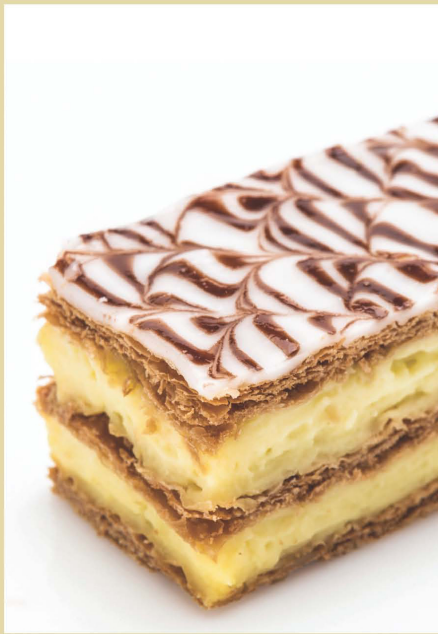
SECOND EDITION

Fats in Food Technology

Edited by

Kanes K. Rajah



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Second edition

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Preface

This updated second edition is fresh and exciting in a number of ways. First, it is a book about fats in food technology – their role, behaviour and the benefits they impart to the foods we consume. Second, it is about fats that are 'naturally present' in foods (e.g. milk fat in cream) or fats that have been added to help with physical and chemical properties (e.g. cocoa butter in chocolate). Finally, it is a book which has useful information about market issues that have driven change and disciplines that have helped to regulate the trade and use of fats and oils in foods.

My initial challenge in the first edition was to find authors who could write to such exacting and wide-ranging requirement. I was privileged to be able to gather together an internationally respected team of authors from several countries, to contribute, either independently or in joint initiatives, a total of nine chapters. In this edition I have been most fortunate that all who still remain active in their specialisms agreed to join me in updating their respective chapters. To fill the gaps created by those who had retired I have been very fortunate in enlisting new authors who are all with senior-level commercial experience of R&D in oils and fats technology and having also direct exposure to technical developments in world markets.

Consequently, all chapters have been reviewed systematically; established products and processes have been investigated for updates while the latest developments have been introduced and new ideas are presented, not only from the recent literature but often from the personal R&D experiences of the authors. Where efficiencies in processing or economy in the costs of raw materials can be achieved, these have – either implicitly or explicitly, by the choice of appropriate examples or formulations – been discussed within the relevant chapters.

Authors have attempted to provide relevant market information in respect of regulation, legislation or directives currently enforced in the major markets, especially within the United States and Europe. Market trends and changes which facilitate a better understanding of the scope and potential for fat technology are also presented. In an integrated approach, the issues concerning greater consumer awareness of health, diet and lifestyle are interwoven into some of the relevant chapters, such as, typically, lower fat products and high moisture emulsions. The technology of non-aqueous fat systems has been brought up-to-date water-in-oil and oil-in-water emulsions are discussed far more extensively in this book than previously.

The book begins with a presentation of the physical properties of fats and emulsions in Chapter 1. Chapter 2, on bakery fats, deals with solid, fluid and powdered fats. New developments in water continuous emulsions and dairy cream technology are explained in Chapter 3. Cream liqueur and ice cream production processes are

also included. Hydrogenation and fractionation, which are the most widely used techniques of fat modification, are covered as separate subjects in Chapter 4. Products from these processes often replace, complement or supplement each other. This is evident from the discussion and also in the examples seen in those chapters dealing with end-use, e.g. bakery, spreads and confectionery. Chapter 5 on confectionery products has been widened to cover both chocolate and sugar confectionery fats. Chapter 6 on spreadable products includes the results of specific secondary market research on important developments in butter, margarine and low fat spreads technology and packaging. The significant growth in fat-based sweet and savoury spreads is also acknowledged in this important chapter. The treatment of emulsifiers is comprehensive and Chapter 7 guides the reader through the technology of current products used in, for example, recipes and formulations to ensure that shelf-life, emulsion stability and anti-spattering properties are optimised. We have introduced a unique new chapter, Chapter 8 on 'Food Safety and Quality Issues of Dairy Fats' consists of the most up-to-date information on the subject. Finally, culinary fats appear as a separate chapter (Chapter 9) because they focus on some of the unique features and benefits of fats, frying oil, ghee and vanaspati and speciality fats in the kitchen and discuss these in terms of flavour, eating quality, texture, aroma and benefits to health.

This book should be helpful to anyone who is interested in the technology of fat-containing products. Food technologists in either the dairy industry or the edible oils industry and indeed the food industry generally should find that this volume provides important ideas for product and process development. For scientists in academic research establishments, the book offers important insights into some of the more significant scientific developments that have been commercialised. The book will also serve as a useful source of reference to traders and marketing personnel in the oils, fats and butter industries.

This has been yet again a major challenge and a creative experience for all of us. It has been possible only because those who participated in crafting both editions gave of their best, unflinchingly. My warmest thanks, therefore, to the following much valued colleagues who have retired but whose original chapters remain with new authors taking up the task to update: Tetsuo Koyano, John Podmore, Ralph E. Timms, David Robinson and Clyde E. Stauffer. I am saddened that Ian M. Stewart, a much admired and highly respected colleague passed away. He will be missed greatly. Finally, Timothy P. Guinee and Barry A. Law were unable to update their chapter on 'Role of milk fat in hard and semihard cheeses' and so their original chapter in the first edition remains as the reference point on the subject and is not included in this second edition. I record my gratitude to all our colleagues who had contributed to the first edition.

A special thanks to my fellow authors in this book for their hard work and for generously sharing their knowledge, insight and experience in producing such excellent chapters. Any perceived shortcomings in this book are entirely my own responsibility. I am equally grateful to Dr Graeme MacKintosh as the Publisher who invited me to

undertake the first edition, and to the Commissioning Editor of this edition Mr Andrew Harrison and to Fiona Seymour – Senior Project Editor, who took over from him. Thank you to all on the Wiley team for your invaluable assistance and unstinting support at all times.

Finally, to the three special people in my life who make me still want to undertake such projects, to Heera, Tamara and Tara, thank you.

1

Physical properties of fats in food[1]

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1.1 Introduction

Oils and fats are important ingredients in a wide variety of manufactured foods, and constitute a significant part of food recipes. The major foods in which they are used are all discussed in detail in this volume. However, it is important to note that the forms in which oils and fats are made available to food manufacturers have changed significantly over the years, particularly since the 1960s, largely because of the major shifts that have taken place in consumer lifestyles and the increasing concerns with health, food safety and a balanced diet. Many of the food products that are now available to consumers reflect this new direction. Important examples arising out of the lipid research that has followed are *trans-free* fatty acids, reduced high-melting, in particular saturated, fats, very-low-yellow fat emulsions, spreadable butter, aerated fats, structured oils, molecularly designed structured fats with new nutritional advantages, and so on. All these initiatives have required an in-depth understanding of the behaviour of the fats concerned so that they can be used effectively as ingredients in food. Consequently, the study of their physical properties is of major interest and is covered in this chapter.

In general, fats form networks of crystal particles, maintaining specific polymorphic forms, crystal morphology and particle–particle interactions (Marangoni, 2005). The control of the physical properties of food fats has therefore been of importance in research efforts and can be considered under five headings:

- clarification of molecular and crystal structures of triacylglycerols (TAGs) with different fatty-acid moieties (Kaneko *et al*., 1998; Kaneko, 2001);
- crystallisation and transformation mechanisms of TAG crystals (Sato, 1996, 1999; Sato and Koyano, 2001; Sato and Ueno, 2005);

[1]The original chapter was written by Tetsuo Koyano and Kiyotaka Sato.

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- clarification of formation mechanisms of mesoscale and macroscale fat crystal network starting from nanoscale primary fat crystals (Acevedo *et al*., 2011);
- rheological and texture properties that are dominated mainly by fat crystal networks (Boode *et al*., 1991; Marangoni and Hartel, 1998; Marangoni *et al*., 2012; Walstra *et al*., 2001);
- influences of external factors such as shear, ultrasound irradiation, minor lipids on fat crystallisation kinetics (Martini *et al*., 2008; Mazzanti *et al*., 2011; Smith *et al*., 2011; Wright *et al*., 2000).

The first topic is of an introductory nature and so will not be elaborated in this chapter (for more details, see the cited references). The remaining four topics are related to observed systems of food fats, with which this chapter is mainly concerned.

The chapter begins with a brief review of the three basic physical properties of fats by collecting together recent work on the crystallisation and transformation of the fats in bulk and in emulsion states. We will then focus on fundamental aspects of the crystallisation and transformation of fats employed in real food systems, through describing the use of important examples, such as cocoa butter, palm oil and palm mid-fractions. Since these natural fats are multi-TAG systems, knowledge of the fundamental properties of pure TAGs composing the natural fats may be necessary, as will be argued. Those who wish to compare real fats with pure fats are directed to the literature (Himawan *et al*., 2006; Sato, 1996; Sato and Koyano, 2001; Sato and Ueno, 2001; Sato *et al*., 1999).

1.2 Basic physical properties of fat crystals

The physical properties of the food fats are influenced primarily by three factors: (1) polymorphism (structural, crystallisation and transformation behaviour); (2) the phase behaviour of fat mixtures; and (3) the rheological and textural properties exhibited by fat crystal networks. In this section we cover the fundamentals and look at recent research work on these three properties.

1.2.1 Polymorphic structures of fats

Polymorphism is defined as the ability of a chemical compound to form different crystalline or liquid crystalline structures. The melting and crystallisation behaviour will differ from one polymorph to another.

Table 1.1 summarises the basic physical properties of the three typical polymorphic modifications of α, β′ and β. Polymorph α is least stable, easily transforming to either the β′ form or the β form, depending on the thermal treatment. Polymorph β′, the meta-stable form, is used in margarine and shortening because of its optimal crystal morphology and fat crystal networks, which give rise to optimal rheological and texture properties. The most stable β form tends to form large and plate-like crystal shapes, resulting in poor macroscopic properties in shortening and margarine.

Table 1.1 Three typical polymorphic forms of fats and their main physical properties.

Form	Stability	Density	Melting point	Morphology
α	Least stable	Lowest	Lowest	Amorphous-like
β′	Metastable	Intermediate	Intermediate	Rectangular
β	Most stable	Highest	Highest	Needle-shaped

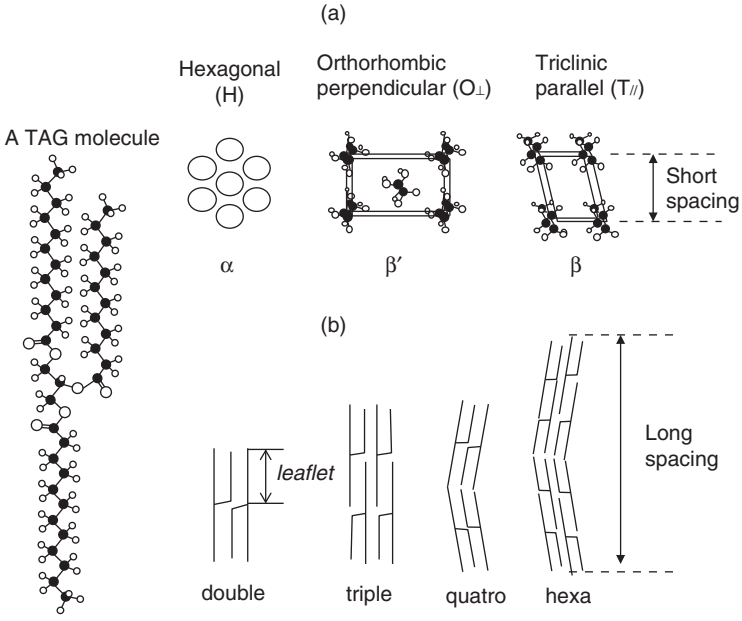

Figure 1.1 Polymorphic structures of three typical forms of triacylglycerol (TAG). (a) Subcell structures and (b) chain length structures.

The three main polymorphs, α, β′ and β of fats, are defined in accordance with subcell structure: α polymorphs have a hexagonal subcell (H); β′ polymorphs have an orthorhombic–perpendicular subcell ($O_{\perp}$); and β polymorphs have a triclinic–parallel subcell ($T_{//}$) (Larsson, 1966; see Figure 1.1 (a)). The subcell structures can be determined most clearly by measuring X-ray diffraction (XRD) short spacing patterns of poly-crystalline samples.

Figure 1.1 (b) shows the chain-length structure, illustrating the repetitive sequence of the acyl chains involved in a unit cell lamella along the long-chain axis (Larsson, 1972). A double chain-length structure (DCL) is formed when the chemical properties of the three acid moieties are the same or very similar. In contrast, when the chemical properties of one or two of the three chain moieties are largely different from those of the moieties, a triple chain-length (TCL) structure is formed because of chain sorting. The relevance of the chain-length structure is revealed in the mixing phase behaviour of the different types of the TAGs in the solid phase: when the DCL fats are mixed

with the TCL fats, phase separation readily occurs. The chain length structures can be determined solely by measuring the XRD long spacing patterns of the poly-crystalline samples.

In food fats, transformation from polymorph β′ to polymorph β often causes deterioration of the end product, mostly because of changes in the crystal morphology and network, as indicated in Table 1.1. The β-type polymorph is found in confectionery fats made of cocoa butter (Timms, 2003). There are two β-type crystals: a meta-stable β_2 form is more useful than the more stable β_1 form (Sato and Koyano, 2001; Van Mechelen *et al*., 2006a, 2006b). Atomic-level structure analyses of the TAGs have been attempted to resolve the microscopic mechanism of the polymorphic β′–β transformation. Results were reported first for the β forms (as reviewed for the β forms in Kaneko, 2001), and have been reported for the β′ form (Sato *et al*., 2001; van Langevelde *et al*., 2000). Mechanistic processes of solid-state transformation from β′ to β forms in trilauroyl-glycerol crystals were observed by a cutting-edge method with synchrotron radiation microbeam XRD (SR-μ-XRD) (Ueno *et al*., 2008), as will be presented below.

As the physical properties of food fats are greatly influenced by fat polymorphism, it is a prerequisite for those who are engaged in the material production of oils and fats to know how the fatty-acid composition influences the fat polymorphism. Two categories of fatty-acid composition may be considered: (1) mono-acid TAGs in which the three fatty-acid moieties of the TAG are of the same type; and (2) mixed-acid TAGs in which different fatty-acid components are connected to three different glycerol carbons on the TAG. The following diversity in fatty-acid composition of TAGs can be found:

- Mono-acid TAGs:
  - the acids may be saturated;
    - the number of carbon atoms in the fatty-acid chain, N_c, may be odd or even;
  - the acids may be unsaturated.
    - the number of carbon atoms in the fatty-acid chain, N_c, may be odd or even;
    - there may be a *cis* or a *trans* conformation around the double bond;
    - the number of double bonds may vary;
    - the position of the double bonds may vary.
- Mixed-acid TAGs:
  - there may be three saturated acids with different chemical species;
  - there may be three unsaturated acids with different chemical species;
  - there may be three acids containing saturated and unsaturated species;
  - the different fatty acids may be connected to carbon atoms of different stereospecific number (*sn*).

In 1988, Hagemann summarised the melting behaviour of TAGs with different combinations of fatty-acid moieties with different chemical species (Hagemann, 1988).

Hagemann showed a general tendency in the melting behaviour of mono-acid TAGs to be as follows:

- In saturated mono-acid TAGs, the melting points of the α, β′ and β forms increase when N_c is increased from 8 to 30. With respect to the quantitative dependence of the melting point of the polymorphs on N_c, the melting points of the α form increase smoothly with N_c, whereas the melting points of the β′ and β forms increase in a 'zig-zag' manner with N_c odd or even.
- In the mono-unsaturated mono-acid TAGs, the melting points of the β forms are available, showing specific dependence on double-bond conformation and on the position of the double bond. For example, *trans* unsaturated TAGs showed higher melting points than those of *cis* unsaturated TAGs at every double-bond position.

Since 1988, much work has been done on the polymorphic behaviour of mixed-acid TAGs. It is important to understand such behaviour as natural oils and fats contain these mixed-acid TAGs (for reviews, see Larsson *et al*., 2006; Sato *et al*., 1999; Sato and Ueno, 2001; Sato and Ueno, 2005).

The fatty-acid compositions of TAGs are closely related to β′-tending properties. TAGs containing different types of fatty acids are more stable in the β′ form, as exemplified in pure TAGs (Hagemann, 1988). In natural fats, milk fats having long-chain and short-chain saturated and unsaturated fatty acids are β′-tending; palm oil is also categorised as a β′-tending fat because of the presence of asymmetric mixed-acid TAGs such as POO (1-palmitoyl-2,3-dioeloyl-*rac*-glycerol) and PPO. Recent work on single-crystal structure analyses of the β′ form of 1,3-dilauroyl-*sn*-2-caproyl-glycerol (CLC; van Langevelde *et al*., 2000) and 1,2-dipalmitoyl-*sn*-3-myristoryl-glycerol (PPM; Sato *et al*., 2001) has indicated that chain–chain interactions through methyl end stacking combined with glycerol group conformations may stabilise the β′ structures (Hernqvist and Larsson, 1982).

The polymorphic behaviour of mixed-acid TAGs differs greatly from that of mono-acid TAGs. For example, Table 1.2 shows variations in polymorphic occurrence and the melting behaviour of a series of TAGs in which the two fatty-acid chains at the *sn*-1 and *sn*-3 positions are stearic acid, and in which the fatty acid at the *sn*-2 position may be stearic (to give SSS), elaidic (SES), oleic (SOS) (Sato *et al*., 1989), ricinoleic (SRS) (Boubekri *et al*., 1999) linoleic (SLiS) (Takeuchi *et al*., 2000), α-linoleic (SLnS) or eicosapentanoic acid (SEpS) (Sato *et al*., 2009). Three typical polymorphs of α, β′ and β polymorphs are revealed in SSS, all stacked in a DCL structure. Substitution of the *sn*-2 acid with elaidic acid (SES) caused a decrease in the melting point for the three polymorphs, which exhibit basically the same properties as those of SSS. However, large differences are produced when the *sn*-2 acid is replaced by oleic, ricinoleic or linoleic acid, revealing a new polymorph, γ, and variation in chain-length structure from double (α form) to triple (the other, more stable, forms). In addition, the β form is absent in SRS and SLS, and the β′ form does not occur in SLiS. Quite recent work

Table 1.2 Polymorphic occurrence and melting points (°C) of SSS, SES, SOS, SRS, SLiS, SLnS, and SEpS.

Polymorph[a]	SSS	SES	SOS	SRS	SLni	SLnS	SEpS
α-2	55.0	46.0	23.5	25.8	21.6	–	–
β′-2	61.6	58.0	–	–	–	–	–
γ-3	–	–	35.4	40.6	34.5	35.9	32.5
β-2	73.0	61.0	–	–	–	–	–
β′-3	–	–	36.5	–	–	–	–
β'_2-3	–	–	–	44.3	–	–	–
β_2-3	–	–	41.0	–	–	–	–
β'_1-3	–	–	–	48.0	–	–	–
β_1-3	–	–	43.0	–	–	40.1	–

Note: SSS, tristearoylglycerol; SES, 1,3-distearoyl-2-elaidoyl-*sn*-glycerol; SOS, 1,3-distearoyl-2-oleoyl-*sn*-glycerol; SRS, 1,3-distearoyl-2-ricinoleyl-*sn*-glycerol; SLiS, 1,3-distearoyl-2-linoleoyl-*sn*-glycerol; SLnS, 1,3-distearoyl-2-α-linolenoyl-*sn*-glycerol; SEpS, 1,3-distearoyl-2-eicosapentanoyl-*sn*-glycerol.
[a]Suffixes 2 and 3 refer to double and triple chain-length structures, respectively.

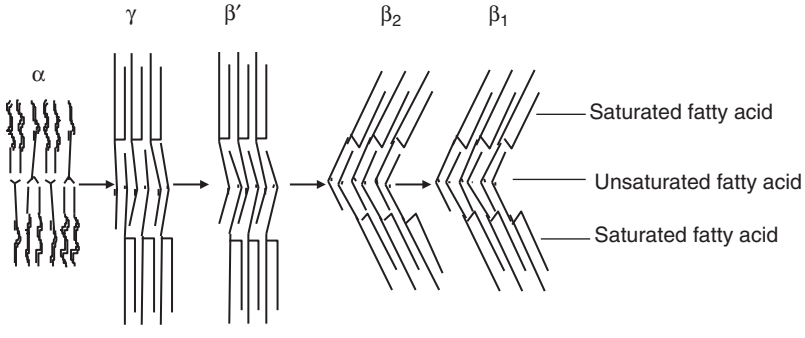

Figure 1.2 Polymorphic structure of 1, 3-stearic-2-unsaturated mixed-acid TAGs.

on SLnS and SEpS (Sato *et al*., 2009) unveiled the following properties of the TAGs exhibited in Table 1.2, and as illustrated in Figure 1.2.

(a) In the mixed-acid TAGs exhibited in Table 1.2, the unsaturated and stearic acid moieties form different layers, resulting in the TCL structure.
(b) Because of the strong van der Waals interactions between the stearic acid layers of the TCL structure, not only the mono-unsaturated fatty acid but also the poly-unsaturated fatty-acid moieties may exhibit extended chain conformation as illustrated in Figure 1.2.
(c) As a result, the melting points of the two TAGs including the poly-unsaturated fatty-acid moieties are actually decided by van der Waals interactions among the stearic acid moiety, and become much higher than those of the poly-unsaturated fatty acids in the free fatty-acid state.

Van Mechelen *et al*. have recently studied β forms of SOS and POS by using polycrystalline samples grown from the melt phase (van Mechelen *et al*., 2006a, 2006b), confirming the existence of two β forms of the TCL structure. They claimed that the differences between β_1 and β_2 may mostly be revealed in the layered structures, in which

β_2 is TCL whereas β_1 is a hexa-layer structure composed of two TCL structures which are stacked with the alternation of the inversion–centre relation shown in Figure 1.2.

The peculiar properties of mixed-acid TAGs involving unsaturated fatty-acid moieties may be partly understood in terms of chain–chain interactions between the saturated and the unsaturated fatty-acid moieties (Kaneko *et al*., 1998; Sato and Ueno, 2001). Much work, however, should be done to clarify the molecular mechanisms that cause such complicated polymorphic occurrence and structures such as those illustrated in Table 1.2 and Figure 1.2.

The variation in polymorphic properties of saturated–unsaturated mixed-acid TAGs (see Table 1.2) may have critical significance for our understanding of the polymorphism of natural oils and fats such as milk fat, palm oil and cocoa butter, which contain large amounts of mixed-acid TAGs (Gunstone, 1997).

1.2.2 Polymorphic crystallisation of fats

The macroscopic aspects of fat polymorphism concern the behaviour at melting and crystallisation and the subsequent transformation. With respect to the melting temperature, T_m, for the three forms of any particular TAG, a general tendency is that T_m is lowest for the α form, intermediate for the β' form, and highest for the β form. In contrast, the crystallisation behaviour is more complicated and is determined primarily by the type of crystallising medium, the crystallisation temperature, and the rate of cooling. In general, the β form is usually crystallised from the solution phase, but all three forms may be crystallised from neat liquid. When crystallisation is from the neat liquid, the relative rates and extents of crystallisation of the three polymorphs are determined by the rate of nucleation, which is highest for the α form, intermediate for the β' form and lowest for the β form. Schematic illustration of polymorphic crystallisation of the three forms of TAG is shown in Figure 1.3. This behaviour was measured with precision for tripalmitoyl glycerol (PPP) (Sato and Kuroda, 1987) and for the other fat crystals (Blaurock, 1999). Stop-and-return DSC method combined with the XRD

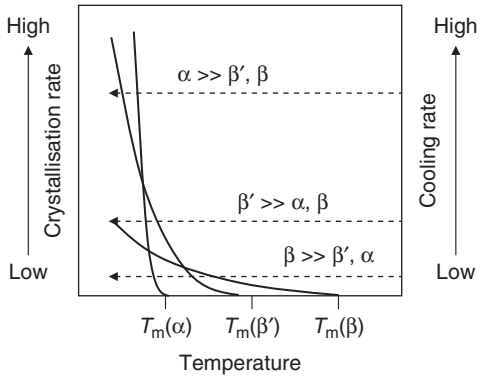

Figure 1.3 Schematic illustration of relative rates of crystallisation of three typical polymorphic forms of TAG in comparison with the rate of cooling.

analysis also showed polymorph-dependent crystallisation kinetics of various natural fats (Foubert *et al*., 2008). DSC and a synchrotron radiation X-ray diffraction study of POP clearly measured the polymorph-dependent crystallisation rates of OPO, POP, OOO and OOL (L: linoleic) (Bayes-Garcia *et al*., 2011, 2013a, b).

Based on the polymorph-dependent crystallisation kinetics, it is necessary to find the optimal rate of cooling in accordance with the preferred rate of crystallisation of the three polymorphic forms, when one tries to selectively crystallise a specific polymorphic form from the liquid state. For example, the α form should be crystallised at the highest cooling rate, and the β form can crystallise at the lowest cooling rate. However, it is quite difficult to predict the optimal cooling conditions for specific polymorphic forms, which have been examined by chance or experience rather than by theoretical prediction in the actual production processes of edible fats. Furthermore, concurrent crystallisation of multiple polymorphic forms may occur, because the nucleation of crystals is determined by probabilistic phenomena. From the practical point of view, however, it is often necessary to crystallise the more stable forms much more rapidly with higher selectivity. For this reason, the following methods have been applied to modify the crystallisation behaviour of the polymorphic forms.

1.2.2.1 Template/additive

Adding foreign materials on purpose to the crystallising liquid, called templates or additives, is widely applied to modify the crystallisation behaviour of inorganic and organic substances, including fat crystals (Sangwal, 2007). The necessary conditions for the template/additive to successfully modify the polymorphic crystallisation may be summarised as follows:

1. *Similarity in molecular shape and polymorphism*. Similarity in molecular shapes as saturated or unsaturated fatty acids or their chain lengths between the template/additive and fat crystals is required. The same properties may be applied to the polymorphic structures between the template/additive and fat crystals.
2. *Thermal stability*. Template/additive materials should not dissolve when they are added to supercooled liquid of lipids, having higher melting points than the fat materials to crystallise.
3. *Optimal supercooling*. When the supercooling is high enough to induce spontaneous nucleation, the effects of the template/additive may be minimised, because unwanted polymorphic crystals are formed without the effects of templates/additives. Therefore, the rate of cooling and the range of supercooling ΔT ($= T_m - T_C$, T_m and T_C are melting and crystallisation temperatures) may be moderate so that spontaneous nucleation is limited.
4. Very limited studies have been performed on the effects of templates or additives on the polymorphic crystallisation of fats. The effects of crystal seeding of high-melting TAGs on the crystallisation of cocoa butter were studied (Hachiya *et al*., 1989a, 1989b; Koyano *et al*,. 1990). The effects of the addition of high-melting emulsifiers on the fat crystallisation in oil-in-water (O/W) emulsion were also examined, as will be described in Section 1.2.2.2.

1.2.2.2 Dynamic temperature variation (tempering)

It has been understood that dynamic temperature change after the crystallisation of the metastable forms is effective to obtain the optimal polymorphic forms through melt-mediation or solid-state transformation (see Section 1.2.3.1). Such a process is called *tempering*, as applied in the polymorphic crystallisation of cocoa butter in chocolate production (Timms, 2003). Also, the tempering method was applied to form β-fat gel, in which tiny crystals of β polymorph of high-melting fats were formed to exhibit organogel, which is composed of several wt.% of high-melting fat crystals and >95% liquid oil (Higaki *et al*., 2003, 2004). During this tempering process, the least stable α form crystals of high-melting fats were formed by very rapid cooling, and subsequent re-heating caused the melt-mediated transformation into the β form, and thus the formed β crystals were so tiny, compared with those formed by simple cooling, that the organogel was formed.

Figure 1.4 illustrates the formation process of the β-fat gel composed of high-melting fat (fully-hydrogenated rapeseed oil, rich in behenic acid, FHR-B) and sal fat olein (SFO) (Higaki *et al*., 2003). The melting temperatures (T_m) of α and β forms of FHR-B crystals decreased with decreasing concentration of FHR-B, with the differences between $T_m(\alpha)$ and $T_m(\beta)$ of 18°C unchanged at all the FHR-B concentrations in the

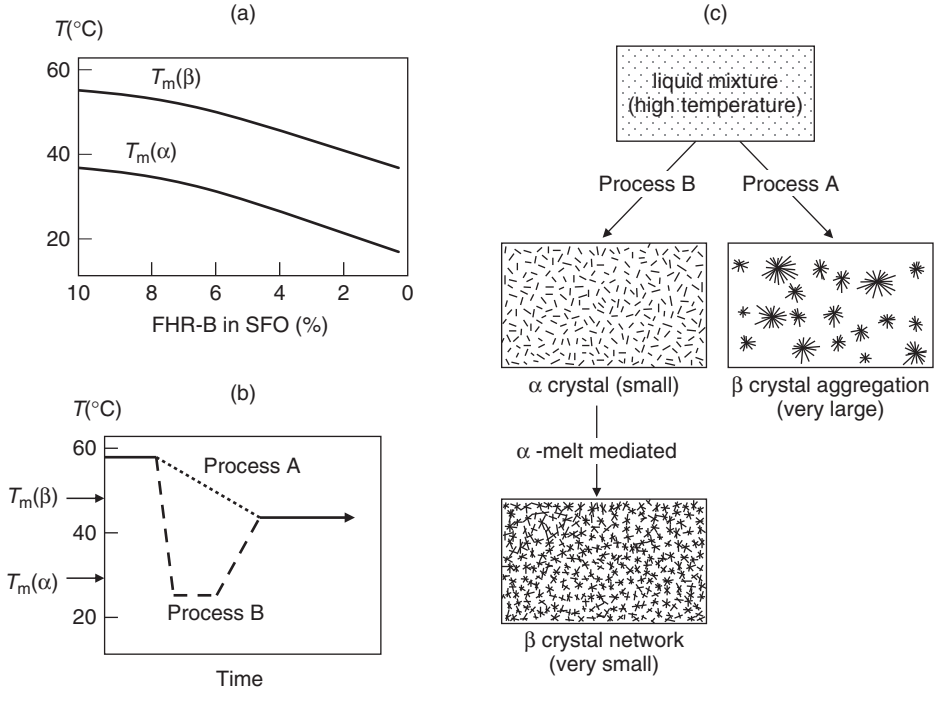

Figure 1.4 Formation mechanisms of β-fat gel made of a high-melting fat (FHR-B) and liquid oil (SFO) mixture (abbreviation, see text). (a) Phase behaviour of α and β forms; (b) temperature variation scheme; and (c) crystallisation behaviour.

mixtures of FHR-B and SFO examined (Figure 1.4 (a)). After the crystallisation process A, during which the molten mixture was slowly cooled to the temperature below $T_m(\beta)$, large β crystals of FHR-B were formed and the gel phase was not formed (Figure 1.4 (b) and (c)). By contrast, the gel phase was formed after the crystallisation process B, in which the molten mixture was rapidly cooled to below $T_m(\alpha)$ and heated to the temperature between $T_m(\alpha)$ and $T_m(\beta)$. After this tempering process, many small β crystals were formed and randomly distributed in the SFO oil which was entrapped by the β crystal betwork of FHR-B. Such a network formation was caused by the melt-mediated transformation from α to β forms, because the nucleation rate of α crystals was high enough to make the transformed β crystals randomly distributed, rather than aggregated as formed by the slow cooling process A.

1.2.2.3 Application of shear

The study of fat crystallisation under shear has been carried out over many years, as reviewed by us (Sato and Ueno, 2001). Since this review was published, more detailed work on cocoa butter and milk fat has been reported by many groups (MacMillan *et al*., 2002; Mazzanti *et al*., 2003, 2007, 2008, 2009, 2011; Padar *et al*., 2009). In these studies, it was evident that the rates of polymorphic crystallisation and transformation were largely increased by applying shear. Furthermore, Mazzanti *et al*. (2003) discovered the preferred orientation of fat crystal particles under shear by observing XRD patterns taken during the crystallisation processes with two-dimensional (2D) detectors.

For example, variations in the XRD intensity were monitored during the crystallisation processes of of cocoa butter at 18°C under sheared condition (1440 sec^{-1}) as shown in Figure 1.5 (Mazzanti *et al*., 2003). Of the six polymorphic forms of cocoa butter (Forms I–VI) (Wille and Lutton, 1966), Form III first crystallised, and

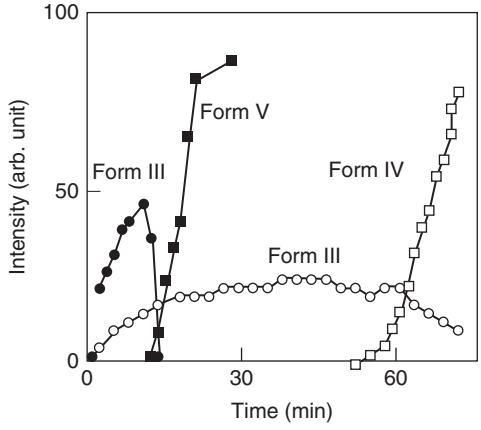

Figure 1.5 Effects of shear application (shear rate 1440 s^{-1}) on crystallisation of cocoa butter at 18°C. Without shear (open) and with shear (filled).

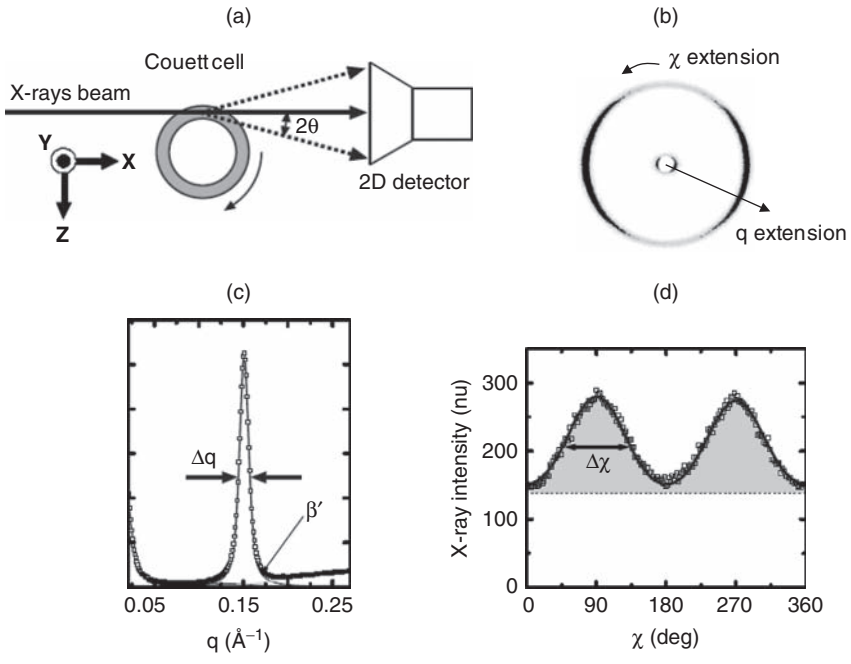

Figure 1.6 Synchrotron radiation XRD patterns from milk fat crystals crystallising under shear. (a) Experimental set-up; (b) two-dimensional XRD pattern; (c) θ-extension pattern; and (d) χ-extension pattern.

conversion into Form IV occurred during further crystallisation when shear was not applied. However, the conversion from Form III to Form V was observed and the rate of crystallisation was increased when shear was applied.

Figure 1.6 shows the effects of shear on the orientation of tiny crystals of anhydrous milk fat (AMF) present in the shear flow, which was determined by synchrotron radiation XRD analysis (Mazzanti *et al*., 2009). AMF was crystallised in a Couett cell under sheared condition ($1440\,\text{sec}^{-1}$) after 1 hour at 17°C. By using two-dimensional X-ray detector, information on the crystals growing in the Couett cell was obtained: (1) polymorphism revealed by observing the q-extension, in which $q = 2\pi/d = \sin\theta \times 4\pi/\lambda$ (where d = lattice parameter; θ = diffraction angle; λ = wavelength of X-ray beam); and (2) orientation of the crystals with respect to the shear direction by observing the χ-extension. Figures 1.6 (c) and (d) show that the AMF crystals grown under shear are of β′ polymorph and the crystals are highly oriented, since sharp arc XRD patterns with narrow Δχ values are observed. These results contrast with the crystallisation without shear, since α and β′ forms crystallised at the same time and no crystal orienatation was observed (Mazzanti *et al*., 2009).

The effects of shear have a practical significance for the crystallisation in edible fats, most remarkably for the crystallisation of cocoa butter in chocolate production (Dhonsi and Stapley, 2006; Maleky and Marangoni, 2011, Maleky *et al*., 2011, 2012).

1.2.2.4 *Irradiation of ultrasound wave (sono-crystallisation)*

For decades, ultrasound has been applied in different applications of the characterisation of microstructures and the process control of materials. In the areas of food fats, there has recently been an increasing interest in the application of ultrasound waves to the crystallisation of fats (sono-crystallisation). Sono-crystallisation has been examined in pure TAGs, confectionery fats, vegetable fats and milk fats, indicating that the rates of polymorph-dependent crystallisation, crystal size and morphology are modified by sono-crystallisation (Higaki *et al*., 2001; Martini *et al*., 2005, 2008; Suzuki *et al*., 2010; Ueno *et al*., 2003).

The sono-crystallisation of tripalmitin (PPP) and cocoa butter has been studied (Higaki *et al*., 2001). The main observations of these preliminary experiments can be summarised as follows: (1) the nucleation rate of PPP was enhanced and the induction time was shortened by the ultrasound application; and (2) the polymorphic Form V of cocoa butter was directly crystallised when the ultrasound was applied under optimal conditions of temperature and short period of sonication.

Martini *et al*. recently applied high-intensity ultrasound (HIU) to the crystallisation of palm kernel oil (PKO), anhydrous milk fat (AMF) and shortening (Martini *et al*., 2005, 2008; Suzuki *et al*., 2010). They observed the following results. HIU induced primary and secondary nucleation of fat crystals, generating smaller crystals. As a consequence, harder materials were formed when HIU was applied at higher crystallisation temperatures as observed for AMF, and when HIU was applied after the first crystals were formed as observed for PKO and shortening. In addition, the fat crystal network in AMF and shortening obtained after HIU application revealed steeper and sharper melting profiles compared with not-sonicated samples. For example, Figure 1.7 shows the effects of the application of HIU at different temperatures on the induction

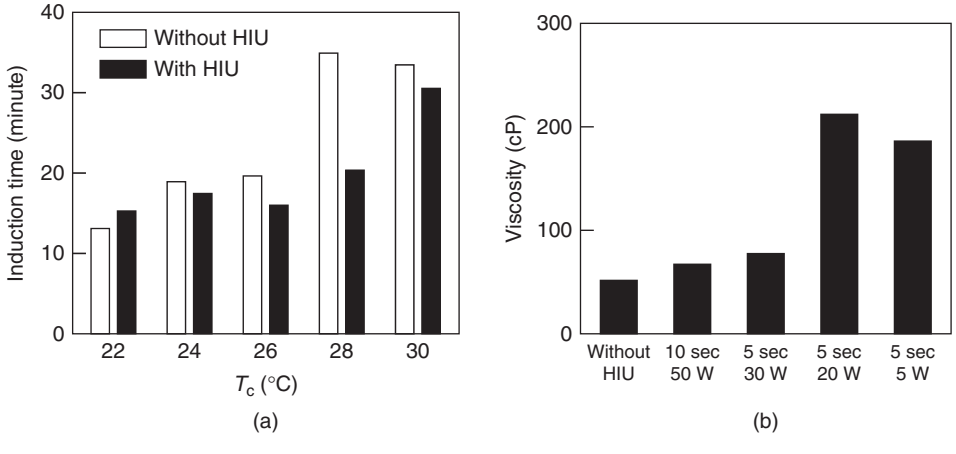

Figure 1.7 Effects of application of high intensity ultrasound (HIU) on crystallisation behaviour of anhydrous milk fat (AMF). (a) Induction time for crystallisation at a different crystallisation temperature (T_c); (b) viscosity of crystallised AMF with different sonication conditions at $T_c = 30^{\circ}$C.

time and viscosity of a crystallised sample of AMF. It was evident that the induction time was shortened when HIU was applied at 26°C and 28°C, and viscosity increased as the sonication time and HIU power were decreased.

To observe the kinetic influences of ultrasound irradiation, *in-situ* observation of the crystallisation processes of PPP and LLL was performed by using synchrotron radiation time resolved small-angle X-ray diffraction (SAXD) and wide-angle X-ray diffraction (WAXD) simultaneous measurement (Ueno *et al*., 2003). Without ultrasound application, both forms of β′ and β crystallised in the melt of each substance. With ultrasound treatment of the melt, the following effects were observed: (1) a marked decrease of induction times for crystallisation of both PPP and LLL; (2) an increased nucleation rate; and (3) crystallisation of only β forms for both PPP and LLL under conditions of initial crystallisation temperature of 50°C and 30°C, respectively, and applied ultrasound of 2 sec. Based on the dynamic nucleation of PPP and LLL crystals induced by collapsing cavitation bubbles, we argued that a pronounced decline in induction times, and an increase in the nucleation rate, result from the melting points shift due to high pressure pulses associated with collapsing bubbles.

The studies reviewed above clearly indicate that ultrasound does affect the crystallisation behaviour of fats in many ways. However, it is still unclear which particular mechansisms are responsible for these effects. To improve our knowledge and predictability in terms of the desired polymorphism, induction times, and nucleation rates that are all influenced by sono-crystallisation, a better understanding of the following issues is crucial: (1) to establish a P-T phase diagram for polymorphic forms, since the primary effect of sono-crystallisation may be due to high pressure when the sonication-induced cavity is collapsed; (2) the stability (lifetime) of different polymorphic forms as a function of the supercooling temperature; (3) the mechanism and lifetime of collapsing cavities; and (4) the basic mechanism of the dynamic nucleation, in the vicinity of a collapsing bubble (Ueno *et al*., 2003).

1.2.3 Polymorphic transformation of fats

Once the less-stable forms are crystallised, they transform to more stable forms in a post-crystallisation process in solid phase or through liquid mediation (Sato *et al*., 1999). As a consequence, the morphology of fat crystals is determined by the polymorphic modification, by the thermal processes of crystallisation and by subsequent transformation. It is worthy of note that various morphologies of β′-form PPP crystals have been found for different temperature treatments. In particular, the β′-form showed needle-like crystals after slow crystallisation, similar to β-form crystals, which usually exhibit a long needle shape (Kellens *et al*., 1992).

Recent studies have shed light on the microscopic structures of polymorphic transformation of fats, which are reviewed as follows.

1.2.3.1 Solid-state and melt-mediated transformations

Two types of transformation processes occur from less stable to more stable polymorphic forms, when crystal-free energy values of α, β′ and β forms are depicted,

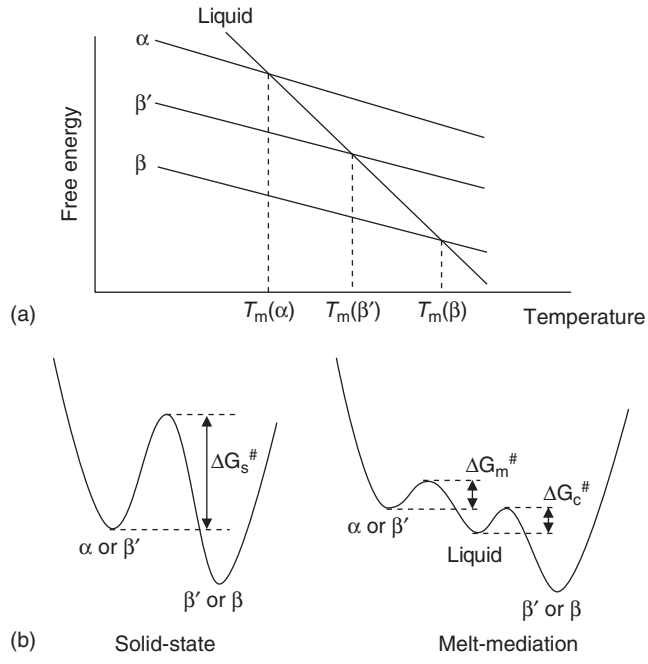

Figure 1.8 Schematic illustration of polymorphic transformations in TAG. (a) Thermal properties of three forms; (b) activation free energy barriers for solid state transformation and melt-mediated transformation.

as in Figure 1.8 (a). As each polymorphic form has its own melting temperature T_m, polymorphism having this property is called monotropism.

Solid-state transformation occurs when the metastable form of α or β′ is stored below their T_m. The rate of solid-state transformation is basically determined by the magnitude of the activation free energy barrier $\Delta G_s^{\#}$, which may include the energies to enable the conversions in the subcell and chain length structures and other molecular structural changes, as illustrated in Figure 1.1.

By contrast, melt-mediated transformation occurs when α or β′ forms are heated to the temperatures just above their T_m, where melting of α or β′ is associated with the crystallisation of the more stable forms of β′ or β. In this case, the rate of transformation is basically determined by the magnitude of activation free energy barriers of melting $\Delta G_m^{\#}$, and crystallisation $\Delta G_c^{\#}$, as depicted in Figure 1.8 (b). As one may expect that $\Delta G_m^{\#}$ is much smaller than $\Delta G_c^{\#}$, the rate of melt-mediated transformation may actually be governed by $\Delta G_c^{\#}$. $\Delta G_c^{\#}$ may include activation energies for nucleation and crystal growth of the more stable forms from the liquid which is formed soon after the melting of the less stable forms. We cannot simply compare the rates of solid-state transformation and melt-mediated transformation, as the factors included in $\Delta G_s^{\#}$ and $\Delta G_c^{\#}$ are quite different. However, it can be expected that heterogeneous nucleation of the more stable forms will reduce the values of $\Delta G_c^{\#}$, and thereby the melt-mediated transformation occurs more rapidly than that in the solid

state (Kashchiev and Sato, 1998). This property was observed for the polymorphic transformation in SOS (Ueno *et al*., 1997). The effects of heating rates on the polymorphic transformation on the transformation pathways, either through solid-state or melt-mediation, were observed for POP polymorphs (Bayes-Garcia *et al*., 2013a).

As for the application of the polymorphic transformations in the processing of food fats, so-called *tempering* corresponds to the melt-mediated transformation from α to β′ in the case of margarine, fat spread and shortening, and from Form IV to Form V in the case of cocoa butter crystals in chocolate.

1.2.3.2 Molecular aspects of solid state transformation examined with SR-μ-XRD

Particular interest has been focused on the solid-state transformation mechanisms, including the variations in molecular orientation of the long-chain axes with respect to the lamellar plane and the subcell axes between α or β′ and β. However, little information on molecular-level understanding of the transformation mechanisms has been available due to the difficulty of growing single crystals of TAGs, both for the metastable and stable polymorphs, unlike the cases of saturated fatty-acid crystals (Larsson *et al*., 2006). Another interest concerning the solid-state transformation may involve the formation of spherulites of fats, which are the main causes of the deterioration of texture in fat-based products, for example, granular crystal formation in margarine, fat spread and chocolate (fat bloom). It was believed that the polymorphic transformation from β′ to β is related to the formation of spherulites, but no microscopic information has yet been obtained to verify this.

We recently reported on the microstructure of spherulites of trilaurin, which are formed by crystallisation and solid-phase transformatio, and which were measured by the synchrotron radiation microbeam X-ray diffraction method (SR-μ-XRD) (Ueno *et al*., 2008). This was the first study involving the structural analysis of the texture of fat crystals using an X-ray microbeam method. Before this work, there had been no study using SR-μ-XRD in the research area of food science except for the study of the microstructure of starch (Buleon *et al*., 1997; Chanzy *et al*., 2006; Lemke *et al*., 2004).

The basic principle of SR-μ-XRD technique relies on X-ray focusing optics and the synchrotron radiation X-ray source, enabling us to use highly brilliant X-rays and to generate an intense X-ray microbeam with a divergence small enough to perform X-ray diffraction studies. By scanning the X-ray microbeam on a thin section of the sample in two dimensions with steps on the order of the beam size, and by collecting each two-dimensional (2D) X-ray diffraction pattern with a 2D X-ray sensitive area detector, we can construct 2D images of a micrometer-dimension in real space.

In the study of spherulite analysis, we applied a microbeam small-angle X-ray diffraction (μ-SAXD) technique using an X-ray microbeam having a width of $5 \times 5\ \mu m^2$ so that the lamellar planes of the fat crystals within a droplet could be clearly observed. Figure 1.9 illustrates the information obtained from a 2D μ-SAXD pattern from the fat crystals present in a 2D space of the microbeam area. The polymorphic structure can be determined by a lattice parameter by calculating the diffraction angles (2θs) shown in Figure 1.9 (a), which is basically identical to the

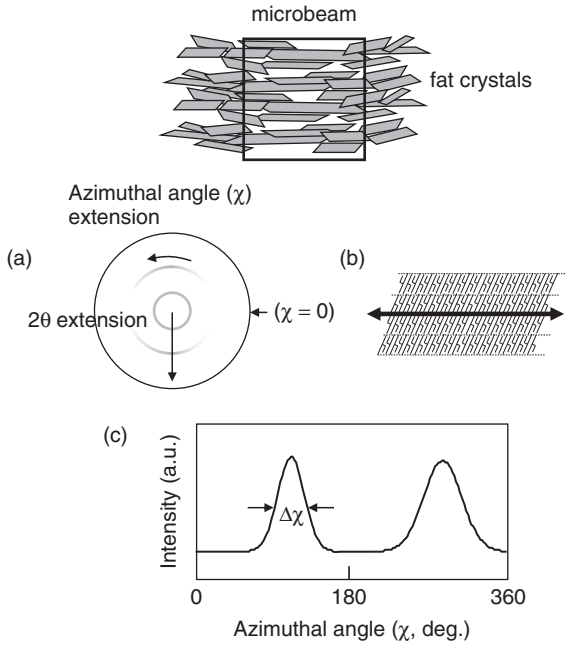

Figure 1.9 Relationships between lamellar plane direction noted by an arrow in (b) and the polymorphism of fat crystals and two-dimensional small-angle XRD patterns examined by SR-μ-XRD.

q-extension shown in Figure 1.6. When all the fat crystals are arranged in a highly ordered manner, two sharp 2D diffraction peaks (arc peaks) should appear. In this case, the average direction of the lamellar planes of the fat crystals is directed normal to the direction connecting the two arc peaks (Figure 1.9 (b)). When the fat crystals are randomly oriented, however, the 2D diffraction patterns must appear in almost all directions with equal intensity. In our previous study, we successfully used a scanning μ-SAXD method to analyze the spatial distribution of the lamellar planes on the fat crystals in spherulites by observing the occurrence and direction of lamellar planes expressed in sharp arc peaks. These properties are basically the same as those presented in Figure 1.6 to observe the effects of shear on fat crystallisation.

Figure 1.10 shows the results of optical and SR-μ-XRD analysis of the solid-state β′ to -β transformation occurring in the same spherulite of trilaurin grown within thin spaces between PET films (Ueno *et al*., 2008). The following results were obtained. The two-dimensional spherulites of β′ were composed of nanometer-sized crystals in which the lamellar planes were oriented parallel to the radial direction of the spherulites, except for the centere position. At the centere position, the lamellar planes of the first-occurring crystals are oriented randomly, indicating that numerous crystal nuclei of β′ form are formed with random orientation at the first stage of spherulite formation. It was also verified that, following the solid-state transformation from β′ to β, the orientations of the long-chain axes of the β form remained unchanged with respect

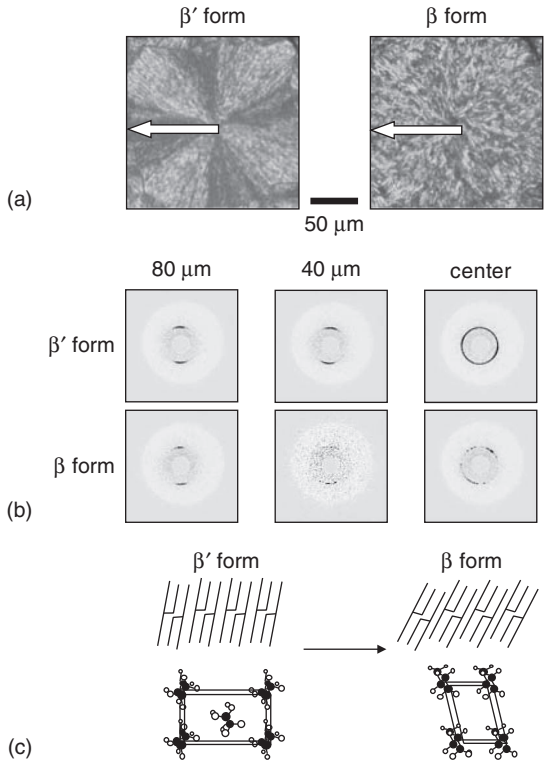

Figure 1.10 (a) Polarised optical micrographs of spherulite crystals of β′ and β forms of trilaurin; (b) small-angle SR-μ-XRD patterns taken at the positions from the centre to left directions noted by arrows in (a) of the same spherulite before and after the β′ to β transformation; (c) variation in lamellar structures and subcell structures during solid-state β′→β transformation.

to those of the β′ form. This suggests that the molecular arrangements of trilaurin during the β′→β polymorphic transformation occurred through template effects of the lamellar structures of the mother phase of β′ as shown in Figure 1.10 (c).

1.2.4 Phase behaviour of fat mixtures

Naturally occurring fats and lipids are mixtures of different types of TAG. The complicated behaviour they exhibit with regard to melting, crystallisation and transformation, crystal morphology and aggregation are partly a result of the physical properties of the component TAGs (discussed above) and, more importantly, partly a result of the phase behaviour of the mixture. To resolve this complexity in mixed-fat systems, a fundamental study of the binary and ternary mixtures of specific TAG components is necessary (Rossel, 1967).

Three typical mixture phases occur in binary solid mixtures of fats in the case where the two components are miscible, for all concentration ratios, in the liquid state.

These are: solid solution phase, eutectic phase and compound formation. For TAG mixtures, two factors affect the mixing phase behaviour simultaneously: chain–chain interactions and polymorphism. Chain–chain interactions are influenced by the chemical nature of the component TAGs varying with chain length (N_c), the saturation or unsaturation and the isomeric conformation (*cis* or *trans*) of the unsaturated chains. The effect of polymorphism is revealed in the formation of miscible and eutectic phases, miscible mixtures being formed with less stable polymorphs (the α and β′ forms) and eutectic phases tending to occur with the stable polymorph (the β form). In addition, differences in chain-length structure (DCL or TCL) affect the mixing systems, the formation of the miscible phase for fats with different chain-length structure being prohibited. Three examples illustrate the effects of polymorphism and structure on the binary mixture behaviour of TAGs (Table 1.3).

In the mixture of saturated mono-acid TAGs, a eutectic phase with a limited region of miscible phase was formed for the stable polymorph when the difference in N_c is no greater than 2, as shown for the mixture of PPP and SSS. However, a miscible mixture was formed for the α and β′ polymorphs in the mixture of PPP and SSS. This means that, when the mixed PPP and SSS liquid is chilled to form the α or β′ form, and when further polymorphic transformation into the β form is induced, the mixture changes from being miscible to separated. This was clearly demonstrated by an *in-situ* X-ray diffraction measurement by using a synchrotron radiation X-ray beam (Kellens *et al*., 1991). The same results were observed in the mixtures of PPP, MMM and LLL (Takeuchi *et al*., 2003). These results indicate the importance of the effect of polymorphism on the mixture system and must be kept in mind when one is seeking an optimal blend of TAGs for use in food where the phase separation of fats is not preferred.

The formation of molecular compound crystals has been observed in mixtures of saturated/unsaturated mixed-acid TAGs. The formation of a molecular compound may be viewed as a special case of eutectic mixing systems that occurs as a result of specific molecular interactions between the component TAGs. Two examples are shown in Table 1.3: for an SOS/OSO mixture (Koyano *et al*., 1992) and for a POP/PPO mixture

Table 1.3 Typical binary mixing behaviour of triacylglycerols (TAGs).

TAG polymorphic form[a]	Mixing phase and polymorphic form
PPP α-2, β′-2, β-2 SSS α-2, β′-2, β-2	Miscible phase: α-2 and β′-2 Eutectic phase: β-2
PPP α-2, β′-2, β-2 MMM α-2, β′-2, β-2	Eutectic phase
SOS α-2, γ-3, β′-3, β_2-3, β_1-3 OSO α-2, β′-2, β-3	Compound formation: α-2, β′-2, β-2
POP α-2, γ-3, β′-3, β_2-3, β_1-3 OOP α-3, β′-3	Eutectic phase

Note: PPP, tripalmitoylglycerol; SSS, tristearoylglycerol; MMM, trimyristoylglycerol; SOS, 1,3-distearoyl-2-oleoyl-*sn*-glycerol; OSO, 1,3-dioleoyl-2-stearoyl-*sn*-glycerol; POP, 1,3-dipalmitoyl-2-oleoyl-*sn*-glycerol; OOP, 1,2-dioleoyl-3-palmitoyl-*rac*-glycerol.

[a]Suffixes 2 and 3 refer to double and triple chain-length structures, respectively.

(Minato *et al*., 1997). In both mixture systems, a common result was obtained in that the polymorphic behaviour was largely different for the component TAGs, yet the molecular compound was formed for all three polymorphic forms. It is worthy of note that all of the molecular compounds were packed in the DCL structure, although DCL and TCL structures are revealed in the component TAGs. A mechanistic treatment has been carried out on the formation of molecular compound systems of SOS/OSO and POP/PPO, taking into account chain–chain interactions (Kaneko *et al*., 1998; Sato *et al*., 1999). The significance of the formation of a molecular compound in food applications is that the rate and extent of the $\beta'-\beta$ transformation in molecular compound systems are remarkably higher than those occurring in the component TAGs.

In this regard, quite interesting results were observed in the binary mixtures of SOS-OOS and POP-OOP, which are the mixtures of symmetric saturated-oleic-saturated mixed acid TAGs (SOS and POP) and asymmetric oleic-oleic-saturated mixed acid TAGs (OOS and OOP) (Zhang *et al*., 2007, 2009). The two mixtures showed the same results as summarised in the following.

Thermal and X-ray diffraction experiments on binary mixtures of SOS-OOS and POP-OOP exhibited immiscible monotectic or peritectic mixing behaviour. The differences between the SOS-OOS and POP-OOP mixtures were in the polymorphic behaviour of the fractions of POP and SOS. No difference was found in the mixing behaviour between optically active (*sn*-OOS) and racemic mixture (*rac*-OOP) as an asymmetric oleic-oleic-saturated acid TAG. From the two results, it was concluded that an immiscible phase was formed in the binary mixtures of symmetric saturated-oleic-saturated TAGs and asymmetric oleic-oleic-saturated TAGs, both for racemic and optically active molecules of asymmetric oleic-oleic-saturated TAGs. This result stands in contrast to mixtures of SOS-OSO, SOS-SSO, POP-OPO and POP-PPO, all of which exhibited molecular-compound-forming behaviour with molecular compound crystals in an equal ratio to the binary mixtures. Molecular-level mechanisms to explain this difference are discussed, based on the possible roles of glycerol groups acting during the mixing processes of saturated-unsaturated mixed-acid TAGs.

Figure 1.11 presents a hypothetical structural model of a molecular compound of SOS and *sn*-OOS, though such mixing behaviour was not observed. Figure 1.11 illustrates that there would be difficulty either in arranging the glycerol groups or with lateral chain packing of stearic and oleic acid moieties, if we draw the molecular compound crystal as a double-chain-length structure. In model (1), the arrangements of the glycerol groups may have a discrepancy in the directions of the glycerol groups, as denoted by arrows, although the oleic acid and stearic acid moieties are packed in separated leaflets. In model (2), however, the aliphatic chain packing may have steric hindrance because of the coexistence of stearic acid and oleic acid chains in each leaflet, though the glycerol groups are well arranged. To conclude, it is difficult to construct a molecular compound crystal with SOS and *sn*-OOS, and therefore eutectic mixing behaviour was observed for SOS-OOS and POP-OOP mixtures.

The effects of chain length, saturation and unsaturation of fatty-acid moiety, and glycerol structure on the mixing behaviour of TAGs are summarised in Figure 1.12. The mixing properties thus summarised may provide important indications of the fat

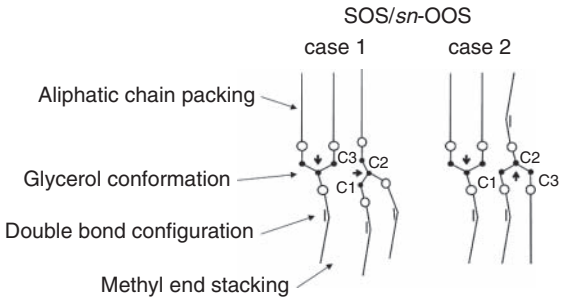

Figure 1.11 Structural models illustrating glycerol groups of a hypothetical molecular compound structure of SOS-*sn*-OOS.

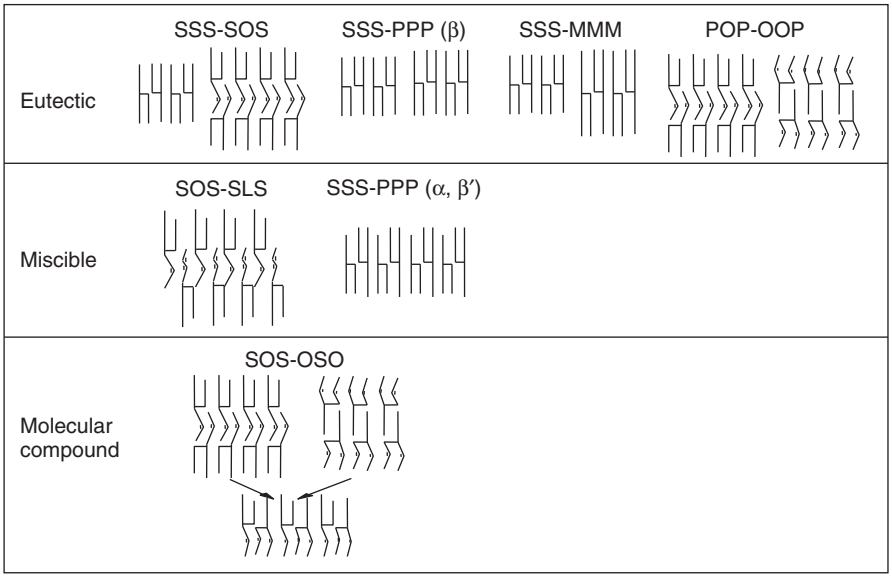

Figure 1.12 Note: For abbreviations, see Table 1.3.

blending of edible and confectionery fats, and the separation of high-melting and low-melting fractions of natural semi-solid oils such as palm oil and milk fat.

It should be noted that the formation of a molecular compound in the binary mixture of POP-OPO was observed, not only in the neat liquid but also in the diluted n-dodecane solution (Ikeda *et al*., 2010).

1.2.5 Microstructure, texture and rheological properties

One of the most important macroscopic physical properties of food fats is the rheology, affecting the spreadability of margarine and other spreads, the 'snap' of chocolate and the smoothness, mouth feel and stability of bulk fats and emulsion products

(de Man, 1999; van den Tempel, 1961). In addition, control of rheological properties is necessary in the production processes in a factory.

The rheological properties of food fats are determined by many factors that can be grouped into two categories (Marangoni and Hartel, 1998):

- internal factors, involving the molecular compositions of fats (TAGs, ingredients and additives), the polymorphism of crystals of the constituent TAGs and the microstructure of fat crystals (morphology, crystal size distribution and crystal network formation);
- external processing conditions, involving temperature variation, shear, flow velocity, and so on.

Of the internal factors, the microstructure of the fat crystals greatly influences the rheological properties (Marangoni, 2005; Marangoni *et al*., 2012).

Much progress has been made by Marangoni and his colleagues on the analysis of fat crystal microstructure. These workers discussed the macroscopic physical properties of food fats in terms of formation and internal assembly of fat microstructures, the rheological properties of the final products being assessed by conventional analytical methods such as thermal measurements, and the determination of solid fat content (SFC) and turbidity. One aspect of their research was focused on the hardness of chocolate made with Salatrim® (a trademark of Pfizer), which is much softer than chocolate made with cocoa butter (Narine and Marangoni, 1999). This phenomenon of hardness is caused by differences in the microstructure of chocolate fats. The TAGs involved in Salatrim® consist of asymmetric molecules ($C_3-C_3-C_{18}$) that result in strong repulsive interactions between TAG molecules in the crystal and induce platelet structures. In contrast, cocoa butter consists of symmetric TAGs such as POP and SOS that pack together densely to make tightly packed crystals. Hence, macroscopic structure is a consequence of the interaction of microstructures and is thus affected by microstructure characteristics. In the case of Salatrim®, a random macrostructure is formed because there are few attractive interactions between the constituent microstructures, thus the macroscopic structure is weak. In the case of cocoa butter, a strong three-dimensional crystal network is formed.

The effects of chemical interesterification on crystallisation, SFC, fat microstructure and rheological properties of various fat blends have also been examined quantitatively with a framework of fractal concepts by Marangoni and co-workers (Marangoni and Rousseau, 1998a, 1998b; Rousseau *et al*., 1998; Tang and Marangoni, 2006).

Most recently, cryo-transmission electron microscopic (cryo-TEM) observation was carried out on edible fat crystals (Acevedo and Marangoni, 2010a, 2010b; Acevedo *et al*., 2011). Blends of tristearoylglycerol (SSS) and trioleoylglycerol (OOO) were prepared in proportions between 20 and 100% w/w to achieve a wide range of supersaturations. Spherulites of SSS were formed by cooling of the molten fat blends, and subjected to mechanical disruption using isobutanol at 10°C for visualisation with the cryo-TEM process. Spherulite structures were broken down into their primary crystals of nanoplatelets of approximate sizes of $150 \times 60 \times 30\,nm^3$ to $370 \times 160 \times 40\,nm^3$

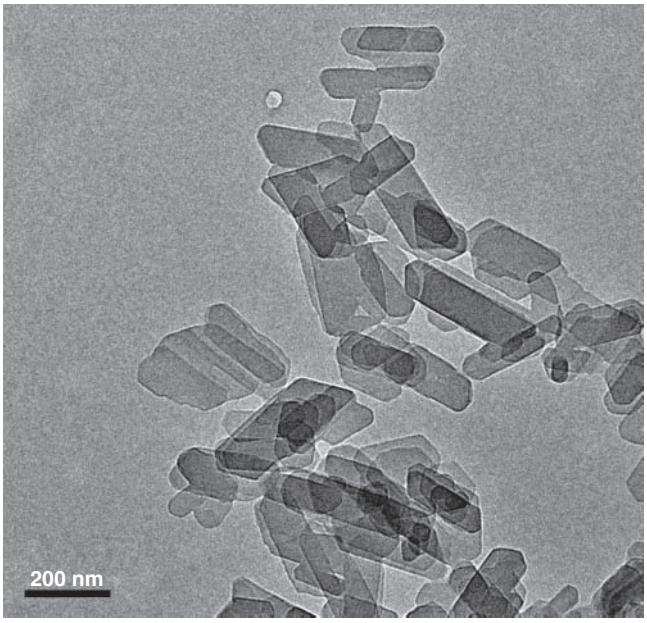

Figure 1.13 Primary crystal particles of SSS in OOO taken with cryo-TEM observation. *Source:* N. C. Acevedo. Reproduced with permission of Dr. N. C. Acevedo, Iowa State University, Ames, IA, USA.

depending on supersaturation conditions (Figure 1.13). This method also allowed the visualisation of bimolecular triacylglycerol lamellae within a cross-section of a nanoplatelet. Acevedo and Marangoni claim that their work opens up the possibility of nanomanipulation of the microstructure of fats to target specific physical properties which govern the texture and rheological properties of edible fats.

1.3 Structure–function relations in food fats

In this section we discuss how the fat structures discussed above influence the macroscopic functions of foods in bulk, in oil-in-water (O/W) emulsion states and in water-in-oil (W/O) emulsion states, looking at specific example materials for each case.

1.3.1 Fats in bulk phase

First, we discuss the physical properties of fats in a bulk phase, taking cocoa butter in chocolate as a model. Cocoa butter forms a continuous fat phase in chocolate, with small particles of sugar, cocoa mass, milk powder (in milk chocolates) and other ingredients, including food emulsifiers, dispersed within it. Compositional effects on rheological and textual qualities in chocolate are largely affected by fats together with sugar, milk and other dairy components and emulsifiers. In particular, sensory

perception of chocolate is determined by the melting behaviour of cocoa butter, whch is affected by the extent of crystallisation of the cocoa butter at ambient temperature, and by the formation of O/W emulsion through phase inversion from W/O emulsion with saliva within the mouth (Afoakwa *et al*., 2007).

1.3.1.1 Crystallisation processes

In the preparation of most commercial-grade chocolates, the temperature treatment of the sample, called tempering, is varied in the manner shown in Figure 1.14, after the mixing, blending, grinding and conching processes. In the following we will describe the events occurring at each stage of tempering in which the extent and polymorphism of cocoa butter crystals are most critical. There are six polymorphs of cocoa butter: Forms I to VI (Wille and Lutton, 1966). The polymorphism of the cocoa butter crystals described above is of Form IV (β' type) and Form V (β type); fat bloom is caused by the transformation from Form V to Form VI. Note that both are of a β-type polymorph. The snapping, appearance and demoulding properties of chocolate are best when the cocoa butter crystals are of Form V (β type), but the formation of fat bloom is a serious problem and is a result of the growth of needle-like crystals after the transformation to and crystal growth of Form VI.

- Stage A (cooling period): This consists of the nucleation and crystal growth of metastable forms of cocoa butter as a result of heterogeneous interactions between cocoa butter molecules and preexisting high melting fats. The metastable forms such as Form IV cause fat bloom if no further tempering is applied.
- Stage B (reheating): This comprises the transformation from the metastable forms to the stable form (Form V) of cocoa butter crystals by raising the temperature. The Form V crystals dominantly formed at this stage serve as seed crystals, leading the rest of cocoa butter liquid to crystallise in Form V. Transformation and further crystal growth of cocoa butter in Form V are accelerated by shear force operated in the tempering machine (Ziegleder, 1985; MacMillan *et al*., 2002).
- Stage C (cooling): crystal growth of Form V develops, with the consequence that shrinkage of the cocoa butter occurs so that demoulding is enabled. Rheological properties at this stage are extremely important in producing chocolate bars or indeed any other enrobed chocolates,[2] the critical step being delicately determined by the solid fat content of the fat.
- Stage D (storage): storage of chilled chocolate enables stabilisation of the fat crystal network and size distribution.

Various techniques have been applied to control the crystallisation and transformation processes of cocoa butter. Blending of different fats with cocoa butter, in

[2]Enrobing is a process involving covering nuts or baked snacks, for instance, with chocolate. In this process, stabilisation of the chocolate viscosity is critical in ensuring the chocolate coating is of uniform thickness.

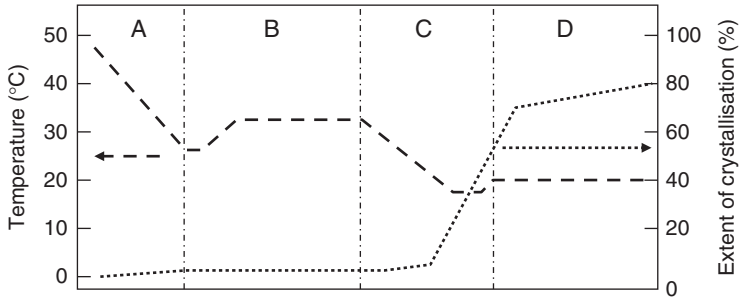

Figure 1.14 Temperature variation with time during chocolate production.

accordance with regulations for blending (which differ from one country to another) is one of the main ways to modify the melting and crystallisation properties of chocolate fats (Timms, 1980, 2003; Faulkner, 1981; Hogenbirk, 1984; Uragami *et al*., 1986, Koyano *et al*., 1993; Ali and Dimick, 1994; Sabariah *et al*., 1998; Narine and Marangoni, 1999). Emulsifiers are added to chocolate fats to modify the rheological properties so that interactions between fat crystals, hydrophilic particles such as sugar and milk powders and water phases are mediated through the emulsifiers (Katsuragi, 1999). The emulsifiers also affect fat bloom stability, acting at growing crystal surfaces of cocoa butter (Aronhime *et al*., 1988).

The addition of high-melting fats having the same crystal structure as Form V, namely form β_2 of 1,3-dibehenoyl-*sn*-2-oleoyl-glycerol (BOB), is quite effective in crystallising cocoa butter in Form V without the need for tempering (crystal seeding; Hachiya *et al*., 1989a, 1989b; Koyano *et al*., 1990). This property was employed to produce enrobing chocolate at temperatures as high as 38 °C at which the viscosity of the chocolate was so decreased that enrobing conditions became very stable. The addition of high-melting fractions of cocoa butter, particularly SOS β crystals, is also employed as a crystal seeding technique. In this case, the temperature at which the seed crystals are added to the molten chocolate liquor should not be as high as those for the case of BOB seed crystals, because of the lower melting temperature of SOS crystals.

External forces, such as shear stress and ultrasound irradiation, are also effective in modifying the crystallisation rate and the polymorphic transformation of cocoa butter, as already described above.

1.3.1.2 Fat bloom problems

Even after the whole production process has been completed, the fat bloom phenomena may arise, causing further problems (Padley, 1997). This can become a serious problem if, during the winter, the chocolate is stored in warehouses, sales outlets or in the home of the consumer, where temperatures can drop to extremely low levels. Similarly, during the summer, temperatures may rise considerably.

Without a doubt, fat bloom is an unwanted phenomenon, which causes serious deterioration of the surface as well as the inner texture of chocolate. Fat bloom frequently occurs when chocolate is stored over a long period at an elevated temperature (Sonwai

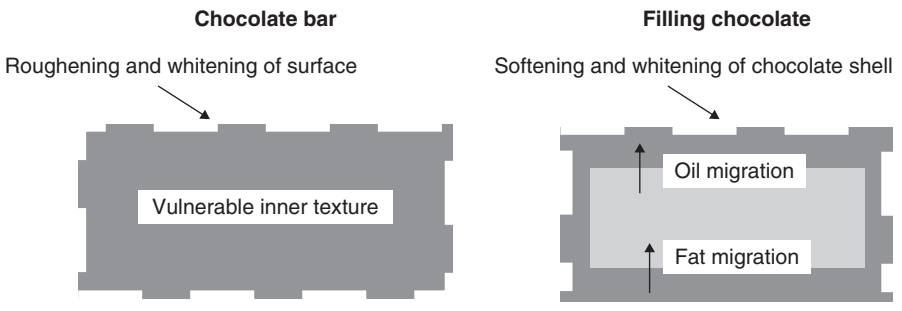

Figure 1.15 Fat bloom phenomena in chocolate.

and Rousseau, 2006) or when optimal tempering was not applied during the production of the chocolate (Lonchampt and Hartel, 2006). Two types of fat bloom are well known, depending on whether chocolate includes an oily filling in it (filling chocolate) or not (chocolate bar), as depicted in Figure 1.15. In both cases, fat bloom makes the chocolate surface white due to light scattering (Briones and Aguilera, 2005), and the inner texture vulnerable due to coarsening of the cocoa butter crystals. Therefore, not only a deteriorated physical appearance but also a sandy taste and worse organoleptic feeling are caused by fat bloom. Many factors are involved in the formation processes of fat bloom (Timms, 2003; Lonchampt and Hartel, 2004) and there is not sufficient space to fully discuss them in this section. Instead, some remarks will briefly be mentioned about fat bloom in terms of crystallisation and polymorphic transformation of cocoa butter crystals.

Common properties of fat crystals in bloomed chocolate may be summarised as follows:

1. Polymorphic transformation from Form V to Form VI of cocoa butter occurs in tempered chocolate. In the case of incompletely tempered chocolate, the transformation from Form IV to Form V also causes fat bloom.
2. Recrystallisation including the polymorphic transformation increases the average size of the cocoa butter crystals from sub-μm (normal chocolate) to tens of μm (bloomed chocolate). As a result, the physical appearance becomes worse and the sharp melting feature disappears.

An interesting observation was made using an atomic force microscope (Rousseau, 2006), that, when the chocolate was stored at temperatures at 25$\sim$27°C, porous surface structures were revealed and crystal growth occurred in the vicinity of the pores. Rouseau indicated a relation of the presence of pores in cocoa butter crystal network in chocolate to the fat bloom formation.

As to the fat bloom in filling chocolate, the migration of liquid oil from inside to outside the chocolate shell and also the migration of the cocoa butter into the filling core occur at the same time (Smith *et al.*, 2007). As the oil content increases by

migration into the chocolate, recrystallisation of cocoa butter is promoted, causing serious fat bloom. The driving forces for such migration processes come from the difference between the melting points of liquid oils included in the filling and the cocoa butter (Khan and Rousseau, 2006). Then the rate of oil migration-driven fat bloom is influenced by the rate of diffusion of liquid oil in chocolate, the interfacial area of the contact of filling with chocolate, the crystallinity of the cocoa butter crystals in chocolate, and the overall rate of recrystallisation of the cocoa butter.

Methods to retard fat bloom formation are, in general, summarised as follows:

1. Decrease the storage temperature (Depypere *et al*., 2009).
2. Select oil components in the filling so that the driving force for oil migration is minimised.
3. Increase the perfection of the cocoa butter crystal network to avoid the formation of defects through which liquid oil may migrate.
4. Use cocoa butter equivalent (CBE) to retard the recrystallisation rate of the chocolate fats.
5. Use food emulsifiers which may promote cocoa butter crystallisation so that tiny and well-dispersed crystals are formed and retard the polymorphic transformation of cocoa butter and the associated re-crystallisation (Lonchampt and Hartel, 2004).

In addition, stability against fat bloom can be improved by fat blending (Lohman and Hartel, 1994; Tietz and Hartel, 2000; Timms, 2003). The effects of the addition of milk fat on the retardation of fat bloom formation have been well known for a long time, but the exact mechanism is still open to question. The true mechanism that underlies the effect of bloom inhibition may involve interactions between the various TAGs involved in milk fats and the polymorphic nature of cocoa butter, and some other components such as minor lipids. It has been reported that the high-melting fraction in milk fat exhibits an anti-bloom effect (Kaylegian, 1997), and that the lipid content, in particular polar lipids such as diacylglycerols and phospholipids, involved in milk fat can have a significant effect on the retardation of fat bloom (Tietz and Hartel, 2000). Bricknell and Hartel (1998) also studied the effects of chocolate microstructures with respect to sugar particles on fat bloom formation. Whatever components are found to improve anti-bloom properties, a microscopic understanding of the fat bloom processes is needed (Sato and Koyano, 2001).

1.3.2 Fats in oil-in-water emulsions

O/W (i.e. water-continuous) emulsions in food are observed in the main body of whipped cream, ice cream, coffee cream, and so on, and their production processes involve pre-emulsification, homogenisation, pasteurisation, rehomogenisation and cooling. Although some details differ from one product to another, the most preferable physical properties of O/W emulsions containing a fat phase are optimal melting and solidification properties, emulsion stability when chilled during storage and during

the final usage stage, and a good crystal morphology and network exhibiting optimal rheological and whipping properties. Partial coalescence of oil droplets is one of the prerequisites for making whipped cream and ice cream. Many factors are involved in the partial coalescence of O/W emulsion droplets, and fat crystallisation is the key to them (Frederick *et al*., 2010). The interactions of emulsifiers and proteins in the oil and water phases are of immense significance but are beyond the scope of this chapter.

The crystallisation of solid fats in O/W emulsion droplets influences the stability, rheology and appearance of emulsions (Boekel and Walstra, 1981; Boode *et al*., 1991; Dickinson and McClements, 1996, Thanasukarn *et al*., 2004, 2006). Furthermore, fat crystallisation largely influences the flavour release (Ghosh *et al*., 2006, 2007) and the digestibility of lipids (Mun *et al*., 2007). Therefore, it is important to analyse the fat crystallisation processes in O/W emulsions. The rate and extent of crystallisation, the effect of polymorphism and emulsifiers, the influence of emulsion droplet size and droplet–droplet interactions and the effect of rate of cooling and subsequent temperature history on fat crystallisation behaviour must be clarified (Povey, 2001; Coupland, 2002).

The elucidation of these complicated crystallisation processes in O/W emulsions can be achieved through two-step studies: (1) by monitoring *in situ* the crystallisation process under a well-defined simple model; (2) by extending this model to more complicated systems containing polymorphic fats under varying temperature treatments, and so on.

For this purpose, ultrasonic velocity measurement has been employed to monitor *in-situ* crystallisation processes (Dickinson *et al*., 1991; Gulseren and Coupland, 2007a, 2007b) based on the principle that the event of crystallisation of a liquid oil phase dispersed in a water phase can be monitored by means of the ultrasonic sound velocity, which increases as the transformation from the liquid to the solid phase progresses. In addition, DSC is also effective for monitoring fat crystallisation in O/W emulsions (Katsuragi *et al*., 2001).

Our recent studies on the kinetic properties of the nucleation processes of palm oil, palm mid-fractions (PMFs) and palm kernel oil in O/W emulsions have shown a remarkable acceleration when highly hydrophobic food emulsifiers such as sucrose fatty-acid oligoesters (SOEs) and polyglyverine fatty-acid esters (PGFEs) are added in the oil phase (Awad and Sato, 2003; Sakamoto *et al*., 2004; Arima *et al*., 2007; Arima *et al*., 2009). Furthermore, the simultaneous addition of two types of SOE additives having hydrophobic and hydrophilic properties to the PMF emulsion remarkably improved the emulsion stability, when the PMF was crystallised in the droplets and fat-crystallised emulsion was stored at a chilled temperature over a long period (Arima *et al*., 2009). In addition, SR-μ-XRD analysis has unveiled that the texture of the PMF crystals in an emulsion droplet changed with the SOE additive compared with the droplet without the additive, as summarised in the following (Arima *et al*., 2009).

Scanning small-angle SR-μ-XRD experiments were performed by irradiating a synchrotron radiation X-ray microbeam having a width of $5 \times 5\ \mu m^2$ at different positions in a 50 μm-diameter emulsion droplet after the crystallisation of PMF by chilling the emulsion at 5°C. Every SR-μ-XRD pattern was recorded with a two-dimensional

(2D) detector, which enabled spatial analysis of polymorphic structures and the orientation of lamella planes of PMF crystals at different positions inside the emulsion droplet. Particular attention was paid to compare the crystallisation behaviour of the PMF in two types of emulsion droplets: hydrophilic polyoxyethylene sorbitan monooleate (Tween 80) alone (Tween 80 emulsion), and Tween 80 and hydrophobic sucrose palmitic acid oligoester (P-170) (Tween 80+P-170 emulsion). The DSC study revealed that the crystallisation temperature of PMF in the Tween 80+P-170 emulsion droplets increased by 3°C compared to the Tween 80 emulsion because of the effects of the P-170 additive in promoting the crystallisation of PMF in the emulsion droplets.

The SR-μ-XRD studies revealed the following results:

1. The lamella planes of the PMF crystals near the outer edges of the droplet in the Tween 80+P-170 emulsion were mostly parallel to an oil-water interface, whereas the lamella planes of the PMF crystals were not always aligned with the oil-water interface in the Tween 80 emulsion droplet.
2. The degree of orientation of the lamellar planes of the PMF crystals, which were evaluated from the values of full width at half maximum of SR-μ-XRD patterns with respect to the χ-extension ($\Delta\chi$, see Figure 1.6 (c)), was remarkably higher in the Tween 80+P-170 emulsion than in the Tween 80 emulsion.
3. Polymorphic transformation from α to β′ of PMF in the Tween 80+P-170 emulsion was retarded, compared to that in the Tween 80 emulsion.

The conclusion (1) was drawn from the χ-extension patterns acquired at the pixel positions in the two droplets of Tween 80 emulsion and Tween 80+P-170 emulsion noted by A through H, both of which are placed more or less equidistantly along the circles near the oil-water interface (Figure 1.16). In the case of the Tween 80+P-170 emulsion droplet, every pixel had single or double peaks, and the double peaks included sub-peaks separated by 50° at most. Furthermore, the differences in the χ values of the χ-extension peaks corresponded well with the differences in the positions of every pixel in the anticlockwise χ direction, except for pixel G. This tendency is clearly indicated by the arrows in Figure 1.16 (b), as the χ values of the peaks increase straightforwardly as the position moves from A to H except for pixel G. By contrast, the χ-extension patterns from the Tween 80 emulsion droplets showed broader peaks and no correlation between the χ values of the χ-extension peaks with the differences in the positions in the droplet, as shown in Figure 1.16 (a).

From these results, it was confirmed that the P-170 additive caused interfacial heterogeneous crystallisation (Krog and Larsson, 1992) through hydrophobic interactions at the oil-water interfaces in the emulsion, which influenced the arrangements of fat crystals so that the lamellar planes of fat crystals were parallel to the oil-water interface (Figure 1.17). Thus, crystallised PMF emulsion droplets were stabilised against partial coalescence due to the irregular morphology of the fat crystals in the droplet, which may occur in the droplets without the additives.

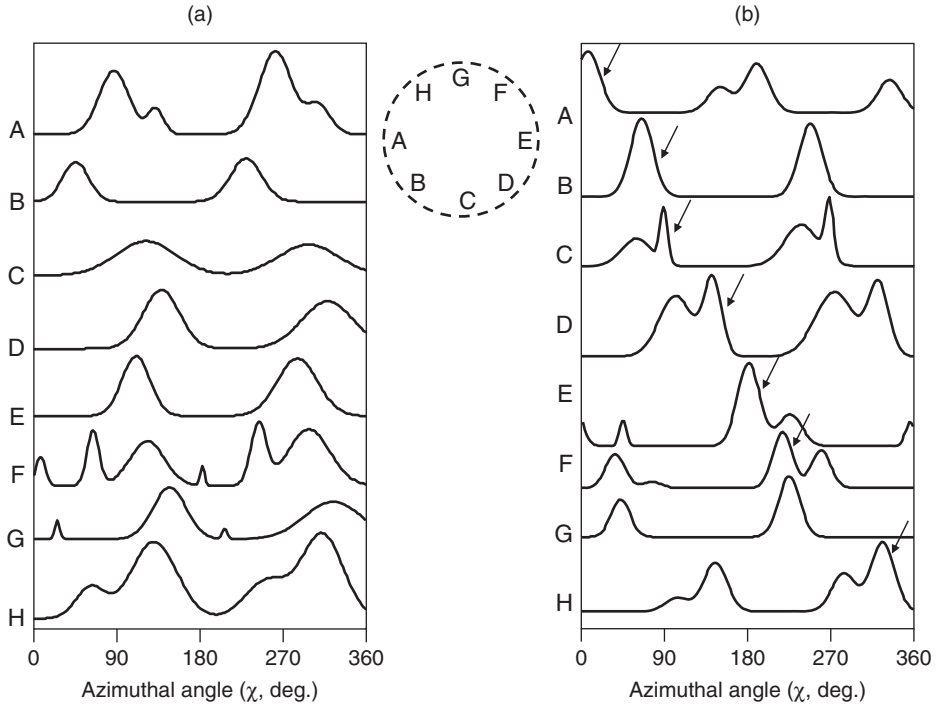

Figure 1.16 χ-extension of the SR-μ-XRD patterns of PMF crystals in emulsion droplets. (a) eight positions of the Tween 80 emulsion droplet; (b) eight positions of the Tween 80+P-170 emulsion droplet.

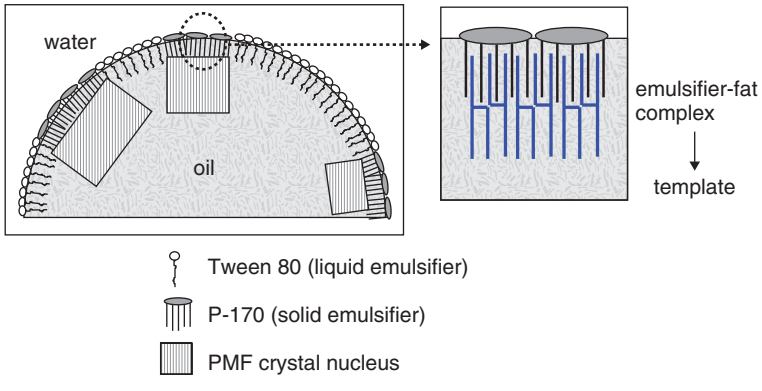

Figure 1.17 A model of interfacial heterogeneous crystallisation of fats in O/W emulsion with the additives.

1.3.3 Fats in water-in-oil emulsions

Margarine and spreads are typical food fats found in the form of W/O emulsions and consist of vegetable fats and oils. The optimal functional, and by implication, physical properties required of margarine and spreadable fats are spreadability, plasticity and consistency (de Man, 1983; de Man *et al*., 1992; Bot *et al*., 2003; Chrysan, 2005). Stabilisation of water droplets against coalescence and water-oil separation is also very important (Rousseau and Hodge, 2005; Ghosh and Rousseau, 2009; Rousseau *et al*., 2009). For this reason, semisolid fats are to be preferred, with optimal SFC values of 50%–60% at around 5°C, which gradually decrease with increasing temperature, until complete melt at about 38°C. Furthermore, special texture and spreadability are needed for margarine for industrial uses, such as the roll-in type used in bakeries. Fat blending of high-melting-point (40–55°C), medium-melting-point (20–40°C) and low-melting-point (< 20°C) fats has been tried, and it has been found that the medium-melting-point fats play an important role, exhibiting optimal spreadability for margarine.

The preferable polymorphic form of margarine or spreadable fats is β′, since β′ crystals exhibit a very fine crystal network which comprises two types of particle–particle interactions: primary and secondary (de Man, 1982; Naguib-Mostafa *et al*., 1985). Primary interactions with strong binding forces form a three-dimensional crystal network throughout the continuous fat phase. Secondary interactions result in small crystals with weaker binding forces. The transformation from the β′ to the β form causes serious deterioration, giving a sandy texture, hardening, reduced spreadability and oil–fat separation and coalescence of water droplets (emulsion instability) in extreme cases. These properties result from, in part, granular crystals of the β form, which tend to grow with rectangular needle morphology (Bennema *et al*., 1992).

In connection to the fats to be employed for margarine and fat spread, *trans* fat alternative issues should be discussed. Due to health claims, reduction of the use of *trans* fats, which are produced by partial hydrogenation of vegetable oils, is required. From the point of view of physical and chemical functionality, however, *trans* fats possess such advantageous properties as a fine crystal network, easy control of melting range, and high stability against oxidation. The fats which are employed as *trans* fat alternatives (Kodali and List, 2005), must possess these properties to be employed for frying oil, margarine, fat spread, shortening, confectionery, etc. The technologies for the production of *trans*-free fats or low-*trans* fats are the combination of esterification and full-hydrogenation of vegetable oils, the separation of semi-solid oils such as palm oil and palm kernel oil, the esterification of semi-solid oil, the use of high-melting emulsifiers, the use of wax crystals, etc. In particular, palm oil may be a promising resource for the *trans* fat alternative materials (Smith, 2001; Aini and Miskandar, 2007). Despite numerous efforts, however, there still remain many disadvantageous problems in *trans* fat alternative technologies, one of which is the formation of granular crystals during long storage of the end products.

Figure 1.18 shows the formation of granular crystals in a model margarine containing the oil and fat phase (70% in total), including fully-hydrogenated rapeseed oil (2 wt.%), soybean oil (48 wt.%) and palm oil (20 wt.%). It is evident that granular

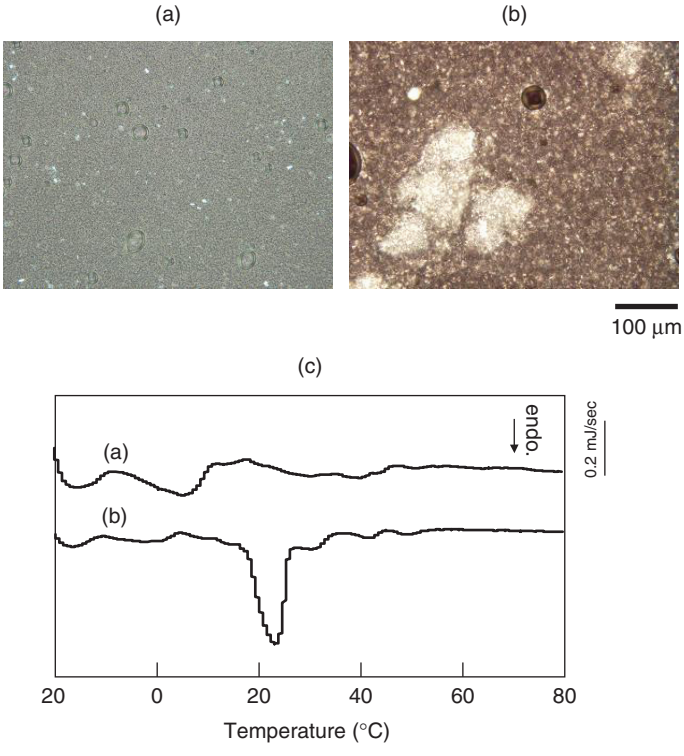

Figure 1.18 Polarised optical microscope images of palm oil-blended margarine. (a) 1 day after keeping at 5°C; (b) 5 days after thermal thawing; and (c) corresponding DSC heating thermopeaks.

crystals grew over 5 days under thermal thawing between 7°C and 15°C for every 12 hours, and the DSC heating thermogram of the granular crystal portions showed a large melting peak around 23°C (Tanaka *et al*., 2009). Conventional XRD study of the granular crystals showed that β-fat crystals of a TCL structure melted below the melting of β′-fat of a DCL structure. Such granular crystals cause a sandy taste and bad physical appearance of the end products, and formation of such crystals should be avoided.

The formation mechanism of granular crystals in fat blends similar to those of margarine fats containing palm oil and other vegetable oils was analysed at the polymorphic level (Miura and Konishi, 2001; Tanaka *et al*., 2007; Watanabe *et al*., 1992). Although palm oil is categorised as a β′-tending fat, fats containing palm-oil fractions show formation of granular crystals in long-term storage. Chemical and physical analyses of TAG compositions, polymorphism and melting points of the granular crystals led to the conclusion that the granular crystals are of β polymorph of POP (1,3-dipalmitoyl-*sn*-2-oleoyl-glycerol). As shown in Figure 1.19, an SR-μ-XRD study showed that the fat crystals of the DCL structure were observed in the granular crystals (region A). However, the fat crystals of the DCL and TCL structures were simultaneously observed

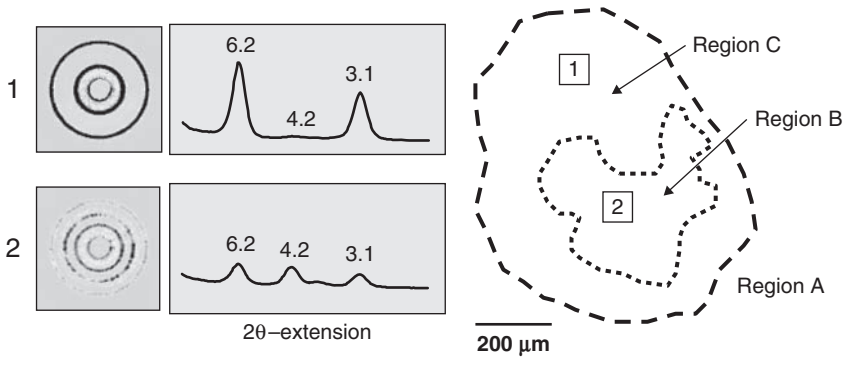

Figure 1.19 SR-μ-XRD patterns taken at two positions in a granular crystal formed in palm-based margarine. Note: Unit nm.

in the central region of a granular crystal (region B, position 2 long spacing values of 6.2 nm and 4.2 nm and 3.1 nm), whereas the fat crystals of the TCL were predominantly present in an outer region of a granular crystal (region C, position 6.2 nm and 3.1 nm). From these results, the microstructures and the formation processes of granular crystals are closely related to the fractional crystallisation of the β form of POP promoted by crystallisation and transformation of PPP and SSS fractions (Tanaka *et al*., 2009).

Various ways of preventing crystallisation and transformation into the β form in margarine and fat spread have been developed, through many techniques, as reviewed by Chrysan (Chrysan, 2005). For example, one can choose β′-tending fat resources (such as cottonseed oil) and blend them with β′-tending fats (such as soybean, safflower, etc.) (Wiedermann, 1978). One can add food emulsifiers that retard transformations from the β′ to the β form (Aronhime *et al*., 1988; Garbolino *et al*., 2005; Sato and Kuroda, 1987). One can add diacylglycerols (Mohamed and Larsson, 1992), or one can use interesterification techniques with different fats and oils (Chrysan, 2005).

The formation of fat crystals in a continuous oil phase is largely influenced by food emulsifiers, which are employed not only for emulsification itself, but to control the fat crystallisation occurring at the water-oil interfaces. Such effects were recently observed in W/O emulsions by adding a high-melting monoacylglycerol (Wassell *et al*., 2012) and by applying shear (Ghosh and Rousseau, 2012).

1.4 Conclusion

The crystallization and transformation properties of fat materials deserve further study regarding fundamental aspects, as discussed in this chapter. It is worthy of note again that the interrelations between polymorphism, solidification kinetics and crystal particle networks underlie the apparently complicated physical behaviour of various food fats. Although not reviewed in this chapter, the physical properties of fats in

organogels and aerated systems (whipped cream, ice cream, aerated confenctions, etc.) are very important.

As for experimental techniques, many advanced methods such as synchrotron radiation X-ray diffraction, ultrasonic velocity techniques, AFM, cryo-TEM technique, etc., have great potential and applicability in such studies. Further research should be carried out in this area.

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2
Bakery fats[1]

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2.1 Introduction

Fats and oils have been used throughout the years in food preparation to provide structure, flavour and nutritive value. Geography and agricultural practices have influenced the fat used in food preparation. For example, people in northern climates have tended to use plastic fats such as butter and suet, whereas in more southerly climates liquid oils such as olive oil are more popular.

Economic conditions and population growth led to the invention of margarine (Young and Wassell, 2008a) as a substitute for butter, and developments in refining technology and fat modification techniques allowed the use of a widening range of fats in margarines and as alternatives for lard and suet.

Progress in the technology of butter production, oil refining and modification and in margarine and shortening manufacture has provided the food processor with a wide variety of fats and oils with differing functional properties to meet product and process needs.

The structural and crystalline properties of fats determine their functionality in food. This is readily illustrated in the manufacture of baked products such as short pastry, cake and puff or flaky pastry. Advances in emulsion technology and emulsifier systems have been applied to bakery products, giving improvements in bread volume and shelf-life as well as leading to recipe balance in other baked products and altering the requirement for plastic fats so that fluid and liquid shortenings can be used (Podmore, 1996). The use of powdered fat and fat powders can add convenience in a number of food sectors (e.g. in prepared cake mixes, toppings and bread improvers).

In the more developed countries, nutritional demands (Mozaffarian *et al.*, 2010; NICE, 2010), combined with rapid changes in lifestyles and eating habits which require quicker and easier food preparation at the point of use, have challenged suppliers in several important ways. These demands require the manufacturer of oils and

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fats to deliver products with the desired functionality but with improved nutritional and health characteristics – such as lower fat content, high in polyunsaturated and mono-unsaturated fatty acids and with a lower component of '*trans*' fatty acids. Since publication of the first edition of this book (Podmore, 2002), much of the aforementioned has already gone through significant change. More changes are now driven by further nutritional requirements to meet new legislation (SACN, 2007; Stender *et al*., 2006, 2009; Wassell *et al*., 2010a). Continued developments will lead to a search for novel oils and altered approaches to blending and modification (Marangoni, 2007; Shigemi, 2006; van Duijn *et al*., 2006).

The acceleration of economic globalisation has created a situation where consumers in once so-called 'less-developed countries' also require the latest and most available technologies. Growth economies such as Brazil, India, and China have enormous populations to feed. However, as these economies continue to strengthen, they are already developing the technology to exploit oils that are readily available to them (Wang *et al*., 2012). For instance, Malaysia and Indonesia use the fractionation process and some of the most up-to-date technology to produce a range of palm-oil-based bakery fats and margarines.

Fats in their natural state have been used as a bakery ingredient for countless years to improve the palatability and nutritive value of foods. However, increasing industrialisation and population expansion in the later part of the nineteenth century led to a shortage of traditional fats. These conditions stimulated the invention of the first substitute food – margarine. Margarine was invented in 1869 by a French chemist, Mégè Mouries (French patent 86480), and the invention was exploited by Dutch butter exporters. Starting from modest beginnings, the margarine industry has developed into an important and sophisticated food-processing industry. Additionally, it has had important repercussions on the agricultural industry, for as margarine production has expanded, it has stimulated an expansion in the production and export of tropical oils and oilseeds, and these now represent a substantial proportion of world trade in agricultural products.

Progress in the understanding of the function of the ingredients in food now means that the fat processor and food manufacturer can work together to improve the food products available to the consumer. Crystalline form and product consistency have a profound influence on the performance of fats in foods, particularly in baked products. Thus, an understanding of physical properties such as crystallisation behaviour, polymorphism and crystal structure in fats is necessary to control production processes so that they can be 'tailor-made' to suit particular applications.

2.2 Production of margarine and shortening

The modern processor has available bland oxidatively stable and low coloured edible oils of vegetable and animal origin, achieved by the processes shown in Figure 2.1. The quality standards for edible oils continue to be raised and so handling and refining practices are being continually improved which, combined with a clearer understanding

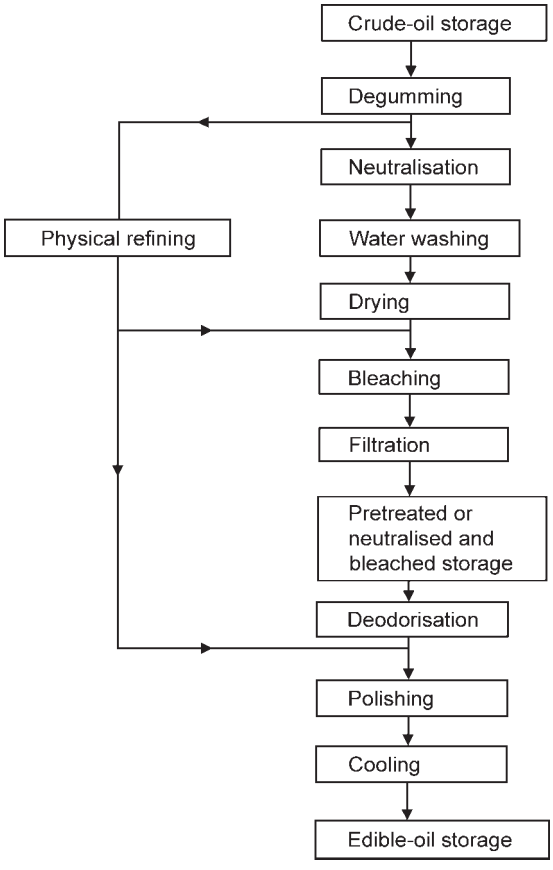


Figure 2.1 The stages of oil and fat refining.

of the influence of the minor components on shelf-life and flavour stability, leads to modified refining methods.

The refining process must be carried out to remove those impurities that have an adverse effect on oil quality but to avoid damaging the triacylglycerols. There is also a requirement that beneficial minor components be retained. Important minor components to be retained are tocopherols and phytosterols, which are biologically active and show antioxidant activity. Lower-temperature methods of refining and deodorisation are being applied to minimise this loss.

The refiner has the option of chemical or physical refining. The choice between the two methods depends on the economics of the processes. Most types of vegetable oil can be physically refined, a major exception being cottonseed oil because of the presence of gossypol (de Greyt and Kellens, 2000). These natural oils can be modified by hydrogenation, interesterification and fractionation, used either singly or in combination, to produce fats that bear no relation to the original material.

In the 1990s there was a change in emphasis away from hydrogenation as the way of providing the hard stock for the formulation of shortening and margarine oil blends. There were two main reasons for this change. The first reason is the ready availability of relatively inexpensive palm fractions and increasing confidence in their performance in bakery fat formulations (Sundram, 2005). The second reason is the finding that '*trans*' fatty acids are implicated in the development of coronary heart disease (Willett *et al*., 1992; Stender and Dyerberg, 2003). Since the hydrogenation reaction can generate high levels of '*trans*' fatty acids, there has been a trend toward reducing reliance on hydrogenated oils in formulations. Instead palm stearins from the fractionation of palm oil have been found to be a valuable alternative to hydrogenated oils (Morin, 2006). However, the use of palm stearins, with their flat melting profile, gives rise to higher solid fat contents in the 30–40°C temperature range. This has led to increased use of interesterification in order to lessen this effect.

Blending oils and fats to achieve the required solid-to-liquid ratio is a major part of the processor's skill as it is critical to the firmness and texture of the finished product. Added to this is the influence of the crystal habit of the oils and fats selected and their polymorphism. Thus, the processor requires an understanding of these characteristics when preparing blends for margarines and shortenings (Narine and Marangoni, 1999; Wassell and Young, 2007).

Irrespective of how the hard stock is obtained, the basic requirements for blending are unchanged in that the desired solid-to-liquid ratios and crystallising characteristics be achieved in order to provide a stable finished product of the correct firmness, texture and crystal form.

2.3 Crystallisation behaviour

In common with all other long-chain molecules, fats and fatty acids exhibit polymorphism – that is, the ability to exist in more than one crystalline form and so possess multiple melting points. Triglycerides occur in any one of three basic polymorphs, designated α, β′ and β (Bailey, 1950):

- the α form is the most loosely packed arrangement and hence is the least stable and has the lowest melting point;
- the β′ form is more stable than the α form but transforms irreversibly to the β form;
- the β form is the most closely packed and is the polymorph with the highest melting point.

Work by Timms (1984) describes the behaviour of a monoacid triglyceride, showing that, with rapid cooling, the α form is obtained which, on slow heating, melts to resolidify and give the β′ form. After further slow heating, it melts and resolidifies in the β form. Most fats possess an α form that is so unstable that it can be ignored; some also possess both β′ and β forms; others possess only a stable β′ or a stable β form. Some examples are shown in Table 2.1.

Table 2.1 Crystallisation performance of some natural edible oils.

β′ form	β form
Cottonseed oil	Soybean oil
Palm oil	Sunflower oil
Tallow	Groundnut oil
Butter fat	Coconut oil
High-erucic-acid rapeseed oil	Palm kernel oil
	Lard
	Low-erucic-acid rapeseed oil

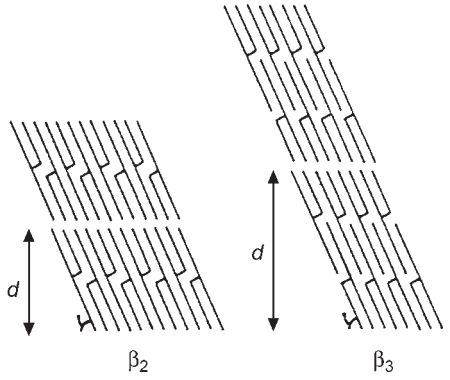
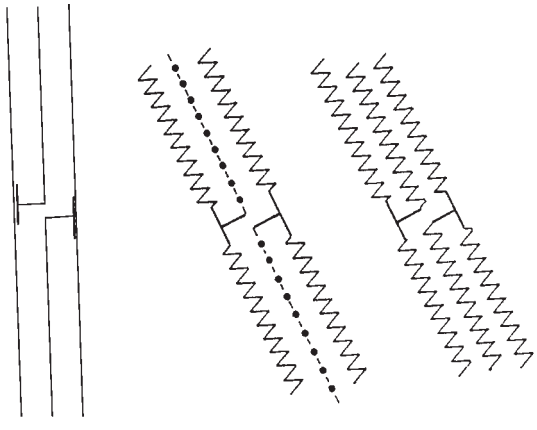


Figure 2.2 Triglycerides in the β_2 and β_3 polymorphic forms.
Source: de Jong (1980) as cited in Timms (1984).

X-ray studies on tristearin have shown that the triglycerides pack side by side in separate layers. The triglyceride molecules form the shape of a chair, and the molecules are arranged in pairs, head to tail. Figure 2.2 shows the packing arrangements possible in pairs of two or three fatty acids. Figure 2.3 shows the main features of the molecular packing of the three polymorphs of tristearin. It can be seen that for the α form, the fatty-acid chains are perpendicular to a basal plane (that plane containing the methyl end-groups). In the β′ form, the fatty-acid chains are tilted at an angle to the basal plane. Each fatty acid has its hydrocarbon chain in regular zig-zag formation in a plane perpendicular to its neighbour. The β form, which also has the fatty acids tilted to the basal plane, has the zig-zag planes of the hydrocarbon chains parallel to the same plane. These descriptions show an increasing closeness in packing and hence increasing melting point and stability.

Where there is a wide variety of molecular size and type of triglyceride, (e.g. cottonseed oil and beef tallow), the β′ form rather than the β form predominates because it is more able to accommodate the distortion of the chain packing necessary for a solid solution.

From the preceding comments it can be seen that each triglyceride has its own polymorphic and melting behaviour. However, in a mixture of triglycerides the individual



	α	β'	β
	Vertical oscillating chains	Tilted chains with adjacent zig-zags in different planes	Tilted chains with all zig-zags in same plane
Short spacing:			
	0.414 nm	0.418 nm 0.378 nm	0.368 nm 0.386 nm 0.459 nm
Layer spacing (*d*):			
	5.06 nm	4.68 nm	4.52 nm
Melting point:			
	54°C	64°C	73°C

Figure 2.3 Comparison of the polymorphic forms α, β′ and β, as exemplified by tristearin (StStSt).

triglycerides do not behave independently but take on a totally new character in terms of crystallisation behaviour. The systems are so complex that it is easier in the case of natural fats to describe them in terms of their different phases; thus, the physical properties of a fat can be discussed in terms of its phase behaviour. In a fat or fat blend at a given temperature, there will always be a liquid phase and a solid phase, and the solid phase can have several components, which can change with temperature and composition.

A phase diagram (Birker and Padley, 1987) can be used to show how blended fats interact, for example, to produce minima points (eutectic behaviour) or maxima points (solid solutions). Where the fats are compatible, the isosolids line is horizontal for all compositions.

Thus, to summarise, the major features defining the firmness, texture and performance of a blended margarine and shortening are (Opfer, 1975):

- the proportion by weight of crystals, which is governed by the solid-to-liquid ratio;
- the melting point of the crystals;

- the crystal geometry; that is their size, shape and alignment;
- the degree of formation of mixed crystals;
- the ability of the crystals to flocculate into a network which increases firmness.

Normally, the greater the quantity of solid triglyceride, the greater the rigidity of the network due to the increased number of crystals and cohesive forces between them in the bulk and at the interface (Ghosh *et al*., 2011; Wassell *et al*., 2012). The latter prevent flow at stresses below those appropriate for the desired consistency. Changes in temperature will obviously change the product's firmness and plastic behaviour by altering the quantity of crystals present, the hardness and the viscosity of the liquid triglycerides.

The crystal modification present will also influence the firmness and texture of the finished product in that the smaller and finer β′ crystals can stabilise more liquid component than can the larger and coarser β crystals.

Fat crystallisation is initiated by nucleation in a supercooled system. In the manufacture of margarine and shortening, the cooling rate, agitation and degree of supercooling, control the rate of crystal growth and thus crystal size and crystal agglomeration, which affect the textural and melting properties of the fat product (Basso *et al*., 2010; Humphrey and Narine, 2004).

Bell *et al*. (2007) neatly describe the effects of shear where they show that the rheological changes of a plastic shortening can be related to the size and number of spherulites that determine the space occupied in the matrix by the crystals. They also say that the extent of structuring of a given semi-plastic shortening is also shown to be heavily dependent not only on the dynamic shearing conditions during crystallisation, but also on the triacylglycerol composition. These authors also note that a higher solid fat content leads to a higher value of the elastic modulus (G'), and of course the nature of this is affected by the liquid-to-solid ratio, the crystal size, packing, shape, and polymorphism.

As stated previously, occurrence of the β′ polymorph can be highly influenced by the presence of, the type of, and amount of fats present, where their natural polymorph is β′. The presence of a percentage of *trans* isomer also affects the fat crystallisation kinetics, where it can influence the formation and crystal form towards the β′ form, even though the natural tendency is towards the β form. Therefore, replacing the *trans* isomer may require that another kinetic mechanism is present to drive polymorphism towards the preferred form. Thus, simply decreasing *trans* fats could negatively impact the functionality unless care and attention are taken to crystal form details (Flöter and van Duijn, 2006; Mayamol *et al*., 2004; Sato and Ueno, 2011).

The need to improve the rate of crystallisation is highlighted in Figure 2.4, which shows three different fat blends having similar SFC profiles but quite different crystallisation kinetics.

Improving the rate of crystallisation of *trans*-free fat blends can be highly beneficial, allowing the fats to reach a specific SFC, often within certain limitations of the process. This issue is fundamentally critical, because where a given fat blend is not optimally crystallised during manufacture, for example, margarine, then 'uncontrolled'

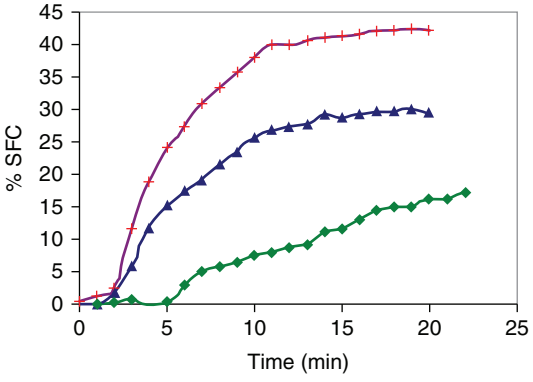


Figure 2.4 Rate of crystallisation for three different fat blends which have similar SFC, while measured under static conditions using Bruker p-nuclear magnetic resonance. *Source:* Wassell and Young 2007. Reproduced with permission of John Wiley & Sons.

post-crystal changes will occur. Therefore, simply selecting a portfolio of oil blends and expecting these to run on 'standard' process conditions is not always a guarantee of success. In some cases manufacturers have been running long-established oil blends on old 'trustworthy' processes and equipment for many years. However, the increasing necessity to either reduce *trans* isomers and/or total saturates, to produce alternative oil formulas with similar rheological profiles, can be complicated and troublesome, especially when attempting to maintain economically viable production rates. If the plant operator's scope to compensate within the process, that is, increase supercooling, etc. is exhausted, then other strategies will have to be sought out and adopted (Wassell and Young, 2007).

Control of the rate of crystallisation can be governed by the addition and concentration of additives (Smith *et al*., 2011). Kristensen and Wassell (2006) have shown the effect of diacylglycerol (DAG) adjusted palm oil (Figure 2.5). The increasing use of palm oil to solve the *trans*-free problem places further pressure to gain control over crystallisation, since it is known that the presence of DAG slows the crystallisation process and changes the melting behaviour (Siew, 2002; Siew and Ng, 1990). The slowing of the crystallisation process leads to post hardening during storage of palm-based margarines. By gaining control over the DAG content of palm oil, it is observed that not only control but also improvement of the crystallisation rate is possible. Figure 2.5 shows the effect of reintroducing DAG into the palm oil under controlled conditions. The DAG was first adjusted enzymatically and then added again, so that the concentrations achieved were 1.7, 3.7 and 5.7% (Kristensen *et al*., 2005). The results showed that the lower the DAG concentration, the faster the rate of crystallisation, which in turn has other process implications of shorter induction times and higher SFCs compared to samples where the DAG content had not been adjusted. It would be interesting to observe the effects of crystallisation on palm oils containing higher (>10%) DAG concentrations.

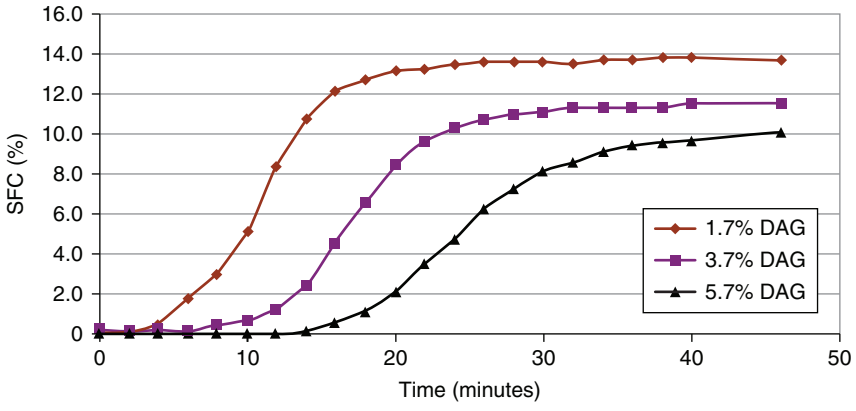


Figure 2.5 Crystallisation curve of palm oil with varying amounts of DAGs (1.7%, 3.7% and 5.7% DAG); crystallisation temperature 25°C.
Note: The reference product contains 5.7% DAG.
Source: Wassell and Young 2007. Reproduced with permission of John Wiley & Sons.

2.4 Processing

The vast majority of margarines and shortenings are now manufactured on scraped surface heat exchangers (Joyner, 1953), and although there is varation in design, these all work to very similar operational principles. The tubular heat exchanger, known as 'A-units', are made of two concentric tubes and in the annular space thus created a compressible refrigerant is circulated. The inner tube has a heated shaft which runs the length of the tube on which are mounted floating or tension-mounted scraper blades. As the shaft rotates, these blades scrape the internal surface of the tube.

In the process the liquid emulsion or fat blend is pumped along the tube at a fixed speed and the rotating blades remove the chilled product from the walls. This constant renewal of the cooling surface and the turbulence created leads to supercooling and the initiation of crystal nuclei and hence crystallisation. The supercooled and partly crystallised product can then be pumped to a worker unit where crystallisation is completed and the heat of crystallisation is released.

It can be seen that it is important that the flow rate of product does not vary, irrespective of the fact that, as it is chilled, there is a viscosity increase. There is also a temperature differential across the product flow, leading to a range of crystalline compositions being created; so, in order to minimise product variability, tight and continuous control must be maintained at all stages of the evaporation rate of the refrigerant.

The worker unit (or 'B-unit') is also tubular and can contain a system of beaters to ensure that the crystal structure is developed in a dynamic environment, hence controlling the size of the crystal aggregates and giving a smooth plastic texture. It is also possible to make no provision for mechanical agitation to induce growth of large crystals from the mass in order to provide a product firm enough to pack into wrapped units.

Systems of much greater complexity are now available to improve the texture and plasticity of a widening range of blend types and that meet greater specificity in the requirements of the user. Factors such as shaft rotation speed, scraper blade design, size of the annular space and size and location of worker units, can all affect the final texture of the product. An excellent overview of these factors is given by Alexandersen (2005).

2.5 Plastic bakery fats

Fats and oils in their natural state have been used as a bakery ingredient for many years to improve the mouth feel and palatability of the finished foods. The growing sophistication of the bakery industry, in terms of both product range and automation techniques, requires greater control of the ingredients used, including fats. The bakery industry is also now becoming more concentrated, with bakery plants becoming larger, more automated and more specialised. These changes, in turn, mean that process control can be substantially improved and fats specified to meet precise performance criteria.

In designing shortenings and margarine for bakery use it is important to understand the application so that the functional properties required can be designed into the product by way of the oil blend used. This is particularly important where relatively inexpensive palm oil and its fractions are used. However, once the blend is selected, the quality and the process control techniques necessary to maintain the desired properties must be applied (Cerdeira *et al*., 2006). Wassell and Young (2007) suggest that apart from the oil or fat blends, the combination of emulsifiers and other minor components (Smith *et al*., 2011), are also important as their interaction and influence on the fat components can change the crystallisation kinetics and adjust the texture, hence a multidisciplinary approach to solving some these problems is favoured (Wassell *et al*., 2010a).

Modification techniques have been shown to offer the chance to minimise and control the *trans* content of oil blends, and can be used to successfully formulate *trans*-free hard stocks. However, the combination of these techniques leads to a greater variety of hard stocks with a wider range of physical properties such as solid fat phase and melting point behaviour. This is particularly important for fats where they are expected to have specific performance. Addressing the functionality issues of replacing *trans* fatty acids, SFC, and crystalline elements are the main physical success criteria of a *trans*-free solution. Therefore, to effectively solve the challenge, performance phenomena such as creaming, crystallisation and emulsification also need to be considered. Thus, to exclusively focus purely on the physico-chemical aspects but neglect the fat's required functional role within the final application is likely to lead to serious and significant developmental problems. The dangers of addressing SFC in isolation when considering the degree of saturation or indeed *trans* fatty acid content of commercial fat blends are highlighted in Table 2.2.

Attempts to match the physical properties of a commercial fat blend to a specific application are often based on the solid fat profile, melting point and textural qualities,

Table 2.2 Three commercial fat shortening/margarine blends of similar SFC at the working temperature of 20°C but with quite different degrees of saturation and *trans* content (inter blend = 60% Pst/40% PK).

Fat blend	1	2	3
Palm oil	20	40	35
Rape seed oil	30	30	40
hPO_mp43			25
Inter blend		30	
hSB_mp35	50		
SFC% (Bruker pNMR)			
5°C	46	44	42
10°C	40	37	37
20°C	19	19	20
30°C	5	7	8
35°C	3	5	6
40°C	0	2	0
Melting point (°C)	33.6	41.5	37.8
Nutrition%	1	2	3
sats.	24	42	34
monos.	38	42	47
polys.	12	15	16
% *trans* acid content	26%	<1%	3%

Source: Wassell and Young 2007. Reproduced with permission of John Wiley & Sons.

whereby the commercial fat blend's plastic range might be expected to be within a given tolerance.

Comparison of the rheological properties of butter with those of margarine shows there are major differences. Butter is a considerably more complex system than is margarine. The fat system of butter is less homogeneous than that of margarine as butter is made up of liquid and crystalline fat, fat globules and globule membrane fragments interspersed with moisture droplets (Mulder and Walstra, 1974).

The globular fat influences the texture and consistency in that the solid fat inside each globule causes it to go rigid with increase in firmness. However, these globules cannot form solid networks with the crystals outside. Thus, when butter and margarine consistency are compared, a margarine with less solid fat than butter may be equal in firmness to the butter.

The functions of fat in bakery applications are (Hodge, 1986):

- shortening power and lubricity
- batter aeration
- emulsifying properties
- provision of an impervious layer
- improvements in keeping properties
- provision of flavour.

The functionality of fat will be discussed in terms of short pastry, cake and puff or flaky pastry in order to demonstrate how fat contributes to the structure and eating

Table 2.3 A range of formulations for industrial pastry margarine.

Fat blend	Suggested fat blend	Alternative fat blends			
	A	B	C	D	E
Palm oil	15	35	30	50	40
Hydrogenated palm oil, MP = 43°C	–	–	50	30	–
Palm stearin	55	50	5	–	25
Liquid oil	20	15	15	20	20
Interesterified fat (60:40, palm stearin/palm kernel oil)	10	–	–	–	15
Solid fat content by pulsed NMR (IUPAC method):					
10°C	58	57	48	49	48
20°C	42	41	28	27	29
30°C	24	26	20	11	14
35°C	18	19	12	6	8
40°C	12	14	4	2	5
Saturated fatty acids (%)	52	52	47	43	49
Mono-unsaturated fatty acids (%)	36	37	43	41	38
Polyunsaturated fatty acids (%)	12	11	10	13	13
trans fatty acids (%)	–	–	–	3	–

quality of the product and hence how the fat can be blended and processed to maximise these functions (Pyler, 1973). Table 2.3 provides some typical fat-blend recipes.

Reviews discussing various strategies in selecting alternative *trans*-free options, or to lower total saturated fats are found in the literature (Menaa *et al*., 2013; Wassell and Young, 2007; Wassell *et al*., 2010a).

2.5.1 Short pastry

Short pastry is used in a wide range of savoury and fruit products. The major ingredients are simply flour, fat and water. When mixing flour and water, the wheat proteins are hydrated to form ‘gluten’ during the preparation of the dough.

Wheat contains four classes of protein, based on solubility in certain solvents: albumins, which are water soluble; globulins, which are also water soluble; glutenins, which are acid and alcohol soluble; and gliadins, which are soluble in aqueous alcohol. It is the glutenins and gliadins that provide the gluten of the wheat that gives rise to the tough and extensible network in flour–water doughs.

The development of an elastic flour–water dough requires access to water of the wheat protein, sufficient water to hydrate the protein in the flour and sufficient energy in mixing to cause the glutenins to aggregate and develop into an elastic mass.

When a flour–water dough is baked, it develops into a hard brittle texture, often described as being ‘flinty’. The function of the fat in a flour–water system is to coat the flour particles and so limit the extent of hydration by minimising moisture ingress. The interruption in development of the gluten results in planes of weakness and so the product becomes ‘shorter’ and more inclined to melt in the mouth. In simplistic terms, it can be seen that too little fat will result in a tough and harsh eating pastry, and too much will so interrupt the gluten development so that the dough will be loose and soft to handle and too fragile when baked.

The same comments apply when the shortening or margarine is too firm or too soft. A firm fat with very high solid triglyceride content will not smear easily and so will not distribute itself successfully in the dough to interrupt gluten development. Consequently, use of such fats lead to a flinty product exhibiting shrinkage. Liquid or fluid shortening, at the other extreme, leads to sloppy and soft and unworkable doughs. Thus, a fat for short pastry should be of firm consistency so that when being mixed into the dough it retains sufficient body under shear conditions to be distributed as protective thin films and droplets throughout the dough.

There are three types of short pastry:

- sweet paste, for use in fruit pies, jam tarts, and so on;
- savoury paste, for use in meat pies, pasties, quiche Lorraine, and so on;
- rich paste, containing little or no added water, typified by Viennese and confectioners' biscuits such as Shrewsbury biscuits (basic recipes are given in Table 2.4).

In sweetened pastes, the sugar reduces the water availability, thereby reducing the gluten development. Sweet pastes are made by either the 'rubbing-in' method or the 'creaming' method. In the former, fat and flour are mixed together before the addition of other ingredients, with the sugar in solution, after which the ingredients are mixed to a paste in the shortest possible time. When creaming is used, equal parts of fat and flour are creamed together, then the rest of the ingredients are added followed by the balance of the flour.

Savoury pastries may be subdivided according to two principal methods of production: boiled paste, used for items such as pork pies; or cold-water paste, used for Cornish pasties or quiche Lorraine. Boiled pie paste is made commercially by rubbing the fat into the flour and then adding boiling water, which contains salt. A relatively stiff paste results as a result of the gelatinisation of flour starch, which can be either 'blocked-out' into tins or hand raised. The pastry when baked has a crisp and slightly

Table 2.4 Basic recipes for short pastry doughs

	Ingredient (%)[a]						
Pastry	Flour	Baking powder	salt	Fats	Sugars	Water	Milk
Sweet	100	0	0.78	50	18.75	0	16.63
Unsweetened	100	3.13	3.13	50	0	27.5	0
Rotary-moulded short biscuit	100	1–2	1	32	30	12	1
Shortbread	100	0	0	50	25	0	0
Sweet paste	100	0	0	50	18.75	0	0
Wine biscuits	100	0	0	62.5	50	0	0
Shrewsbury biscuit	100	0	0	31.25	25	0	0
Viennese biscuit	100	0	0	65.6	25	0	12.5
Choux paste	100	0	0	50	0	125	0

Note: [a]Amount as a percentage of the weight of flour.

greasy feel. The fat used generally has a higher melting point than that used for sweetened paste, as it is necessary for the fat to solidify as the temperature falls to avoid fat loss, to give an oily paste. The fat must also show a good plastic character and not become hard or brittle. Animal fats such as lard and tallow are favoured for this application, although vegetable-oil blends are also used. Animal fats have the additional advantage of contributing to the flavour of the meat filling.

In cold-water paste, cold water is substituted for hot or boiling water. Basic recipes are shown in Table 2.5. In some cases the fat is creamed with some flour before the water is added. These pastes have a high potential for gluten development, which affects the handling characteristics and influences the texture of the baked pastry to make it firm and slightly brittle, as the final eating quality will be influenced by the filling.

The fat used for a savoury paste is the same as that used in sweetened paste; that is, one that can give good distribution during the minimum mixing time. The traditional fat used for short pastry for savoury products is lard, which, because of its particular triglyceride structure (Carlin, 1944), crystallises in the β polymorph, which has led to the belief that the β form is preferred for short pastry manufacture. However, compounded shortenings containing β and β′ polymorphs have been found to perform well in short pastry recipes to give a good 'short' texture and good mouth feel.

A feature of considerable importance is the ability of the fat to retain its plastic characteristics over a wide temperature range: realistically, 15–30°C and probably higher in warmer climates. This is a function of the solid-to-liquid ratio of the fat blend and a relatively high proportion of triglycerides with three saturated fatty acids, so that a significant proportion of solid crystalline material is retained at higher temperatures. There is a balance to be achieved in formulating shortening blends in ensuring that undue firmness is not achieved but that adequate solids are present at higher temperature. One must also bear in mind that the fat will contribute to the short pastry flavour, and thus a high content of residual solid material could detract from the flavour.

Products such as margarine and butter are not extensively used alone in short pastry as, on a strict weight-for-weight basis, more has to be used because these products are only 80% fat (the functional ingredient); thus, they are often combined with lard or shortening in order to enrich the flavour of the pastry. Butter has a place

Table 2.5 Recipes for savoury pastries.

Ingredient[a]	Pork pies[b]	Cornish pasties[c]	Quiche Lorraine[c]
Flour (%)	100	100	100
Shortening (%)	44	45	48
Water (%)	31	20	38
Salt (%)	1.5	1	1
Baking powder (%)	0	0	1.2

Notes: [a]Amounts are given as a percentage of the weight of flour.
[b]Boiled-water method.
[c]Cold-water method.

in high-quality sweet paste because of the superb flavour and the textural 'bloom' it can impart to the pastry.

2.5.2 Cake

The mechanism by which a fat functions in a cake has been the subject of a considerable amount of research work. The process has been described by Shepherd and Yoell (1976) in terms of batter preparation and of the changes taking place throughout the period of baking. It has been shown that cakes are highly dependent on fat for proper aeration; as well as ensuring successful aeration, fat also contributes to crumb texture and mouth feel.

The first step in making, for example, a maderia cake is to blend the ingredients; the method of blending the ingredients has some influence on the fat particle size in the batter. The traditional methods of batter preparation are the sugar batter method, in which the sugar and fat are creamed together first, or the flour batter method, in which the fat and flour are blended first. The all-in method, where the batter preparation is completed in one stage, has become more popular with the introduction of high-speed mixers. Popular in large commercial bakeries are continuous mixers, where a loose slurry of ingredients is fed to a mixing head, where air is injected into the batter.

Examination of batters prepared by these various methods has shown that the air is held initially in the fat phase (when plastic fats are used), the method of batter preparation having an influence on the distribution and fineness of the fat particle size in the batter. The finer the distribution of the fat and air, the better the final cake volume and crumb structure. It has been suggested (Gillies, 1974; Stauffer, 1996) that, in the case of single-stage mixing, when the air is trapped in the water phase rather than in the fat phase, the protein present stabilises the foam. The risk of foaming by the fats and oils present can be prevented by the inclusion of α-tending emulsifiers such as propylene glycol monoesters of acetylated monoglyceride which in sufficient concentration form a film at the oil–water interface, which protects the protein foam (Wassell, 2006a).

Figure 2.6 shows results from a simple 'creaming test', where fat and sugar are beaten together, and demonstrates that the plastic properties of the fat are important in its ability to incorporate and retain air. By definition, a plastic material contains solid and liquid portions, and this is the case with a plastic shortening or margarine. In the creaming process there must be enough liquid oil available to envelop the air bubble, and sufficient crystalline fat to stabilise the system. The small β' crystals are the most effective in stabilising air bubbles, as they can readily locate at the air–oil interface and so stabilise the air bubble.

Crystal aggregates that break up during the process can also stabilise the system. The proportion of crystalline triglyceride at the working temperature must be above a certain minimum, which practice has shown to be 5%. However, traditionally, most commercial bakery fats contain about 20% solid triglyceride at the working temperature. The increasing use of all vegetable-oil blends, combined with the demand for more nutritionally acceptable formulations, has led to the use by major bakeries of

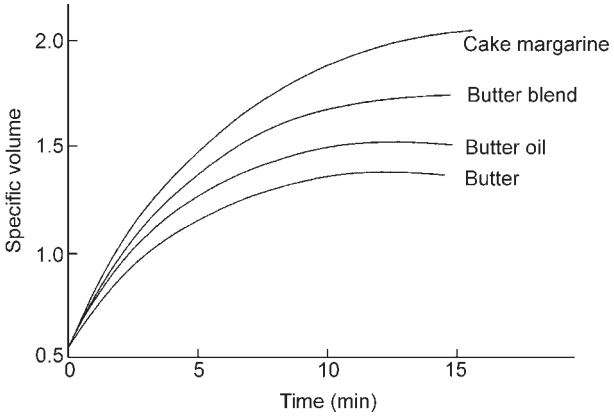


Figure 2.6 Rate of incorporation of air into a fat–sugar cream.

shortenings and margarine with crystalline contents nearer the 5% level, particularly as factory environments now have improved temperature controls.

The creaming test demonstrates the plastic behaviour of the fat and its resistance to work softening, which, if it happens to a significant degree, results in the coalescence of the air cells and a loss of volume in the cream. The creaming curves in Figure 2.6 show the expected behaviour of the texturised butter oil as it initially creams very quickly and then fails. Butter also demonstrates the limitations of a low solid-to-liquid ratio, leading to a short plastic range. The incorporation of butter oil as a margarine oil blend component significantly improves the performance, though it still does not match the 'tougher' cake margarine.

Furthermore, it is also the case that once the fat blend and emulsifier system has been chosen, then the preferred system will require several degrees of optimisation through plant processing conditions. Figure 2.7 demonstrates this aspect for creaming performance by the reduction of specific gravity.

Following the incorporation of the aqueous ingredients and flour, it can be seen that the final batter is a multiphase system where flour particles are suspended in the aqueous phase, but the water continuous phase still has parts that are water-in-oil (W/O) emulsion. The application of heat to this system at the start of the baking process has little effect; however, at about 37°C the irregularly shaped fat particles begin to melt and become droplets of oil; at this point the W/O emulsion parts of the batter invert to being an oil-in-water (O/W) emulsion. As the temperature continues to rise, the fat withdraws from the air bubbles, which are left in the more viscous aqueous phase, to produce a foam, probably stabilised by the egg protein preventing coalescence of the air bubbles. The flour particles and fat droplets are now distributed through the continuous aqueous phase.

Convection currents in the still fluid batter cause bulk flow such that the air bubbles act as nuclei, for the increase in volume of the total batter, as the carbon dioxide and water vapour moves into them. Studies by Carlin (1944) have shown that no new air

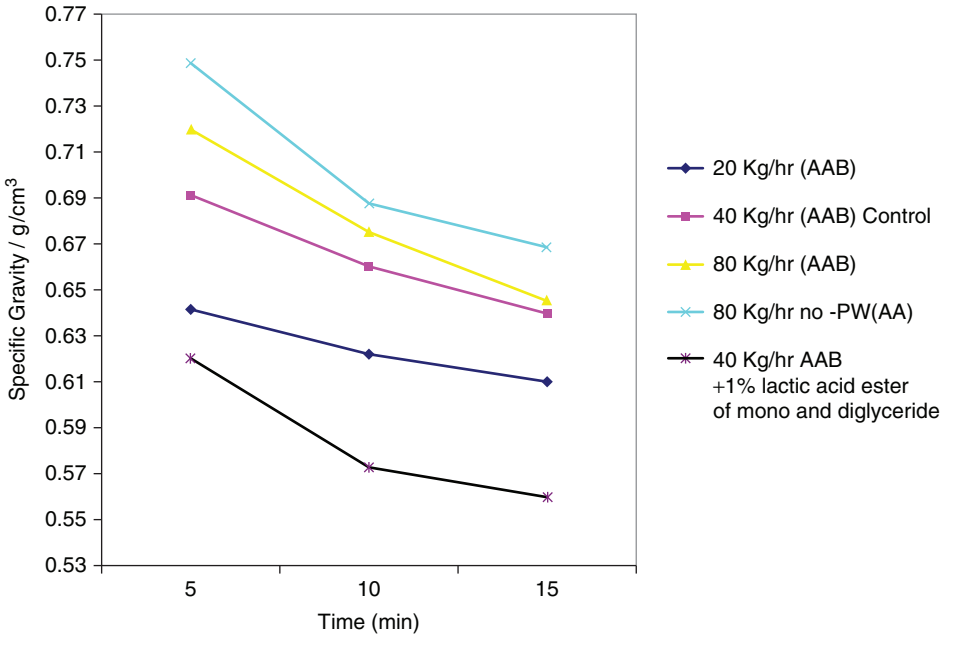


Figure 2.7 Creaming performance of a *trans*-free industrial margarine containing 0.5% of a fully saturated distilled mono and diglyceride, produced on a Gerstenberg Schroder pilot plant. The A units (700 r.p.m.) refer to scrape surface heat exchangers and the B unit refers to pinworker (250 r.p.m.).
Source: Wassell and Young 2007. Reproduced with permission of John Wiley & Sons.

cells are created during baking; thus all the air cells that create the cake texture are introduced during batter preparation.

A continued rise in temperature to 65–70°C results in the start of the gelatinisation of the flour and coagulation of the egg protein. The expansion of the air bubbles is very rapid and at 95–100°C the structure becomes fixed.

Plastic fats by design must be easily whipped into a batter and yet retain sufficient structure in order to retain the incorporated air. These characteristics are achieved by using an oil blend with a flat melting profile to ensure the solid fat content at low temperatures is not so great as to cause hardness or brittleness and with sufficient solid fat content at higher temperature to ensure there is sufficient crystalline material present to stabilise the incorporated air. The oil blend when processed must also preferentially crystallise in the β′ modification.

Figure 2.8 demonstrates the effects of toughness and wide plastic range on a finished cake. The volumes of cake made with butter and a range of commercial margarines show that use of butter or butter oil gives a lower volume and lighter texture compared with a retail packet margarine. Special cake margarine shows a finer distribution of air cells in the finished cake and this can be achieved when milkfat is included in the formulation. In this case again, butter confers a richness of flavour not achieved by margarine.

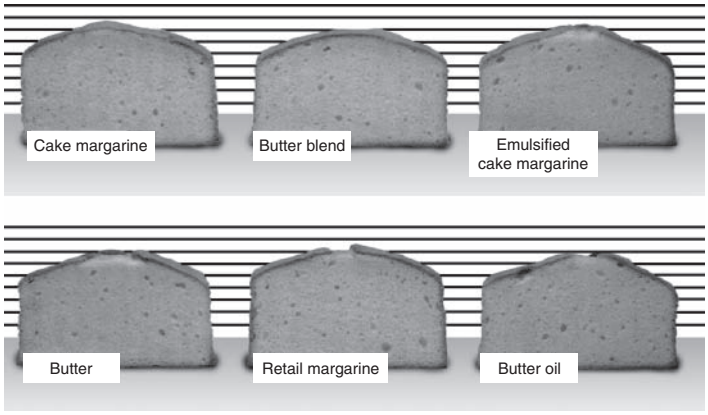


Figure 2.8 Commercial Madeira cake made with a range of margarines and fats. Top row, from left to right: cake margarine, butter blend, emulsified cake margarine. Bottom row, from left to right: butter, retail margarine, butter oil.

Shortenings can be designed to be general purpose in that they can be used in cake and short pastry applications. However, margarine is preferred in cake manufacture since it not only has the functionality described above but also can contribute a richness and flavour to a cake not normally found with shortening. Butter is of particular value in giving a highly characteristic flavour. However, margarines are an excellent vehicle for emulsifier systems, which can significantly improve performance.

Emulsifiers now have an important position in the manufacture of bakery products. This is best illustrated by a consideration of high-ratio cakes. These cakes were developed from a better understanding of the function of all the basic ingredients in a cake recipe – flour, sugar, egg and fat. The 1930s saw the development in the USA of superglycerinated, or high-ratio, shortenings, which brought about a significant change in the baking industry. Emulsifiers, mainly monoglycerides and diglycerides, were introduced into shortenings. The monoglycerides and diglycerides contributed to a finer dispersion of the fat particles and so a greater number of smaller fat globules. As a result, the emulsifier strengthened the batter, which allowed the introduction of additional liquids, which in turn allowed increased sugar to be dissolved in the system. Recipe amendments now became possible. These are illustrated in Table 2.6 (Hartnett, 1977). The more typical recipe balance is for the weight of sugar to be equal to that of the flour, for the total weight of liquids to equal that of the flour and for the proportions of fat and egg to be the same. These proportions were important, as too much sugar affected starch gelatinisation, whereas too much liquid weakened the structure. The introduction of emulsifier allowed the use of greater proportions of sugar and liquids relative to flour weight.

As well as the addition of emulsifiers, the flour used to make a high-ratio cake must be milled to a finer particle size, and treated with chemicals or heat treated, in order to allow it to absorb greater quantities of liquid, with the gluten-forming proteins largely broken down. This type of cake altered the rules of recipe balance and the methods

Table 2.6 Yellow layer cake.

Ingredient	'Old' formula (%)[a]	'New' formula (%)[a, b]
Flour	100	100
Sugar	100	140
Shortening	50	55
Eggs	50	65
Milk	50	110
Baking powder	2	6
Salt	2	3

Notes: [a]Amounts are given as a percentage of the weight of flour.
[b]High ratio of sugar to flour.
Source: Based on data from Hartnett 1977.

of mixing the ingredients, allowing simplification and automation and achieving cakes that were generally moister and more tender.

Sponge goods, that is, those based on egg, sugar and flour, were traditionally considered as a separate product type from cake because the presence of small amounts of fat could dramatically interfere with the aeration and stability of the sugar and egg foam. In traditional sponge manufacture the egg and sugar are whisked together to form a stable foam and the flour is carefully folded in to avoid loss of whipped-in air. There are variations on this method to improve aeration and industrial efficiency (Bent, 1997).

The development of enriched sponges has now begun to blur the differences between cake and sponge goods in that many large manufacturers now include fat in sponge goods for products such as gateaux bases, the fat content varying widely from 5–25% relative to the egg content. The function of the fat in an enriched sponge is to improve flavour, mouth feel and shelf-life. In making an enriched sponge the structure is first formed during the whisking of the egg and sugar; the fat or oil is then added very quickly at a high temperature (93°C) on slow mixing just prior to folding in the flour. Butter is a preferred fat in enriched sponges because of the distinctive flavour contribution it makes, although margarines are used. Liquid vegetable oils are used extensively as they add succulence and tenderness.

2.5.3 Puff pastry

Puff pastry is an important example of another basic and unique type of bakery product in that it has a light flaky and layered structure, which during baking increases in volume up to eight times compared with the original dough. In the preparation of puff pastry, layers of dough, with a well-developed gluten network, are arranged so that two layers of dough enclose a layer of fat; then, by a complex system of folding and rolling, a structure of alternate layers of dough and fat is built up. The layers of fat behave as impervious barriers to the moisture vapour and gases generated during baking. The retained gases expand and so stretch the gluten network to give the well-known puffed or flaky texture.

There are essentially three basic methods for the manufacture of puff pastry, namely, the English, French and Scotch methods. They differ mainly in how the laminating

fat is used. The following descriptions of the manual methods of manufacture of puff pastry illustrate the methods:

- English: a rectangular sheet of dough is covered to two-thirds of its area with a layer of fat or margarine. The uncovered part of the dough sheet is folded over half of the fat layer and then the remaining half of the fat layer and adhering dough is folded over the first fold to create a unit with two fat layers and three dough layers. The piece is turned through 90° and then sheeted out to its original length. This process of 'half turns' is repeated until the desired number of layers is achieved.
- French: this method starts like the English method, but in this case half the dough sheet is covered with a layer of fat and the uncovered dough is folded over the fat layer. Formation of the alternate fat and dough layers then proceeds as described for the English method.
- Scotch: this is an all-in mixing method. The fat is cut into cubes of roughly 2–3 cm, and these are added to the mixer with all the other ingredients. After a short mixing time, to ensure the laminating fat is retained as distinct lumps, the dough is sheeted out and then folded and turned as described for the English method.

The fat blend for a puff pastry margarine must have a tough and plastic texture as it is required to be rolled and stretched and sheeted out to as thin a layer as possible and yet remain continuous. The mechanical stress of the rolling process must not cause the margarine to soften unduly as this would lead to the loss of its property as a layering fat. Further, any brittleness in the texture may cause penetration into the dough during manufacture (Madsen, 1981). The melting point of the fat blend must be such that it keeps the dough layers apart in the initial stages of baking without giving the final baked product a 'waxy' mouth feel.

Butter is often used in the manufacture of puff pastry but it requires handling in such a way that the applied stress is kept below the yield value of the butter to ensure that its plastic behaviour is good and that it layers well. The low solid-to-liquid ratio of butter at ambient temperatures means its layering capability is poor. Figure 2.9 shows examples of puff pastry made with butter and with refrigerated milk fat. Additionally, a processed sample of fractionated butter improved the performance as did the chilling of the butter at the point of usage. Butter and butter oil fractions confer the benefits of a characteristic flavour and of being easily digestible as they melt below body temperature.

The laminating of the dough and fat into the paste involves a series of folding and reduction steps. As the number of laminations increases, the baked specific height increases (height per unit weight of paste). There is an optimum of 162 theoretical fat layers, above which there is a fall in specific height.

Table 2.7 shows a basic puff pastry recipe. Within a particular recipe it is possible to vary the relative amounts of dough fat and layering fat, which influences the structure and volume of the baked pastry. For example, by increasing the relative amount of

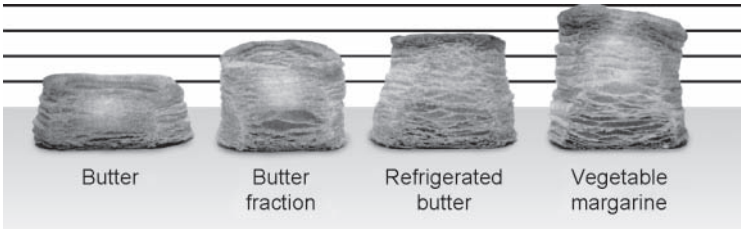


Figure 2.9 Comparison of layering fats in puff pastry. From left to right: butter, butter fraction, refrigerated butter, vegetable margarine.

Table 2.7 The main basic puff-pastry recipes.

Ingredient	Half paste	Three-quarter paste	Full paste
Flour	3.178	3.178	3.178
Salt	57	57	57
Cake margarine	227	284	398
Water	1.532	1.475	1.419
Layering fat	1.362	2.090	2.781
Total fat	1.589	2.374	3.179

Notes: Quantities are in grammes.

dough fat, the paste becomes softer to handle and shorter to eat; however, the final volume will be reduced.

Danish pastry is another form of laminated product, having one type of fat in the dough and a second type of fat for layering. A good Danish pastry will have 25% layering fat (based on flour). Danish pastry dough is softer than that found in puff pastry. The dough in Danish pastry is enriched and contains yeast (rather like a rich bun dough) and is given a short fermentation time. The layering fat is added by the English method, though the number of half-turns is reduced in order to restrict the volume increase. The product is cut into the desired shape, gently proved and then baked. Butter is finding a widening application in the manufacture of Danish pastry and croissants as it enriches the product but maintains a light eating quality. The volume increase expected is much less than in puff pastry; even so, the butter is often refrigerated before use.

Puff-pastry margarines are made from oil blends that have a high solid-to-liquid ratio, often at the expense of the final melting point. Slip melting points of 42°C and higher are not uncommon. In manufacture, the margarine emulsion is shock chilled from a high temperature in order to give quickly a very stable crystal network, which is then subjected to a heavy working and kneading routine to prevent the establishment of larger-crystal networks and to obtain a proper balance of reversible and irreversible bonds to prevent the finished margarine becoming too rigid, causing brittleness and flintiness in use.

Puff-pastry margarine is made in specially designed tubular chillers (refer to Section 2.4) to give the shock chilling and plasticising necessary at the high pressures experienced. Today there are still some who prefer to manufacture on the chilling drum and complector system, which is claimed to give better plasticity. In this case the oil

blend or emulsion is spread across the surface of a rotating horizontal drum chilled internally with liquid ammonia. As the drum rotates, the layer of fat or emulsion is rapidly chilled and crystallises. The flakes are then stored usually in a hopper to allow crystallisation to be completed as shown by a significant rise in temperature. The flakes are then plasticised by forcing them through a tube with one or two rotating screws to be extruded in blocks ready for wrapping. The post-crystallisation working can be adjusted to the final hardness desired.

2.6 The influence of emulsifiers in baking

Emulsifying agents, particularly those esters formed from fatty acids and polyvalent alcohols such as glycerol, propylene glycol, sorbitol and sucrose, and their modifications made by esterification with organic acids such as acetic acid, citric acid, lactic acid and diacetyl tartaric acid, have been used extensively in bakery products and other foodstuffs. The function of emulsifiers (Krog and Laurisden, 1976) in food systems falls into three broad categories:

- stabilisation of emulsions and aerated systems;
- improvements to texture and shelf-life of starch-based products;
- dough conditioning by interaction with wheat gluten.

In the stabilisation and aeration of cake batters, emulsifiers can play a very important role, and the physical state of the emulsifier has a marked influence on the batter. The effect of an emulsifier incorporated in the fat or margarine was mentioned in Section 2.5.2 regarding high-ratio shortenings, and in more conventional recipes the emulsifier improves the distribution of the fat and so promotes the distribution of the air. In addition, hydrates of emulsifiers have been used for many years to improve aeration in cake batter, in particular in fat-free sponge cakes. It has been demonstrated (Krog, 1975; Krog and Vang Sparsø, 2003) that with distilled monoglyceride dispersions in water at varying concentrations and temperatures, a series of liquid crystalline mesophases can be formed. These mesophases are a result of hydration, where water penetrates through layers of the polar groups of the crystalline monoglyceride above the Krafft point (the critical temperature at which micelles are formed). On cooling, the hydrocarbon chains crystallise again and the water between the lipid bilayers forms an α crystalline gel structure. As well as the lamellar type of mesophase, cubic and hexagonal structures have been identified. Monoglycerides based on saturated fatty acids form viscous gels where the lamellar structure dominates, whereas unsaturated fatty-acid monoglycerides predominate in a cubic structure. Figure 2.10 is the phase diagram of a distilled monoglyceride in water. Figure 2.10 shows that above 50°C the monoglyceride absorbs water to form a dispersion, at 60–65°C. This is a lamellar structure with the water fixed between the polar groups of the monoglyceride. In this form the monoglyceride is at its most effective in forming complexes with starch.

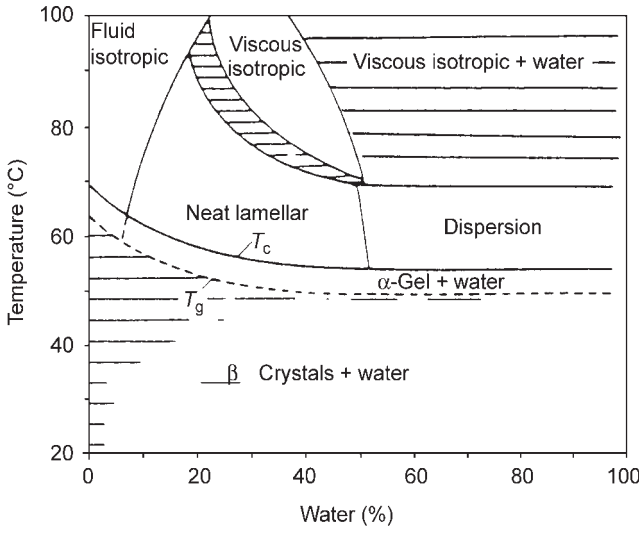


Figure 2.10 Phase diagram of a monoglyceride in water.
Source: Krog 1975. Reproduced with permission of Elsevier.

Table 2.8 Comparison of the performance monoglyceride gels with high ratio shortenings in some cake recipes.

	High ratio shortening			Hydrate 2–4% on flour (typical use levels)		
Cake	Batter gravity	Vol.	Crumb and grain	Batter gravity	Vol.	Crumb and grain
115% White cake	0.96	1878	Sl. Open Sl. irreg.	0.86	2085	Sl. irreg. good
130% White cake	1.04	1580	Compact Sl. irreg.	0.93	1865	Sl. closed good
100% Yellow cake	1.02	1680	Sl. irreg.	0.90	1980	Sl. irreg.

Note: Sl., Slight.

The use of these gels in cake batter has been shown to give a much more uniform air distribution than the shortening containing monoglyceride or monodiglyceride. The finer air distribution increases the viscosity, which leads to a better cake volume and texture. Table 2.8 shows improvement in the cake and batter volumes in high ratio cake recipes when the emulsifier is used as a hydrate compared with when it is incorporated in the shortening. The reasoning for the better performance of the hydrated form of the monoglyceride compared with the simple solution in a shortening oil blend is that the monoglyceride has a very fine crystal size in the aqueous dispersion, which ensures optimum distribution in the batter.

There are several other emulsifiers that show crystalline properties in water dispersions and that have been found to improve batter aeration properties, such as lactic acid esters of monoglycerides and propylene glycol esters of fatty acids.

Work on starch-based products (Krog and Nybo Jensen, 1970) has shown that certain emulsifiers, particularly distilled monoglycerides, have crumb-softening and

anti-staling properties in wheat bread. The process of bread staling has been shown to be a result of the amylose fraction of wheat starch. During baking, some amylose leaks out of the starch granule and dissolves in the water available to form a gel between the swollen granules of the fresh bread. On cooling of the baked bread, the gel contributes to the initial firmness of the bread crumb; however, with time, the amylose recrystallises (retrogrades) to its insoluble form and so the bread becomes hard and brittle.

It is now generally accepted that amylose in its helical form has a lipophilic core; hence in this form the amylose can be stabilised by straight-chain hydrocarbon molecules, such as those found in fatty acids. The saturated distilled monoglycerides have a steric configuration that can easily be enclosed in the amylose helix. The insoluble helical complex raises the gelatinisation temperature of the starch and thus reduces the total gelatinised starch in the bread crumb. The monoglyceride-complexed amylose will not retrograde as does the unreacted amylose, thus leading to less amylose being available to be part of the starch gel, to give a softer crumb. Additionally, the amylose–monoglyceride complex does not take part in transporting moisture from the surrounding protein network, with the result that this network becomes less rigid and hence gives a softer crumb.

Anionic emulsifiers such as the sodium or calcium salts of stearoyl 2-lactylates, diacetyl tartaric esters of monoglyceride and succinylated monoglycerides have been found to impart dough strengthening characteristics in fermented doughs. The effect of dough strengtheners or conditioners is to improve dough processing characteristics and also to give increased volume and a finer texture to the baked product.

During the processing of a dough, a gluten network is developed which traps the carbon dioxide produced by the yeast to give the final volume and texture to the finished bread or cake. Any weakening of the gluten during processing will lead to a loss of gas and will result in poor volume. The emulsifiers used as dough conditioners interact with the gluten to improve gas retention and dough elasticity to provide tolerance to variations in fermentation time and temperature and to mechanical shock.

There is still some doubt about the mechanism of the interaction of gluten and emulsifiers; however, it has been shown (Larsson, 1980) that the emulsifier can replace some of the flour lipid in association with the gluten, suggesting there are lamellar emulsifier structures in the aqueous films at the interface between the gluten strands and starch.

2.7 Control of quality in margarine and shortening manufacture

Since the fat blend is the major component in the manufacture of margarine and shortening, most analytical control effort is directed towards ensuring not only that the oil blends used are of good edibility and oxidative stability but also that they have the specified solid-to-liquid ratio and the correct crystal habit.

The tests used to judge the quality and edibility of fats and oils are well documented (Cocks and Van Rede, 1966). Classical tests for free fatty-acid content, peroxide value

and colour are well known and have been supplemented by tests such as the anisidine value, used to assess secondary oxidation products, and accelerated stability tests, such as the active oxygen method (Swift's test) and the Rancimat test, which are both based on bubbling air through the oil or fat at an elevated temperature. Finally, the flavour of the oil must be judged by an expert panel to ensure it is bland or near bland. The processor will receive these oils from the refinery with the assurance that qualitative standards have been achieved. It is then important to ensure the blend and solid characteristics of the oils are correct (Chrysan, 2005; Zurcher and Hadorn, 1979).

The margarine and shortening manufacturer can either receive refined, deodorised oils which must then be blended, or, by consultation with the refiner, the manufacturer can receive complete blends. There are arguments for and against both types of operation in terms of quality, efficiency and process control. The system selected usually depends on the way the processor's production organisation has been built.

Establishment of the correct blend for the duty the margarine and shortening are to perform requires close consultation with the user and an understanding of the user's process by the margarine manufacturer. A knowledge of the fatty-acid composition and the triglyceride structure of the fats available, using gas chromatographic techniques (Christie, 1993), ensures the crystal habit of the fat is correct.

It is important to know the extent to which a fat or fat mixture crystallises at the temperatures of practical interest and the extent of crystallisation at various temperatures. The modern method for measuring the solids content of fats is based on the difference in molecular mobility in liquid and solid triglycerides (Waddington, 1986) and, as the solid-to-liquid ratio varies with temperature, then a temperature profile of the solids content of the blend can be obtained. The technique in question is wide-line nuclear magnetic resonance (NMR). Pulsed NMR has replaced the much more time-consuming technique of dilatometry, which measures the solid fat content by volume contraction during crystallisation. Recently, attempts have been made to investigate SFC and rheological properties of fats, using real-time dynamic conditions (Wassell *et al*., 2010b; Young *et al*., 2008).

The phase behaviour of oil blends can be evaluated by plotting pulsed NMR solids content data as a function of temperature and composition. The interaction of two oils or triglyceride types can be shown with these diagrams. These so-called isosolid diagrams show components are compatible by giving horizontal isosolid lines. However, where eutectics or compounds are formed, the isosolid lines are not horizontal and so product defects can be forecast; for example, a margarine may rapidly develop a grainy or brittle texture as a result of compound formation (Birker and Padley, 1987).

The analyses discussed above, that is, gas chromatography and solids content determination, are commonly used to establish the oil blend in terms of the user's requirements for performance and eating qualities. Once the parameters are established, then blend control can be effected by routine analyses, such as of the solids content of the individual and blended oils and the iodine value, supplemented with gas chromatography of the fatty-acid methyl esters.

In the production of margarine the manufacturer is faced with additional control problems in that a product is being made that has two phases, which, when processed, must be completely stable. Also, the fat and water levels must reach the statutory levels, and any added salt must attain the level specified by the consumer (Andersen and Williams, 1965).

The production of stable W/O emulsions is facilitated by the addition of emulsifying agents; traditionally monodiglycerides (Vereecken *et al*., 2010) have been used. The influence of emulsifiers on such features as air incorporation, batter stability, etc., has led to a greater sophistication. The emulsifiers also ensure that the water droplets in the emulsion are small (about 5 μ), which leads to a good bacteriological standard and prevents their coalescence. The presence of large droplets would provide a medium with sufficient nutrients where bacteria could grow (Delamarre and Batt, 1999).

The phases in margarine manufacture can be mixed either by means of a batch process or continuously. The batch process is the more traditional method, the oil phase and aqueous phase, with their soluble ingredients, being premixed in the form of a suspension at a temperature sufficiently high to ensure that the crystallisation of the highest melting component does not take place. The 'premix' is then fed to a chiller by way of a buffer tank. In many factories, continuous metering systems have been installed where proportioning pumps blend the fat and aqueous ingredients immediately prior to the chiller, and the system relies on the agitation and shear characteristics in the chilling tube to give a correctly distributed water globule size.

Both systems can be found in modern factories and can be substantially automated. Most modern systems now include in-place cleaning facilities, and emulsions can receive a high-temperature treatment similar to pasteurisation prior to chilling. Automation of the process relies principally on monitoring the product temperature, refrigerant demand and product back pressures. The desired targets are fixed experimentally and then automatically monitored within fixed ranges to ensure a consistent final product. The parameters are fixed on the basis of the solids profile of the oil blend and its rate of crystallisation.

Moisture content can be automatically monitored with in-line equipment as well as by evaporation loss. Fat and salt contents are measured by conventional laboratory tests. Bakery margarines can include milk solids, either in the form of whey solids or spray-dried skimmed milk powder. These products are added to improve the flavour, and the presence of the lactose can improve crust browning. There has been a move to simplify bakery margarines by removing the milk solids and making them into simple fat–water emulsions. This step has been supported by the improved quality of the flavours used and a desire not only to lower the cost but also to ensure microbiological standards are more easily achieved (Delamarre and Batt, 1999).

In modern margarine factories the possibility of microbial contamination has been almost completely eliminated. However, the finished product must be regularly examined for the presence of spoilage organisms, yeasts, moulds, lipolytic bacteria and food-poisoning organisms, and the surface and the atmosphere should also be monitored. Additionally, close control of the pH value of the aqueous phase of the margarine,

combined with maintaining a small water globule size, inhibits the proliferation of spoilage organisms (Charteris, 2007).

As discussed earlier, the processing conditions have some influence on the texture of the finished fatty product; hence the chilling and working conditions need to be very closely defined; for example, attention must be paid to parameters such as emulsion or oil-feed temperature, throughput speed, refrigerant evaporation temperature and product temperature. These controls will lead to a consistent product, and the firmness can be confirmed by estimation of the yield value. Final quality testing is done by user tests; for example, one can measure the air incorporation achieved in a standard bakery mixing-machine, one can manufacture a basic cake that is sensitive to fat performance and, in the case of puff-pastry fats, one can make test vol-au-vent cases in order to measure the volume increase. These user tests can be supplemented by the use of objective tests such as penetrometer tests to show hardness and texture, profile analysis to indicate initial firmness, plasticity, brittleness, gumminess, and so on, which affect the functionality of the product.

Bakery fats can be processed into products other than the plastic fat described so far. These other forms will be discussed later.

2.8 Liquid shortenings

Liquid shortenings by definition are clear and fully liquid at ambient temperature. As discussed in Section 2.5.2, batter aeration is dependent on the ability of a plastic fat to retain air; liquid oils do not have this property. However, the advent of high-ratio cakes showed that dependency on the fat's plasticity for aeration was reduced by the inclusion of emulsifiers. Thus the developments in continuous methods for cake mixing and the need for bulk storage of ingredients have led to the introduction of fully liquid shortening. In early applications it was shown that shortenings made by dissolving various emulsifiers in liquid vegetable oils provided an effective alternative to plastic fats (Hartnett and Thalheimer, 1979). The use of liquid oils containing emulsifiers (Kumari *et al*., 2011) or emulsifier combinations in place of plastic shortening in cake manufacture appears to maintain the tenderness and moistness of the cake for longer. This may be, in part, due to the high level of liquid oil being used in the cake recipe making the cake initially more tender. Moreover, an additional advantage is that there can be up to one-third reduction in total fat in the recipe, compared with a plastic fat, without loss of volume or eating qualities (Hegenbart, 1993). Investigations into the design of the oil blends used for liquid shortening systems have shown that inclusion of a β' promoting hard stock (palm oil) in liquid oil to form liquid shortening was beneficial in increasing the specific volume of the cake. It was also shown that at certain inclusion rates of the liquid shortening to a cake batter system, it is possible for a reduction in the total emulsifier load (Wassell, 2006b).

Liquid shortenings have been exploited principally in the USA (O'Brien, 1998) but historically have failed to gain popularity in the UK, in part because of the high cost of

the emulsifier systems and because the systems have a much greater temperature sensitivity than claimed. For example, at cooler temperatures (18–20°C), the emulsifiers are often precipitated from solution, with the consequence that the product becomes highly variable. Today, given the requirement for fat systems with reduced overall saturated fatty acids, it is envisaged that liquid systems still have advantages to the modern cake and bread plant manufacturers.

Liquid shortenings have now largely replaced solid fats in bread manufacture. Liquid shortenings, when used in place of plastic fats, give lower loaf volumes and a more open crumb structure. The use of liquid shortenings in bread doughs requires the use of dough conditioners to overcome the shortcomings mentioned above. Typical dough conditioners are sodium steroyl lactylate and/or calcium steroyl lactylate and diacetyl tartaric esters of monoglycerides. Their function in the dough system arises from their ability to form a hydrogen bond complex with both the protein and the starch fractions of flour, with the effect that the starch–water–protein matrix is strengthened during the critical rising and setting stages of baking.

Dough strengtheners, because of their ability to complex with the starch in wheat, also behave like dough softeners in the same way that the monoglycerides of fatty acids do, as described in Section 2.6.

2.9 Fluid shortenings

These are pourable shortenings but are distinguished from liquid shortenings in that they contain suspended solid particles. Fluid shortenings were principally developed as frying media to provide a stable but pourable frying oil. Oils such as soybean oil and rapeseed oil, with a relatively high content of linolenic acid, were 'brush' hydrogenated to reduce the linolenic acid level and hence improve the oxidative stability. Instead of winterising the product, to give a clear oil, the addition of a small quantity of a fully hydrogenated fat and a technique for maintaining the solid material in suspension led to a pourable 'slurry'.

A variety of techniques have been patented (Schroeder and Wynne, 1968; Rossen, 1970) for creating a slurry-like fluid over a wide range of temperatures. The critical feature of the suspended particles is their size; if too large, they will settle quickly, and if too small, though settling slowly, they will pack closely. It has been found that β' crystals are too small, and β crystals are better as they are too large to pack closely. Treatment to prevent aggregation of the crystals ensures a stable slurry.

The systems described (Haighton and Mijnders, 1968) usually require slow crystallisation of the shortening following the addition of a high melting fat component to a liquid vegetable oil and a final homogenisation of the flocculent precipitated crystalline mass. These products can also be made on scraped-surface heat exchangers where the control on the rate of cooling is critical to ensure the correct crystal modification is created.

Slurry shortenings still rely heavily on added emulsifiers for their functionality. A number of emulsifier systems have been shown to work well, and experience

with pilot-scale trials has shown that acceptable performance can be achieved with blends containing α monoglycerides, polyglycerol esters, propylene glycol monostearate, lactic acid monoglycerides and sodium steroyl lactylate. Used in high-ratio cake recipes these give finished cakes approaching the volume and texture of a cake made with conventional high-ratio shortenings. Acceptable quality cakes have been obtained with a reduction of fat in the cake recipe.

As previously mentioned above, it is established that the preferred crystal polymorph is beta (β) (Thomas, 1978; Widlak, 2000) and β′ should be avoided because the spatial packing of the latter will increase the viscosity. Patents have clearly highlighted this point (Gillies, 1974). However, some evidence suggests the possibility of maintaining the β′ form (Podmore, 1996), providing functional benefits to the cake batter. It has been found that by the introduction of an additive (e.g. sorbitan tristearate), into a fluid shortening formulation, a higher solids content can be achieved and fluidity maintained. This then allows the shortening to function adequately in a range of cake and short pastry applications without addition of other emulsifiers (Wassell, 2006a, 2006b).

Fluid shortenings have temperature limitations in the same way as liquid shortenings. Storage at temperatures below 12–14°C can lead to the product setting, and temperatures in excess of 35°C cause some melting of the crystals formed, and subsequent cooling will cause the formation of large crystals which will settle.

2.10 Powdered fats, flaked fats and fat powders

The claimed advantages for fat powders, powdered fat and flaked fat are ease of handling in transport, dosing and simplified storage. Blending with the growing number of other dry ingredients is eased.

Before considering the manufacture and application of these forms of fat, it is necessary to define the differences between them. Powdered fats and flaked fats are both similar in that they are entirely made of fat or of fat and emulsifier. However, they are manufactured by different methods, as their names imply, though there is some overlap in their application. Fat powders, though they do contain substantial amounts of fat, also contain non-fatty material which acts as a carrier. This applies a restriction in their use in that the nonfatty component must be compatible with the final recipe of the user.

2.10.1 Methods of manufacture

2.10.1.1 Powdered and flaked fat

In the manufacture of powdered, granulated and flaked fat there are certain common features to be considered. The fat in its final form must be a solid at ambient temperatures, and the flake or particle must be such that the crystallisation must go as quickly as possible to completion so that late crystallisation of the liquid core does not release sufficient heat to cause lumping or caking in the product.

The technique of cooling and crystallising on a cooling drum to create a flaked product has long been used in the margarine industry. The method is similar in creating flaked fat though generally the flakes are thicker so that they can be handled easily in conveying and packaging. Additionally, so that they can crystallise quickly, the fat is usually of a high melting point with high solid fat content at ambient temperature (e.g. a pulsed NMR measurement of 70% at 20°C and of 30% at 30°C). Any fat hydrogenated to a high enough melting point can be used. However, a fat with a wide variety of triglyceride types exhibiting little polymorphism is preferred. The inclusion of coconut or palm kernel oils in their hydrogenated form in the fat formulation can assist in achieving the required percentage solids while slightly improving mouth feel.

Flaked fats can be further pulverised to make them more granular in texture, to improve the flow properties. However, this requires the application of low temperatures.

Powdered fats (Lamb, 1987) are manufactured by the technique of spray chilling, that is, by dosing the fully liquid fat or fat blend into a tower through which cold air is being circulated. The fat (Munch, 1986) must be injected into the upper portion of the tower as a fine spray. Since the globule size is a critical factor in the success of the operation, a range of systems have been developed such as rotary atomisers, both disc and centrifugal, and high-pressure nozzles to control the globule. The system is selected on the requirements of the processor and of the products, that is, the requirements for flexibility, throughput, product viscosity and formulation complexity.

The major parameter for the successful spray cooling of fat is that the globule size should be such that the total particle is fully solidified before leaving the tower. It can be such that the holding time in the cold air stream is also important. The difference between the air temperature and the melting point of the fat also plays a part. Thus, in principle, the smaller the droplet radius and the greater the difference between the melting and the air temperatures, the more rapid the solidification. Other features that have an influence are product temperature, viscosity and the injection pressure. These influence the droplet size and the amount of energy to be removed in the cooling.

Liquid nitrogen has been tested as the cooling medium in the manufacture of powdered fats. The great differential between the melting point of the fat and the liquid nitrogen at -70°C means that the rate of crystallisation is enhanced, ensuring crystallisation is complete before the fat leaves the cooling chamber, and there is also the possibility that the particle size can be varied without risk of a molten core, thereby widening the range of applications.

The design of the tower is of great importance in that the powder take-off system must not allow outside air or moisture into the tower, and the chilled air must be filtered and cooled for reuse.

It can be seen again, that a relatively high melting fat is required in this system so that rapid hardening is achieved and lumping in store is prevented. The advantage of this type of fat over flaked fat is easier control on dispensing and easier dispersion with other ingredients. This is particularly important when emulsifiers or fats containing high levels of emulsifiers are being introduced as an ingredient, as the quantity is likely to be very small and so its successful distribution is more difficult.

2.10.1.2 Fat powders

Fat powders are popularly made by the technique of spray drying (Blenford, 1987). The fat is first made into an O/W emulsion with an aqueous solution of carrier powder (e.g. milk power, starch, dextrin). The emulsion is then supplied to the spray tower atomiser by a high-pressure homogeniser to ensure the feed is homogeneous. The fine spray of emulsion droplets is projected into a hot air stream to evaporate the moisture. The moist air and fine particles are collected in a cyclone, and the dry fat powder is collected at the base of the drying chamber.

The design of spray driers has advanced significantly from the single-stage spray-drying system, in which the drier discharge tended to be at a relatively high temperature, to the double-stage and triple-stage systems, which reduce the energy consumption so that the product can be produced at lower temperatures. Thus more temperature-sensitive and high-fat products could be handled. Figure 2.11 shows the layout for a simple single-stage system.

As with powdered fats, the design of the atomiser is critical to the success of the plant. The geometry of the spray chambers is also very important, where the air flow can be counter or concurrent, and it is important that the spray must not strike the tower wall until dehydrated, otherwise it will stick and burn onto the wall and ultimately interrupt the air stream. The volume of air, its velocity and temperature must be controlled to be consistent with the heat sensitivity of the product.

Microencapsulation. Microencapsulation of fats and oils has now been developed to a considerable extent. The method gives a product where the fat is at the core of a nonfatty substance; thus, liquid oils can be used without risk of leakage and the temperature sensitivity of the product is reduced.

Microencapsulation utilises a spray-drying technique. The fat and oil are thoroughly emulsified with a water solution of the water-soluble coating material, such as gelatine, gum arabic, starch or dextrin. The water is evaporated off as described above to leave

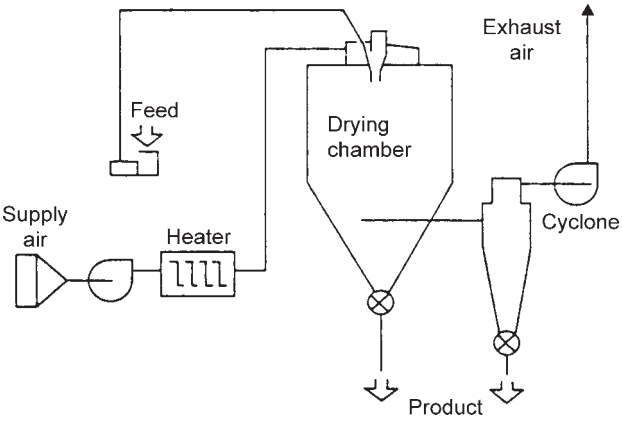


Figure 2.11 A single-stage spray-drier system.

dry particles in a shell or capsule of dry colloid in which the fatty material is embedded or encapsulated in the form of a minute droplet.

Various other processes. There are several other methods for manufacturing fat powders, for example systems have been developed where molten fat can be sprayed into a stream of dry particles in a spray chiller. This simple expedient of feeding a 'carrier'-like flour into the area of atomisation in a spray chiller gives the opportunity for lower melting fats to be used. The system can be used for the manufacture of dry food mixes. Simple mixing of a powdered fat with a dry component can be used to manufacture fat powders. In this system, heating takes place as a result of the mechanical and shear forces applied; thus a cooling phase prior to packaging of the product is required.

There are also a number of recently patented systems for the manufacture of fat powders. For example, European Patent Application 0289069 (Hamaguchi, 1988) describes a system of blending a fat or oil with a hydrophilic base substance (such as starch, caseinate or gelatine) and a small proportion of polyol-like glycerol or propylene glycol to give a free-flowing powder that rapidly gives up the oil when dissolved in water, thus being valuable for the manufacture of the seasoning of soups.

2.10.1.3 Butter powders

Butter powder deserves special consideration when discussing fat powders. A considerable amount of development work has been carried out on this product in order to achieve an 80% butter fat product that performs well in bakery applications and can withstand higher ambient temperatures than butter itself.

The powder is made by way of standard spray-drier technology (Frede *et al*., 1987) from an emulsion of milk powder solution and anhydrous milk fat that is homogenised as a 40% total solids solution and then spray dried. The mechanical stability of the powder is improved by the inclusion of trisodium citrate, possibly because of its influence on the fat–protein interface. Emulsifier, usually monodiglyceride, is included in the product, even though it has been found to adversely affect the mechanical stability of the powder, as it improves the aeration of the cake batter.

The risk of caking or clumping of the power can be reduced by using a higher melting fraction of butter fat and by cooling the powder immediately on leaving the spray tower as this creates many crystal nuclei, which help to retain the state over a wide range of temperatures. If the cooling is rapid enough, the crystalline structure can also give benefits in bakery applications. Butter powder is useful as a bakery ingredient as it is dispersed easily and quickly in the mix and imparts the richness to the product associated with butter.

2.10.2 Applications of fat powders and powdered fats

At a time when the demand for convenience foods is increasing, the use of powdered products has increased. Powdered products that can be easily reconstituted are now of considerable importance. The best-known examples come from the dairy industry where there is a considerable range of milk and milk proteins in powdered form being

used as ingredients and nutritional supplements. There is also the opportunity for efficiency improvements in industrial situations where powders give easier handling and storage (Hogenbirk, 1984).

Powdered fat is now being used as a bread improver. This kind of product often includes emulsifiers. Flaked and powdered fats have a limited application because they have a high melting point; however, they play a major role as crystallisation accelerators in products such as fondant and as a stabilising agent for paste products such as peanut butter. In addition, lauric hard butters in powder form are used as easy adjusters for the fat content of compounded chocolate for coatings. Flaked and powdered lauric fats are used in the preparation of ice-cream mixes.

Fat powders can vary considerably in their fat content, from as low as 15–20% in microencapsulated powders, through coffee creamers and whippable toppings at 30–40%, to butter powder with greater than 80% fat content, used as a bakery ingredient.

The presence of nonfat dry solids in fat powders means that lower melting fats and fat blends can be used in fat powders than in powdered fats, which widens the range of applications compared with powdered fats, though, as mentioned above, some constraint is placed on fat powders in that the carrier must be compatible with the other final recipe ingredients.

Instant desserts and whipped toppings that can contain up to 40% fat and emulsifier are popular convenience foods relying heavily on the added emulsifier system to ensure good aeration.

Prepared cake mixes for both catering and domestic outlets have been available for many years. The traditional manufacturing method was to distribute a conventional boxed shortening or a pumpable shortening throughout the flour and other dry ingredients or to inject a softened shortening as small droplets into a haze of flour. In both cases the crystal structure of the fat is maintained in order to ensure good bakery performance in the finished mix. The high-fat powders, which contain between 70% and 85% fat, now give the opportunity for bakery mixes to be prepared by mixing all the dry ingredients together. The difficulty that is found is that the fat will not necessarily be in the correct crystalline modification for optimum performance. Developments in emulsifier systems in these products have substantially improved their performance.

It is not only necessary to compare the advantages and disadvantages of using fat powders and powdered fats; it is also important that these two forms of processed fats be compared with fats manufactured as plastic, fluid and liquid shortening.

In comparing powdered fat and fat powders it can be seen that because of the presence of a carrier in fat powders, there is a greater microbiological hazard than in the all-fat powdered fat. It has been noted that fat powders deteriorate oxidatively more rapidly than does powdered fat because of the contact with the carrier. However, the comparison is confused by the fact that most fat powders are less saturated than are powdered fats.

Fat powders and powdered fats are easy to handle and store, as are boxed fats. However, liquid oils in bulk require expensive temperature-controlled storage installations.

Where boxed fats are melted prior to use, this gives a significant disadvantage because of equipment, energy consumption and handling of the melted fat.

Boxed fats have considerable advantages over fat powders and powdered fats in recipe versatility, although the method of incorporation can be more expensive than for powders in terms of energy consumption. The selection of the form a fat product is in depends on the final food product, the ease of handling, incorporation and, most importantly, the quality of the finished food.

2.11 Fat in biscuit baking

Biscuit manufacture is a major and highly specialised sector of the baking industry and is seen as being wholly separate from bread and confectionery baking. Biscuits appear in a wide variety of types, the majority of these requiring fats in the recipe, with some of the functionality described earlier for other baked products. However, biscuits differ from the majority of other baked products in that they are baked to have a much lower residual moisture content in order to ensure a long shelf-life; as a consequence, the fats used must also exhibit good resistance to oxidation and to the development of off-flavours.

Biscuit manufacturing is probably the most mechanised and automated baking activity, yet many of the biscuit types that are still popular and so are regularly manufactured were made in the home before factory manufacture was introduced. In the early days, only fats such as butter and lard were used, which restricted the shelf-life of the higher-fat biscuits. The introduction of vegetable oils and hydrogenation improved this situation.

The function of fat in biscuits will be discussed in relation to the various biscuit types. However, biscuit coatings will not be considered here as chocolate and confectionery fats are dealt with elsewhere in this book.

A problem associated with fat in biscuits is the appearance of fat bloom, that can appear in biscuits containing particular fat blends and during storage in conditions where there is temperature cycling. The biscuits take on a dull unappetising appearance. This feature of how fat functions in biscuits will be discussed later.

2.11.1 The function of fats in biscuits

Fats are used in biscuit doughs, cream fillings and as surface sprays. Fat is also employed in biscuit coatings, the main example being chocolate. Before considering how fat functions in biscuit doughs, it is necessary first to attempt to classify biscuit types. This is particularly difficult for a product that appears in so many forms with many overlapping qualities. Table 2.9 (Manley, 1983) shows a classification that attempts to take account of a range of parameters and properties in order to classify biscuit types. Those biscuits more influenced by the addition of fat will be considered here.

Table 2.9 Classification of biscuit types.

			Short		
	Crackers	Semi-sweet	High-fat	High-sugar	Soft
Moisture in dough (%)	30	22	9	15	11
Moisture in biscuit (%)	1–2	1–2	2–3	2–3	≥3
Temperature of dough (°C)	30–38	40–42	20	21	21
Critical ingredient(s)	Flour	Flour	Fat	Fat and sugar	Fat and sugar
Baking time (min.)	3	5.5	15–25	7	≥12
Oven band type	Wire	Wire	Steel	Steel	Steel

Source: Based on data from Manley 1983.

2.11.1.1 Short-dough biscuits

This is the largest group, spanning the fat-rich shortbread and the sugar-rich, fat-lean ginger snap, as well as digestive biscuits, and biscuits filled with cream. The biscuit dough is in principle made from fat, water, sugar and syrup, into which the flour is blended and, as in short pastry, the fat in the dough shortens and texturises the finished biscuit. Biscuits by design are crisp, and the presence of fat ensures they do not become hard.

In high-fat short-dough biscuits the fat prevents the sugar solution reacting with the flour to develop gluten. The fat also reduces the starch swelling and gelatinisation to give a soft-textured biscuit. The high level of fat also has a lubricating function that helps to control the amount of water used in the recipe.

In high-sugar biscuits the fat still functions to control gluten development but its principal function is to limit the extent to which the syrup solution develops to be a vitreous and brittle solid on cooling after baking.

The fats used in these doughs are plasticised, as in the case for short pastry, so that they can be smeared through the dough in small particles in order for the resulting dough to be cohesive and lacking in elasticity. The mixing times are closely controlled in order to control gluten development (these biscuit doughs are usually allowed to stand for a period before they are rotary moulded or wire cut).

The oil blends used in the production of biscuit dough fats are structured to ensure that the solid fat content at the dough temperature is high enough that the fat can be smeared through the dough, but low enough at body temperature to avoid a waxy mouth feel when the biscuit is eaten. Further constraints are that biscuits are expected to have a long shelf-life, so that fats used to formulate the blend must exhibit good oxidative stability. Hence oils with high contents of polyunsaturated fatty acids are usually avoided, and it has been found that fat blends with steep melting curves can lead to the development of bloom. Typical blends are shown in Table 2.10.

2.11.1.2 Semi-sweet and hard sweet biscuits

Although for this type of biscuit a dough fat similar to that used in soft dough biscuits will be used, semi-sweet and hard sweet biscuits have a well-developed gluten

Table 2.10 Short-dough biscuit recipes.

	Biscuit		
Ingredient[a]	Digestive	Lincoln	Ginger snap
Shortening	121 (30.3)	100 (25.0)	73 (18.25)
Sugar	86 (21.5)	107 (26.8)	202 (50.5)
Molasses or syrup	10.5	20	88
Skimmed milk powder	20	13	0
Biscuit crumb	0	0	23
Salt	5	2	3
Colour or flavouring	q.s.	q.s.	q.s.
Water	57	51	57
Bicarbonates	8.5	1.75	4
Ginger	0	0	6
Flour	400 (100)	400 (100)	400 (100)
Oatmeal	14.25	0	0

Notes: q.s. *Quantum satis*.
[a]Amounts are in kilogrammes. Figures in parentheses are percentages relative to the flour content.

structure. They are sheeted and baked to give a smooth surface with a slight sheen and an open, light texture.

2.11.1.3 Laminated biscuits

In the manufacture of puff biscuits, there is an analogy to the manufacture of puff pastry, though the layering is much less well defined owing to the fact that the layering fat distribution is nonhomogeneous during lamination. A tough, extensible dough is made free of fat and then the fat is folded into it. The fat is distributed in fine lumps or flakes to cause flakiness in the areas where they are located.

The fats used need to have a high solids content at the laminating temperature, but because the product is eaten cold the solids content at 35°C must be low to prevent waxiness. The fats used are palm kernel oil or hydrogenated rapeseed oil delivered into the dough mass as flakes, often after crystallisation, on a rotating chilling drum. This equipment consists of a horizontal revolving drum cooled internally by brine or liquid ammonia. The unit operates such that the melted fat is fed into a trough, which spreads the fat in a thin layer across the surface of the drum. As the drum rotates, the fat is rapidly cooled and crystallised, to be scraped off as flakes by a scraper blade located near the feed trough.

Cream crackers are another form of laminated biscuit, but in this case a fermented dough is used. The dough fats discussed above can be used in these products as there is even less requirement for distinctive layering than in the case of the puff biscuits.

2.11.2 Biscuit filling creams

Biscuit filling creams are principally sugar, fat and flavourings. The fat in a filling cream is usually in the range of 25–30% of the cream. The fats used in the filling creams are selected to give the cream some specific characteristics:

- The cream must be firm enough at ambient temperatures to hold the two biscuit shells together and to avoid being squeezed out of the ‘sandwich’.
- The cream must give the consumer a firm bite yet melt quickly to give a cooling impression on the palate and release the sugar and added flavourings.
- The cream must solidify sufficiently rapidly after spreading so that the two biscuit shells are held together during transport and packaging.

The fats used in this application must have low solids content at body temperature and yet have a relatively high solids content between 15°C and 25°C to ensure the biscuit shells remain ‘keyed’ together. The fats preferred today are derived from blends containing whole natural oils and fractions. This will likely include lauric fats and interesterified vegetable oils. Table 2.11 shows a preferred range to target acceptable solid fat profiles.

2.11.3 Spray fats

Fat is sprayed onto the surface of savoury crackers to give them an attractive sheen and also enables added salt to adhere to the surface. The requirements of the fat in this application is that it should be liquid at room temperature but must also show good resistance to oxidation because it is exposed to the atmosphere as a thin film. Blends containing lauric fats, palm oil, palm oleins, and so on are favoured in this application, as shown in Table 2.12.

Table 2.11 SFCs for cream fat blends for biscuit filling.

Solid fat content (SFC) pNMR	
20°C	48–58
35°C	1–5

Table 2.12 Spray-fat blends (SFC and ratio).

	Percentage
Blend A:	
Hardened rapeseed oil	35
Coconut oil	65
Solid fat content	
20°C	22–28
35°C	0.5[a]
Blend B:	
Palm oil	50
Palm kernel oil	50
Solid fat content	
20°C	18–22
35°C	0.5[a]

Note: [a]Maximum.

2.11.4 Fat bloom

Fat bloom in biscuits becomes evident as a white powder on the surface of a biscuit, giving a dull appearance. The powdery substance on the biscuit surface consists of fat crystals. These crystals are caused by fractionation of the biscuit fat and migration of the liquid portion to the biscuit surface, where it recrystallises as fine powdery crystals.

Temperature cycling of biscuits during storage encourages the development of bloom. Fat bloom has also been associated with fats such as palm oil and lard, which show an ability to separate quickly into fractions. Fat bloom in biscuits can also be caused by the mixing of cream fats and dough blends, which in many cases leads to the production of a eutectic mixture in the fat system, and the new mixture of triglycerides more easily fractionates and migrates to cause bloom.

2.12 Conclusion

There will continue to be a demand for fats for use in baked products, though nutritional and life-style changes will continue pressure for change. Concerns about obesity and the impact of saturated and *trans* fatty acids on heart disease will influence the choices of the oils and fats manufacturer (van Duijn *et al*., 2006; NICE, 2010; Swinburn *et al*., 2011; Wang *et al*., 2011).

Bakery fats now tend to have a lower content of hydrogenated oils and increasing quantities of liquid vegetable oils, both to raise the levels of mono-unsaturated and polyunsaturated fatty acids and to reduce the levels of saturated and *trans* fatty acids consumed (Wassell *et al*., 2010a). These shifts in blend characteristics have led to the increased use of fractions and the growing use of enzymatic interesterification, to help achieve functional products with lower solids contents. Functionality, coupled with relatively lower saturates, is the aim of an increasing interest in liquid shortenings (Zhou *et al*., 2011).

There has already been a considerable amount of work done towards the use of reduced fat emulsions in bakery products, designed to maintain good functionality particularly with respect to eating quality. The greater use of emulsifiers and emulsifier–stabiliser systems is likely to be combined with changes in bakery recipes and processing methods in order to meet consumers' desire to have what appear to be traditional products but with lower fat content (Young and Wassell, 2008b).

Some bakery products could be used as a source of functional food. Thus the fat manufacturer may be expected to supply fats and emulsions containing, for example, phytosterols or that are enriched with vitamin E, as well as to supply fat replacers such as inulin, which is a dietary fibre (de Dekere and Verschuren, 1999). Wester (2006) discusses a range of approaches to solving nutritional and texturising issues of fat blends, and neatly describes and presents the background to the prior art and concludes with a description of the use of combinations of stanol and sterol fatty acid esters or their blends, and as forming crystal networks with similar properties to those of conventional hardstock triglycerides. The use of phytosterols, organogels and

specific fatty acids is also shown to offer structure and textural properties in edible oil mixtures, (Bot and Agterof, 2006; Bot *et al*., 2011; Wright and Marangoni, 2006; Bech, *et al*., 2013). Rogers (2009) has reviewed novel structuring strategies for unsaturated fats, and suggests the 'next hurdle for industrial manufacturers to overcome is the ability to modify the physical properties using simple processing techniques' (Rogers and Marangoni, 2008).

The search for nutritional improvement could lead to the use of sucrose polyesters, which have been developed by Procter and Gamble, to the point where they are being used as frying media for certain snack foods in the USA. It is not hard to visualise that by changing the fatty acids esterified to the sucrose molecule, a sucrose polyester could be produced with the required functional properties. The same approach can be applied to other carbohydrate polyesters based on sorbitol, trehalose, raffinose and stachyose, which are also indigestible.

Medium-chain-length triglycerides are structured lipids, which have been used in spreads for many years. Medium-chain-length fatty acids do not increase plasma total cholesterol in the same way that lauric myristic and palmitic acids do, and they can contribute to weight reduction in obesity because of their lower energy content compared with longer-change-length triglycerides.

Currently, the biggest and probably the most challenging development for the oils and fats industry is to find solutions that not only deal with removal of *trans* fats, but also remove significant amounts of saturated fats (Gortmaker *et al*., 2011; Menaa *et al*., 2013; da Silva Lannes and Ignácio, 2013; Wassell *et al*., 2010a). To satisfy all the necessary technical and functional requirements will prove challenging (Piller, 2011).

The impact of genetic and or enzymatic modification will be felt in the production of bakery fats. The possibility of genetic modification of oilseed crops to produce oils with many of the desired characteristics already present in the oil will allow processors to simplify operations and hence supply a cost-effective and functional ingredient to the baker.

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3
Water continuous emulsions

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3.1 Introduction

The mammary epithelium of the udder cells of mammals undergoes remarkable changes in order to secrete the white biological fluid termed milk. Humans have used this wholesome food from early periods in history and developed techniques to produce specific food commodities using some of its major components, such as fat. Milk from sources other than cows has also been used in many parts of the world as the main source of food supply. For example, the milks of buffalo, goat, sheep, yak and horse have in some parts of the world been the main source of vital nutrients to supplement the native food supply. Milk exists in the form of an emulsion. The food emulsion exists in two basic forms: the oil-in-water type (O/W) or the water-in-oil type (W/O).

Creams, ice cream, mayonnaise and salad oils (dressings) are some of the two-phase O/W emulsions where water or the aqueous phase is continuous. These emulsions are constantly under threat from possible destabilisation caused by microbiological activity or by chemical or physical changes. In creams and ice creams, the pH is in the neutral range and that, together with the continuous aqueous material, provides an ideal environment for a large cross-section of microorganisms to thrive. In the case of salad dressings and mayonnaise, the pH is low (3–4), and such acid conditions are an unfavourable environment for many microorganisms, including pathogens. The aqueous phase in O/W systems contains a variety of nutrients, which can easily be digested by bacterial cells and therefore act as a good substrate for them to feed on.

An important variation on O/W emulsions is that found in ice cream. Its components – water, dissolved solids and salts – all exist in a frozen state. In addition to being able to withstand the freezing process, it should also hold fine air bubbles. Incorporation of air into ice cream and whipped cream means that these emulsions consist of a third phase.

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3.1.1 The structure of water continuous emulsions

In defining an emulsion it is important to be aware of descriptions of other closely associated systems such as solutions, colloidal solutions, suspensions and foams. A genuine solution is the simplest of all physicochemical states, whether it be solid, liquid or gaseous. A simple example of a genuine solution is that of sugar dissolved in water. The solute particle size is less than 0.001 μm. In a colloidal solution the particle size varies from about 0.001–0.1 μm. The complex calcium salts in milk exist in colloidal form together with albumin and casein. According to basic principles, there is very little difference between an emulsion and a suspension. The most striking difference is that the particles of an emulsion are liquid, whereas those of the suspension are solid. In both systems the particle size (diameter) is greater than 0.1 μm and could be as large as 1 mm. The fat in milk exists in this form. Foam can be considered to be a suspension where the particle size (i.e. the diameter of the air cells in the foam) is about 30–100 μm.

An emulsion is defined as a mixture formed by combining two immiscible fluids in which one is uniformly distributed in the other without separation. As indicated, the particle size ranges from about 0.1 μm to visible size. In food emulsions the two main components are oil and water, with other semisolids or solids dispersed either in the continuous or in the dispersed phase. These systems are either O/W or W/O, and the semisolids and solids may also exist as crystals, as in ice cream or butter. Figure 3.1 shows the basic structure of O/W and W/O emulsions. In milk, the fat content, which is approximately 4%, is dispersed in an aqueous phase containing protein. Similarly, the higher fat milk emulsions such as creams also contain protein in the aqueous phase but to a lesser extent. However, milk, creams and dairy ice cream differ from other emulsions that have been formed by mixing vegetable oils and water. In milk the fat exists uniquely in globular form, with each globule surrounded by a membrane. The aqueous phase may be described as a colloidal phase because of the presence of proteins, salts, carbohydrates, microcomponents and other aqueous-phase materials.

Milk and creams are considered to be natural O/W emulsions whereas ice creams, soups and salad creams are considered to be engineered O/W emulsions. Milk inside

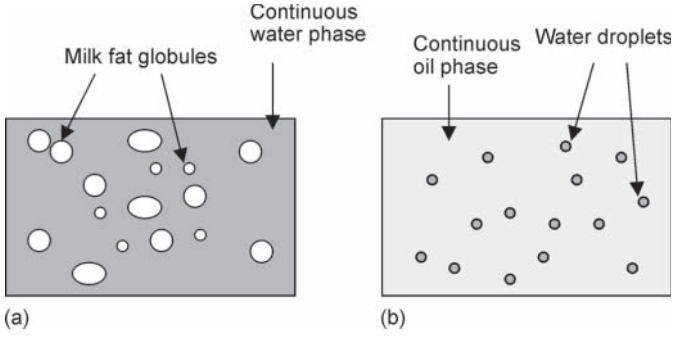


Figure 3.1 (a) Oil-in-water and (b) water-in-oil emulsions.

the cow udder is a stable emulsion with the dispersed phase (fat) uniformly distributed without separation. However, once the milk exits the udder, the tendency is for the fat globules to rise because of the difference in density between fat globules and the aqueous phase. This separation is also referred to as creaming and milk and cream storage silos and tanks are kept in gentle agitation at regular intervals to minimise this creaming effect. This natural separation of the fat phase in milk was used in early periods to prepare high-fat milk products.

3.1.2 Milk fat globule structure

A unique difference between milk fat and vegetable fat is that in its natural state milk fat is found in a globular form enrobed by a very complex membrane. This membrane protects the fat inside the globule from chemical and lypolytic action by the chemicals and enzymes present in the aqueous phase. The membrane also extends protection against mechanical damage during handling in the farm as well as in the dairy. This thin protective membrane also prevents the globules from flocculating and coalescing. The milk fat globule membrane (MFGM) is estimated to be about 5–10 nm thick (Mulder and Walstra, 1974) and 10–50 nm by Keenan and Mather (2006). Scientists describe the fat globule as consisting of two basic layers: an inner core of fat surrounded by an emulsifier system. A recent study by Evers *et al*. (2008) reported that using liphophilic probes and fluorescence microscopy, the MFGM is structurally and chemically heterogeneous both within and among globules. The fluorescence study also highlighted the presence of a bilayer consisting of phospholipids and glycoprotein in the MFGM. The MFGM surface is hydrophilic and maintains the fat in an emulsified state. The membrane is composed of a complex mixture of phospholipids, protein, vitamin A, carotenoids, cholesterol, high-melting-point glycerides and various enzymes. Figure 3.2 shows the layout of the milk fat globule components to highlight the main layers, the inner layer being the triglycerides surrounded by the membrane. Chemical components such as lecithin hold the lipids and the aqueous material together. Other components such as casein units organise themselves around the aqueous layer to form the outermost layer. This biological membrane is formed during the milk secretion process in the mammary epithelium of the udder cells of the cow.

In a recent publication, Thanh *et al*. (2013) showed that O/W emulsions prepared using microfiltered butter milk and protein/soybean oil produced a uniform particle size (3.5 μm) when homogenised at 9/2 MPa and observed no droplet aggregation compared to separate emulsions prepared using butter milk powder, skimmed milk powder and sodium caseinates. The authors suggest that a superior emulsion stability of this nature shows potential for future development of new products.

The fat content of milk varies more than the other major constituents and is influenced by environmental and other biological factors. As the fat fraction of milk tends to separate from the aqueous phase in most species, the fat content varies throughout milking or suckling, generally increasing as the gland is emptied. Apart from this, the fat content in all species is influenced by the stage of lactation, age, the breed type and

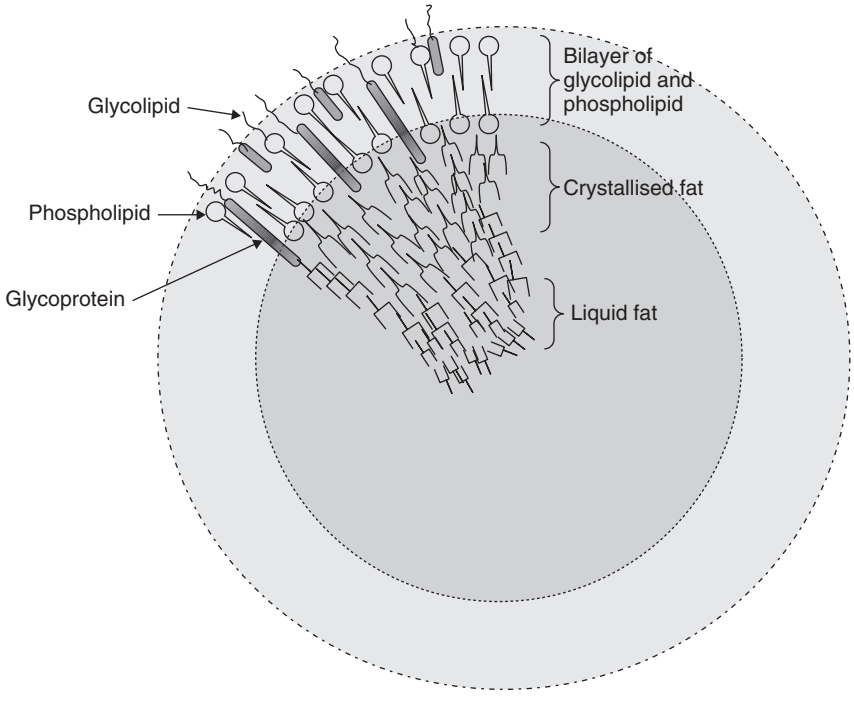


Figure 3.2 Milk fat globule system.

diet. It is estimated that the mean fat globule diameter is about 3 μm for cows' milk and about 2 μm for goats' milk. In different breeds the size of the globules tends to vary with the fat content of the milk. Therefore, the mean for Holstein milk is 2.5 μm and that for Channel Island cattle is 3.5 μm (Ling *et al.*, 1961). However, it was found that Ayreshires are an exception though the milk has a higher fat content than Holstein milk, the size of the globules is the same. As lactation advances, the fat globules tend to become smaller.

The long-chain fatty acids of the phospholipid are buried in the fat and the hydrophilic part of the molecule is directed outwards. It is likely that the carotenoids, vitamin A and cholesterol associated with the membrane are in the phospholipid layer. The characteristic nature of the globule surface is such that at normal temperatures (8–20°) the globules are grouped together in the form of clusters, which play an important part in the rising of cream.

Milk fat begins to melt at about 28°C but is not completely liquid until the temperature has reached about 33°C. The liquid fat sets over a similar but lower temperature range (24–19°C). At the time of secretion the fat globules are liquid. However, when milk is cooled, crystallisation commences and this may take up to 24 hours to reach completion. The reason for this lengthy period could be attributable to the complexities of the crystallisation process rather than to solidification. Also with the liquid fat being

in the dispersed phase, there is no opportunity for the hastening effect of 'seeding', which usually operates when the liquid is in a continuous phase.

As with other fat material, milk fat is soluble in fat solvents such as petroleum and ether but it is not possible to extract milk fat by merely shaking it with these solvents. This is because of the protection it receives from the fat globule membrane. In quantitative solvent extraction the fat globule membrane is first removed by the action of acid or alkali. The membrane materials change constantly to keep in equilibrium with the components in the aqueous phase. This means that some membrane material may leave and join the aqueous phase, and vice versa. Therefore, the thickness of the membrane is variable.

Such clear demarcation of layers in the fat globule structure indicates that boundaries can be defined based on the components associated with each layer. The outer boundary is that associated with the components outside the fat globule and belongs to the membrane materials. The inner boundary consists of the triglycerides in the core of the globule at the fat–water interface. However, the membrane undergoes rearrangement as a result of homogenisation and cooling.

3.2 Preparation of water continuous emulsions

3.2.1 Dairy creams

It is known from ancient writings that butter was used in food preparation in India between 2000 bc and 1400 bc (McDowall, 1953). It has also been reported that in 1480 cream was recovered by skimming the surface of milk and used for butter-like product manufacture in Italy. This therefore provides the evidence that, historically, the effect of differences in the density between oil and water has been utilised to recover cream and to produce dairy products from fats in milk. This also includes fat from mammals other than the cow.

Similarly, a denser material in milk will eventually settle to the bottom of the container holding the milk. The flotation or sedimentation velocity of particles in an emulsion (O/W) follows Stokes's law, as follows:

$$V_g = \frac{d^2(p_1 - p_2)}{18\eta}\mathrm{g} \tag{3.1}$$

where

V_g is the flotation or sedimentation velocity
d^2 is the particle diameter
p_1 is the particle density (kg m^{-3})
p_2 is the density of the continuous phase (kg m^{-3})
g is the gravitational pull of the earth
η is the viscosity of the continuous phase (kg m^{-1} s^{-1}).

Equation (3.1) indicates that a larger particle will rise or sediment faster than will a smaller particle, that the velocity increases with increasing difference in density between the particles and continuous phase, and that the velocity increases with decreasing viscosity of the continuous phase. Equation (3.1) can be used to calculate the flotation velocity of a fat globule. For milk η is about 1.4×10^{-3} kg/m.s, p_1 is 980 kg m^{-3} and p_2 is 1.03 kg m^{-3}. The average globule diameter varies based on the mechanical and shear forces acting on the globule, leading to size reductions. However, the fat globules that form clusters or that aggregate rise faster because of the increase in overall diameter and become less dense.

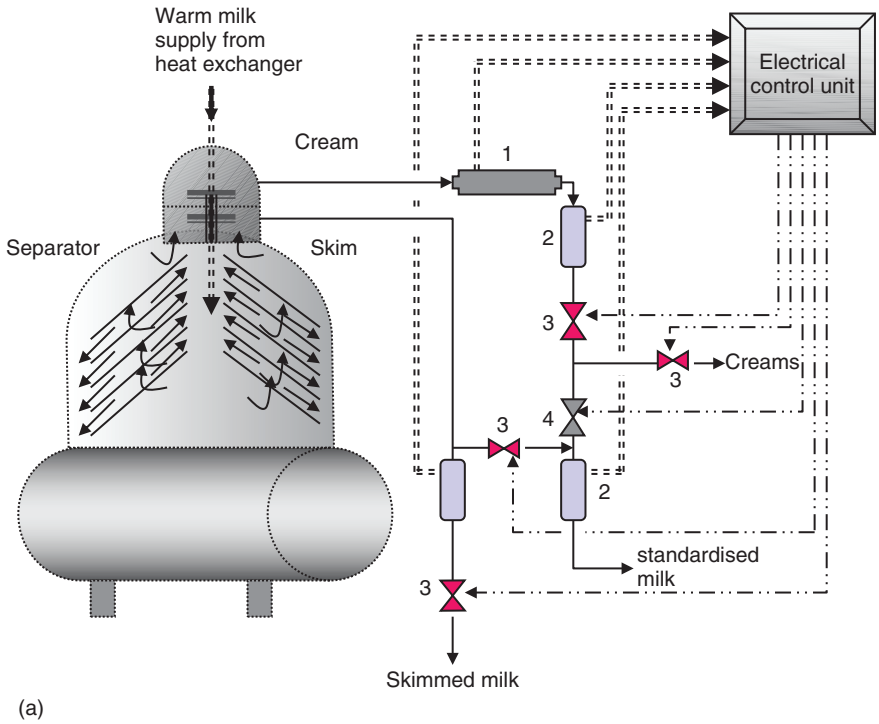
3.2.1.1 Clarification of milk

The cooled, stored raw milk is either filtered or clarified prior to processing and separation. A clarifier is used in almost all modern, medium-to-large dairy installations. A clarifier works on the same principle as a centrifugal separator. Centrifugal force is generated from the rotational movement of the material. The magnitude of the centrifugal force is dependent on the radius and speed of rotation and on the density of the material being rotated. Milk produced under good hygiene conditions will be substantially free from foreign matter as it will have passed through a filtering system in the farm. In all dairies milk passes through a filtering system (filter cloth, etc.) or through a centrifugal clarifier. Clarification is generally conducted in the cold and, unlike the case of a separator, the heavier and lighter fractions do not exit separately from the machine. The insoluble matter is thrown to the rotating bowl, where it is discharged at regular intervals.

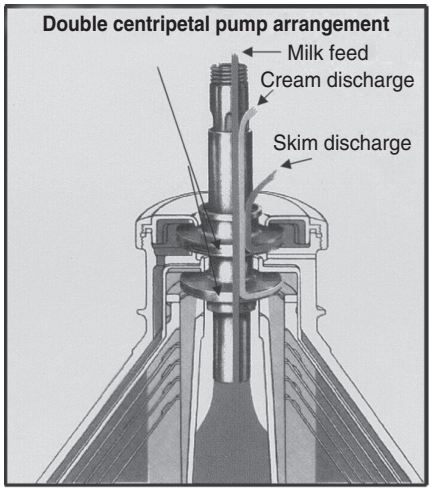
3.2.1.2 Centrifugal separation

The dairy industry pioneered the development of centrifugal separation to produce cream fractions for the manufacture of high-fat dairy products. A dairy centrifugal separator is specially designed to separate the fat phase in milk with minimum damage to the fat globules. In early designs, fat globules travelled a significant distance inside the unit prior to being separated by the centrifugal force. The centrifugal force throws the denser material away from the centre spindle, and the lighter phase moves towards the centre. In modern separators, however, the inner cavity of the separator bowl is fitted with a series of conical discs arranged one on top of the other to form a stack. This arrangement separates the milk into thin layers (Figure 3.3 (a)). Such an arrangement increases the efficiency of the separation process. In each disc holes are arranged for the distribution of milk. The sediments and other heavy particles are also separated as sludge and are collected at the sidewall of the bowl. In small and medium throughput separators (up to about 5000 l h^{-1}) the sludge is removed manually when the separator is dismantled for cleaning.

The operating principles of separators vary with design features present. There are three main categories of separator: the open design, the semi-enclosed type and the hermetic type. These names relate to the separator bowl design and to the arrangement of the entry and exit ports.



(a)



(b)

Figure 3.3 (a) A milk separation and standardisation circuit; 1, density transmitter; 2, flow transmitter; 3, flow-control value; 4, isolation valve; dotted line, control circuit. (b) Centrifugal method for extracting skimmed milk and cream: the centripetal pump system is fitted internally, with milk fed into the system from the top of the separator. *Source:* Part (b) based on data from Westfalia Separator, UK and Diotte Consulting & Technology, UK.

As already described, the denser material moves to the wall of the rotating bowl and the lighter fraction moves towards the centre spindle. The centre spindle is mechanically linked to the motor and gear system, which rotates the spindle at 7000–9000 rpm. In the dairy separator the open design introduces milk from the top of the bowl, usually via a float arrangement. The skimmed milk and cream exit the bowl from the top via an overflow into collecting spouts or trays. In this system, milk, skimmed milk and cream are exposed to the outside environment, hence the name 'open design'.

Semi-enclosed separators differ from the open type in that there are paring discs fitted at the top of the bowl to pump the cream and skimmed milk (see Figure 3.3 (b)). These are also called centripetal pumps. The exit ports are fitted with throttle valves to maintain back pressure and to control the fluid flow.

All modern dairy separators designed to operate at a higher flow rate are able to isolate the separator rotating components and products inside the bowl (milk, cream and skimmed milk) from the outer environment. Such separators are of the hermetic type.

3.2.1.3 Control of fat content in cream

In the early period, up to the nineteenth century, cream recovered from milk was used mainly for the manufacture of butter-type products. The development of the dairy separator was an important process innovation which led manufacturers to launch added-value products with a high fat content, creams as well as low-fat and 'no-fat' milks such as semi-skimmed and skimmed milk, respectively. The method of preparation included either using the skimmed fraction or whole milk to dilute the cream to obtain the desirable fat content in the final product. In these techniques the fat content of each fraction must be analysed in order to formulate the appropriate combination required. The dairy industry regularly standardises creams and milks.

To adjust the fat content accurately, Pearson's rectangle is used. The basic method is demonstrated in Figure 3.4. The example given illustrates that cream containing 50 g per 100 g fat may be diluted with skimmed milk in the ratio 4:1 to obtain cream containing 40 g per 100 g fat. In high-throughput separators, an in-line densitometer automatically makes the fat adjustment. A simple diagrammatic illustration of in-line automation for fat standardisation is given in Figure 3.3 (a).

The basic requirement is to use flow meters, densitometers and control valves to adjust the fat content by mixing the correct proportion of skimmed milk and cream.

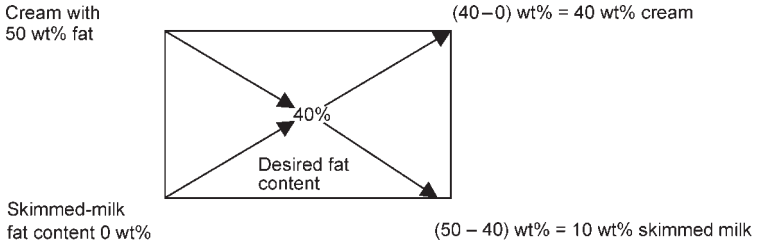


Figure 3.4 Pearson's rectangle for cream standardisation. Note: Figures are in grams per hundred grams.

The actual fat content of the streams is continuously monitored by the densitometer and the information is communicated back to the control unit for comparison with the preset parameters corresponding to the required fat content in the cream. The density transmitter is capable of detecting small changes in the density of the cream when the fat content changes. An increase in fat content in cream results in a decrease in density; the opposite is true when the fat content decreases. This means a relationship exists between fat content and density; that is, the fat content in cream varies inversely with density.

Factors such as entrained air in milk and cream influence the density measurement. If the processing circuit linking the separator has the tendency to suck air in because of poor flow control in the system, then the cream produced will be lighter as air bubbles will be pushed towards the cream by the centrifugal force. This means that the process circuit must be airtight and, in addition, some installations include an in-line de-aerator to ensure that the oxygen content of raw milk is reduced to a uniform level prior to being separated.

It is possible to estimate the theoretical yield of cream of known fat content by using the following formula:

$$T_f = \frac{F_m S}{100} \tag{3.2}$$

where

T_f is the total fat flowing through the system (kg h^{-1})
F_m is the fat content of the incoming milk (g 100 g^{-1})
S is the flow rate of the separator (kg h^{-1}).

If the separator is adjusted or programmed to achieve 40 wt% fat cream, the cream yield Y (in kg h^{-1}), would be given by

$$Y = \frac{100 T_f}{40} \tag{3.3}$$

If T_f is the pure fat flowing per hour, then $Y - T_f$ is the skimmed milk fraction flowing per hour included in the 40 wt% fat cream. These values calculated as shown can be used for approximate setting of the separator to obtain the desired cream fraction. For example, in separators where the flow is manually adjustable the skimmed milk and cream exit ports are fitted with throttle adjustments to restrict the flow. They are adjusted so that the system pressure as well as the cream flow rate can be balanced as specified for a particular separator. The system pressure adjustment is in the skimmed milk outlet and, when the cream exit port is set to the correct flow rate in the flow indicator, the fat content of the cream exiting the separator will be close to the desired value. Table 3.1 lists the categories of cream in use in the United Kingdom.

The efficiency of separation is reflected in the quality of skimmed milk obtained and the level of free fat in the cream. Efficient separation produces skimmed milk with less than 0.05 wt% fat and low amounts of free fat in the cream. Figure 3.5 shows the microstructure of single cream. The free fat level will increase if damage is caused to the fat globule membrane from mechanical and shear action in the circuit

Table 3.1 Cream categories in the United Kingdom, with minimum fat content measured in g per 100 g.

Type	Minimum fat content
Half cream	12
Single cream	18
Whipping cream	35
Double cream	48
Sterilised cream	23
Clotted cream	55

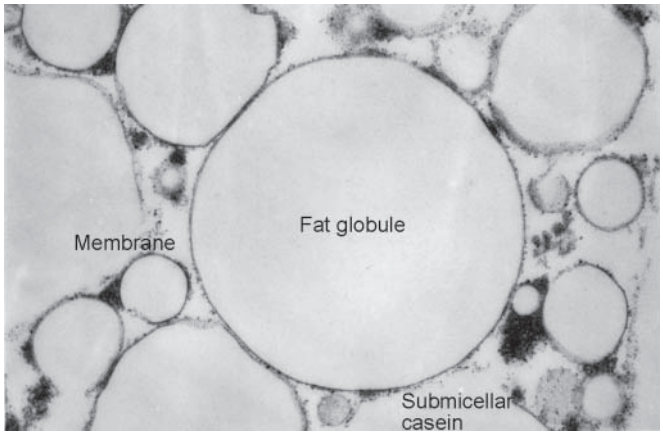


Figure 3.5 The microstructure of cream. *Source:* Diotte Consulting & Technology, UK. Reproduced with permission of Diotte Consulting & Technology, UK.

and pumps. Milk is usually warmed to at least 40°C prior to separation, and the feed to the separator should be adjusted to ensure that it is within the design specification of the manufacturer. A lower than optimum feed rate into the separator can cause the fat fraction to stay in the separator longer than necessary, causing further damage to the fat globule membrane as a result of shear. Once the globule membrane is damaged, the free fat can escape into the aqueous phase. A high percentage of free fat leads to high quantities of free fatty acids (FFAs) in the cream, resulting from lipolysis by indigenous lipase enzyme. Not all FFAs are formed by this method; some are formed as a result of poor quality milk or poor handling practice. In poor-quality milk a high concentration of the microbial enzyme lipase is available to hydrolyse the triglycerides and thus increase the FFA content. Therefore, it is important to reduce the occurrence of FFAs in the raw milk that may originate from poor microbiological quality or handling methods.

3.2.2 Recombined creams

The formulations and procedure for recombined creams have been known to the food and dairy industries for quite some time. Buchanan and Smith (1966), Zadow and

Kieseker (1975) and Towler and Stevenson (1988) studied the manufacture and properties of these products. The manufacture of such products was originally achieved by using butter oil, skimmed milk powder and water. However, the main drawback with this recombination process was that the resulting cream had a very poor overrun or no foaming at all: high-fat recombined cream should be pourable as well as thick enough to use as a dessert cream. Therefore, in formulating a recombined cream, various ingredients are selected to enhance the desirable qualities and to make the process cost-effective. Recombined creams are popular in countries where real cream is in short supply or is not available and where cream is popular in bakery applications. For bakery applications high-fat products can be specially formulated by using stabiliser–emulsifier systems to minimise serum drain and to improve foam quality. Some details of emulsifiers and stabilisers are given in Section 3.2.3.1. Emulsifiers, such as distilled monoglycerides, were found to produce acceptable overrun, and lecithin gives the desirable stiffness to the foam.

Zadow and Kieseker (1975) reported that use of anhydrous milk fat, nonfat milk solids and an emulsifier such as glycerol monostearate could produce good-quality whipping cream (35 wt% fat). A two-stage homogenisation step was used at pressures of 1.4–2.1 MPa at the first stage, and 0.7 MPa at the second stage. The optimum temperature for homogenisation was found to be about 48°C. In the formulation 0.1 wt% of the emulsifier was used and it was found the product could withstand process conditions used in ultra high temperature (UHT) treatment.

The steps involved in the preparation of recombined cream are as follows:

1. Dissolve the nonfat milk solids and emulsifiers in water at about 40–50°C with the use of a high-speed mixer.
2. Melt the fat (e.g. anhydrous milk fat, butter, etc.) at about 40–45°C and add it slowly to the liquid mix.
3. Continue mixing to ensure that a homogeneous mix is formed that is free from lumps and oil droplets.
4. Heat treat (i.e. pasteurise or UHT) the mixture (see Section 3.2.4).

3.2.2.1 Nondairy creamers or cream alternatives

The manufacture of these products is similar to that of recombined dairy cream. The most common ingredient that is substituted in making a nondairy cream is the fat source. Milk fat is replaced with vegetable oil in most nondairy preparations. Substitution of milk fat with vegetable oil is attractive for the manufacturer because of its substantially lower cost as well as because it is easy to obtain in various parts of the world. In some formulations fat replacers are used so that these products are suitable for those who prefer fat-free products. Other components such as nonfat milk solids have been replaced with alternative nondairy components. For example, nonfat solids originating from soya powder or soya slurry extract have been used in varying proportions together with stabilisers and emulsifiers in nondairy cream formulations.

Table 3.2 Constituents of coffee whitener.

Constituent	Quantity
Vegetable fat	10–12
Carbohydrate[a]	8–12
Sodium caseinate	1–2
Emulsifier[b]	0.15–0.25
Stabiliser[c]	0.04–0.06
Polyphosphate	0.04–0.2
Flavouring	as required
Water	Remainder

Notes: Quantities are given in g per 100 g.
[a]Sources: dextrose monohydrate, polydextrose and maltodextrin.
[b]For example, monoglycerides.
[c]For example, carageenan.

Development of such products tends in most cases to be protected by patents. A simple nondairy emulsion is a coffee whitener where the fat content is in the range 10–12 g per 100 g. Some of the components in coffee whitener are given in Table 3.2.

Coffee whitener products became popular in the marketplace in the mid-1980s, their production being aided by the development of sophisticated emulsifier–stabiliser systems and much improved recombination technology. Similar to other recombined water continuous emulsions, nondairy creams were prepared with care to achieve the desirable physical and organoleptic characteristics. Products containing vegetable oil have been formulated to include a certain proportion of dairy fat and solids so that these products closely resemble real dairy creams. For example, butter milk or butter milk powder is frequently used in nondairy products as these ingredients provide the characteristic creamy taste as well as the emulsifying ability of O/W emulsions. The selection of emulsifiers is important to achieve desirable characteristics such as an increase in the whitening ability of the coffee creamers and also to reduce the homogenisation pressure required to disperse the oil phase uniformly. The whitening power of a coffee whitener reflects the surface area created by the dispersed particles. The higher the surface area, the greater the light reflectance from the dispersion, and thus the greater the whitening effect. However, overhomogenisation also has its drawbacks, as it disrupts the fat globules and leads to fat oxidation.

3.2.2.2 Cream liqueurs

Cream liqueurs were developed in the mid-1970s and are water continuous dairy emulsions of high added value. Cream liqueurs are simply a combination of milk-protein-stabilised cream emulsion with high alcohol content. These emulsions are now produced commercially in large volumes and they are a popular product, especially in Ireland, the United Kingdom and mainland Europe.

The manufacturing methods are described by Banks and Muir (1985). The procedure can progress in two ways: via single-stage or two-stage processing. In the single-stage process homogenisation is carried out after the addition of alcohol, whereas in the

Table 3.3 Composition of a typical cream liqueur.

Constituent	Quantity
Cream (40 wt% fat)	30.0
Added sugar	18.0
Sodium caseinate	2.8
Alcohol (40% v/v)	38.0
Water	11.2

Note: Quantities are in g per 100 g.

two-stage process the homogenisation step takes place prior to alcohol addition. A typical formulation for cream liqueur is given in Table 3.3. In both methods the starting point is to prepare a cream base. It is prepared by mixing sodium caseinate powder and sugar into water. Cream is incorporated into this mix together with citrate by gentle agitation to form the cream base. Alcohol is added slowly with gentle agitation. This mixture is then homogenised twice at about 30 MPa at about 50–60°C and is then cooled. In the two-stage process the cream base is homogenised at 50–60°C, cooled to about 10–15°C and the alcohol is added slowly with gentle agitation. Banks and Muir (1988) observed that there are fewer large fat globules if the homogenisation is carried out in the presence of alcohol. As much as 97% of the fat globules in the emulsion has a diameter less than 0.8 μm when the product is homogenised twice at 30 MPa. In view of the relatively small diameters of these fat globules, the corresponding increase in total fat surface requires additional protein material to cover them adequately, and this protein is derived from the sodium caseinate incorporated in the cream base.

In some formulations either all or part of the sodium caseinate may be replaced with a suitable low molecular weight emulsifier. A heat-treatment stage is not required for cream liqueurs as they are protected from microbiological activity by the presence of the alcohol (14–17% v/v).

3.2.3 Ice-cream mix

An ice cream is both an emulsion and a foam containing ice crystals. Various components contribute to the stability of the system. Physico-chemically it is a very complex system, probably the most complex of all dairy products. The complexity is partly a result of the choice of ingredients and the use of sophisticated emulsifier–stabiliser systems.

A typical simple ice-cream mix contains the ingredients listed in Table 3.4.

Table 3.4 Typical ingredients of a simple ice-cream mix.

Ingredient	Quantity
Water	63.0
Sugar	15.0
Nonfat milk solid	11.5
Fat	10.0
Emulsifier–stabiliser system	0.5

Note: Quantities are averages and are expressed in g per 100 g.

3.2.3.1 Sources and functions of ingredients

The desired chemical and physical properties and organoleptic quality can be achieved through the selection of appropriate ingredients. The selection of ingredients varies from manufacturer to manufacturer, from regions of the same country to another and from country to country. Such variation exists because the ingredients used in making up an ice-cream mix will vary in character and may fluctuate significantly from one formulation to another. Commercially, the composition is a vitally important factor, contributing to characteristics such as eating quality, demand and competitiveness of market price. Manufacturers will favour the combination that will best stimulate demand and at the same time be made at a favourable cost.

Fat. Fat present in ice-cream products may be derived from animal or vegetable sources. In dairy ice cream, common sources of fat are whole milk, creams, butter, butter oil, sweetened condensed milk, evaporated milk, and milk concentrated by membranes (e.g. ultrafiltration and reverse osmosis). Other sources are milk powders, butter milk and whey. The minimum level of fat in ice cream varies according to national regulations. For example, in the United Kingdom ice cream is defined in the Food Labelling Regulations (1996), which state it should contain not less than 5% fat. This also applies to other European Union countries. Similarly, dairy ice cream should contain a minimum of 5% fat consisting exclusively of milk fat.

In some countries the description ‘ice cream’ may only be used if the fat is derived from cows’ milk. Regardless of the origin of the fat it must be free from off flavours and undesirable taste characteristics otherwise these will carry through to the finished products. Vegetable oil has a neutral taste, whereas dairy fat provides a characteristic creamy flavour. In addition, the melting characteristics of fats are important to achieve stability during storage.

Nonfat milk solids. These may also be called simply nonfat solids. They play an important role in the final eating quality of ice cream and therefore must not be used as a filler to increase the total solids content, as, above an optimum amount, nonfat solids can lead to a sandy texture resulting from the formation of lactose crystals. At the optimum level of addition they give body as well as enhance the aeration properties. Incorporation of nonfat solids supplements the use of proteins, milk salts (e.g. salts of calcium, magnesium, potassium and sodium, and chlorides, citrates and phosphates) and some vitamins (e.g. B, C and folic acid).

Sugars and sweeteners. The main function of added sugar in ice cream is to provide sweetness and therefore to increase the palatability. It also, for example, increases the food value and alters the physical properties, such as the freezing point, of the product. An increase in sugar content relative to the water content has a tendency to depress the freezing point of ice cream.

Sugar is derived mainly from cane and sugar beet. In formulations where sweetened condensed milk is used in significant quantities, it may not be necessary to add further sugar to the ice cream mix. Other sources such as malt sugar and corn sugar or corn

syrup may be used to replace 'normal' sugars (sucrose from sugar cane or sugar beet). An important consideration is that the sugar, either in solid or in liquid form, must not present handling problems in commercial use.

The majority of consumers show a preference for relatively sweet ice creams; in some recipes the total sugar content may be as high as 20%. Most products generally contain about 15% sugar. The level of addition plays an important role in adjusting the required final total solids content.

Stabilisers. The function of stabilisers is to prevent large crystals from forming during freezing of the ice-cream mix. The most commonly used stabilisers are derived from two main sources: gelatine, of animal origin, and food hydrocolloids, such as alginates, carrageenan, carboxymethyl cellulose (CMC) and gums, of plant origin. The quantity of stabiliser used is very small and tends not to induce undesirable organoleptic characteristics. Desirable qualities expected from the use of stabilisers are a smooth body, good textural properties, the presence of small ice crystals throughout the storage period and an increase in product viscosity.

Emulsifiers. Food emulsifiers serve a number of purposes. They promote the emulsification of the oil and the aqueous phase without separation, they have a starch-complexing ability, they interact with proteins, they modify fat crystallisation and the viscosity characteristics of food ingredients, they control foaming and antifoaming, they disperse solids in water and they provide lubrication. Hence, in addition to providing basic emulsification, there are other extremely important functions performed by emulsifiers. These functional properties are key factors in determining their suitability for various applications. The use of an emulsifier increases the ease of formation and promotes the stability of emulsions by reducing the amount of work required to form a homogeneous mixture of two usually immiscible phases (e.g. oil and water). This function is possible if the chemical structure of the molecule consists of hydrophilic (i.e. water-soluble) and lipophilic (i.e. oil-soluble) groups. The emulsifier can then partially dissolve in each of the phases and thus unite those phases in the form of a homogeneous emulsion. Figure 3.6 illustrates O/W and W/O emulsions.

3.2.3.2 Hydrophilic–lipophilic balance (HLB)

The hydrophilic–lipophilic balance (HLB) is used to classify emulsifiers. A number is assigned to each emulsifier that expresses the balance of the number and strength of its hydrophilic groups as compared with its number of lipophilic groups. In general terms, the HLB represents the oil and water solubility of an emulsifier. The HLB value can be calculated with knowledge of the chemical structure of the emulsifier, determined experimentally by comparison with emulsifiers of known HLB. For a homologous series of esters of polyhydric alcohols and fatty acids the simplest method is to calculate the value from analytical data by using the following formula:

$$HLB\ value = 20\left(1 - \frac{s}{a}\right) \tag{3.4}$$

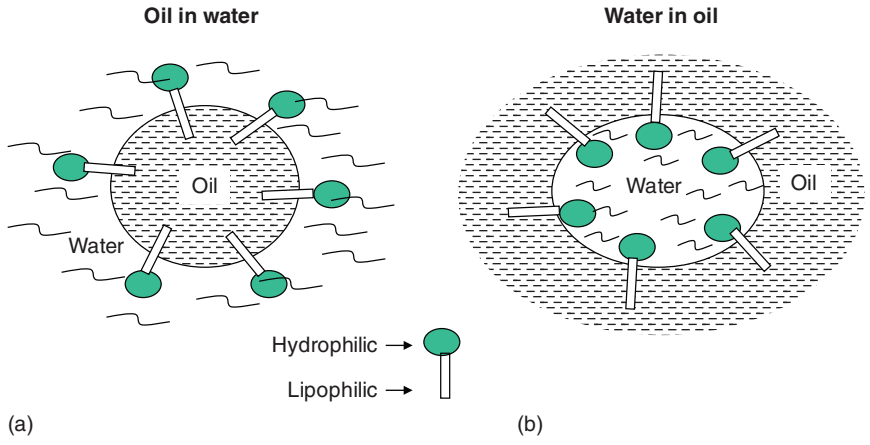


Figure 3.6 The role of emulsifiers in the formation of (a) oil-in-water emulsions and (b) water-in-oil emulsions.

where *s* is the saponification number of the ester, and *a* is the acid value of the fatty-acid radical. This method, which is based on weight percentages is satisfactory for emulsifiers that are nonionic. However, there are difficulties in determining the saponification value of some esters, and ionisation of the hydrophilic group in ionic emulsifiers will tend to exaggerate their hydrophilic character.

Table 3.5 shows that as the HLB value increases, the emulsifiers become more soluble in water and their function changes from being W/O emulsifiers to being O/W emulsifiers. Ice cream is essentially an O/W emulsion, and one would expect the most effective emulsifiers to have HLB values in the range 8–14. In fact, however, saturated monoglycerides with HLB values in the range 3–4 are by far the most widely used

Table 3.5 Common emulsifiers, categorised by hydrophilic–lipophilic balance (HLB) and application.

HLB value 3–6: water-in-oil emulsions
monoglycerides
glycerol lactopalmitate
propylene glycol monostearate
sorbitan esters
HLB value 8–14: oil-in-water emulsions
diacetyl tartaric acid esters
polyoxyethylene sorbitan esters
sucrose esters
decaglycerol distearate
HLB value 14–18: detergents
soaps
lecithin
decaglycerol monolaurate

emulsifiers in ice cream. This apparent anomaly arises from the fact that the function of the added monoglycerides is not emulsification per se but interaction with the milk proteins present to form a protective hydrophilic layer of adsorbed protein around the fat globules. These layers prevent the globules from coalescing and thus stabilise the fat emulsion. In addition, some bonding takes place between neighbouring protein layers, causing the fat globules to clump. This clumping effect is responsible for the dryness, texture and stand-up properties of ice cream. The fat globules containing adsorbed protein also help to stabilise the air bubbles incorporated into the ice cream during the freezing and whipping process. Emulsifiers generally used in ice-cream manufacture are monoglycerides and diglycerides (saturated, and polysorbates). Monoglycerides are used in the range 0.25–0.5%. They function to control fat destabilisation to confer dryness at extrusion, to provide resistance to shrinkage, to ensure good melt-down properties and to control overrun.

3.2.3.3 Other ingredients

Egg products. Egg yolk increases the nutritive value of ice cream but, equally, it is an expensive ingredient. Egg yolk also provides a characteristic flavour to ice cream and gives it body and texture. Egg yolk is rich in lecithin, which has emulsifying properties and therefore improves aeration and increases the viscosity. Therefore, in some ice-cream recipes it is used as a filler.

Starch. As with solids from egg products, starch may be used as a filler in ice-cream recipes or in special ice creams. In some recipes starch may be used as a substitute for gelatine.

Flavours and colours. Addition of such components to ice-cream mixes varies, depending on consumer preferences. There are many flavouring materials available. Commonly used flavouring materials in ice cream are vanilla, chocolate, fruit and fruit extracts, nuts and spices. Flavours may be harsh or delicate but, in general, the consumer will tolerate high concentrations of delicate flavours but may object to harsh flavours even in low concentrations. Therefore, finding the right flavour balance is important, especially when a product is made from mixed flavours. The intensity of the flavours should only be sufficient for the consumer to perceive it.

Colours are chosen in accordance with flavour. Fruit-flavoured ice creams may require only a small amount of added colour as the fruit itself may give sufficient colouring. Colours are not generally required for chocolate ice cream made with cocoa powder.

3.2.3.4 Creating a balanced ice-cream mix

As already mentioned, ice cream is a very complex product and requires careful selection of ingredients and close calculation of the proportions required to bring out the desirable organoleptic qualities and economic advantage for the manufacturer. Calculation methods are illustrated in detail by Arbuckle (1986). In the formulation of a balanced ice-cream mix it is important that initially the ratio between the fat and

the nonfat milk solids or that between the fat and the total solids be calculated to establish that the minimum requirement is satisfied for the various ingredients used in the formulation. Further addition of specific ingredients is possible provided that the level of addition is not detrimental to the organoleptic quality of the ice cream.

In such calculations the adjustment of fat will be similar to that for creams, described in Section 3.2.1.3, using Pearson's rectangle (Figure 3.4). In modern calculations computers are used to simplify quantitative specifications for ice-cream mixes. In addition to formulation work, such methods are used for assessing and comparing costs across various recipes.

3.2.3.5 Preparation of ice-cream mixes, and freezing

Preparation. Ice-cream mixes are formulated from many ingredients derived from a variety of sources. The key components are fats and oils, liquid dairy ingredients, powdered dairy and food ingredients, stabilisers and emulsifiers. To achieve the best from each individual ingredient in the formulation, optimum conditions should be ensured. This can be achieved by taking care in the order of incorporation and by using appropriate timing for inclusion.

Figure 3.7 illustrates the procedure for mixing ice cream to produce an O/W emulsion. The ice-cream mix should be heat treated (i.e. pasteurised). In the batch method the warm ingredient mix is homogenised and collected into a batch pasteuriser (for minimum heat-treatment conditions, see Section 3.2.4.1). In the continuous method, the preheating stage in the heat exchanger raises the temperature to 40–50°C. The mix is homogenised at 40–50°C and is then returned to the heat exchanger for pasteurisation. The normal pressure ranges for most formulations and homogenisers are given in Table 3.11 (on p. 115). Homogenisation can also be carried out after pasteurisation and cooled to about 45–50°C. In all the methods discussed here, the ice-cream mix must be cooled to below 10°C, preferably to less than 7°C. The cooled ice-cream mix is aged for at least 4 h or preferably overnight to allow fat crystallisation and the emulsifier–stabiliser system to take effect.

Freezing. Very small batches of ice cream can be frozen by using the batch method. However, all industrial operations use the continuous freezing method. A scraped-surface heat exchanger is used for freezing ice-cream mixes in the batch method and in the continuous method. The central shaft of the scraped-surface unit is fitted with scraper blades, and the shaft rotation speed can be altered in most industrial units to allow optimisation of product quality. Air is introduced into the mix either by suction of the feed pump or through injection into the freezer entry port. The scraped-surface freezer unit continuously whips the air into the ice-cream mix, with a concomitant reduction in temperature to freeze the water into small ice crystals. Figure 3.8 shows a cross-section of a scraped-surface freezer.

The freezing process thickens the consistency of the mix as the temperature is reduced to below about 0°C. The scraper blades, in addition to whipping air, continuously scrape the frozen layer of the product from the inner surface of the freezer barrel to facilitate good heat-exchange performance. The refrigerant material is circulated through the space between the product tube and the outer tube.

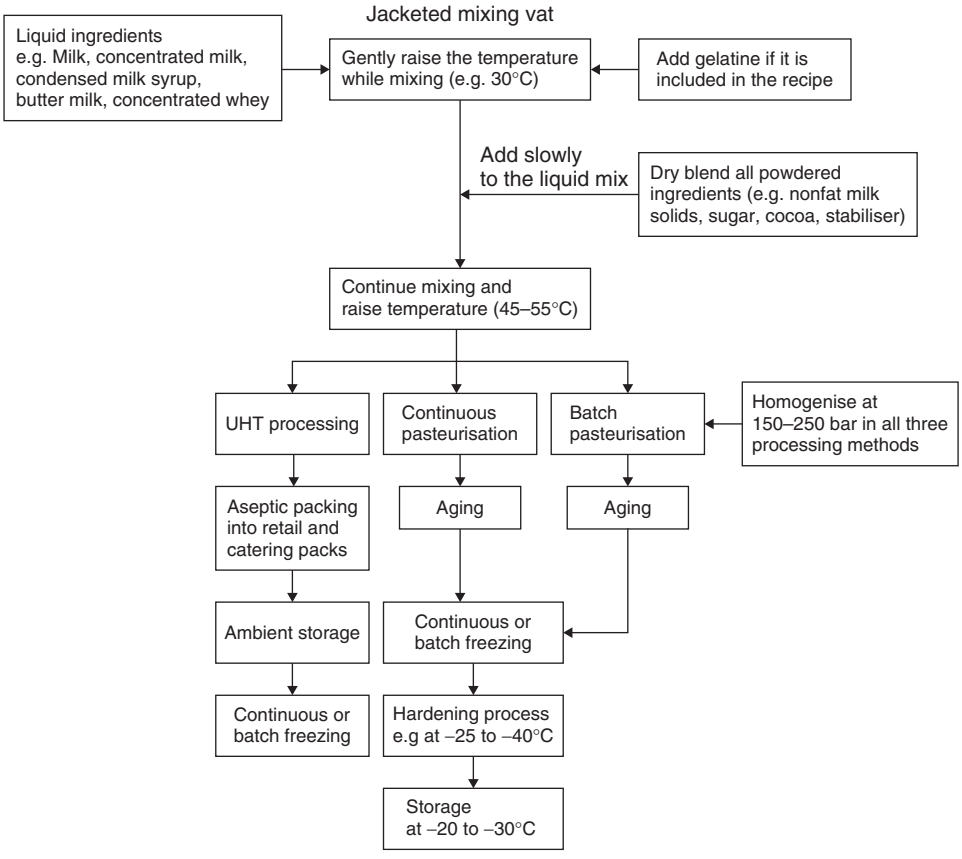


Figure 3.7 Flowchart for the manufacture of ice cream.

In the continuous phase there exist unadsorbed whey proteins, salts, high-molecular-weight polysaccharides and other macromolecules. After homogenisation, where the fat globules are reduced in diameter, new membranes are formed to cover the new fat globules. The membrane formation is completed during the ageing process, and some proteins are displaced by the emulsifiers.

In the freezing stage the air is uniformly distributed and forms a dispersed phase of air bubbles. Emulsifiers enhance the process of fat crystal formation due to nucleation during cooling and aging. They also enhance the whipping quality of the mix, the production of drier ice cream and facilitate moulding and various extrusion requirements. Dryness implies the absence of surface gloss and also a short nonsticky texture.

Ice cream exits the freezer unit at about -6°C to -8°C. At the exit from the freezer there is a back-pressure valve to generate the required pressure inside the scraped-surface unit. Ice cream exiting the unit is directed to the filling system for filling into individual servings and/or bulk packages. These containers go through a hardening process either in a batch process at -25°C to -30°C or in a continuous process by being passed through a tunnel. Hardened ice cream is stored at about -20°C to -25°C.

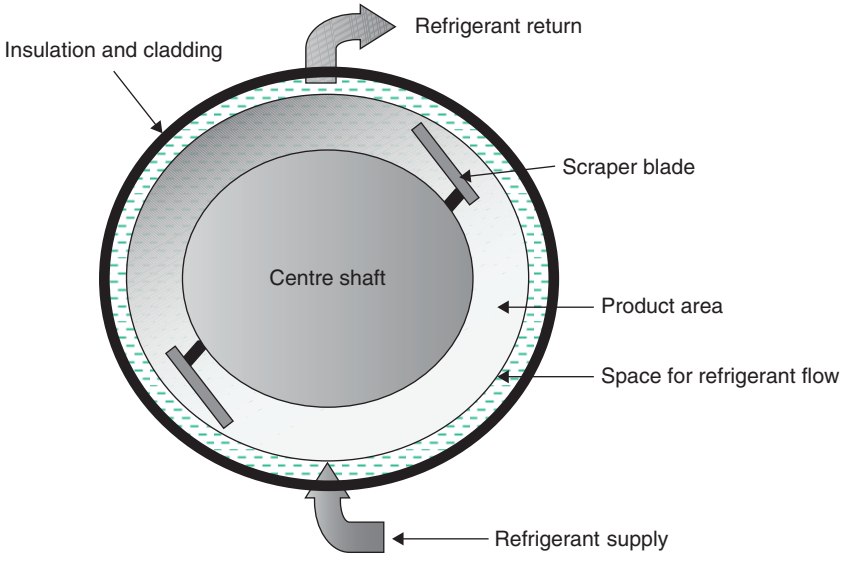


Figure 3.8 Cross-section of a scraped-surface freezer barrel.

3.2.4 Heat treatment of emulsions

The primary objective of a heat-treatment process is to ensure food safety, to comply with hygiene requirements and to facilitate those ingredients that require heat to activate and initiate functional properties. This applies to water continuous emulsions. Milk separation may be carried out as part of the heat-treatment process (e.g. pasteurisation). In many continuous heat-treatment applications on farms, a separator is linked to the heat-exchange unit either in the heating cycle or after the final heating stage and during the cooling cycle. In either arrangement the separation temperature used is in the region of 40–45°C. In the former method the separated fractions, skimmed milk and cream are further heat treated to pasteurise and are then cooled. The heat-treatment regimes designated, for example, in the Dairy Products (hygiene) Regulations (1995) are used for heat treatment of milks, creams and ice cream (see Section 3.2.4.1).

3.2.4.1 Pasteurisation

Pasteurisation methods can be either of the batch type or of the continuous high-temperature short-time (HTST) type.

- *Batch method*. In this method the product is heated to a temperature of not less than 65.6°C and held at that temperature for at least 30 min.
- *High-temperature short-time method*. In this method the product is heated to not less than 72.0°C and held at that temperature for at least 15 s (continuous

method), or it is heated to some other temperature for some other time regime, to have an equivalent effect to eliminate pathogens.

- *Ice-cream high-temperature short-time method*. Here, the product is heated to 79.4°C for not less than 15 s and is cooled to less than 7.2°C within 1.5 h before freezing. If frozen ice cream reaches above −2.2°C at any time during storage, it must undergo pasteurisation again before sale.

In each method the ice cream must be cooled to less than 10°C, preferably less than 7°C. Figure 3.9 illustrates the product flow arrangement for a continuous plate pasteurisation system. Some important design features in a HTST heat-treatment plant are as follows.

- The pasteurisation temperature sensor is located in the early part of the holding tube.
- A divert valve is fitted at the end of the holding tube.
- A continuous recording method is used for probes monitoring the temperatures of pasteurisation, hot water and the final product cooler.
- A pressure differential measurement and indicating device should be fitted to monitor the raw and pasteurised products. If the pressure differential is not monitored, a valid pressure-test certificate should be available for inspection by the licensing authority (every 12 months).

3.2.4.2 Ultra high temperature treatment

Long-life creams and ice-cream mixes have been produced successfully for many years in Europe. Long-life ice-cream mixes have become popular in many other parts of the world. The ultra high temperature (UHT) process was originally applied successfully to milk. The same basic processing methods were later adapted for creams and ice-cream

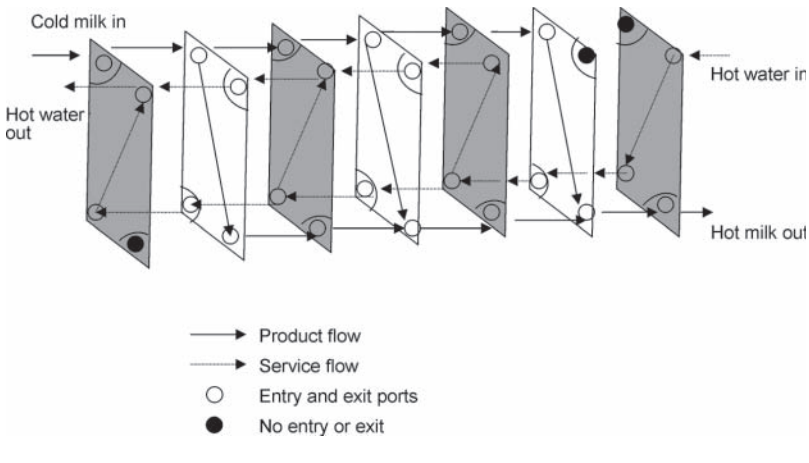


Figure 3.9 Flow arrangement in a plate heat exchanger.

mixes. The UHT process regimes used in the United Kingdom are defined in the Dairy Products (Hygiene) Regulations of 1995.

The minimum heat treatment required is defined as follows:

- Heat the product to not less than 140°C and hold that temperature for not less than 2 s

or

- Heat the product under other temperature and time regimes having an equivalent lethal effect on vegetative pathogens and spores.

The normal heat-treatment regimes used in commercial operations are 136–145°C for 2–6 s. For ice-cream mixes it is necessary to raise the temperature to not less than 148.9°C for at least 2 s. The regulations may vary according to the food process control measures introduced in individual countries.

Process plants have been developed and mechanised to be able to withstand heat-treatment duty and to satisfy hygiene and food safety requirements and the organoleptic quality preferences of the consumer. Heat-exchange systems are divided into three main types based on the method of construction: plate, tubular and scraped-surface. The most commonly used in the dairy industry is the plate-type heat exchanger. Plate heat exchangers are efficient in terms of energy usage and some plants have been designed to operate with 95% energy efficiency. The method of heat transfer is also divided into two main groups based on how the transfer is carried out: direct or indirect. The direct method may involve steam injection, in which high-pressure steam is injected into a stream of product, steam infusion, in which the product is injected into a chamber containing steam under pressure, or it may involve electrical heating, in which a high voltage passes between two electrodes placed inside a stainless steel tube carrying the product, the resistance to electrical conductance producing the necessary heat. Commercial plant using electrical heating are called simply 'ohmic heaters' and are supplied by the APV Company, England (for a description of this process, see Murray, 1985). In the indirect method, heat-conducting material such as thin plates or tubes separates the product and the heating medium. The heating medium may be steam, superheated water or electrical energy.

The time–temperature profiles of typical commercial UHT plants are given in Figure 3.10. Ranjith and Thoo (1984) described a procedure for producing fresh-tasting milk and milk products after UHT. This process is in commercial production in the United Kingdom. Burton (1988) has documented a comprehensive account of UHT processing. The heat treatment given to a product was originally quantified in terms of lethality values based on work carried out in the food canning industry. For example, the lethality value given to food products is described in terms of F_o values with reference to the death rate of the organism *Clostridium botulinum*. An F_o value of 1 is given when a product receives a heat treatment of 121.1°C for 1 minute. A simplified formula used in the calculation to derive F_o values in high-temperature processes is as follows:

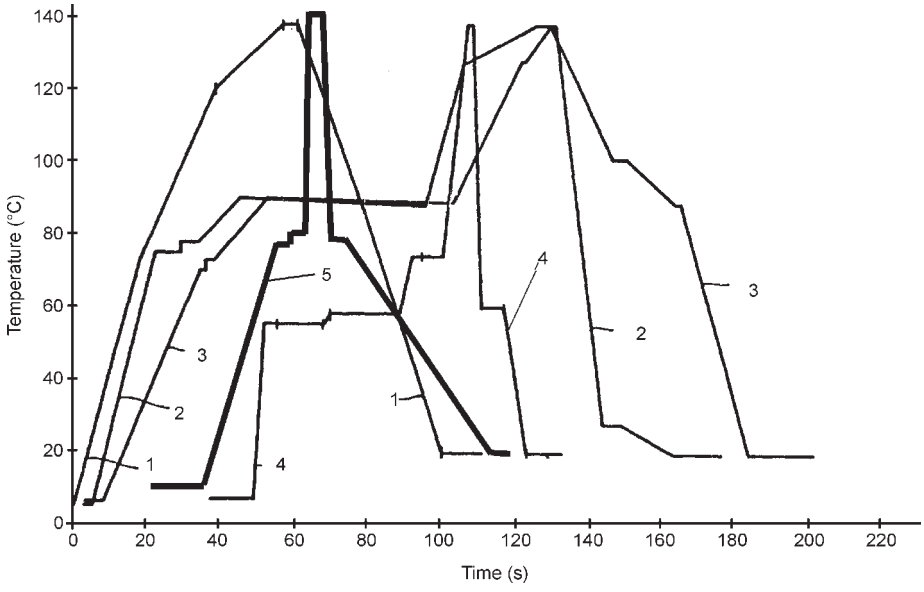


Figure 3.10 Temperature–time profiles for some commercial high-temperature plants. 1, Indirect plate, 85% regeneration; 2, indirect plate, 95% regeneration; 3, indirect tubular plate, 60% regeneration; 4, indirect plate, 70% regeneration; 5, indirect steam injection. *Source:* Ranjith and Rajah, 2001. Reproduced with permission of Taylor and Francis.

$$F_o = 10^{(T-121.1z)}t \tag{3.5}$$

where

T is the temperature (°C) of the process
t is the time (min)
z is the change in temperature (°C) required for the thermal death time to transverse one $\log_{10}$ cycle.

Kessler and Horak (1981) described alternative dimensionless values for quantifying the lethal effects of a heat treatment: the B^* and C^* values. A B^* value of 1 refers to a heat treatment when the spores of *Bacillus stearothermophillus* were reduced by 10^9 $\log_{10}$ cycles. A C^* value of 1 refers to a heat treatment where vitamin B_1 (thiamine) is reduced by 3%. For milk and cream processing it is necessary to achieve a higher B^* value and a C^* value as low as possible. These values can be calculated by using graphical methods (Kessler, 1981; Kessler and Horak, 1981).

Ultra high temperature (UHT) products are always stored and filled under aseptic conditions, without which a long shelf-life at ambient temperatures would not be possible. An aseptic system in commercial production is shown in Figure 3.11. A key feature in such a system is that every point where a valve isolates the sterile product

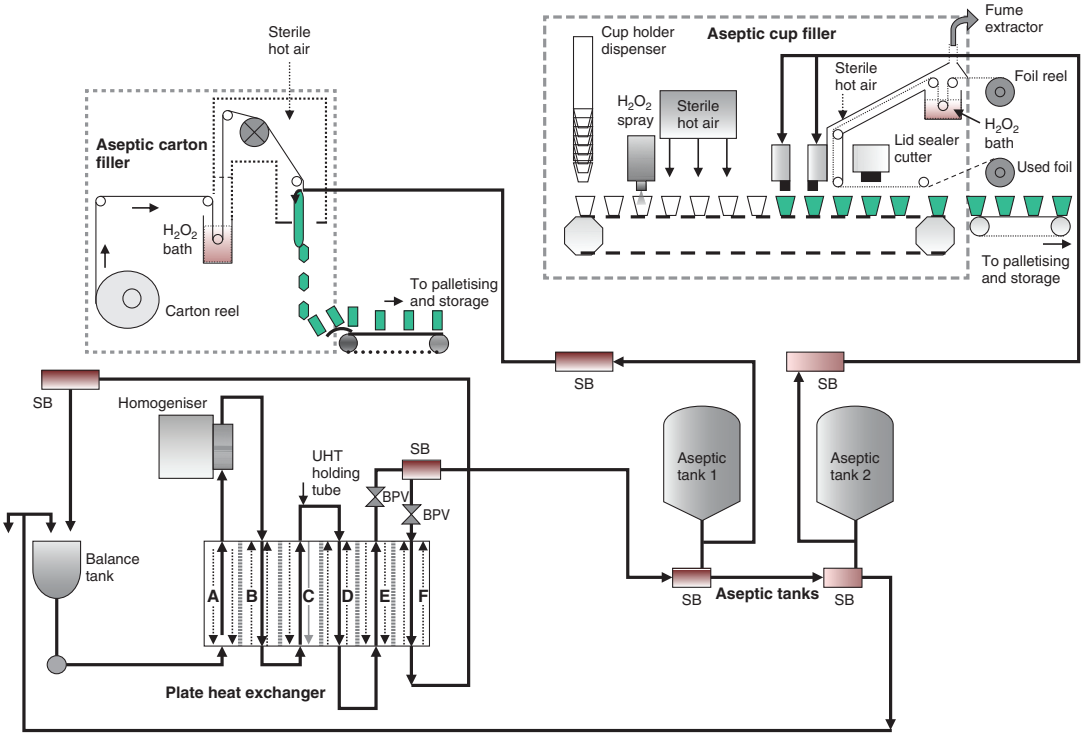


Figure 3.11 An industrial ultra heat treatment (UHT) processing and aseptic filling system. SB, steam barrier valve; BPV, back-pressure valve; A, preheater 1; B, preheater 2; C, UHT heater; D, cooler 1; E, cooler 2; F, sterilising cooler. *Source:* Diotte Consulting & Technology, UK. Reproduced with permission of Diotte Consulting & Technology, UK.

from a nonsterile environment (air, water, cleaning material), a steam tracing device exists to protect the product from contamination. In addition, where the product is diverted to aseptic storage tanks and aseptic filling machines, an aseptic valve cluster is installed to facilitate product diversion, steam barrier functions and cleaning in place (CIP). The sequence of valve operations and monitoring of events are very complex in an industrial installation and require a programmable controller. The program itself is carefully prepared to control a specific installation so that coordination of events and all necessary precautions are taken to ensure that recontamination does not take place.

3.2.4.3 Extended shelf-life processes

A systematic investigation into the poor keeping quality of milk and creams commenced in the United Kingdom in the early 1970s by the Milk Marketing Board (MMB, England and Wales). At that time it was well known that the storage life of cream, milk and other fresh liquid milk products was very short. For example, when these products are stored at ambient temperature (e.g. $10-20^{\circ}C$) for a few hours, the microbiological quality can reach unacceptably high levels even when they are subsequently stored under refrigerated conditions. The shelf-life of such products can be prolonged by storing the products under refrigerated conditions ($5^{\circ}C-8^{\circ}C$) immediately after heat treatment. Such low-temperature storage conditions prolong the shelf-life from perhaps 1 or 2 days to perhaps 4 or 6 days, but prolongation of shelf-life by this extent is of limited value industrially. The deterioration in the quality of milk, cream and other fresh liquid milk products is due to microbiological activity that generally develops within a few days of storage to such a level that the product takes on unacceptable flavour characteristics and frequently undergoes unacceptable physical changes. The microbiological activity that gives rise to these unacceptable changes is not prevented by conventional pasteurisation treatment. The bacteria in refrigerated bulk raw milk consist mainly of Gram-negative psychotrophs. Some of these organisms synthesise extracellular proteases and lipases that are resistant to heat (Griffiths *et al*., 1981; Law, 1979) and therefore control of their numbers in milk is important. Pasteurisation of dairy products is a thermal treatment to destroy pathogens that may be present. However, it also destroys a large proportion of the nonpathogenic bacteria. Thus the thermal treatment makes the product safe and improves the keeping quality but it does not improve the organoleptic quality of the product. Recently, the E-coli 0157 strain has been found in heat-treated milk in the United Kingdom and elsewhere. This was not due to survival from heat treatment but was mostly due to post-process contamination. This highlights the problems faced in delivering milk with good keeping qualities and 'freshness'.

Microbiological quality of raw milk. Cows' milk is an almost perfect food for human beings and is the perfect food for calves. Unfortunately, it is also a good source of food for microorganisms. Milk from the udder of a healthy cow contains very few organisms (not more than about $300\,ml^{-1}$) and these are of no danger to the consumer. Therefore, milk is contaminated generally by post-production handling, including milking equipment and the general hygiene of operatives. The keeping quality of raw milk is

determined mostly by the initial number of microorganisms present in the milk and by the temperature at which it is retained after production. Hygienic milk production has advanced in most countries, and in the European Communities the standards are defined for the maximum allowable total viable counts per millilitre of raw cows' milk. Raw milk viable counts are becoming an important factor in modern dairy processing as the time interval between milk production and processing has increased. Other factors such as alternate day collection and changes to factory operation methods further extend this time interval. Delay in processing means that psychotrophic bacteria can proliferate. It is the psychotrophic spores in large numbers that can undermine a heat-treatment regime, as the microbial inactivation follows first-order reaction kinetics. For example, if the heat-treatment regime were capable of reducing the number of colony-forming units (cfu) by a factor of 10^4, an initial count of 10^5 cfu ml^{-1} would leave 10 cfu ml^{-1} after processing. This is the scenario with heat-resistant organisms, but not with vegetative pathogens. Thermodurics are defined as those organisms that survive a temperature of 63°C for 30 min; endospores can survive a temperature of 80°C for 10 min (Lewis, 1999). Therefore, the quality of raw milk will vary depending on general production hygiene, the equipment used, the environment, and organism population and type.

High-temperature pasteurisation. Pasteurisation of milk and milk products by the continuous flow method applies a heat-treatment regime of 72°C for 15 s. These conditions destroy pathogens in milk, in particular *Mycobacterium tuberculosis*. However, a pathogen *Mycobacterium paratuberculosis* was found to survive this pasteurisation regime, and many milk processing dairies have already extended the holding time from 15 s to 25 s in order to destroy this organism.

One drawback of the present pasteurisation process is that the whole system is vulnerable to post-process contamination. Thus, the shelf-life of the product may vary from one day to another, depending on the total counts in the final product after heat treatment and depending on fluctuation in storage temperature. It is difficult to guarantee the hygiene standard of milk holding tanks, filling machines, packaging materials and the packaging environment. If contamination is high, then the shelf-life may be reduced significantly. Therefore, a method to extend the shelf-life of creams and milks is desirable in order to minimise losses through microbiological spoilage.

Consequently, there is still a need for a heat-treatment process that will inhibit the microbiological activity in fresh milk and milk products to an extent that will permit the product to be stored under refrigeration for prolonged periods of time (e.g. in excess of 4 weeks), and at the same time avoid the difficulties of an unacceptable 'sterilised' flavour. The method described here is based upon careful selection of temperature and time combinations suitable for milk and milk products to inhibit microbiological activity when they are stored at 5–10°C for periods of up to 7 weeks or longer. Any heat-treatment process showing poor organoleptic characteristics was considered to be unacceptable.

The microbiological development of milk after a heat-treatment regime in the range 74–81.5°C (using an indirect plate heat exchanger) is shown in Figure 3.12 (a).

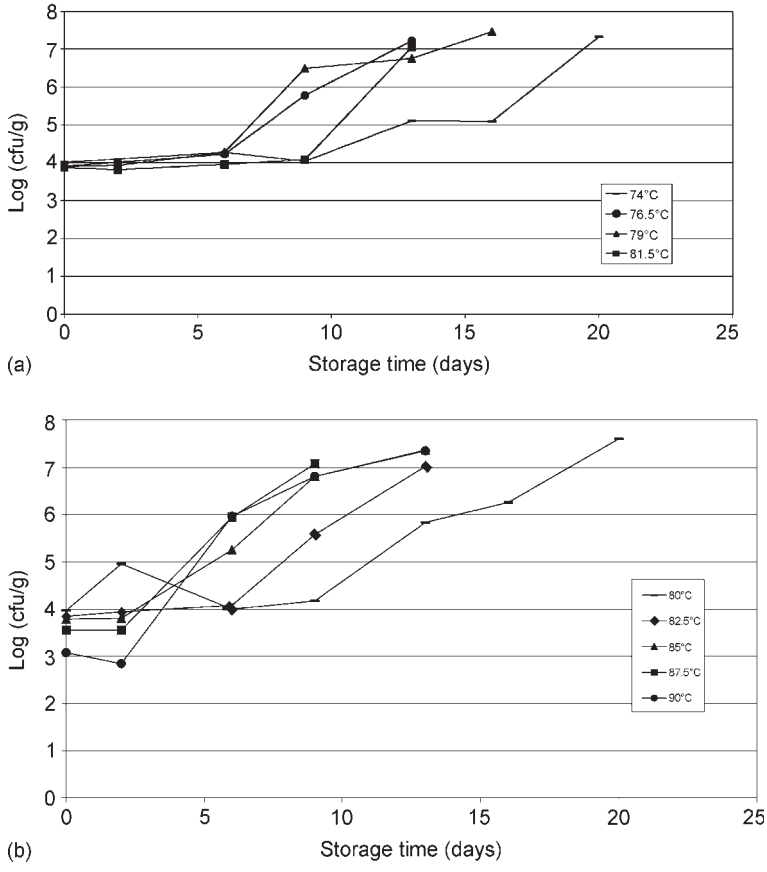


Figure 3.12 Microbiological development in heat-treated cream stored at 7°C: (a) pasteurisation at temperatures in the range 74–81.5°C (holding time 15 s); (b) flash pasteurisation at temperatures in the range 80–90°C (holding time 1 s). Note: CFU, colony-forming units.

Contrary to the general belief that by increasing heat-treatment temperature, shelf-life will be prolonged, results indicate that bacteriological counts increase during storage. For example, in this experiment, cream was treated at the lowest temperature and had a shelf-life of 20 days whereas that treated at the highest temperature (81.5°C) was unacceptable after 13 days at 7°C.

In flash pasteurisation heat-treatment temperatures in the range 80–90°C are used commercially with a holding time of 1 s or less. Figure 3.12 (b) shows microbiological development in heat-treated cream stored at 7°C. The end result shows that the microbiological quality obtained with this treatment was similar to that obtained with the higher temperature pasteurisation as illustrated in Figure 3.12 (a). Comparing the results in Figures 3.12 (a) and (b), one can see that the holding time plays a significant part in the shelf-life of milk and milk products. For example, the cream heat treated

Table 3.6 Pasteurisation effect (P^*) of various heat-treatment regimes.

	Temperature (°C)							
Time (s)	72	75	79	80	81.5	82.5	85	90
15	1	2.4	7.5	10.0	15.4	20.5	–	–
1	<0.1	0.16	0.5	0.7	1.03	1.4	2.8	11.9

at 80°C for 1 s had a longer shelf-life than that treated at 79°C and 81.5°C for 15 s. It can be seen from Figure 3.12 (b) that 20 days shelf-life was achieved for heat treatment at 80°C for 1 s, whereas creams treated at 82.5°C, 85°C and 90°C for 1 s were unacceptable after 9 days.

The pasteurisation effect P^* of each heat-treatment regime was calculated according to Kessler and Horak (1981) and the results are listed in Table 3.6. The recommendations of the International Dairy Federation (IDF) for minimum conditions for pasteurisation (72°C for 15 s) was given as $P^* = 1$. The pasteurisation effects at 72°C for 15 s and at 80°C for 1 s were close, and the total microbiological development after storage at 7°C for 20 days was comparable. However, the pasteurisation effect was 15-fold more at 81.5°C for 15 s, yet the shelf-life was limited to 13 days. Similarly, at 82.5°C up to 90°C for 1 s, the pasteurisation effect was more severe than at 72°C for 15 s but the shelf-lives were limited to 9–13 days at 7°C.

The reason for this contradiction is associated with the microbiological development of those organisms that are tolerant of high temperatures. The aseptic packing techniques in the sample production ensured that other organisms did not enter the system to cause post-process contamination downstream of the highest temperature in the system. Therefore, bacteria present in the cream had survived the heat treatment and were able to grow at 7°C. The results of thermoduric and spore counts at various heat-treatment regimes are listed in Table 3.7. Of the thermoduric group of organisms, *Bacillus cereus* is able to grow rapidly at 7°C and therefore would limit the shelf-life of the product.

Scientists have known about the activation of thermoduric organisms such as *Bacillus cereus* by high-temperature pasteurisation for a long time (Brown *et al*.,

Table 3.7 Thermoduric and spore counts of heat-treated cream stored at 7°C.

Heat treatment		Thermoduric	Spores	Shelf-life
Temperature (°C)	Time (s)	count/g	count/g	(days)
74.0	15	1.02×10^4	1.85×10^3	20
76.5	15	2.75×10^4	1.71×10^4	13
79.0	15	1.08×10^4	1.00×10^3	16
81.5	15	2.36×10^4	1.55×10^4	13
80.0	1	1.07×10^4	8.55×10^2	20
82.5	1	2.44×10^4	2.60×10^4	13
85.0	1	1.48×10^4	1.75×10^2	13
87.5	1	4.70×10^3	2.70×10^2	9
90.0		7.8×10^3	1.69×10^4	13

Source: Brown *et al*., 1980. Reproduced with permission of John Wiley & Sons.

1980; Kessler and Horak, 1984; Schroder and Bland, 1984). It was believed activation is caused by the heat shock on the spores resulting from high-temperature treatment regimes. However, investigations by Barrett *et al*. (1999) into the lactoperoxidase system (LPS) in milk found that the high-temperature inactivation of LPS also plays an important role in the poor keeping quality. The antimicrobial activity of LPS was attributable to its oxidation product, with a hypothiocyanite group, being able to oxidise the sulfhydryl (–SH) groups of bacterial cell walls (Reiter and Harnulv, 1981). Therefore, if the LPS were inactivated by a heat-treatment regime, the level of antibacterial activity could also be reduced. Barrett *et al*. found that inactivation of LPS was temperature sensitive, with *z* values of about 4°C. The inactivation appears to take place close to 80°C, and Lewis (1999) reported that when hydrogen peroxide and thiocyanate were added to heat-treated milk (to enhance the LPS), they increased the keeping quality of milk heat treated in the region of 72–76°C for 15 s when kept at 30°C, but no such increase was detected in the region 78–90°C. This showed that at the higher temperatures, the LPS had been inactivated.

In the absence of antimicrobial activity from LPS, the preservation of milk and milk products requires more severe heat treatment to reduce the thermodurics and spores. Table 3.8 shows the microbiological development in cream heat treated to 115°C, 117.5°C, 120°C, 122.5°C and 125°C.

A heat-treatment temperature range of 120–125°C for 1 s tends to increase the keeping quality of cream to an acceptable standard when tested after storage for 49 days at 7°C. As before, post-process contamination was avoided by using aseptic filling techniques.

An acceptable product with very low surviving thermodurics and spores was obtained by the high-temperature heat treatment, but it was also desirable that the final product be similar to pasteurised milk and cream in terms of organoleptic characteristics. The organoleptic qualities of milk and cream after heat treatment are shown in Table 3.9. Freshly prepared pasteurised milk and cream were used for organoleptic assessment. The organoleptic characteristics for high-temperature heat-treated milk and creams stored for more than 37 days (more than 49 days for single cream) were similar to those of pasteurised products. A heat-treatment temperature range of

Table 3.8 Microbiological development in heat-treated cream stored at 7°C (total counts per gram).

	Heat-treatment temperature (°C)[a]				
Age of cream (days)	115	117.5	120	122.5	125
0	9	7	2	<1	1
2	10	8	1	1	<1
6	7	3	2	3	<1
9	3150	700	105	3	1
13	$>3 \times 10^6$	$>3 \times 10^6$	20	4	3
20			15	10	10
41			40	15	15
49			<10	<10	<10

Note: [a]For a duration of 1 s.

Table 3.9 Organoleptic quality of milk and creams after heat treatment and storage at 7°C.

		Mean acceptability score[a]		
Product	Shelf-life (days)	120°C, 1 s	125°C, 1 s	74°C, 15 s
Milk	>37	7.7	7.6	7.8
Single cream	>49	7.7	7.6	6.75
Whipping cream	>37		6.9	7.6
Double cream	>37		6.8	6.9

Note: [a]A value of 1 indicates the product is unacceptable; a value of 10 indicates the product is good and fresh.

Table 3.10 Lethal and chemical effects of some UK heat-treatment methods.

Heat treatment	B^*	C^*	Lactulose ($mg\,l^{-1}$)
Extended shelf-life	0.006	0.013	<40
Ultra heat-treatment			
direct	3.55	0.27	80–100
indirect	1.20	0.19	200–500
Sterilisation	1.00	5.50	550–750

Note: $B^* = 1$ for $\log_{10}$ 9 reduction of thermophilic spores; $C^* = 1$ for 3% reduction of thiamine (vitamin B_1).
Source: Diotte Consulting & Technology, UK. Reproduced with permission of Diotte Consulting & Technology, UK.

120–125°C for 1 s tends to increase the keeping quality of cream to an acceptable standard when tested after storage for 49 days at 7°C. As described before, the use of aseptic filling techniques prevented post-process contamination.

The results of total counts and organoleptic quality assessment provide sufficient information to design a high-temperature pasteurisation method to extend the shelf-life of milk and milk products with use of a standard dairy heat exchange system. Table 3.10 compares the lethal effects of high-temperature pasteurisation with some commercial heat-treatment methods. The values increase as the severity of the heat treatment increases. The aim is to achieve a high B^* value and low C^* and lactulose values to produce a safe product with good keeping quality and acceptable organoleptic characteristics.

To guarantee an extended shelf-life of more than, for example, 30 days in chilled distribution, it was necessary to include aseptic filling to prevent post-process contamination.

A method based on high-temperature pasteurisation was first commercially operated in the United Kingdom in 1980. The extended shelf-life (ESL) process together with aseptic filling was also robust, withstanding fluctuations in chilled temperature distribution in commercial operations.

Microfiltration. In membrane filtration technology, microfiltration is the specified area where the particle size ranges from about 0.09 μm to about 9 μm. This size range is able to reject molecular weights greater than 100 000. In the ESL process the membranes have a nominal pore size of about 1–2 μm and are capable of reducing the bacterial cells and spores in the product by more than 99%.

In the microfiltration process the milk is first separated at about 60°C, and the skim fraction is then cooled to about 50°C. The membrane filters in the circuit then separate the permeate and retentate in a form of concentration process. The microbial cells and spores are also rejected and get collected along with the retentate. This is a very small fraction and is either discarded or heat-treated to destroy the cells and spores before the fraction is added back to the microfiltered skimmed milk. The microfiltered skimmed milk, permeate and cream can be mixed in appropriate proportions to formulate various milks and creams and can then be pasteurised.

Bactofugation. This process was developed based on the principles of centrifugal separation, where the dense bacterial cells and spores are collected as a single fraction after separation. A hermetic centrifuge called a bactofuge is employed as the main unit to carry out the separation of the bacterial cells and their spores. There are three main methods of bactofugation:

- two-phase bactofuge with continuous discharge of bactofugate;
- single-phase bactofugate with intermittent discharge of bactofugate;
- double bactofugation with two single-phase bactofugates in series.

Bylund (1995) gives details of the third system. In essence, it can be described as being a two-phase bactofugation with continuous discharge and sterilisation of bactofugate. The milk is separated into cream and skimmed milk, the skimmed fraction being rich in bacterial cells and spores. The skimmed fraction is subjected to separation by a two-phase bactofuge. The bactofuge separates the bactofugate, which is rich in spores and other microbial cells, as it is denser than the rest of the skimmed milk. This bactofugate is subjected to sterilisation by steam infusion. The sterilised fraction is mixed with part of the skimmed fraction to cool prior to adding it to the main stream skim flow in the circuit. The skimmed milk resulting from bactofugation and heat treatment is mixed with cream to formulate standardised milk and creams. These products can be pasteurised according to the standard methods described in Section 3.2.4.1.

3.2.4.4 Homogenisation of emulsions

A homogeniser is simply a high-pressure pump usually designed to operate with a three-piston arrangement. It was invented in 1899 by a Frenchman, August Gaulin. The general method of homogenisation of creams and other dairy products involves pumping the liquid by a positive displacement pump arrangement into a homogeniser valve chamber or head. The head encloses the valve arrangement, with a very narrow gap allowing the product to exit. When the product is allowed to exit through the narrow slit, the product particle velocity undergoes a sudden increase, which breaks down the coarse material and incoming fat globules (up to about 20 μm in diameter) to a much finer particle size ($<1\,\mu$m). The term 'homogenisation' is also used by equipment suppliers for equipment that carries out high-shear mixing of products in batch operations. For example, high-shear mixers and colloid mills are used to incorporate powders and other ingredients into liquids to ensure uniform distribution

of particles. This type of operation does reduce the particle size and disperse the ingredients uniformly, but the size-reduction capability is not comparable with a high-pressure homogeniser. Particle-size reduction by ultrasonic waves has also been used but practical, economic and commercially viable units are not as yet available in the food and dairy industries.

With the inclusion of a homogenisation step in the process one would expect to achieve a stable emulsion as a result of particle size reduction, a smoother mouth feel as a result of the smaller fat globules, the need to use less stabiliser, a shorter ageing time, better overrun and a decreased tendency to churn fat in the freezer in ice-cream mixes. Therefore, even small variations from the optimum process conditions can lead to significant deterioration of consistency and texture. The design of the homogenising valve has been improved over the years, and Phipps (1985), Stistrup and Andreasen (1966) and White (1981) have reported on the performance of various commercially available systems.

There are four main valve designs: the bell-flow, flat, conical and liquid whirl. The particle sizes vary significantly for the different valves. In the flat-valve design the pressure must be almost double that of the liquid-whirl design to achieve the same particle sizes. It is important to note that the homogenisation procedure may be either single-stage or two-stage, depending on the design of the head. The second stage involves simply routing the product through a similar path as the first stage.

The main components in a homogeniser are the piston driving unit, the high-pressure head and the homogenising valve housing. The movement of the pistons out of the high-pressure head shuts the exit valves and opens the inlet valve and allows the product to enter the chamber. When the pistons move into the head the inlet valve shuts and opens the exit valve to allow the product to reach the homogenising valve (or valves in a two-stage process) under pressure. The product exits through a restriction and then through a second restriction (called the first stage and second stage, respectively) or, in the case of the liquid-whirl design, two steps in the same valve allow two homogenisation stages. In both methods the increase in pressure is achieved by manually operating a plunger (forcer) or by hydraulic pressure, to close the product exit gap between the two faces of the homogenising valve (or to restrict the exit orifice of the product). When the product is forced to flow through a very narrow orifice, the particles (mainly fat globules) must go through a size-reduction stage, their new size reflecting the size of the gap from which they escape. The second-stage homogenisation pressure is lower than the first-stage pressure, and its main purpose is to break up the clusters of fat globules formed after the first-stage homogenisation. For example, if the total pressure specified for homogenisation of cream were 200 bar, then the first-stage pressure could be set at 17 MPa, and the second-stage pressure at 3 MPa. Table 3.11 indicates some homogenisation conditions used for fresh creams and ice creams with use of a flat-valve homogeniser. In Table 3.11, a range of values is given, reflecting the conditions used in the dairy industry and taking into consideration variables such as the throughput of the homogeniser, the temperature used at different installations and the efficiency of the valves in the head.

Table 3.11 Homogenisation pressures and temperatures used in the commercial production of creams and ice creams.

		Homogenisation pressure (MPa)	
Product	Temperature (°C)	Stage 1	Stage 2
Cream			
12% fat	45–70	15–20	3–6
18% fat	45–70	10–32	3–8.5
Ice cream	50–75	16–20	3–5

The product itself can determine the optimum conditions, as the ratio of nonfat milk solids to fat is important to ensure sufficient solid material is available to reduce interfacial tension. Sommer (1944) reported that for cream a ratio greater than 0.85 would prevent fat clumping. A ratio in the range 0.6–0.85 could lead to some clumping. A ratio less than 0.6 significantly increases the clumping of fat globules. The ideal homogenisation conditions for creams are best established by conducting trials to select the most appropriate parameters to produce the desired product characteristics.

In long-life milks, creams and ice-cream mixes the homogenisation can be done after the sterilisation stage and the cooling section of the process (downstream). To be able to homogenise in this downstream position, the pistons and pressure-adjustment devices must be fitted with steam tracing to protect the product from post-process contamination.

Double homogenisation. Information on double homogenisation or multiple homogenisation is limited. Geyer and Kessler (1989) reported that double homogenisation of 12% fat cream showed improvement in physicochemical properties. Stistrup and Andreasen (1966) were among the early investigators to establish the effect of single-stage, two-stage and double homogenisation of ice-cream mixes. Their results showed that fat-globule dispersion in ice cream was better with the liquid-whirl valve design compared with the flat-valve and conical valve designs in single-stage homogenisation. Two-stage homogenisation did not improve the degree of dispersion in comparison with single-stage homogenisation, whereas double homogenisation gave a higher degree of dispersibility than single-stage or two-stage homogenisation. Four linear relationships were found to exist between the logarithm of optical dispersion (a measure of light scattering) and the logarithm of pressure applied, for all methods.

Homogeniser care. Basic care of the components of the homogeniser not in contact with food is as equally important as for the homogenising head and valve arrangement. Components such as drive belts, crankshaft, oil pump and seals should be regularly checked for wear and tear to ensure that running efficiency is optimal. In the homogenising head the chevron seals can easily be damaged by abrasive food components such as cocoa powder. This is also true for the pistons. Ordinary pistons are hardened and coated with a thin layer of chromium oxide to withstand excessive wear. Other materials such as ceramic-coated pistons have been used successfully for processing emulsions containing abrasive material.

The inlet and exit valve seat surfaces in the homogeniser head should be free from pitting and crevices. They require regular inspection, and, if necessary, surface cutting and grinding should be carried out according to the supplier's instructions. Similar checks are necessary for homogenising valves. One problem is the appearance of extensive wear on the face of valves, forming a specific pattern of erosion rings caused by separation and cavitation (Phipps, 1985). A sharp-edged inlet arrangement increases flow separation, and at low homogenising pressure the valve seating develops flow patterns. A suitable valve with the correct inlet angle should be used for efficient homogenisation.

The seals in the homogenising valve chamber must be checked regularly, as faults in these seals can allow unhomogenised product to leak out. The seals when fully compressed tend to leak under high pressure. The result of such a leak is the formation of a fat ring on top of UHT milk when it has been left standing for a few days.

3.2.5 Preparation of dressings

Salad dressings are designed to form an O/W colloidal macroemulsion but, unlike creams and ice cream, they are acidic food products with a pH in the range of 3–4. There are two basic categories of dressings: the mayonnaise-type salad dressings made with cooked starch paste, and the French-type dressings.

The basic ingredients in mayonnaise are oil, water, stabilisers or thickeners (eggs, edible gums), flavouring and colouring materials. Some regulations specify 65% as the minimum oil requirement for mayonnaise, but many commercial products contain 75–80% oil. Table 3.12 gives an example of ingredients used for high-fat and medium-fat mayonnaise formulations.

Salad dressings contain a slightly lower oil content compared with mayonnaise (30–40%). The ingredients are cooked starch, emulsifiers and stabilisers (i.e. gums to provide stability and thickness). There are two types of French dressing: the separating type and the nonseparating type. The separating type is a temporary O/W emulsion containing oil, vinegar, lemon juice and seasonings. Table 3.13 lists an alternative

Table 3.12 Formulation of mayonnaise.

	Oil content	
Ingredient	80%	50%
Vegetable oil	80.0	50.0
Stabiliser	0.0	1.0–4.0
Emulsifier	9.0	6.0
Salt	0.5	1.0
Sugar	0.5	4.0
Vinegar[a]	6.0	15.0
Mustard	0.5	1.0
Seasoning	optional	optional
Water	remainder	remainder

Notes: Quantities are in g per 100 g.
[a] 10% acetic acid.

Table 3.13 Formulation for a French dressing.

Ingredient	Quantity
Sugar	2.5
Dried mustard	2.5
Salt	2.5
Worcestershire sauce	1.5
Vegetable oil	60.0
Vinegar	31.0

Note: Quantities are in g per 100 g.

formulation for a typical French dressing. The main ingredients in nonseparating French dressings are egg yolk and/or other emulsifying ingredients (to keep the oil in suspension) and stabilisers such as gums to provide extra stability to the emulsion.

Mayonnaise is used to enhance the flavour and texture of some foods and also functions as a spread. Applications for salad dressings are much more diverse and the products are supplied in a variety of flavours and thicknesses. Therefore, a wide range of products also exists based on the modifications to physical characteristics. Such perceived physical characteristics (viscosity, body and thickness) have a direct relation to the ingredients used as stabilisers and to oil-phase volume in the recipe.

Mayonnaise is a stiff product whereas salad dressings are somewhat thinner and can be made to a pourable or spoonable consistency. Consumer demand is responsible for such a wide variety. Reducing the oil content and substituting oil with fat replacers also produces the low-fat and no-fat varieties. Thickeners are added to compensate for the loss of oil and to restore the required physical characteristics.

3.2.5.1 Manufacturing procedure

In the manufacture of mayonnaise and salad dressings, salad oils are used for the oil phase and, typically, vegetable oils such as soybean, sunflower, corn, rapeseed, olive and cottonseed oils are used. Soybean has been the most cost effective and widely used oil but other oils, typically rapeseed oil (also known as canola), can be a more economic alternative. The term ‘salad oil’ is generally reserved for those products that remain substantially liquid at refrigerator temperatures (4–7°C). This property is referred to as resistance to graining at chilled storage. They have varying degrees of flavour and oxidative stability, depending on the main oil and manufacturing standards. Most oils are refined, bleached and deodorised to remove flavour and are sometimes lightly hydrogenated. An exception to this concerns olive oil, which is generally not deodorised because it lends a special flavour quality desirable for dressings. Those salad oils that have high melting oil fractions that solidify in refrigerated storage are put through a process called ‘winterisation’ to remove these fractions. Sometimes, crystal inhibitors such as polyglycerol esters and methylsilicone are added to further protect the oils from grain formation or crystallisation.

Salad oils contain a high proportion of unsaturated fatty acids and are easily oxidised. The oils contain natural vitamin E in small concentrations and provide protection against oxidative rancidity.

Flavour in salad dressings and mayonnaise is derived from the oils used, the spices added as solids finely dispersed in the emulsion, water-soluble salts, alcoholic products or from flavoured vinegars and vegetable preparations such as tomato products. The aqueous phase in these products is usually the vinegar, which is a weak solution of acetic acid (at least 2.5% by weight). Highly flavoured products such as cider, wine or malt vinegar are also used. Equally, other well-established flavouring components are citric acid and lemon juice.

For mayonnaise and salad dressing production in industry (the batch method), equipment such as jacketed stainless-steel tanks fitted with temperature-control devices and agitators are used, together with colloid mills or high-shear mixers. In the production of mayonnaise, initially the egg and flavour ingredients are mixed thoroughly to form a base to which oil and vinegar are added by continuous agitation. Once the ingredients are mixed, the mixture is passed through a high-shear mixer such as a colloid mill. The final consistency and texture of the emulsion are affected by the rate of addition of the oil during the premixing stage. For example, to obtain fine oil droplets, the oil is dispersed by using a high-shear mixer, increasing the viscosity of the product. The mixing and colloid mill treatment are carried out at about 10°C.

In the manufacture of salad dressings, gums are mixed with an acidic aqueous phase; this process may include a heating profile to hydrate the solid particles. Gums are added to increase the viscosity, as the oil content is less than that for mayonnaise.

In the manufacture of mayonnaise and salad dressings a heat-treatment stage is not included. The acidity of the final product is sufficiently low to inhibit the proliferation of microorganisms.

The manufacture of mayonnaise and salad dressings can also be automated as well as produced by a continuous production method for large-scale industrial operations. Figure 3.13 illustrates an industrial layout for mayonnaise production.

Originally, salad dressings and mayonnaise products were packed in glass containers. Glass containers provide protection against attack by oxygen. However, polyethylene (PE) based containers have been introduced more recently. PE is not as good as glass as a barrier material against oxygen, but it provides greater protection for it allows antioxidants to be incorporated into the product.

The manufacture of a nonemulsified (separating) type of salad dressing is a simple procedure. It involves only mixing, and the mixture is then filled into containers.

3.3 Factors affecting water continuous emulsions

Water continuous emulsions, where the pH is in the neutral range, provide a good medium in which microorganisms can grow. Therefore, products such as milks, creams and ice-cream mixes provide a good environment for the multiplication of bacteria, yeasts and moulds unless some control measures are taken to limit their number. Salad dressings and mayonnaise-type products are acidic food emulsions, the low pH inhibiting the growth of most microorganisms.

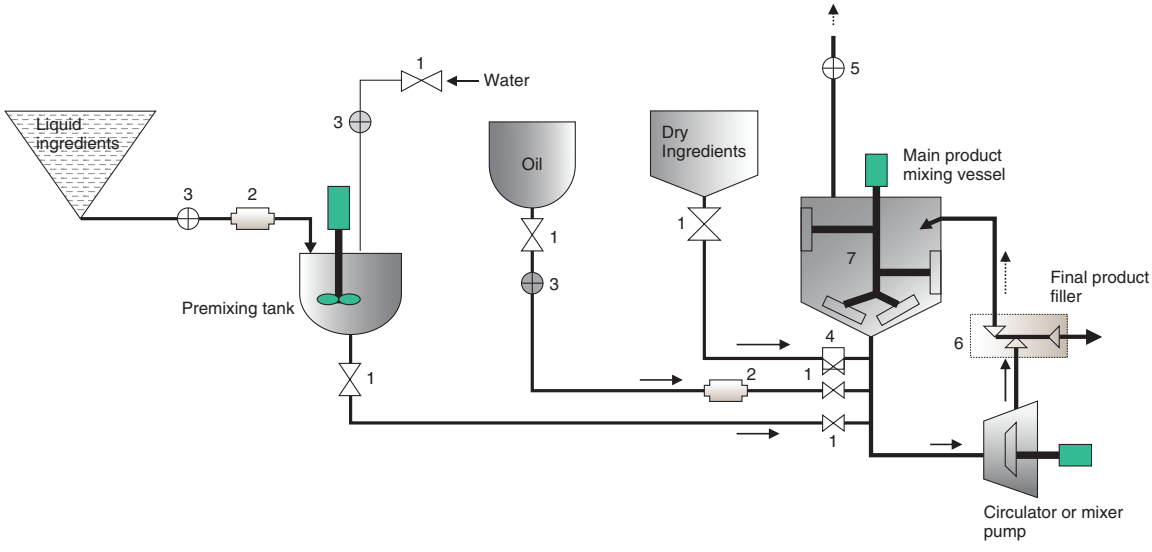


Figure 3.13 A batch industrial mayonnaise production circuit. 1, isolating valve; 2, flow meter; 3, product pump; 4, Venturi power injector; 5, vacuum pump; 6, product divert valve; 7, scraper agitator.

In ice cream the microbiological problems are reduced to some extent because of the low temperature at which it is stored until it is consumed or until the end of its shelf-life (-25°C to -30°C). It is important to ensure that the storage temperature is maintained throughout its shelf-life period. In these emulsions, microbiological activity leads to changes in pH, mainly lowering it depending on the extent of the activity. In milks and creams, such a change in pH (e.g. to a pH less than about 6) would bring about emulsion instability as well as undesirable organoleptic characteristics.

3.3.1 Emulsion stability of high-fat creams

At normal storage temperature, the fat globules in milk show a tendency to form clusters compared with those in a nonrefrigerated environment. Milk silos are kept under slow agitation at regular intervals to minimise cluster formation and fat separation. The size of the fat globules affects the efficiency of the separation of cream from milk, and the optimum temperature for separation will vary depending on globule size. A large proportion of smaller fat globules ($<2\,\mu$m) can reduce skimming efficiency by allowing the fat percentage in the skimmed milk to rise. Larger fat globules with a distinct yellow colour (compared with that of milk from, for example, a Friesian herd) is generally present in milk from Jersey herds. Rothwell (1966) and Foley *et al*. (1971) investigated various processing parameters that influence the emulsion stability of creams. These investigations highlighted the influence of milk separation temperature, cream pumping, pasteurisation, cooling and fat percentage on the physical properties of cream and on damage to the integrity of the fat globules.

3.3.1.1 Physicochemical defects in fresh creams

In many industrial installations equipment designed for products more robust than cream (i.e. milk, skimmed milk, juice drinks) is employed for handling creams. As stated before, the handling and processing circuits need to be very gentle when handling cream in order to minimise shear and mechanical damage.

In the preparation of high-fat creams (e.g. 48% fat cream = double cream in the United Kingdom) there is a tendency for a solid plug of cream to develop and, in some instances the viscosity may rise to unacceptably high levels under optimum process conditions. Defects in cream are associated with the fat percentage of cream and, depending on the use to which the product is put, these defects may come under strong criticism from the end user.

Defects such as oiling off, formation of a cream plug and age thickening have been associated directly with the level of free fat (or solvent-extractable fat) present in the cream, known to increase with fat content, especially above about the 40% fat level. Section 3.2.1.2 highlights the incidence of fat in relation to the use of a centrifugal separator in the preparation of creams.

An O/W emulsion prepared with increased levels of free fat will result in a product likely to show instability immediately after preparation or in the early stages of the shelf-life. The instability has been described in many ways, the most familiar descriptions relating to creaming, flocculation, coalescence and disruption.

The process of fat globules rising to the surface as a result of differences in density between the aqueous phase and the fat globules and the consequent formation of a thick, fat layer is termed 'creaming'. The presence of free fat tends to aggravate this as the crystallised and liquid fat exits the globules as a result of damaged or missing globule membranes and forms a solid fat layer on the surface of the cream.

The fat globules also come together and form floccules, making them much larger particles. These then begin to rise faster than individual globules as the floccules are less dense than the aqueous phase. However, the floccules are fairly redispersible. In floccules, individual fat globules exist but these are bound together with neighbouring globules by weak forces.

Fat globules coming together and bound by strong forces form clusters. These fat globules unite at their contact points and share interfacial layers. The clusters can be redispersed with application of mechanical energy, as in the case in the second stage of the homogeniser. The formation of clumps indicates serious destabilisation of the emulsion, as the clumps are not usually considered to be redispersible. The fat globule membrane material of individual globules come together and form a continuous membrane round them, and the fat forms a continuous mass, completing the clump formation. It is reported that clumps are formed from partly solid globules (Mulder and Walstra, 1974). These clumps will coalesce into one large globule when all the fat becomes liquid (owing to a rise in temperature). Once the cream is cooled, some of the high melting fat fraction will have become crystallised, the crystal formation generating physical forces within the globules. If the cold cream is subjected to mechanical forces as a result of harsh handling methods, the fat globules will tend to become damaged. This leads to further cluster formation. Te Whaite and Fryer (1975) found that gel formation in cream is linked directly with the formation of free fat in creams.

3.3.1.2 Physicochemical defects in ultra heat-treated creams

The most widely manufactured UHT creams in the United Kingdom are the half-creams (not less than 12% fat) and single creams (not less than 18% fat). The general term 'coffee cream' is used for creams with a fat content in the range of 10–20% and is used mainly in catering applications. Other high-fat creams (whipping cream, 35–38% fat; double cream, 48–50% fat) are produced but the demand tends to be seasonal. Since the mid-1980s demand for low-fat whipping cream has increased in Europe and the USA. Mann (1987) reviewed whipping cream, including low-fat whipping cream. Anderson and Cawston (1975) reviewed the progress of research work under the subheading 'The milk fat globule membrane', covering details of the milk fat globule membrane and its composition.

Stability of UHT coffee cream. A common problem associated with some coffee creams is an instability known as 'feathering', which shows coagulated curd-like flocs floating on the surface when the product is added to hot coffee. This phenomenon was reported as far back as the 1920s and 1930s by Doan (1929, 1931). Anderson *et al*. (1977a, 1977b) and Geyer and Kessler (1989) have also investigated the stability

of UHT coffee creams with reference to shelf-life, extending the shelf-life, and the influence of manufacturing methods on feathering.

The stability of cream to hot coffee is affected by the homogenisation pressure and temperature, the homogenisation position (i.e. upstream or downstream position in the circuit), the hardness of the water used to make coffee, the acidity of the coffee, and the temperature of the coffee. This shows that feathering is partly a result of changes brought about by alteration of the structure of milk proteins caused by processing and also, partly, by the harsh conditions of coffee preparation. Usually, these creams are stable to hot coffee immediately after processing (i.e. they resist feathering); the tendency is for the product to become susceptible to feathering on storage at ambient temperature. The exact transformation of various components in the O/W emulsion leading to feathering was not initially fully understood. Early researchers suggested the possibility of changes to the fat–water interface, but Anderson *et al*. (1977a, 1977b) confirmed that an increase in the ratio of fat-phase casein to calcium was associated with the feathering in UHT coffee cream, suggesting that casein is the more important factor. They also observed that susceptibility to feathering is associated with the tendency for adjacent fat globules to become linked by bridges of casein (see Figure 3.14). Most of the fat globules have casein micelles associated with them, and numerous submicellar casein particles appear to be attached to the surface. Therefore, feathering is accompanied by an increase in calcium and casein levels and in the ratio of casein to calcium in the fat phase of the cream. I have investigated single cream prepared by various methods (Table 3.14), including a new method of producing cream involving making adjustments to the diffusible-calcium (calcium in the aqueous phase) content (Ranjith, 1995). In this method, the milk is first subjected to membrane filtration (ultrafiltration) so that the retentate has a total solids content of 35–38 wt%. The permeate is subjected to an ion-exchange process to remove calcium and magnesium (diffusible divalent ions). Deionised permeate is added back to the retentate to reconstitute the original whole milk. The whole milk is then separated to obtain diffusible-calcium-reduced (DCR) cream (single cream or coffee cream).

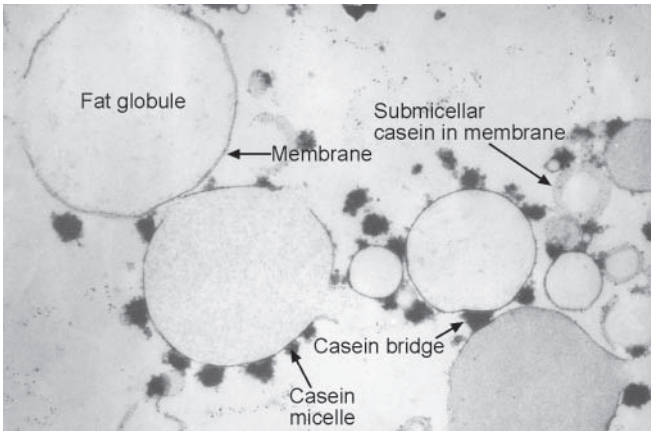


Figure 3.14 Ultra heat-treated cream exhibiting severe feathering. *Source:* Diotte Consulting & Technology, UK. Reproduced with permission of Diotte Consulting & Technology, UK.

Table 3.14 Methods used for the preparation of coffee cream.

Cream	Composition
1	Control cream
2	Cream with calcium content reduced to c. 20% of original level
3	As for cream 2, with 1.5 g per 100 g sodium caseinate added
4	Diffusible-calcium-reduced cream

Note: Fat content 20 g per 100 g product.

Each cream preparation was divided into two equal portions and subjected to UHT treatment by the indirect plate method, with one portion being homogenised in the upstream position at 170/34 bar (170 bar at first stage, 34 bar at second) by using an Aluminium Pressure Vessel (APV) Manton Gaulin homogeniser. The cream was preheated to 55°C prior to homogenisation. In the downstream method after UHT treatment at 140°C for 3.5 s it was cooled to about 60°C prior to homogenisation (170/34 bar). The creams were cooled, in both methods, to 20°C before aseptically filling into 150 ml plastic containers and sealing with an aluminium-foil lid.

When tested, the cream prepared by this method was found to resist feathering for up to six months at ambient storage temperature. More importantly, this cream was very stable to alcohol in the alcohol stability test. It was stable to 95 vol% ethanol when tested after six months at ambient storage. A cream liqueur prepared with use of this cream was stable to retort sterilisation, and the emulsion was stable for more than two years.

The viscosity of coffee cream made by the methods summarised in Table 3.14 were tested, and the results are given in Figure 3.15. All cream samples made by adjustment of calcium content (except batch 3, containing added caseinate) showed a slight

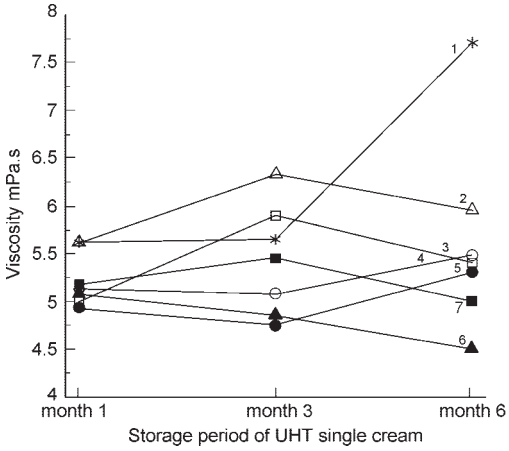


Figure 3.15 The change in viscosity of ultra heat-treated single cream as a function of storage time. Cream 1, control cream, made by downstream homogenisation; creams 2 and 3, calcium-reduced cream, made by upstream and downstream homogenisation, respectively; creams 4 and 5, calcium-reduced cream with added sodium caseinate, made by upstream and downstream homogenisation, respectively; creams 6 and 7, diffusible-calcium-reduced cream, made by upstream and downstream homogenisation, respectively. *Source:* Ranjith, 1995. Reproduced with permission of Dr Heva Ranjith, Diotte Consulting & Technology, UK.

reduction in viscosity after six months at ambient storage. The control cream made by upstream homogenisation developed a thick plug after two months. The control sample made by downstream homogenisation showed thickening after six months (the viscosity increased by 36%) but did not form a plug.

The sample containing added sodium caseinate showed a gradual increase in viscosity, although the total calcium level was reduced by about 20% of the original value. It is possible that calcium adjustment reduces the likelihood of casein bridges forming between fat globules, thereby keeping the viscosity low or even reduced during long-term storage and helping to maintain a uniform, homogeneous O/W emulsion. The increase in casein content could be responsible for the increase in viscosity during storage, with casein bridges being built between the fat globules.

Other experimental work has indicated that the problem of feathering can be minimised by immobilising the calcium in cream by using chemical additives such as phosphates, citrates and carbonates.

Stability of UHT whipping cream. The primary objective of UHT is to achieve a long shelf-life for products at ambient storage with minimum heat damage and minimum changes to organoleptic characteristics compared with the fresh product. However, a homogenisation step is essential in the manufacture of high-fat liquid dairy products to minimise fat separation. An optimum homogenisation pressure is desirable as high pressure tends to be somewhat disadvantageous when one wishes to create a stable foam having about 100% overrun (see Equation 3.6). Kieseker and Zadow (1973) found that milk separation at 43°C was ideal for manufacturing UHT whipping cream (36% fat) with desirable whipping properties. Whipping properties are overrun, serum leakage or seepage, free-fat content and whipping rate (assessed by using a scale of 1 to 5, where 1 is very poor, and 5 is excellent). The overrun can be calculated as follows:

$$O = \frac{W - W^{\text{whip}}}{W^{\text{whip}}} \times 100 \tag{3.6}$$

where

O is the percentage overrun
W is the weight of a specific volume of cream
W^{whip} is the weight of same specific volume of whipped cream.

The control of overrun in industrial whipping equipment is possible as such equipment is provided with devices to adjust the cream feed rate, the air injection rate and the rate of rotation of the worker unit.

The overrun may not be the same for different cream preparations and each batch of cream must be treated differently from previous batches, and fine-tuning and adjustments are necessary to optimise the control parameters to achieve a stable foam.

Excessive shear in the worker unit can be detrimental to the cream and leads to poor overrun and other whipping properties. Table 3.15 lists the parameters affecting the production of good-quality UHT whipping cream. The methods described for

Table 3.15 Effect of preparation and processing on the whipping characteristics of UHT whipping cream.

Parameter and its effect on product properties
Milk quality
Poor microbiological quality causes lipolysis of fat as a result of lipase, originating from bacteria surviving the UHT treatment
Milk separation and cream preparation
A temperature above about 40°C is suitable for milk separation to ensure fat is in the liquid form
Milk supply to the separator must be appropriate for required throughput of the separator to reduce the production of free fat through shear action. The fat content of the cream separated should be as close as possible to the final fat content of the product. This tends to reduce excess free fat in cream.
Permitted stabilisers can be added at this stage by incorporating them into the skimmed milk by using a high-shear mixer; this fraction is then added to the cream with gentle agitation. Stabilisers tend to reduce seepage but also reduce the overrun; therefore optimum level of stabilisers is desirable
Cream pumping
A positive displacement pump is desirable to ensure minimum disruption to fat globules
UHT processing and homogenisation
UHT treatment by indirect or direct methods are suitable, but shear damage to fat globules as a result of steam injection may affect whipping properties
Homogenisation is usually carried out above about 40°C in the preheating stage, but the downstream process (after UHT treatment) may have a slight advantage over this in terms of whipping properties. Two-stage homogenisation with 20–25 bar in the first stage and 7–12 bar in the second stage is a suitable specification for most homogenisers to produce good whipping and storage properties
One-stage homogenisation tends to encourage cluster formation and, depending on the homogenisation pressure, gel formation in the cream is a possibility during storage
Cream cooling methods
Whipping cream is generally manufactured to have low viscosity.
To obtain a low viscosity the cream is rapidly cooled in the heat exchanger to below 10°C.
To obtain a slightly thicker consistency, the cream is cooled to about 25–30°C and filled aseptically into containers and held for 2–4 h at ambient temperature before overnight storage at a chilled temperature below 10°C. This treatment allows the crystallisation of liquid fat and develops the viscosity

whipping cream can also be applied to the manufacture of double creams and other high-fat creams.

3.3.1.3 Foam formation and stability

The formation of air bubbles when handling milk, skimmed milk and creams is a common problem in dairies and food factories. Nevertheless, based on this foaming ability, aerated products such as whipping cream and ice cream have been developed and became established in the markets. Recently, milk for cappuccino coffee has become popular in many countries. As its popularity increases, the consumer will expect a good quality foam when consuming the beverage. For example, the foam in a cappuccino coffee is expected to stay stable until at least half the coffee is consumed. Similarly, whipped cream must produce stable foam after whipping to produce an overrun of about 100%. Additives to improve aeration are not permitted in milk in many countries.

Sometimes milk fails to produce an acceptable level of foam in cappuccino coffee. Whipping cream also sometimes produces a poor overrun or the foam collapses soon

after it has formed. This means that the fundamental mechanism of foam formation must be understood so that appropriate steps can be taken to ensure the desired properties of foam are achieved. In whipped cream the air bubbles in the foam are held in a three-dimensional matrix of partially coalesced fat globules.

The microstructure study of whipped cream also clearly shows partly destabilised fat globules adsorbed at the air–water interface. The gas phase in foam provides specific textural character; for example, the lightness in whipped cream or the scoopability in ice cream. In dairy creams and alternatives the emulsions are stabilised by the proteins. These proteins should be soluble in the emulsion and rapidly diffuse into the oil–water or air–water interface. This is an important functional property of protein, and poor solubility characteristics mean poor emulsion stability as well as poor foaming ability of the emulsion. Other equally important characteristics of the protein is that it should reorient its structure until some degree of unfolding of the molecule is achieved, sufficient to bring about intermolecular interactions leading to the formation of a coherent film. This continuous, cohesive film brings about considerable mechanical strength and viscoelastic properties, which plays an important part in the stability of emulsions and foams.

During aeration the protein diffuses into the air–water interface and gets adsorbed. When more and more proteins are adsorbed, the surface tension at the interface reduces. The protein structure orientation at the interface is important at this stage, as its hydrophobic part must unfold towards the air whereas the hydrophilic part must associate with the aqueous part, or water phase. Interaction and association between proteins are important to the integrity of the film. Emulsion temperature, acidity and ionic strength all affect the protein–protein interactions. The whey proteins, especially β-lactoglobulin, are well known for their foaming properties in milk and milk products. They increase its adsorption rate with increase in ionic strength. This protein exists in globular form and, during pasteurisation, unfolding of the structure causes more charged sites to become exposed to the emulsion, which enhances the adsorption process. Anderson *et al*. (1987) examined the structure of whipped cream by surface electron microscopy and the photographs taken show evidence that the inner surface of air bubbles consists of a continuous air–serum interface through which individual fat globules protrude. In the whipping process fat globules penetrate into the air–water interface and are then attached to the air bubbles. At the same time fat globules clump and form a network, spreading some of the fat on the air bubble surface. A network of air bubbles and fat clumps finally entraps the liquid from the emulsion to provide rigidity and stability to the foam. Therefore, the foaming ability of milks and creams depends on:

- the solubility of proteins, and protein–protein interactions;
- the ability of proteins to reorient and become adsorbed at the air–water interface;
- the formation of a strong and viscoelastic film to entrap air bubbles;
- the formation of fat globule clumps and network over air bubbles and film;
- the ability of the film to hold serum and provide rigidity to the foam.

A high free-fatty acid content in the emulsion tends to give antifoaming properties and causes poor overrun as well as serum drain. Stabilisers help to minimise serum leakage from the foam but they also reduce the overrun of the foam.

3.3.2 Defects in ice cream

In commercial terms the composition of an ice-cream mix is an important factor for two main reasons. The composition influences and stimulates consumers to eat the product and creates demand. The demand is also a reflection, to some extent, of the pricing strategy of the product. A further concern for the manufacturer is the cost of producing a specific volume of ice-cream mix. Therefore, the choice of ingredients together with the cost of production, if optimal, stimulate demand for generating a commercially viable product or process system. Defects in the final product originate from flavour, body and texture, melting characteristics, colour, packaging, microbiological quality and composition.

3.3.2.1 Compositional issues

Too low a fat content affects the palatability and food value of ice cream. A very high fat content is also found to be difficult to assimilate and, owing to its large content of heat units, can become especially objectionable in warm weather. Fat content in the range of 8–10% appears to be popular for most markets. It is equally important to optimise the level of nonfat milk solids as in many formulations it is responsible for good overrun because of the foaming characteristics of casein and whey protein. Therefore, about a 5% level of nonfat milk solids in the ice-cream mix has been used for most formulations as the lower limit, but about 8–12% is frequently used by many manufacturers in commercial products. Figure 3.16 illustrates the structure of ice cream.

The ingredients used to provide the nonfat milk solids could be responsible for one particular defect, which is described as ‘sandy ice cream’. Sandy ice cream arises from the crystallisation of the milk sugar (lactose). Crystallisation of milk sugar is possible under certain conditions, such as those experienced after the mix has been frozen. The other possibility is that sugar crystals already exist in some of the dairy ingredients in the formulation. The level of nonfat milk solids is responsible for a sandy texture, and a level of less than 9% tends to prevent this problem from occurring. Other factors, such as aqueous phase material, could influence the solubility of lactose, but this does not appear to be a significant factor in causing a sandy texture. However, long-term storage of ice cream also allows sufficient time for crystal formation. Therefore, storage period may be an important factor for some formulations. Closely associated with texture defects is the coarse taste resulting from large ice crystals. Gelatine and alternative stabilisers have been used in formulations, as they are capable of influencing the water crystal size during freezing. A smooth texture can be achieved by incorporating, for example, about 0.5% gelatine, but higher levels, apart from being costly, could become organoleptically objectionable, as the ice cream does not melt readily on the tongue.

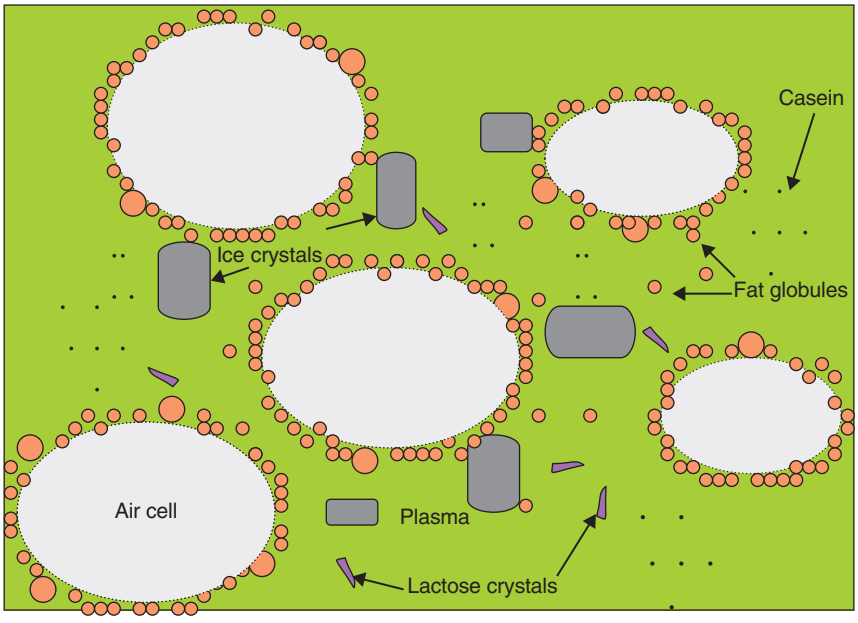


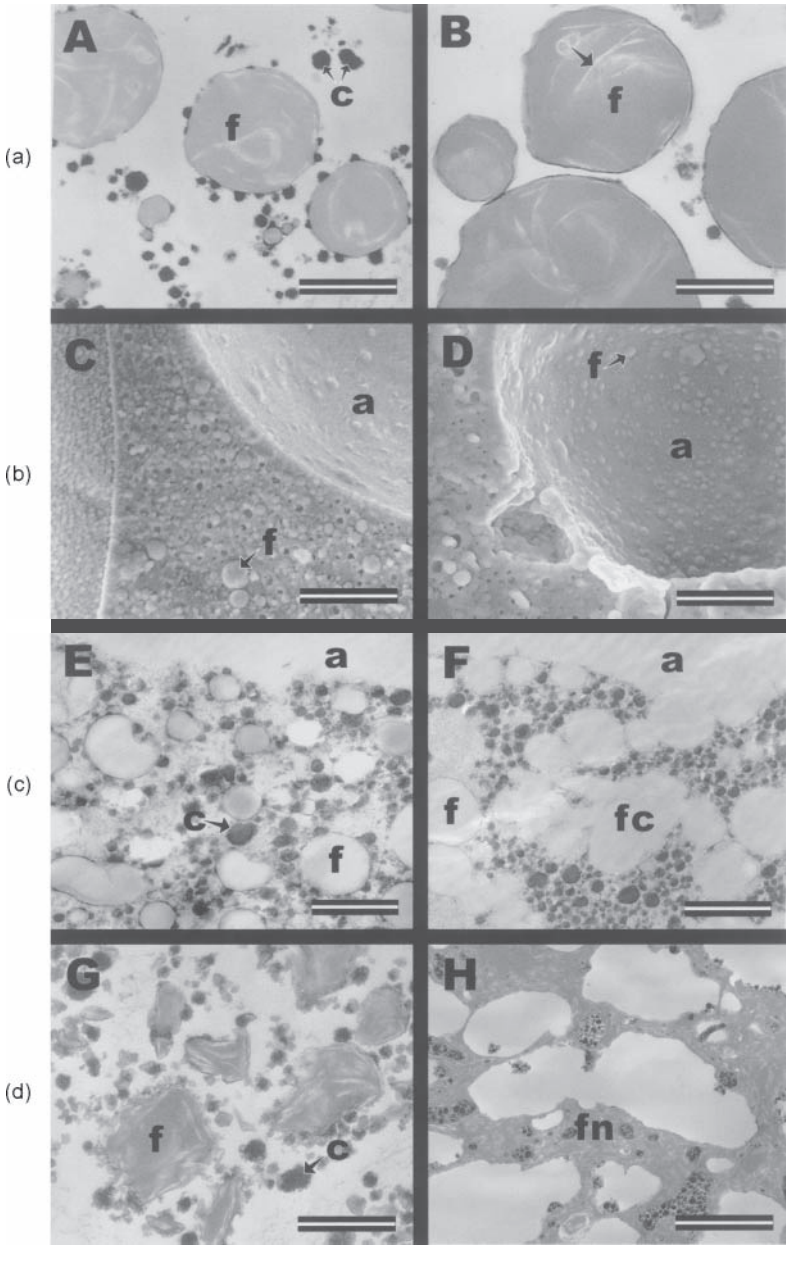
Figure 3.16 The structure of ice cream (not to scale).

3.3.2.2 Shrinkage in retail containers

Shrinkage of ice cream is a problem that is visible in retail containers from time to time without any other obvious defects. The mechanism of shrinkage is attributed to the collapse of lamellae, or the walls between the air cells, caused by changes in the internal pressure together with temperature fluctuation. The exact reason for ice-cream shrinkage is poorly understood and its manifestation is sudden and persists for a period and very often this problem disappears without any known cause.

Goff (2001) reported on the control of ice-cream structure by examining fat–protein interactions. Figure 3.17 shows the effect of adsorbed proteins on the structure of

Figure 3.17 The effect of adsorbed protein on the structure of ice-cream mix, ice cream and melted ice cream. (a) Ice-cream mix with (A) no surfactant and (B) added surfactant, as viewed by thin-film transmission electron microscopy (TEM; for methodology, see Goff *et al*., 1987); double bar = 1 μm; there are high levels of adsorbed protein, especially casein micelles, in the matrix illustrated in part (A). (b) Ice cream with (C) no surfactant and (D) added surfactant, as viewed by scanning electron microscopy (SEM; for methodology, see Caldwell *et al*., 1992); double bar = 4 μm; the lack of a surfactant impedes the adsorption of fat. (c) Ice cream with (E) no surfactant and (F) added surfactant, as viewed by thin-section TEM with freeze substitution and low-temperature embedding (for methodology, see Goff *et al*., 1999); double bar = 1 μm; the added surfactant can be seen to inhibit the partial coalescence of the fat. (d) Melted ice cream with (G) no surfactant (double bar = 1 μm) and (H) added surfactant (double bar = 5 μm), as viewed by thin-section TEM (for methodology, see Goff *et al*., 1987); the absence of surfactant shows rapid meltdown with recovery of mostly intact fat globules. Notes: a, air bubble; c, casein micelle; f, fat globule; fc, fat cluster; fn, fat network; arrow, crystalline fat.
Source: D. Goff, University of Guelph, Canada. Reproduced with permission of Professor Doug Goff.


(a)
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(b)
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(d)
G
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fn

ice-cream mix (Figure 3.17 (a)), ice cream (Figures 3.17 (b) and 3.17 (c)) and melted ice cream (Figure 3.17(d)). Goff's work highlights the importance of a network of partially coalesced fat globules in the formation of ice-cream structure.

3.3.3 Defects in mayonnaise and salad dressing

The formulations of mayonnaise and salad dressings are carefully carried out to ensure the dispersed oil phase is kept uniformly distributed throughout the period of its shelf-life. The only exception to this is for the separating-type French dressings. Oils that contain a high degree of saturated triglycerides are subjected to a process called 'winterisation' to remove the high melting fractions. If these are not removed, they solidify at refrigeration temperatures.

The main problem in salad dressings and mayonnaise is the development of rancidity. The oils in these products contain unsaturated bonds and are easily oxidised by contamination with traces of transition metals, in particular iron and copper, as they act as catalysts in the reaction. Other factors such as the viscosity of the aqueous phase, particle size and influence of water tend to support the oxidation process.

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4
Oil modification processes

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4.1 Introduction

Edible oils and fats are natural products and their physical properties are determined by their agricultural origin. Since many oils and fats are by-products such as, for instance, lard or cottonseed oil, or co-products such as soybean oil, their availability and price depend on a large number of agro-economic factors. Since food producers usually specify certain physical and/or chemical properties for the edible oils and fats to be used in their products, it is therefore up to the refiner to provide fully refined oils, fats or fat blends to meet these specifications at the lowest cost. To meet these goals while using the raw materials available on the market, the refiner uses one or more of the following processes listed below in order of increasing cost per tonne (Kellens, 2000):

- *Blending*. This is by far the cheapest process and it is therefore widely used to produce, for instance, margarine or shortening fat blends by mixing a hardstock with a liquid oil.
- *Fractionation*. This process requires dedicated investment and uses some energy but it does not suffer a yield loss nor does it require auxiliary products. It separates the fat to be fractionated into a higher melting and a lower melting fraction and thus redistributes the triglycerides that provide the fat with its consistency. It is a purely physical process.
- *Interesterification*. Although the investment required for the interesterification process is low, the process itself is more costly than the processes listed above because of yield loss and catalyst usage. The process redistributes the fatty acids over the triglycerides and can thus change a blend with too high a melting point into a fat blend with acceptable mouth feel. The process requires a catalyst, which can be a strong alkali or a lipase enzyme.
- *Hydrogenation*. This is the only process that creates consistency in oils and fats by converting low melting triglycerides into higher melting ones. It was

Fats in Food Technology, Second Edition. Edited by Kanes K. Rajah.

developed at the beginning of the twentieth century (Normann, 1903) to counteract a shortage of solid fats such as edible tallow used in margarine and shortenings. Because it is the only process that converts a liquid oil into a solid fat, and despite its high cost (hydrogen, catalyst, investment), the hydrogenation process is essential to meeting the growing demand for semi-solid fat products. It has also enabled the use of oils like fish oil and whale oil in food products.

An example of how these various modification processes are used to provide a fat blend for producing margarines with good spreadability, melting behaviour and plasticity is given by one of the many Unilever patents (Schmidt, 1986). The said fat blend is produced by *interesterifying* a *mixture* consisting of a liquid oil, a partially *hydrogenated* oil and a *fully saturated* fat, and *fractionating* to obtain a higher melting stearin and an olein which can be used as such or *mixed* with palm oil and/or *hydrogenated* palm oil to produce spreads. The various oil modification processes involved in producing this fat blend have been highlighted by italicisation and this shows that several modification processes are involved more than once.

However, each of the above oil modification processes increases the cost of the oils used as raw materials and which process to select depends on the costs of these raw materials, the cost of modification and the demands the final product has to meet. Which fat blend of liquid oil and modified oils and fats will have the lowest cost can be calculated by linear programming (Dijkstra, 2008a). This calculation also allows manufacturers to meet marketing-oriented criteria such as minimum or maximum levels of polyunsaturated fatty acids (especially ω-3 fatty acids), or a maximum level of *trans* isomers, whereby it should be kept in mind that such additional criteria nearly always lead to an increase in cost.

4.2 Hydrogenation

The hydrogenation process was invented by Normann in the early twentieth century (Normann, 1903); it is also referred to as a ‘hardening’ process because it converts liquid oil into solid fats.

The hydrogenation process is nearly always carried out as a batch process in an autoclave (Figure 4.1). Neutral oil that is commonly but not necessarily bleached is pre-heated to some 120–150°C by the previous batch, the catalyst is added and molecular hydrogen is dispersed in the batch. Because the saturation of double bonds is exothermic, the batch has to be cooled as soon as a temperature of 200–220°C has been reached. The reaction is continued until the reaction product has obtained the properties aimed for, the batch is cooled by heating a subsequent batch and the catalyst is removed by filtration; catalyst residues are subsequently eliminated during the post-bleaching step.

This catalyst is invariably nickel metal on a support which was formerly diatomaceous earth and is now alumina or silica. Other catalytically active materials such as noble metals (Rylander, 1970) have been investigated but so far, they have not

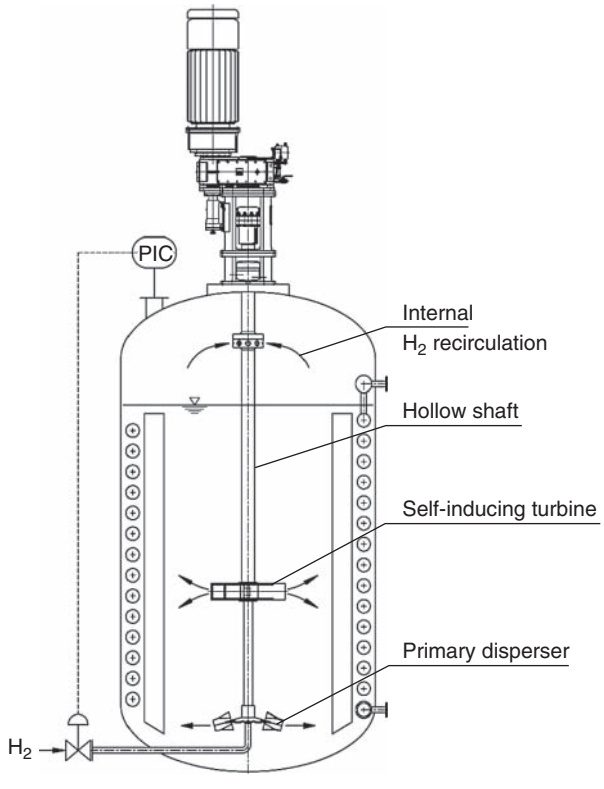


Figure 4.1 Dead-end tank reactor. *Source:* Beers, 2008. Reproduced with permission of John Wiley & Sons.

been used industrially for cost reasons. They are currently receiving renewed interest because they could be effective in producing hardened oil with a reduced content of *trans* isomers (Beers *et al*., 2008; Philippaerts *et al*., 2011).

Hydrogenation processes in the chemical industry such as the production of aniline from nitrobenzene or cyclohexane from benzene and even the oleochemical industry such as the production of fatty alcohols from fatty acid esters aim for full hydrogenation. In this respect they differ from the hydrogenation of edible oils, which is nearly always partial. This means that the hydrogenated oil still contains double bonds and these may have the original *cis* configuration but they may also have isomerised to the *trans* configuration; the extent to which this has happened is described by the isomerisation index or the *trans* selectivity of the hydrogenation. Other selectivities are required to describe the relative rates of reaction of the various unsaturated fatty acids.

4.2.1 Kinetics and mechanism

Three reaction partners are involved in the hydrogenation of the double bonds in edible oils: unsaturated triglycerides, hydrogen, and the catalyst. Since hydrogen is supplied continuously to the reaction mixture, transport mechanisms can also play a role but,

according to Koetsier (1997), the rate constant pertaining to the hydrogen transfer towards the catalyst particles is an order of magnitude larger than the volumetric liquid-side mass transfer coefficient $k_L a$ governing the rate of hydrogen dissolution. Consequently, in industrial hydrogenations, 'the effect of mass transfer rate from the bulk of the oil to the catalyst particles can therefore be neglected'.

Accordingly, the rate of hydrogenation equals the rate of hydrogen dissolution and that is governed by the rate of agitation, which in industrial reactors is constant, and the difference between the hydrogen concentration in the oil and its solubility. If the pressure is constant, this solubility depends only on the temperature (Tiutiunnikov and Novitskaia, 1958; Wisniak and Stein, 1974) but the dependence is small.

In addition to hydrogenation or saturation of double bonds, the bonds can also isomerise, either geometrically as part of the *cis-trans* equilibrium, or positionally by shifting along the fatty acid carbon chain. This ability is explained by assuming that the hydrogenation takes place in two steps (Horiuti and Polanyi, 1934) and that the half-hydrogenated intermediate can dissociate again. The various reactions taking place according to this mechanism are shown in Figure 4.2, in which an asterisk (*) indicates that a species is adsorbed onto the catalyst surface.

When a hydrogen molecule reaches the catalyst surface, it can be adsorbed (reaction 1 in Figure 4.2) and the adsorbed molecule can dissociate into two adsorbed hydrogen atoms (reaction 2). Since these atoms take part in most reactions shown in Figure 4.2, their concentration determines their relative importance. A low hydrogen

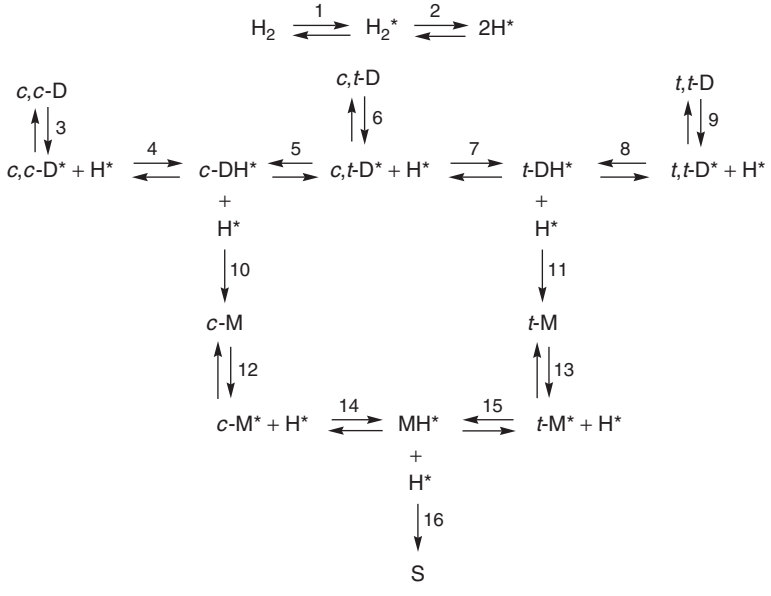


Figure 4.2 Reaction pathways during the hydrogenation of diunsaturated fatty acids D, forming mono-unsaturated fatty acids M and finally saturated fatty acids S. *Source:* Adapted from Dijkstra, 2006. Reproduced with permission of John Wiley & Sons.

concentration will promote isomerisation by providing the half-hydrogenated intermediates with time to dissociate before they react with a second hydrogen atom and become saturated. A low concentration will occur in the early stages of a hydrogenation run when the reaction mixture is highly reactive and can thereby maintain a low hydrogen concentration, or when the catalyst has been poisoned either accidentally by catalyst poisons present in the oil or on purpose when a *trans* promoting catalyst is prepared, by allowing a nickel catalyst to react with sulphur-containing compounds. On the other hand, a high concentration of hydrogen atoms on the catalyst surface promotes saturation of double bonds and this is encountered at the end of a hydrogenation run when the reactivity of the oil has decreased, or at elevated hydrogen pressure.

When an unsaturated triglyceride molecule reaches the catalyst surface, it can be adsorbed through its double bond (reactions 3, 6, 9, 12 and 13) but since edible oil is a mixture of different molecules, this raises the question of how the various structures of these molecules affect their likelihood of being adsorbed. Will the presence of two oleic acid moieties in a triglyceride molecule increase this likelihood by a factor of two in comparison with a triglyceride containing only a single oleic acid moiety? According to the 'common fatty acid pool' concept suggested by Bailey (1946), this factor should indeed be two, but later (Schilling, 1978; Dijkstra, 1997) it was concluded to be somewhat less than two.

And how does the likelihood that a mono-unsaturated fatty acid is adsorbed (reactions 12 and 13) compare with the likelihood that a polyunsaturated fatty acid is adsorbed (reactions 3, 6 and 9)? At one stage it was concluded (Coenen and Boerma, 1968) that mono-unsaturated fatty acids could only isomerise when they were also hardened. Since during a selective hydrogenation mono-unsaturated fatty acids are hardly hardened, it would follow that they hardly isomerise and thus are hardly adsorbed. However, the otherwise elegant experiment using erucic acid as an internal marker (Coenen and Boerma, 1968) was carried out at a very low temperature and was thus not representative of normal hydrogenation reaction conditions. When the experiment was repeated under normal, selective conditions, erucic acid isomerised without being hardened to behenic acid (W.L.J. Meeussen, personal communication). This demonstrates that mono-unsaturated fatty acids are also adsorbed onto the catalyst surface when linoleic acid is being saturated.

It is not clear to what extent the adsorption equilibrium constants involved depend on the number of double bonds in a fatty acid moiety but it is clear that this number affects the subsequent reaction rates. If a diene is adsorbed onto the catalyst surface and a hydrogen atom is added to one of the double bonds (reactions 4, 7, and 8), there is still a double bond left. That residual double bond can also interact with the catalyst surface and cause the half-hydrogenated diene to remain adsorbed onto the catalyst surface. If, on the other hand, a monoene is adsorbed (reactions 12 and 13), it loses its double bond on partial hydrogenation (reactions 14 and 15) and this facilitates dissociation (reactions -14 and -15) followed by desorption (reactions -12 and -13). On the other hand, if the triglyceride molecule containing this monoene contains a further unsaturated fatty acid moiety, the double bond or bonds in this moiety may cause

the triglyceride to remain adsorbed and thereby increase its likelihood to react with an adsorbed hydrogen atom to a saturated fatty acid moiety. This has been observed by reinterpreting the data provided by an experiment in which triolein was partially hydrogenated (Bushell and Hilditch, 1937). According to this reinterpretation (Dijkstra, 2012), individual oleic acid moieties in triolein are more likely to get saturated than the two oleic acid moieties in monostearodiolein and certainly than the single moiety in distearomono-olein. This is an example of triglyceride selectivity, a further deviation from the 'common fatty acid pool' concept.

The difference between mono-unsaturated and polyunsaturated fatty acids also affects the kinetics of the hydrogenation process. Since a half-hydrogenated polyunsaturated fatty acid is more likely to remain adsorbed, the rate of the addition of the second hydrogen atom will depend mainly on the concentration of the half-hydrogenated intermediate ([*c*-DH*] and [*t*-DH*]). This concentration is governed by equilibria 3, 6 and 9. Since this equilibrium involves a hydrogen atom, the values of [*c*-DH*] and [*t*-DH*] are therefore likely to be proportional to the hydrogen atom concentration [H*].

Since the hydrogen atom concentration is governed by a dissociation equilibrium (equilibrium 2), it can be assumed to be proportional to the square root of the concentration of the adsorbed molecular hydrogen [H_2*]. In its turn, the concentration of the adsorbed molecular hydrogen [H_2*] can be assumed to be proportional to the concentration of the dissolved hydrogen [H_2]. Accordingly, the concentrations of the half-hydrogenated adsorbed dienes [c-DH*] and [*t*-DH*] will be proportional to $\sqrt{[H_2]}$.

For the mono-unsaturated fatty acids, the situation is different. There, the hydrogen concentration ([H*]) governs the rate at which the half-hydrogenated intermediate (*c*-M* or *t*-M*) will become fully saturated. As with the dienes, the concentrations of these half-hydrogenated adsorbed monoenes (*c*-M* or *t*-M*) will be proportional to the concentration of the adsorbed hydrogen atoms [H*] and thus to $\sqrt{[H_2]}$. This means that the rate at which they become saturated is proportional to $(\sqrt{[H_2]})^2$ or simply [H_2], and not to the square root of the hydrogen concentration as is the case for the polyunsaturated fatty acids. This difference in order with respect to hydrogen has already been suggested in the literature by Hashimoto *et al*. (1971) and Ahmad *et al*. (1979).

This difference explains why monounsaturated fatty acids are isomerised rather than saturated at low hydrogen concentration. It also explains why the so-called linoleic acid selectivity decreases during the hydrogenation process (Dijkstra, 1997): this decrease coincides with an increase in hydrogen concentration when the reactivity of the reaction mixture has decreased to below a certain value.

From the above mechanism, it is clear that *trans* isomers will be formed when the hydrogen concentration is low (Dijkstra, 2006, 2011) and ways to counteract their formation therefore aim at increasing this concentration (Van Toor *et al*., 2005) by increasing the pressure and/or lowering the temperature. In theory, a decrease in catalyst concentration also leads to an increase in hydrogen pressure but since the low temperature already decreases the rate of reaction, a further decrease by lowering the catalyst concentration would lead to unacceptably long cycle times.

4.2.2 Industrial hydrogenation processes

In principle, industrial hydrogenation processes are just scaled-up versions of laboratory experiments in that they are carried out in an agitated autoclave provided with a hydrogen supply. However, the scaling-up, product quality assurance, safety requirements, and process economics have affected the design of industrial hydrogenation plants and their process control:

- The hydrogenation reaction is highly exothermic in that a drop in iodine value by 1 unit raises the oil temperature by 1.6–1.7°C. This necessitates temperature control of the autoclave content and also permits heat recovery.
- Hydrogen forms explosive mixtures with air. Accordingly, the autoclave is preferably situated outside so that the wind will disperse any hydrogen escaping from the autoclave. If it is situated inside a building, extensive safety precautions including hydrogen detectors are necessary.
- The autoclave is a relatively expensive vessel so that savings in investment can result from using cheaper auxiliary vessels for operations that do not require an autoclave.
- For process control reasons, both the batch weight and the amount of hydrogen supplied to the autoclave must be determined sufficiently accurately.
- To minimise exposure of the operators to nickel, fully enclosed and automated catalyst filters can be used but their large heel makes this type of filter unsuitable if frequent oil type changes are foreseen. In this case, the conventional frame and plate type filter is preferred.

A flow chart of a modern hydrogenation plant is given in Figure 4.3. It incorporates an oil-to-oil heat exchange vessel in which the oil to be hydrogenated flows over spiral tubes before being pumped to a measuring vessel in which the oil can be further heated by steam coils if necessary. From this measuring vessel the hot oil can be dropped into the autoclave where the hydrogenation proper takes place. Accordingly, the autoclave is provided with a means to feed the required amount of catalyst, a hydrogen supply, an agitator that maintains the catalyst in suspension and that dissolves the hydrogen into the oil, and cooling coils. After the reaction, the autoclave is emptied into a drop tank that is agitated to prevent the catalyst from settling. The hot hydrogenated oil is then pumped through the coils of the heat exchange vessel to the catalyst filter.

4.2.2.1 Hydrogenation process conditions

Industrial hydrogenation reactions employing a nickel catalyst require a starting oil temperature of preferably $>150^{\circ}$C. If the previous batch had a final temperature of about 220°C, this starting temperature can be reached in the heat exchange vessel. On the other hand, if a series of lightly hydrogenated products has to be produced (for instance, ‘brush hydrogenated soybean oil’), their final temperature is too low to bring the next batch up to the starting temperature. Then additional heat must be supplied in the holding vessel. Products with an IV-drop in excess of 40 generally require

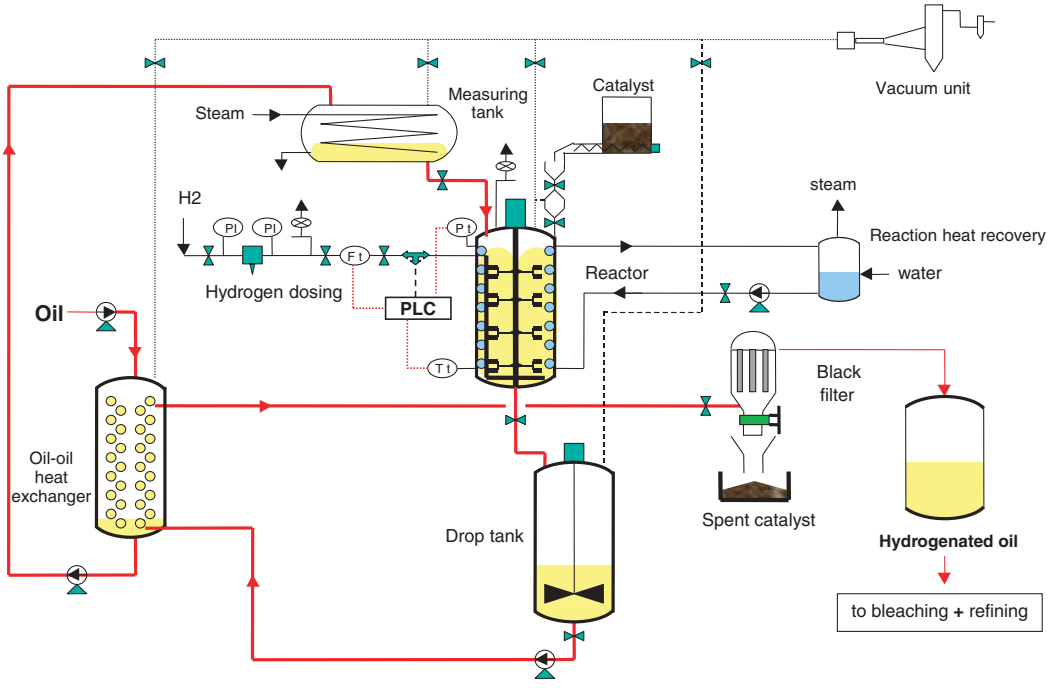


Figure 4.3 Flow chart of fractionation plant. *Source:* Desmet-Ballestra. Reproduced with permission of Desmet-Ballestra.

cooling to avoid the batch temperature exceeding 220°C. In standard practice, the temperature is allowed to increase to this final level before active cooling is instigated. For products with a lower than normal *trans*-isomer content, a low batch temperature throughout the process is required (Hassan *et al*., 2011).

The oil to be hydrogenated should be dry. If not, any water present will react with the oil (hydrolysis) and the resulting free fatty acids will react with the nickel catalyst and form nickel soaps. This latter reaction is of course highly significant when fatty acids themselves are hydrogenated. It is reversible but the metallic nickel resulting from the reverse reaction may not have the same catalytic activity as the original catalyst.

The hydrogenation pressure is determined by what the autoclave can withstand and the product properties aimed for. Normally, the pressure varies (increases) during a run. In the beginning, the highly unsaturated oil tends to be highly reactive and prevents the autoclave pressure from rising. As and when the reactivity decreases, the pressure may increase and be controlled at a certain, safe level (for example, a 5 bar gauge). As will be discussed below, pressure control during the latter stages of a hydrogenation run can effectively ensure batch-to-batch reproducibility.

A high pressure and a low temperature can also be applied on purpose to generate hydrogenation products with a lower than normal *trans*-isomer content (Van Toor *et al*., 2005). However, operating an autoclave at a reduced temperature also reduces the temperature difference between the batch temperature and the cooling medium temperature and hence the rate of heat transfer. This means either a longer batch cycle time or autoclave modification.

4.2.2.2 Catalyst usage

The amount of nickel catalyst to be employed merits some discussion. Some operators prefer to use fresh catalyst for each hydrogenation batch. In the USA, this has been common procedure for a long time, and in Europe, new plants also tend to use the catalyst only once. This necessitates thorough cleaning of the oil by a pre-bleaching step. Then an amount of 0.03–0.05 wt % catalyst will generally suffice for partial hydrogenation. This catalyst consists of metallic nickel supported on alumina or silica particles that are dispersed in a fully hydrogenated fat. The dispersion is pelleted and contains approx. 25 wt % nickel. Full hydrogenation to an IV < 3 benefits from a somewhat higher catalyst loading. Fish oil and rapeseed oil, which contain sulphur catalyst poisons that are hardly removed by bleaching, also need more catalyst to ensure reproducible processing.

Another possibility is to re-use the spent catalyst until its catalytic activity is almost exhausted or catalyst filtration has become too time-consuming. With this method, the catalyst filter cake is slurried in oil when the filter has to be cleaned. This requires additional investment in a reslurry system and a catalyst slurry dosing system (for a flow diagram see Coppa-Zuccari, 1971). Because the catalyst is re-used until almost exhausted, higher catalyst loadings do not immediately raise the process costs. Therefore, higher loadings tend to be used since they make the hydrogenation process more robust, that is, less susceptible to variable concentrations of catalyst poisons.

Because of the steady decrease in catalytic activity of the catalyst lot (as determined by the filter capacity), catalyst loadings are preferably increased each time the lot is re-used until the loading has become so high that discarding the lot represents a saving.

Re-use of catalyst is certainly preferable on cost grounds when a high catalyst loading is required as, for instance, for partially poisoned catalysts used to produce partially hydrogenated products with a *trans*-isomer content that is close to equilibrium; such high *trans* products are used for confectionery fats such as non-lauric cocoa butter substitutes (CBS). Then a high catalyst loading is essential because the poisoned catalyst has a low activity and to further promote geometrical isomerisation by keeping the hydrogen concentration at a low value.

4.2.2.3 Hydrogen dissolution systems

It has been mentioned before that industrial hydrogenation processes are mass transfer limited. Accordingly, the hydrogen dissolution system is an essential process characteristic. Because laboratory autoclaves often use a sparging ring situated beneath the agitator impellers to disperse and dissolve the hydrogen in the oil, industrial autoclaves have also been fitted with this type of dissolving system. However, this system has the disadvantage that a sluggish reaction will cause the concentration of the dissolved hydrogen to become rather high. This decreases the driving force for dissolution, so that hydrogen will collect in the roof of the autoclave until a safety pressure switch cuts off the hydrogen supply and no more hydrogen will dissolve.

This disadvantage has been overcome by extracting hydrogen via a cooler from the roof and then recycling it to the autoclave via the sparging ring by means of an additional hydrogen pump. Another way to overcome this disadvantage is by using an agitator that sucks hydrogen from the headspace into the oil (Weise and Delaney, 1992; Farr, 2001). Such an agitator obviates the need to use a sparging ring and allows the hydrogen to be fed directly into the autoclave headspace.

The Buss loop reactor is yet another system to dissolve the hydrogen into the oil. In this system (Duveen and Leuteritz, 1982), an external pump circulates the oil over the autoclave via a Venturi tube that sucks in hydrogen gas and dissolves it into the oil. The loop also contains a heat exchanger for oil temperature control. Improvements to the Buss loop reactor have been described by Urosevic (1986).

4.2.2.4 Process and product quality control

Process control in hydrogenation should aim for reproducibility and thus ensure that subsequent batches of the same grade have almost identical compositions and thus properties. This means not only that the extent of hydrogenation (drop in IV) has to be controlled but also the various selectivities that characterise a hydrogenation run. In addition, the control has to be quite accurate since small changes in IV and *trans*-isomer content can have a large effect upon the SFC, as illustrated by the equation below (P.J.A. Maes, personal communication):

$$\Delta N_{20} = -1.2\Delta(\mathrm{IV}) + 0.5\Delta(\%trans)$$

This equation shows that for a partially hydrogenated soybean oil (melting point 35°C) a drop in IV of 1 unit will increase the SFC at 20 °C (N_{20}) by more than 1.2% since this IV-drop will be accompanied by an increase in *trans*-isomer content.

The process control should also deal with variations in catalyst activity and catalyst activation and with a variable and often unknown content of catalyst poisons in the oil. Of course, the effect of the latter variable can be reduced by bleaching the oil to be hydrogenated, but this treatment constitutes an additional cost element since the hydrogenated oil also has to be bleached to remove residual nickel.

Given the hydrogenation mechanism described above, it is clear that product reproducibility can only result if the batch temperature and the hydrogen concentration in the oil follow standard profiles in function of the extent of hydrogenation, which can be determined by calculating the accumulated hydrogen consumption from its flow measurements.

According to a method described by Colen *et al*. (1990), good product reproducibility can be achieved if pertinent batch parameters (temperature and hydrogen concentration) are controlled in function of the IV achieved; they replace the variable 'time' by the variable 'degree of hydrogenation'. To this end they constructed a data base comprising:

- the extent of hydrogenation as calculated from the hydrogen flow as measured;
- the temperature;
- the rate of hydrogenation as determined by calculating the rate of drop in IV;
- the hydrogen concentration in the oil.

The dissolved hydrogen concentration is calculated from the mass transfer equation (Koetsier, 1997):

$$J = k_L a \, (C_{\max} - C_{\text{bulk}})$$

where

$J =$ rate of hydrogen dissolution that equals the rate of hydrogenation
$k_L a =$ volumetric liquid-side mass transfer coefficient which is an equipment parameter that is determined separately in a test run (Stenberg and Schöön, 1985)
$C_{max} =$ hydrogen solubility at the prevailing pressure and temperature, whereby:

$$C_{\max} = m(T)\, p$$

and

$m(T) =$ Henry's law constant

$p =$ pressure

$C_{\text{bulk}} =$ dissolved hydrogen concentration.

Having obtained a data set that is characteristic of a certain hydrogenation grade, Colen *et al*. (1990) then ensure that subsequent runs aiming to produce that grade follow the

same temperature and hydrogen concentration profiles. They control the temperature by adjusting the extent of cooling and achieve the same hydrogen concentration by varying the pressure in the autoclave. They also mention that control is more critical in the final stages of the hydrogenation than in the beginning.

Thus, if for one reason or another, a hydrogenation run turns out to be slow (J is lower than normal), this will be signalled by a higher than normal hydrogen concentration as shown by rewriting the mass transfer equation as:

$$C_{\text{bulk}} = C_{\text{max}} - J/k_L a$$

Accordingly, Colen *et al*. (1990) then decrease the autoclave pressure to decrease the driving force for hydrogen dissolution, as a result of which the dissolved hydrogen concentration will fall. Of course, this will slow down the rate of reaction even further, and consequently, the operator will tend to want to increase the pressure to speed up the reaction and thus gain time lost. However, decreasing the pressure will ensure that the various selectivities are controlled at around the values shown by the data set and thereby lead to a similar final product.

To ensure that the final product properties are even closer to specifications, it is advisable to interrupt the hydrogenation before the expected end point and take a sample for quick analysis. One method of quick analysis could be the determination of IV and possibly the *trans*-isomer content by Fourier transform Near Infra Red analysis (Cox *et al*., 2000). Another method could be the fast Solid Fat Content measurement by pulse-NMR (Rutledge *et al*., 1988) involving the crystallisation of the sample in liquid nitrogen. In both cases, tables based on past performance should be used to calculate how much more hydrogen is to be added to the autoclave to obtain the target product.

4.3 Interesterification

Whereas the hydrogenation process discussed above causes the fatty acid composition to alter but does not affect the triglyceride composition according to carbon number, the interesterification process does the opposite; it does not alter the fatty acid composition but it does change the triglyceride composition. When the interesterification is carried out in a single phase, the resulting fatty acid distribution over the glycerol moieties will be random, which means that the triglyceride composition can be calculated on the basis of the fatty acid composition (Baltes, 1960a; Rozendaal and Macrae, 1997; Rousseau and Marangoni, 2002).

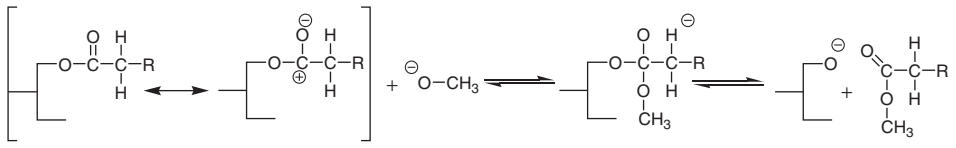
On the other hand, when there are two phases (a liquid phase and a crystalline phase or a liquid phase and a gaseous phase), the interesterification can be directed so that a non-random reaction product results. The directed interesterification process has been used industrially in the USA to improve the plasticity of lard (Hawley and Holman, 1956; Holman and Going, 1959) and in Europe to produce a margarine fat blend with a minimal content of saturated fatty acids (De Lathauwer *et al*., 1980; Holemans *et al*., 1988) but apparently, the processes are no longer used.

4.3.1 Chemical catalysis

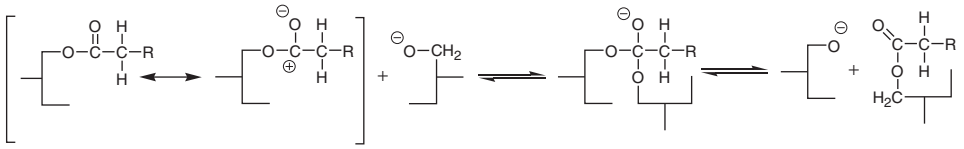
The most commonly used catalyst for the industrial interesterification process is sodium methanolate or sodium ethanolate. Only some of the directed interesterification processes mentioned above used a sodium/potassium alloy and before switching to sodium ethanolate, Unilever used metallic sodium (De Groot and Hilder, 1971). The use of the condensation product of glycerol and sodium hydroxide is mentioned in the literature (Keulemans and Smits, 1986) but it is not clear to what extent this has been used industrially.

4.3.1.1 Mechanism of the chemically catalysed interesterification

The interesterification mechanism that was proposed by Baltes in 1960 and that has been generally accepted for more than 40 years assumed the sodium methanolate catalyst would react with a triglyceride under formation of a glycerolate anion and fatty acid methyl ester according to:

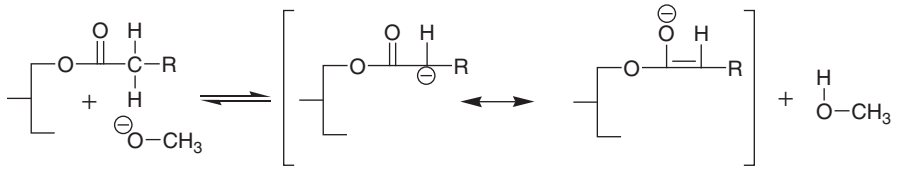


This glycerolate anion would then react with a triglyceride to form another triglyceride and another glycerolate anion and thus effect interesterification according to:

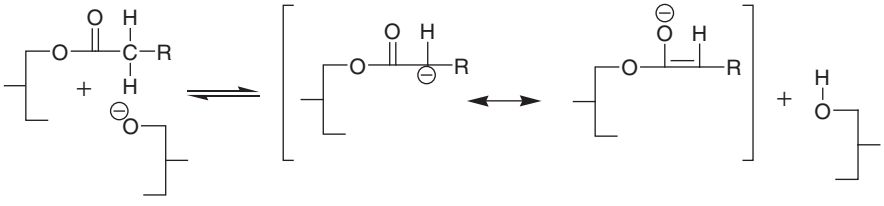


However, the above mechanism does not explain the formation of free fatty acids on catalyst inactivation in amounts that are equivalent to the amount of catalyst used. It does not explain why fatty acids lacking an α-hydrogen do not participate in the interesterification reaction (Liu, 2004), nor why compounds like acetone (Muller and Kock, 1974), dimethylsulfoxide (Artman *et al*., 1968) and dimethylformamide (Sreenivasan, 1973) accelerate the reaction. Accordingly, a novel mechanism has been proposed (Dijkstra *et al*., 2005).

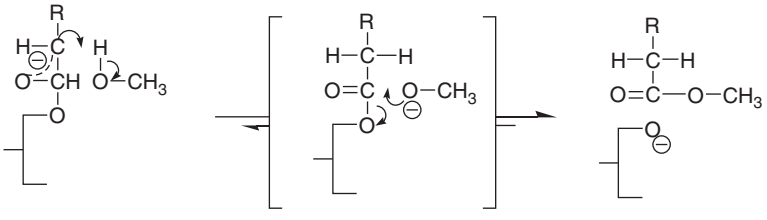
In this novel mechanism the enolate anion that is formed by the abstraction of an α-hydrogen from a fatty acid moiety plays a central role. Underneath, two routes leading to the formation of this enolate anion are shown. The first route involves the abstraction of an α-hydrogen from a fatty acid moiety by a methanolate anion:



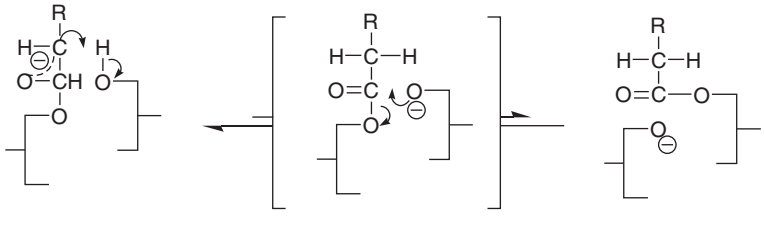
and the second one the abstraction by a glycerolate anion:



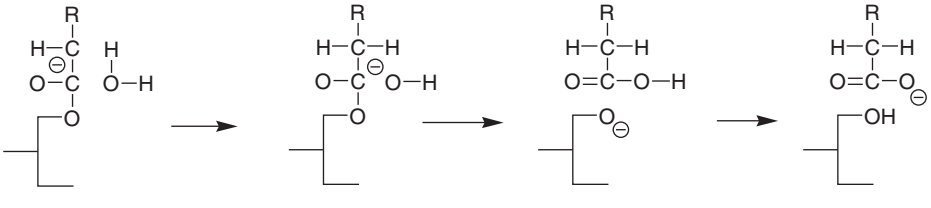
Once formed, the enolate anion reacts with hydroxyl groups. When this hydroxyl group is part of a methanol molecule, a fatty acid methyl ester is formed. This is what happens during the methanolysis of triglycerides, as when producing biodiesel.



In the above reaction, a glycerolate anion results at the same time and this will abstract an α-hydrogen as indicated above and regenerate the enolate anion. Interesterification is effected when the enolate anion reacts with a partial glyceride[1] according to:



Again the glycerolate anion formed simultaneously will regenerate the enolate anion as indicated above but when the latter reacts with a hydroxyl group in water according to:



[1]It would therefore be interesting to investigate to what extent the rate of interesterification depends on the hydroxyl number of the substrate.

the glycerolate anion is likely to react irreversibly with the carboxyl group of the fatty acid formed and form a carboxyl anion. In fact, the inability of the 'glycerolate' mechanism to explain this free fatty acid formation has been an important ground for its rejection (Dijkstra *et al*., 2005).

Another reason for rejecting the original, glycerolate mechanism is that it does not explain why compounds like acetone accelerate the rate of interesterification. According to the 'enolate' mechanism outlined above, the acetone acts as a hydrogen transfer agent by donating a proton to the glycerolate anion formed during interesterification, whereafter the resulting acetonyl anion will abstract a hydrogen from a fatty acid. The acetone molecule is much smaller and thus more mobile than the bulky triglycerides and this explains the acceleration observed. This donation/abstraction has been demonstrated experimentally (Dijkstra *et al*., 2005) by incorporating fully deuterated acetone into the interesterification reaction mixture. When the reaction proceeded, more and more deuterium became attached to the α-position of the fatty acid moieties present in the reaction mixture. The role of the α-hydrogen in the enolate mechanism is also fully in line with the necessity of its presence as argued by Liu (2004).

The formation of the enolate anion had been suggested before (Weiss *et al*., 1961) but then it was also suggested on the basis of IR-spectra that the enolate anion formed would react further to a β-keto ester and that this ester would be the catalytically active intermediate. This latter suggestion was refuted (Heldal and Mørk, 1981) on the grounds that the IR spectrum peak appeared only gradually. These conflicting views have now been reconciled by assuming the β-keto ester to be formed gradually and to have hardly any catalytic activity. In that way, the thermally induced loss of catalytic activity of an interesterification reaction mixture (D. Meert, personal communication) can also be explained.

In 1995, Pelloso *et al*. observed that their attempts to interesterify a mixture of rapeseed oil and triacetin only led to the randomisation of the rapeseed oil; the triacetin did not participate in the reaction at all. Since the addition of tripropionin caused the short chain fatty acid triglycerides to participate in the reaction, the lack of reactivity of the triacetin could perhaps be explained by the lower acidity of the primary α-hydrogen atoms in comparison with the acidity of the secondary hydrogen atoms in longer fatty acid chains. However, it could also be that the triacetin that Pelloso used had a very low free hydroxyl content and could therefore not react with the enolate anions. In fact, a 'catalyst promoter' that furnishes alcoholic hydroxyl groups was already mentioned in 1943 and provides yet another example of a phenomenon that is not explained by the glycerolate mechanism (Baltes, 1960a; Coenen, 1974b).

As only to be expected, the free hydroxyl content of an ester interchange reaction mixture affects the concentration of the various anions, most of which can act as catalytically active intermediate. The latter are shown in Figure 4.4. So during a methanolysis reaction of triglyceride oil, when the free hydroxyl group concentration is high, the reaction mixture will contain more methanolate and glycerolate anions than when triglycerides are being interesterified (Dijkstra, 2008b). This means that the various mechanisms are all acting at the same time but their relative importance

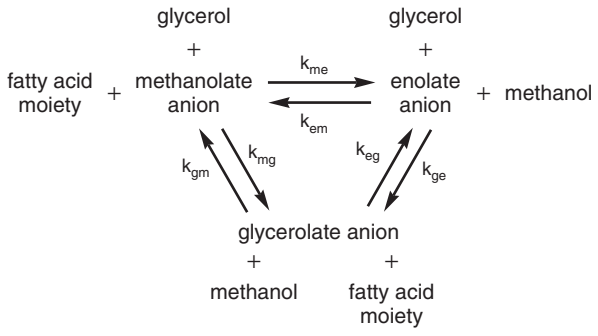


Figure 4.4 The equilibria involving intermediates that are catalytically active during ester interchange reactions. *Source:* Dijkstra, 2008. Reproduced with permission of John Libbey Eurotext.

is not known. They must also operate next to each other when an acetoglyceride is prepared by interesterifying a mixture of triglyceride oil, triacetin and glycerol (Dijkstra *et al*., 2007) since the triacetin participates in the ester interchange.

4.3.1.2 Industrial practice

The chemically catalysed interesterification process is generally carried out as a batch processes and employs sodium methylate or ethylate as the catalyst. Since this catalyst is inactivated by water, FFA or peroxides, a dry and neutral feedstock is mandatory. This can be assured by adding some caustic soda to the raw material after it has been heated to reaction temperature (80–100°C) and removing the water by evacuating the agitated batch (Laning, 1985) and checking for alkalinity. Provided the batch is sufficiently dry and neutral, an amount of 0.05% by weight of sodium methylate suffices to ensure complete randomisation in a few minutes. To be on the safe side, a reaction time of some 30 minutes is usually provided.

After the interesterification equilibrium has been reached, the catalyst is inactivated by the addition of water that may have been slightly acidified. Water addition leads to the formation of soaps, whereas the addition of acidified water leads to FFA formation. Soaps can be removed by water washing or a treatment with silica hydrogel, whereas FFA are removed during the subsequent deodorisation step, which is required anyway to remove the FAME formed after the addition of the catalyst.

The main drawback of the chemically catalysed interesterification process is its yield loss, which is directly proportional to the amount of catalyst used. The addition of sodium methylate (MW = 54) leads to the formation of an equivalent amount of FAME (MW = ~295) and catalyst inactivation leads to a further formation of an equivalent amount of FFA (MW = ~280). In addition, neutral oil is lost on removing the soaps or FFA. Accordingly, the use of 0.1% by weight of sodium methylate will lead to the formation of approx. 1.0% FAME and FFA. In that case, total oil losses (including losses during post-bleaching and deodorisation) can be up to 1.5% (Kellens, 2000).

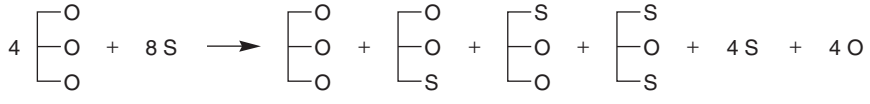
If sodium methylate consumption can be limited to 0.05%, overall oil losses can be reduced to 0.8% or less.

Apart from the oil losses, there are other reasons to limit the amount of catalyst to max. 0.1% or preferably 0.05%. High catalyst concentrations will result in high diglyceride levels and can also lead to the formation of unwanted side-products like ketones (Verhé *et al*., 2006). Even at half the catalyst dosage, yield loss is responsible for about one-third of the total variable cost (Kellens, 2000). Knowing the reasons for the yield loss also provides the means for its prevention (Dijkstra, 2009). Using metallic sodium or preferably, a sodium/potassium alloy (Hawley and Dobson, 1956), sodium hydride (Eckey, 1951) or sodium amide (Nelson and Mattil, 1953) as the catalyst prevents the formation of fatty acid methyl esters and avoiding the presence of water until after the catalyst has been inactivated prevents the formation of free fatty acids or soaps. The use of glacial acetic acid has been mentioned for this purpose (Eckey and Formo, 1949).

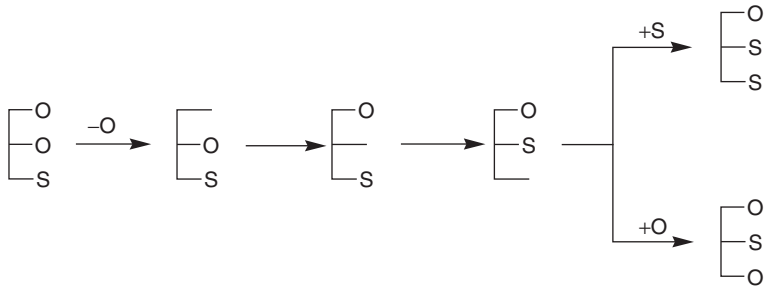
4.3.2 Enzymatic catalysis

The first industrial use of the enzyme lipase (EC 3.1.1.3) for the ester interchange of fats aimed at something chemical catalysis could not achieve by making use of the specificity of enzymes. The extracellular microbial enzyme concerned (*Rhizomucor miehei*) had a positional specificity for the outer positions (*sn*1,3-specificity) on the glycerol backbone (Coleman and Macrae, 1977; Matsuo *et al*., 1981). Accordingly, it could be used to manufacture fats with a high symmetrical mono-unsaturated triglyceride content that are therefore more or less compatible with cocoa butter. These are the so-called cocoa butter equivalents (CBE) that can be used for confectionery applications.

To this end, triglycerides with a high oleic acid content on the 2-position such as, for instance, high oleic acid sunflower seed oil, were allowed to react with a large excess of stearic acid or its methyl ester. This excess is necessary since double the amount that is theoretically needed to convert triolein to distearomono-olein has a yield of only 25% as illustrated below:



Consequently, a large excess of stearic acid or stearic acid methyl ester is required in this process to boost the distearomono-olein (SOS) yield and even then, the reaction product must be purified by fractionation to yield a sufficiently pure final product. As explained by Dijkstra (2007c), there is another reason why this fractionation is required: loss of specificity leading to the formation of triglycerides with a stearic acid (S) at the β-position according to:



By fatty acid interchange, the OSS formed according to the above reaction scheme can be converted into a SSS triglyceride. This loss of specificity is enhanced because thermodynamically, partial glycerides with fatty acids in the α-position are favoured over β-substituted ones. It therefore not only causes the formation of trisaturated triglycerides but also of asymmetrical mono-unsaturated triglycerides (SSO and OSS), which affect the crystallisation behaviour of the confectionery product in which the interesterified and fractionated product has been incorporated. Because the said confectionery product can no longer be called chocolate in the EU (Berger, 2003), the enzymatic interesterification process aimed at maintaining specificity is limited to the production of fats for infant formula (Quinlan and Moore, 1993).

Enzymatic randomisation on the other hand is gaining importance for the preparation of hardstocks for margarine and shortening manufacture (Holm and Cowan, 2008). It employs a number of reactors in series that are filled with the immobilised lipase obtained from a genetically modified *Aspergillus* sp into which the lipase gene from *Thermomyces lanuginosus* has been transferred. Its main problem is the current impossibility of predicting how long the enzyme will remain active. Some progress has been made in this respect in that it has been discovered that the enzyme is very sensitive to acids but other factors acting as enzyme poison remain to be detected. Accordingly, the oil blend to be interesterified has to be extensively purified which, together with the cost of the enzyme, makes the enzymatic process more expensive than the chemical randomisation process, especially when the yield loss, which is the major cost element of the chemical process (Kellens, 2000), is reduced by avoiding the formation of FAME and free fatty acids. Moisture-free silica has been claimed as suitable purification agent in a patent (Dayton and dos Santos, 2013) that also discloses the use and mode of operation of multiple packed bed reactors.

A process using an *sn*2-specific lipase (Song *et al*., 2008) for the production of CBE has been suggested by the author (Dijkstra, 2009). It could use fully hydrogenated fats as substrate and exchange the saturated fat at the *sn*2-position with an oleic acid or it could upgrade an existing CBE by replacing linoleic acid in the *sn*2-postion by oleic acid. This process has several advantages over the original CBE production processes in that only one fatty acid has to be exchanged instead of two and in that the diglyceride produced on enzymatic hydrolysis is the 1,3-diglyceride which is thermodynamically more stable than the 1,2-diglyceride. Accordingly, the use of the *sn*2-specific enzyme causes less diglyceride isomerisation and thus less loss of specificity.

4.3.3 *Interesterification products*

Because glycerol was urgently needed for the war effort, an ester interchange process was developed that uses triglyceride oil and methanol to produce FAME and glycerol (Bradshaw and Meuley, 1942). The FAME could then easily be saponified to produce soap. Subsequently, FAME were also used to produce fatty alcohols and various other oleochemicals such as, for instance, α-sulfo fatty acid esters (MES or methyl ester sulfonates) used as a detergent. More recently, FAME production has been increased substantially to over 10 m tonnes per annum to meet the mandatory incorporation of FAME into petrodiesel fuel. Because of unduly optimistic views of this outlet, FAME capacity has increased to some 50 m tonnes a year, much of which is now surplus capacity.

Interesterification of fats used in food products started with the randomisation of lard on its own (Vander Wal and Van Akkeren, 1951), of lard with a glycerol (Seestrom *et al*., 1961) or by a process of directed interesterification (Hawley and Holman, 1956). These processes all improve the performance of the lard: creaming and plastic range. Another early interesterification process was the randomisation of partially hydrogenated sunflower seed oil, either as such or with some liquid sunflower seed oil (Gander *et al*., 1966) to prevent it from recrystallising in a β-polymorph and causing the margarine to become sandy; with the current *trans* scare it is unlikely that this effective modification is still in use.

Instead, fats made by interesterifying high-melting palm stearin and low melting lauric oils (Fondu and Willems, 1972) now serve as hardstock in margarine and shortening manufacture and their usage can be reduced by hydrogenating the interesterified fats (Delfosse, 1971; Graffelman, 1971; Ward, 1982); this also reduces the saturated fatty acid content of the final fat blend. Recent variations on this theme prescribe the use of fully hydrogenated soya bean oil and liquid soya bean oil (List, 2004).

Interesterification has also been used to prepare various fat substitutes. When this substitute is a triglyceride such as, for instance, Salatrim (Pelloso *et al*., 1995), it can be made by interesterifying the triglycerides providing the fatty acid moieties required in the final product. If this substitute has another polyhydroxyl backbone than glycerol such as, for instance, sucrose, it may be necessary to use FAME to incorporate the fatty acid moieties (Rizzi and Taylor, 1978). Consumers' interest in these substitutes is below expectation.

4.4 Fractionation

As opposed to the hydrogenation process and the interesterification process, both of which entail chemical reactions, the fractionation process is a physical process; its scope is therefore much more limited than that of chemical processes. Nevertheless, marketing departments tend to promote fractionation as the answer to perceived consumer chemophobia, which, if it exists at all, they may well have induced themselves.[2]

[2]Inducing is not only dishonest, it may also backfire. How can you explain to a consumer that conjugated linoleic acid (CLA) may well have nutritional advantages despite its *trans* content?

The first ever systematic study of oils and fats by Chevreul already mentioned their fractionation by treating a fat with boiling alcohol. This results in a solution that 'on cooling splits into two different materials, one with an excess of olein which stays in the alcohol, and another with an excess of stearin which forms a precipitate'. In fact, Chevreul introduced the names 'olein' and 'stearin'.

Dry fractionation has also been developed in France in that Mège-Mouries, who invented margarine in 1869 (Mège, 1869) used beef tallow olein for this application. So he had to 'separate the hard portion that makes the fat coarse grained, causes it to solidify rapidly and sticks to the palate" Mège-Mouries continues by specifying:

> The liquid and clear fat is poured into tubs that have an aperture at the bottom and contain a layer of lukewarm water. Then they are closed by a lid and when the crystallisation is complete on cooling, the water is drained through this aperture, the tub is turned upside down and the mass is allowed to fall on a table where it is cut into slices of 1 to 2 cm thickness, which are wrapped in cloth and pressed between warm plates. In this way about 60% of a mixture of margarin[3] and olein are obtained, having a composition that is identical to lard but with a much better taste. The solid material remains inside the cloth.

In this respect, the process is similar to the dry fractionation process formerly applied to lauric fats (Rossell, 1985).

During the fractionation process, the oil or fat being fractionated is partially crystallised and subsequently, the crystals formed are separated from the mother liquor. The crystals are isolated as a filter cake that is referred to as the stearin fraction and the filtrate is called the olein fraction. In general, olein properties are determined by the filtration temperature. Stearin properties and the yield of both fractions also depend on the filtration temperature but even more on the olein entrainment in the stearin filter cake (Dijkstra, 2002; Hamm, 2005). Accordingly, a higher specificity of the fractionation could only be realised by diluting the olein in the cake with a solvent.

To avoid the use of inflammable solvents, the detergent fractionation process (Seugé and Vinconneau, 1975) was developed. In this process, originally described by Fratelli Lanza of Turin, Italy (1907) and later developed by Alfa Laval as the Lipofrac® process, a surfactant solution in water is used to bring the crystallised fat into the aqueous phase which is then separated from the olein by using centrifugal separators. With improved separation technology resulting from the use of a conical sieve centrifuge fitted with a co-rotating scroll (Maes and Dijkstra, 1985), a high pressure membrane filter press (Willner *et al.*, 1989; 1990) or a decanter (Deffense, 2005), the dry fractionation process has completely ousted the detergent process. The olein content of the stearin obtained by the detergent process (35–52%) is no better than can be achieved with a membrane press (Hamm and Timms, 2006), the cost of the centrifugal

[3]Chevreul suggested that oils and fats consist of compounds formed by a fatty acid and glycerol and that fat properties were determined by the relative amounts of these compounds (Chevreul, 2009). The compound formed by stearic acid and glycerol he called stearin and the compound formed by oleic acid and glycerol, he called olein. He also isolated palmitic acid, which he called 'margaric acid' and the margarin referred to by Mège is the compound formed by this margaric acid and glycerol.

separators and of the surfactant and the resulting water disposal problem are all factors explaining why no new detergent fractionation processes are being installed.

Given the developments outlined above (Hamm, 1995), the present chapter will be limited to the various dry fractionation processes in current use. It will discuss both stationary crystallisation processes and the partial crystallisation of an agitated melt, the various separation processes and their equipment, and the products obtained by these processes.

4.4.1 Fat crystallisation theory

Fat crystallisation affects a large number of food products and processes. It should, for instance, provide chocolate with a snap on breaking and it should prevent margarine from oiling out. On the other hand, some countries prefer the crystals in ghee to sink to the bottom and leave a clear oily supernatant. In puff pastry margarine, the fat crystals should provide the product with plasticity, in physically ripened cream, the crystals should facilitate churning and in dry fractionation, the crystals should permit the olein to be separated from the stearin.

These various demands can only be met by different crystal morphologies and arriving at these different morphologies necessitates using different crystallisation techniques. Tempering for chocolate (Padley, 1997), scraped heat exchangers for margarine (Poot and Biernoth, 1994), a slow cooling for ghee (section 9.5 in Podmore, 2002), patience for cream (section 6.4.3 in Robinson and Rajah, 2002) and an artistic talent for dry fractionation (Tirtiaux, 1990). The situation is complicated by the fact that different fats behave differently. If molten butter is allowed to cool down without being agitated, a deposit of filterable crystals is formed eventually, as observed in ghee. If lard is treated the same way, a grainy plastic solid results.

Apparently, the triglyceride composition of the fat being crystallised affects the resulting crystal morphology but that is not the only factor. Non-triglyceride components such as phosphatides (Smith, 2000) and partial glycerides can also have an influence. High melting diglycerides, for instance, may attach themselves at a crystal growth point, thereby disturbing the regularity of the crystal lattice and preventing it from growing further until the diglyceride has dissolved away again.

Crystallisation comprises several steps (Foubert *et al*., 2006). If the thermodynamic driving force for crystallisation is sufficiently large, crystal nuclei will appear. They can be formed by homogeneous primary nucleation but this requires undercooling by >30K (Kloek, 1998) so that in industrial practice, heterogeneous primary nucleation by dust particles, etc. constitutes the main nucleation mechanism, at least in the beginning of the crystallisation process (Timms, 1991).

In a multi-stage fractionation of palm oil, the first olein may well contain so few of these dust particles that heterogeneous primary nucleation will be impeded. This could be the reason why Maes *et al*. (1995) found that introducing high melting triglycerides by the gradual addition of a small amount of palm oil to the olein while this was being cooled down and crystallised, increased the rate of crystallisation and caused

the resulting crystals to be more readily filterable. Inoculation with seed crystals is another possibility (Rappard and Plonis, 1980; Deffense, 1998).

When crystallisation is under way, new nuclei may also be formed by a process of heterogeneous secondary nucleation, a phenomenon for which Walstra (1998) has given a tentative explanation. He assumed that clusters of more or less oriented molecules diffuse away from the crystal and subsequently form a new nucleus. This requires the crystal growth rate to be rather slow so that the clusters have the opportunity to diffuse away before being incorporated into the original crystal lattice. In the industrial dry fractionation process, secondary nucleation is considered to be responsible for the formation of additional small crystals that badly affect the filtration characteristics of the stearin cake and thus make the process less selective (Timms, 1997). The well-known difficulty of maintaining crystallisation characteristics on scaling up may well arise because secondary nucleation gains in importance with increasing vessel size and linear agitator speed (M. Kellens, personal communication).

After nuclei have emerged, they will grow and form crystals provided the temperature of the melt is lowered. The presence of solvents has little influence on the triglyceride composition of these crystals (Coenen, 1974a; Hamm, 1986; Timms, 1997); this means that diluting the fat to be fractionated with a liquid oil (Van Putte and Muller, 1987) does not lead to the formation of different crystals either. If only one species of high melting triglycerides is present, this is the species that will crystallise, but the natural products processed industrially normally contain many different triglyceride species. This raises the question of which species will crystallise and when.

The different species present in natural fats will form solid solutions. They will not crystallise as separate, pure compounds but as mixtures of slightly different triglycerides. Therefore, they affect each other's solubility. In this respect, they behave quite differently from the way in which, for instance, sugar and salt behave when they are both dissolved in water. The solubility of the salt is not affected by the sugar concentration and vice versa. The salt starts to crystallise as and when the solution becomes supersaturated in salt, irrespective of the amount of sugar present.

When cooling a molten fat, the first crystals will be formed long before the melt becomes supersaturated with the triglycerides with the highest melting point. Similar but different triglycerides with a somewhat lower melting point will form mixed crystals with the higher melting triglycerides and their total concentration determines when the melt becomes supersaturated. On further cooling, the triglyceride composition of newly formed crystalline matter changes in that it starts to contain more and more triglycerides with lower and lower melting points.

There are cases known where different crystal phases can form a eutectic mixture (Smith, 2001). In palm oil, the higher melting phase is mainly PPP and POP while the lower melting phase consists principally of POO. As only to be expected, the study of model systems shows that triglyceride interactions can lead to more complex crystallisation behaviour but in general, this requires higher concentrations of particular triglycerides or a greater substrate purity than encountered in the industrial environment. Moreover, industry has to cope with variable partial glyceride concentrations

that tend to have a greater effect on the crystallisation process than the interactions mentioned earlier.

4.4.2 Industrial practice

Industrial fractionation processes can be classified under the following categories:

- Winterisation processes. In Europe, the term 'winterisation' refers exclusively to dewaxing processes whereas in the USA it can also refer to processes for producing salad oils by the removal of higher melting triglycerides from oils such as cottonseed oil (O'Brien and Wan, 2001) or brush-hydrogenated soya bean oil.
- Fractionation processes employing static crystallisation. These processes are primarily used for oils that are not amenable to suspension crystallisation, the prime example being palm kernel oil.
- Fractionation processes employing suspension crystallisation.

All these processes tend to be batch processes but there is a tendency to move toward semi-continuous and even fully continuous processes.

4.4.2.1 Winterisation/dewaxing

The purpose of the dewaxing process is to ensure that liquid oils that are stored in a refrigerator remain brilliant and do not throw a deposit. A cold stability of 8 days at a temperature of 0°C requires the wax content of the oil to be reduced to 8 ppm. Sunflower seed oil, corn germ oil and rice bran oil are the major oils that need dewaxing. The amount of wax to be removed can vary considerably and in the case of sunflower seed oil, dehulling the seed prior to oil expelling greatly reduces the crude oil wax content. Washing the seeds with hexane before crushing them also removes most of the wax (Morrison III, 1982).

The dewaxing process itself consists of a crystallisation stage that is followed by a separation step. The latter is usually a filtration employing filter aid but centrifugal separators are also used, as in the Lipofrac® process mentioned above in the context of detergent fractionation. The literature describes a large number of different cooling procedures (Dijkstra, 2007a) but in practice, the only procedure to lead to crystals requiring a minimum of filter aid during filtration has been disclosed by Asbeck and Segers (1990); it is also one of the fastest. Their cooling process comprises a quick cooling to just above the cloud point of the oil. In practice, this is usually about 45°C but it depends of course on the type of oil and the amount of wax present. Then a slow cooling stage at 6°C per hour is introduced. According to J. De Kock (personal communication), the rate of cooling can be increased as soon as the oil has reached a temperature of 20°C below its cloud point. Thus, cooling must be slow when nuclei are forming and start to grow but before and after this stage, cooling can be fast without affecting crystal morphology. There is no need to store the crystal slurry in maturation tanks. It can be sent to the separation stage as soon as the lowest temperature (usually some 5°C) has been reached. This cooling process can be carried out continuously.

The most common filter used for the separation of the wax crystals is the pressure leaf filter (Arbeitskreis "Technologien der industriellen Gewinnung und Verarbeitung von Speisefetten", 1996). The filter aid used is usually diatomaceous earth but other products can also be used. Which filter aid to choose depends on how much is needed, its price and the oil retention in the filter cake. In this respect, kitchen salt used as a filter aid (McClain, 1951) has been found to retain very little oil, which facilitates wax recovery. When the wax crystals are separated by centrifuge, it is common to employ an aqueous solution of sodium lauryl sulphate (Seugé and Vinconneau, 1975). They can also be separated centrifugally as part of a degumming process (Ringers and Segers, 1977) or by adding some caustic to acid oil to be subsequently physically refined (Kõvári *et al*., 2000).

4.4.2.2 Static crystallisation

In this dry fractionation process, the melt is allowed to cool and partially solidify in trays without agitation. Formerly, the resulting blocks were then wrapped in cloth and pressed (Rossell, 1985; Soon, 1994) but because the wrapping and subsequent unwrapping are very labour-intensive, ways have been sought to automate the process. Accordingly, Yoneda *et al*. disclose a system (1997) in which the molten fat is pre-cooled by passing it through a heat exchanger, then introduced into shallow trays where it is cooled by circulating air and subsequently, the partially solidified melt is taken out of the tray and passed to a crusher that converts the material to a pumpable paste that is then passed to a membrane press where it is separated into an olein fraction and a stearin fraction.

A further improvement of dry fractionation employing static crystallisation was disclosed by Hendrix and Kellens (2003) who introduced a static crystalliser (Statoliser®) that has some similarity to a membrane filter press. It comprises a series of adjoining narrow chambers but whereas in the filter press, these chambers can be compressed by a membrane with a liquid behind it, in the Statoliser® these chambers are used to cool and crystallise the chamber contents by withdrawing heat through the chamber walls into a cooling medium. Both pieces of equipment have in common that they can be opened to release the chamber contents. In the case of the Statoliser®, these contents are partially crystallised blocks that can be crushed to form a pumpable paste that is then fed to a membrane press for separation into fractions. Accordingly, the crystallisation temperature can be controlled quite accurately, which causes the crystallisation process and the resulting product properties to be quite reproducible; the process is fully automated and requires little labour. It is also possible to pump pre-crystallised oil into a filter press where it is allowed to crystallise further before being pressed (Higuchi *et al*., 1989).

4.4.2.3 Suspension crystallisation

All suspension crystallisation systems involve filling a crystallisation vessel with molten fat that is then cooled to form a crystal slurry. This slurry is then pumped to a separation device for separation into an olein fraction and a stearin fraction.

Because cooling requires heat transfer, the vessels are always agitated and provided with heat exchange elements. The oldest type of crystallisation vessel was a cylindrical vessel fitted with cooling coils and a central multi-speed agitator (Deffense, 1985) that ensures a uniform temperature throughout the vessel and prevents crystals from settling. Cooling is rather slow so that the resulting crystals tend to be fairly uniform in size and easy to filter. On emptying a vessel like that, some crystals may be left behind in the vessel and on the coils and may settle once the liquid level has fallen below the lowest agitator blade. Replacing the cooling coils by vertical cooling fins has reduced the amount of crystalline material left in the vessel. For diagrams of this and subsequent crystallisers, see (Timms, 1997) and (Kellens and Hendrix, 2000).

With the advent of the membrane filter press (Willner *et al*., 1991; Willner and Weber, 1994) crystal uniformity and filterability became less important and this permitted faster crystallisation. This led to the development of the concentric crystalliser that consists of concentric annular vessels that are separated by double walls through which a cooling medium flows. The agitation is ensured by a common agitator but this has the disadvantage that the linear speed of the agitator blades is much higher for vessels near the outside of the crystalliser than for those close to the agitator shaft. Heat transfer in this type of crystalliser is high and this permits fast cooling without requiring a large temperature differential between the melt being crystallised and the cooling medium so that the risk of crystals being deposited on the cooling surface is minimised.

Even better heat transfer is obtained in crystalliser vessels in which the cooling elements have been integrated into the agitator (Homann, 1996; Kellens and Hendrix, 2007). For the STAR-type (STirring ARea) crystalliser, a heat transfer coefficient of 300 W/m^2K has been reported (Weber *et al*., 1998) even though the linear speed of the agitator elements is quite low. This low speed is in all likelihood the reason why this type of crystalliser leads to the formation of very uniform crystals. It may well avoid or suppress secondary heterogeneous nucleation (Walstra, 1998). In addition it has been found that this type of crystalliser does not necessarily cause the temperature to be uniform throughout the entire crystalliser vessel (See Example 3 in Kellens and Hendrix, 2007) and that this lack of temperature uniformity does not cause the crystals to become poorly filterable. Accordingly, this type of crystalliser (Mobuliser®) can in principle be used in a continuous dry fractionation process which also requires a continuous separation step to be fully continuous.

4.4.2.4 Separation processes

The first type of filter to be used to separate the stearin from the olein was a rotary vacuum drum filter (Bernardini and Bernardini, 1975) but this was ousted by the successful vacuum band filter as developed by Tirtiaux (1976) because the belt provides more time for the oil to drain away from the cake (Timms, 2005). Even so, this filter had two disadvantages: it can only handle well-developed crystals and even with those, the filter cake still contains up to 70% entrained olein.

Accordingly, further development was required to reduce the amount of entrained olein. The first development in this direction was by Maes and Dijkstra (1985) who

used a conical sieve centrifuge fitted with a co-rotating scroll (Dijkstra, 1998) which has also been described by Deffense (2000). It allows the olein content of the filter cake to be reduced to 30% and CBE and CBR (cocoa butter replacers) to be produced but only when the crystals exceed a certain size. If they are too small, they pass through the screen and if they block the holes in the screen, they reduce its permeability with the result that the feed flows over the screen without being filtered.

However, with the right kind of crystals, a dry cake results and moreover, the X-proof version of the equipment allows the option of washing the filter cake with a solvent and thereby lowering the olein content even further, as suggested by Timms (2006). Just washing the cake with a solvent would require much less solvent than crystallising from that solvent and would therefore be much cheaper than full solvent fractionation while still yielding comparable results. The rinsing possibility is shown in Figure 4.5, which depicts a cross-section of the conical sieve centrifuge.

A separation process that is less sensitive to crystal size and morphology and that therefore has been widely adopted uses the membrane filter press (Willner *et al*., 1989, 1990; Willner and Weber, 1994; Tirtiaux and Gibon, 1996; Dijkstra, 2002). Early presses suffered from high maintenance costs but this problem has been overcome. The pressure has also been increased from 5 bar to 30 bar which necessitates the use of hydraulic fluids.

The use of a nozzle centrifuge for separating the stearin from the olein has also been reported (Wilp, 2000). The process is continuous and involves a closed system both of which are advantages but the disadvantage of the process is that the nozzles have a fixed discharge capacity for stearin crystals. If these are supplied at a rate that exceeds

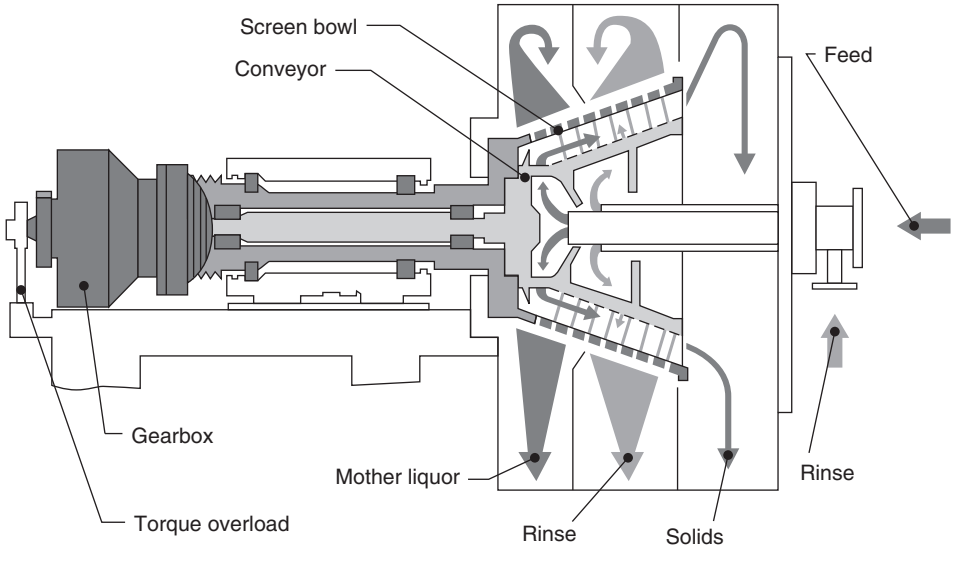


Figure 4.5 The cross-section of the conical sieve centrifuge. *Source:* De Greyt and Dijkstra, 2008. Reproduced with permission of John Wiley & Sons.

Table 4.1 Melting points and yields of beef tallow fractions.

Product	Method of filtration					
	Vacuum belt		Vacuum belt		Membrane press	
	MP (°C)	yield (%)	MP (°C)	yield (%)	MP (°C)	yield (%)
tallow	42.6	(IV = 51.1)	46.2	(IV = 45.0)	44.8	(IV = 46.0)
S-36	48.7	30	51.8	34	52.9	24
O-36	34.7	70	36.2	66	34.0	76
SS-43	53.5	35 (10.5)	55.7	33 (11.2)		
SO-43	43.0	65 (19.5)	47.5	67 (22.8)		
OS-20	43.7	30 (21.0)	41.8	48 (31.7)	43.1	27 (20.5)
OO-20	19.7	70 (49.0)	19.5.	52 (34.3)	20.0	73 (55.5)

Source: Based on data from Deffense, 2001.

this discharge capacity, they leave the separator with the olein and if they are supplied at a lower rate, olein leaves the machine together with the stearin (Dijkstra, 2007b).

The use of a decanter on the other hand does not suffer from this disadvantage. Its use had already been suggested (Example 1 in Maes and Dijkstra, 1985) but it is only recently (Deffense, 2005) that good results have been obtained on an industrial scale.

4.4.3 Fractionation products

As mentioned above, the first fat to be fractionated on an industrial scale was beef tallow (Mège, 1869). It is still being fractionated and the data provided by Deffense (2001) and summarised in Table 4.1 pertain to a multi-stage fractionation. In Table 4.1, S-36 stands for a first stearin fraction that has been obtained by filtration at 36°C. Similarly, OS-20 stands for the stearin fraction obtained by fractionating a first olein fraction (O-36) and filtering at 20°C.

Anhydrous milk fat (AMF) is fractionated industrially (Kaylegian and Lindsay, 1995) to produce a stearin that is used in puff pastry. The stearin has a longer plastic range than butter or AMF so that its use obviates the need for intermittent cooling of the dough. The butter olein is used to make butter spread more easily and also is used in ice cream.

Lard is also fractionated industrially to produce a variety of olein and stearin fractions. A multi-stage fractionation is shown in Figure 4.6, the first stage of which is a dry fractionation process using a filter press (J. Artigas i Brugal, personal communication). The stearin and olein yield of the first fractionation have been calculated from the iodine values as provided. When iodine values of the further fractions are used for yield calculations, the first stearin yields about equal amounts of hard and soft stearin and the mid fraction yields are about 20% in both cases. Accordingly, the overall yield of the 3rd olein fraction is about 35–40%.

As is to be expected, the oleins are enriched in oleic acid and linoleic acid, in comparison with the lard used as starting material, whereas the stearins contain less unsaturated fatty acids than this lard and are enriched in saturated fatty acids. The mid

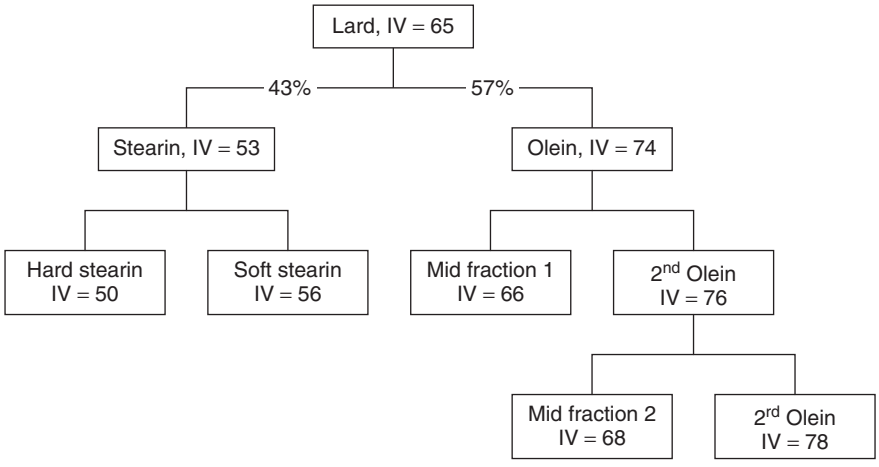


Figure 4.6 Multi-stage fractionation of lard.

fractions contain slightly more oleic acid than the lard but are otherwise very similar. Consequently, the olein yield can be increased by recycling the mid fractions.

Lard is also fractionated industrially by using a Mobuliser® crystallisation vessel (Kellens and Hendrix, 2007). According to the analytical data supplied (J.T. van der Veen, personal communication), a single fractionation yielding an olein with an iodine value of about 70 is produced together with a stearin with an iodine value of 50. If these values are compared with those in Figure 4.6, it can be concluded that the filter cake resulting from the Mobuliser® slurry retained less olein. This could be due to the particular membrane press used to filter the Mobuliser® slurry or because of the good filterability of this slurry.

By far the most important oil to be fractionated industrially is palm oil. The amount of palm oil that was fractionated in 2009 can be estimated at some 30 million tonnes. This yields 6 million tonnes of palm stearin IV 32-34 and 24 million tonnes of palm olein with IV 56–58, some of which is fractionated again to produce palm olein with a lowered could point (W.F.J. De Greyt, personal communication). The palm oil co-product of palm kernel oil is also fractionated to yield palm kernel stearin which after hydrogenation, provides a steeply melting cocoa butter substitute (CBS). Palm kernel oil itself has too low a melting point for this application and the melting point of fully hydrogenated palm kernel oil is too high and gives the product a sticky mouth feel. This is caused by triglycerides containing stearic acid and their concentration can be reduced by using the stearin fraction which contains less oleic and linoleic acid and thus less stearic acid after hydrogenation (Rossell, 1985).

A two-stage dry static fractionation has been described by Calliauw *et al*. (2005). In the first stage, a palm kernel stearin fraction is obtained with an iodine value of 5 that can be used as a CBS without further hydrogenation. The first olein fraction is then fractionated again, yielding a second palm kernel stearin (IV = 7) that is suitable as

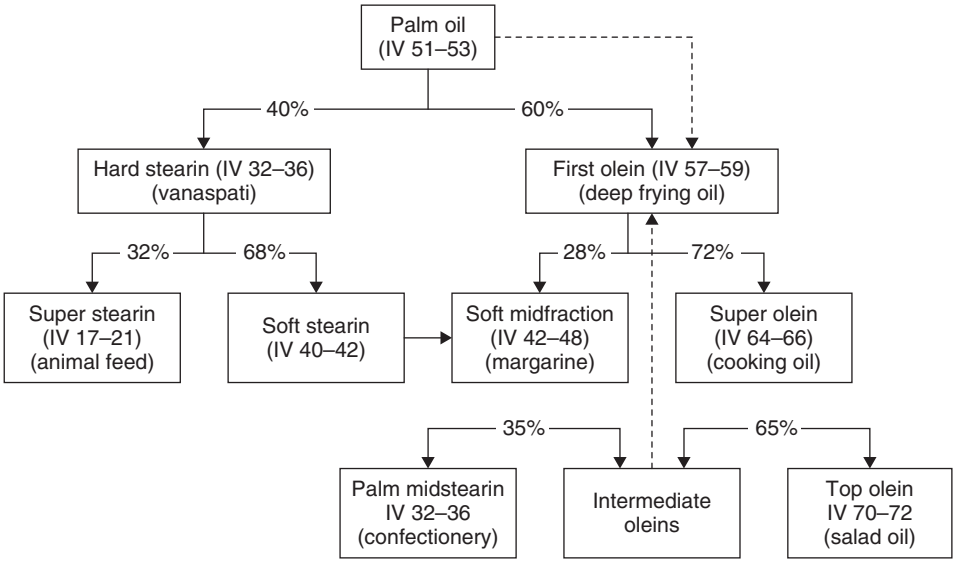


Figure 4.7 Multi-stage dry fractionation of palm oil. *Source:* Adapted from Deffense, 1995.

CBS after full hydrogenation. This two-stage process has the advantage of requiring less hydrogenation capacity and a higher CBS yield.

A multi-stage fractionation scheme for palm oil is represented in Figure 4.7. This indicates via a dotted line that it can be useful to 'seed' the first olein being fractionated by the addition of some non-fractionated palm oil (Maes *et al*., 1995). Another dotted line indicates that intermediate oleins for which no ready application has been developed can be recycled by mixing them with the first olein. High IV superoleins combine a low cloud point with good oxidative stability and are therefore used as salad oil and frying oil. The palm mid-fraction (IV 32–36) can be used as confectionery fat and thereby commands a premium. The higher IV soft mid-fraction is increasingly used in margarine and shortenings as a *trans*-free hardstock.

Another reason for this increased use may be its low cost price. In fractionation, the cost of the raw material (palm oil) and the cost of fractionation are both givens. The selling prices of some of the fractions can also be givens and consequently, the cost price of the fractions that have no immediate outlet can be calculated. If they can be sold at a higher price, the fractionation process makes a profit even when their selling price is low in comparison with other, similar fat products that they may therefore replace. If the selling price is then raised to just below the price of these similar fat products, an even larger profit results.

4.5 Discussion

Among the modification processes, the hydrogenation process, which was developed to remedy a shortage of fats to be used as hardstock in margarine and shortenings, is

the oldest. It has also been used to increase the stability of highly unsaturated oils and utilise raw materials such as whale oil and fish oil. This latter application has almost disappeared since whale oil is no longer produced and fish oil is used more and more in aquaculture feed. The *trans* scare has also reduced the partial hydrogenation of vegetable oils but full hydrogenation of these oils has increased since the resulting fats can be interesterified with liquid oils and then provide a hardstock for margarine and shortening fat blends.

Consequently, more and more fats are being produced by the interesterification process and the importance of this process is believed to go on increasing. Whereas it formerly mainly served to manufacture speciality products such as confectionery fats and fat blends that did not contain hydrogenated fats and were sold in health food shops (Fondu and Willems, 1972), interesterification is now used to produce fats that are similar to those formerly provided by partial hydrogenation but that, sadly enough, are more difficult to process (Gerstenberg, 2008).

The third modification process (fractionation) is also expected to gain in importance, if only because more and more palm oil is being produced. Another reason for its growing importance stems from the technical improvements, several of which are fairly recent and still await full implementation. Among these developments, the change from a batch process or semi-continuous to a fully continuous process constitutes an appreciable saving and since most large fractionation plants operate with few type changes, they are highly amenable to changing to a fully continuous process. This change is therefore also expected.

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5

Fats for chocolate and sugar confectionery[1]

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5.1 Introduction

The traditional fat ingredients for chocolate are cocoa butter (CB) and milk fat (MF). If we add sugar confectionery to this, then we can also include certain vegetable oils, especially coconut oil (CN) used in toffees and fillings. Nowadays, there is a much wider range of fats available, designed mainly to replace the expensive cocoa butter and milk fat, but also coconut oil. As far as fats intended to replace cocoa butter are concerned, these are generally termed 'cocoa butter alternatives' (CBAs). These may be designated by their application (e.g. milk-fat replacer, cocoa-butter extender) but the more systematic approach adopted in this chapter is to designate them according to their chemical composition, which is the fundamental basis of their properties. Historically, three types of CBA have been defined (Gordon *et al*., 1979):

- those based on symmetrical SOS[2] triglycerides;
- those based on hardened (hydrogenated) non-lauric oils that are high in trans fatty acids;
- those based on lauric oil.

To this list we can also add a new type of CBA – those based on fractionated non-lauric oils that are not rich in symmetrical SOS triglycerides.

[1]The original chapter was written by Ian M. Stewart* and Ralph E. Timms.
*(1950–2007)
[2]In this chapter the convention used for abbreviations of fatty acids will be S = saturated, U = unsaturated; L = lauric (C12:0), M = myristic (C14:0), P = palmitic (C16:0), St = stearic (C18:0), O = oleic (C18:1c), E = elaidic (C18:1t), Li = linoleic (C18:2), Ln = linolenic (C18:3), A = arachidic (C20:0).

Fats in Food Technology, Second Edition. Edited by Kanes K. Rajah.

Symmetrical SOS fats are composed of the same triglycerides – POP, POSt, StOSt (see note 1 for nomenclature) – that are found in cocoa butter. Because the unsaturated oleic acid is at the 2 position and the saturated palmitic and stearic acids are at the 1 and 3 positions, the triglycerides are described as symmetrical. These triglycerides are obtained by selecting natural fats that contain them.

Hardened, high-trans fats are complex mixtures of triglycerides with fatty acids of carbon numbers 16 and 18 (C16 and C18) where the unsaturated acids have their double bonds mainly in the *trans* configuration. These triglycerides are produced by hardening (hydrogenating) liquid oils under very selective, trans-promoting, conditions.

Fractionated, non-hydrogenated non-lauric fats are mixtures of fractions of vegetable oils in which palm oil is generally the predominant one. They are a more complex mixture of triglycerides than are found with the symmetrical SOS type of fat.

Lauric-type fats are complex mixtures of triglycerides based on mainly saturated fatty acids with carbon numbers 8 to 18 (C8–C18). Lauric acid constitutes about 50% of all the fatty acids. The triglycerides are obtained from the two main fats containing lauric acid: coconut and palm kernel oils.

In the following sections, we describe the production and properties of cocoa butter, milk fat and the various alternative fats. We then discuss the legal and regulatory aspects governing their use in chocolate before describing their various applications in chocolate and sugar confectionery. In a chapter of this length it is not possible to go into great detail. We have aimed to cover all aspects of the topic succinctly, while providing adequate references to more detailed reviews of particular topics. Two of us have written much more comprehensive handbooks to which reference should be made if more detail is required (Timms, 2003; Talbot, 2006, 2009a).

5.2 Production and properties

5.2.1 Cocoa butter and milk fat

Cocoa butter is the fat extracted from the seed of the *Theobroma cacao* tree (Minifie, 1989; Beckett, 2009). These seeds, which are referred to as cocoa beans, consist of about 15% shell and 85% cotyledon (referred to as ‘nib’), of which about 55% is fat. To extract the fat, the nibs are ground to a paste called cocoa liquor or mass, and the fat is then extracted by hydraulic pressing, screw expelling or solvent extraction. The highest quality cocoa butter is produced by hydraulic pressing and is called ‘pure prime pressed’ cocoa butter. Solvent extraction is used only for extraction of cake residues from the expeller process or of other, waste, residues. The cocoa butter produced is invariably of lower quality and contains higher levels of non-triglyceride materials such as phospholipids and pesticides.

At some stage in the processing of the beans they are roasted to produce the desirable chocolate flavour. Whole beans, nibs or liquor may be roasted (Beckett, 2000). Typically, 100 g of beans produces 40 g of cocoa butter, 40 g of cocoa powder (the residue after extraction, which contains 10–24% fat, most commonly 10–12%) and 20 g of waste materials such as shell, moisture and dirt (Timms and Stewart, 1999).

Most of the cocoa butter added to chocolate, particularly to milk chocolate, which consists of about 80% of total consumption, is deodorised. The main purpose of deodorisation is to moderate the flavour by removing harsh or acidic flavours and off-flavours. A subsidiary purpose is to sterilise the fat. Cocoa butter is deodorised at temperatures of 130–180°C by passing steam through the oil under a vacuum of 1–5 mbar for 10–30 min. (In older, batch, processes operating at lower temperatures (105°C) and poorer vacuums (up to 40 mbar), cocoa butter could be deodorised for as long as 3 hours (Hanneman, 2000).) Under these conditions, deodorisation has no effect on the physical properties (Timms and Stewart, 1999). There may be a small (less than 0.5%) reduction in free fatty acids.

The milk fat used in confectionery may be added as pure fat (butter oil or anhydrous milk fat (AMF)), as full cream milk powder (FCMP) containing 26% fat, as skimmed milk powder (SMP) containing less than 1% fat, or as milk crumb containing varying levels of milk fat and cocoa butter, typically 7% and 9%, respectively (Jackson, 1995; Minifie, 1989) though total milk fat and cocoa butter levels of 31% in milk crumb have also been reported (Haylock and Dodds, 2009). In recent years other dried ingredients have become widely available: buttermilk powder (8% fat), whey powder (1% fat) and high-protein and high-fat powders (Haylock, 1995). Figure 5.1 shows the schematic composition of the four main milk ingredients. Traditionally, butter or even cream was used for the manufacture of sugar confectionery such as toffees, caramels or

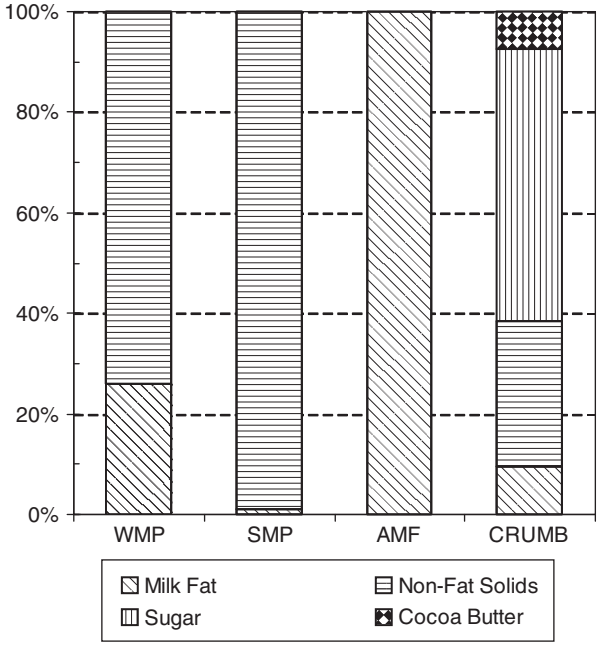

Figure 5.1 The main milk-fat-containing ingredients used in chocolate. Note: WMP, whole milk powder; SMP, skim milk powder; AMF, anhydrous milk fat; CRUMB, milk crumb.

Table 5.1 Typical specification for deodorised cocoa butter.

Parameter	Specification	Method
Appearance	Clear	Visual
Odour	Characteristic, free from rancid, smoky and foreign odours	Taste panel; particular odour and flavour required may need to be agreed with customer
Flavour	Characteristic, free from rancid, smoky and foreign flavours	Taste panel; particular odour and flavour required may need to be agreed with customer
Moisture (%)	0.05 maximum	Karl Fischer
Free fatty acid (% as oleic)	1.75 maximum	Titration (e.g. AOCS Ca 5a-40)
Diglyceride (%)	2.5 maximum	Gas-liquid chromatography after silylation
Unsaponifiable matter (%)[a]	0.35 maximum	IOCCC method 23-1998, for example
Peroxide value (meq kg^{-1})	1.0 maximum	Titration (e.g. AOCS Cd 86-90)
Rancimat induction period (120°C)	32 h	Some companies specify different temperatures but this should meet all requirements
Iodine value	34–38	Titration (e.g. AOCS Cc 13c-92)
Blue value	0.04 maximum	Based on IOCCC method 29-1988
E(1%) 270 nm	0.35 maximum 0.14 maximum after alkali wash	Based on IOCCC methods 18-1973 and 19-1973
Solid fat content (%)		Pulsed nuclear magnetic resonance, with tempering at 26°C for 40 h (e.g. BS684:2.22)
20°C	76.0 minimum	
25°C	70.0 minimum	
30°C	42.0 minimum	
35°C	1.0 maximum	
Jensen cooling curve		Manual cooling curve (BS684:1.13)
T_{max} (°C)	29.5 minimum	
t_{max} (mins)	35–55	
Rise (°C)	4.5–6.0	
Total plate count	1000 g^{-1}	Standard microbiological procedure
Origin processing	As agreed with customer Deodorised to flavour agreed with customer Filtered	Deodorised: no crude cocoa butter allowed

Note: [a]The permitted levels of unsaponifiable matter differ in the various standards set for cocoa butter (Kamphuis, 2009), i.e., EU Directive 2000/36/EC: maximum 0.5%, or maximum 0.35% in press butter); Codex STAN 86-1981, rev 1-2001: maximum 0.7% or maximum 0.35% in press butter.
Source: Timms and Stewart, 1999. Reproduced with permission of John Wiley & Sons.

fudges. Butter and especially cream require particular storage conditions and hygienic handling. Also, the water in these products must be evaporated during confectionery manufacture. It is therefore much more convenient to use AMF (Jackson, 1995).

A typical customer specification for cocoa butter is given in Table 5.1. This example relates to deodorised cocoa butter, but the physical and chemical properties as opposed to the sensory properties are little affected by deodorisation. For the fat technologist, the most important properties of a fat are its melting properties, usually indicated by solid fat content (SFC), and its rate of crystallisation, in this case indicated by the Jensen cooling curve (Figure 5.2). Cooling curves may also be obtained by using the Shukoff method (IUPAC standard method 2.132; IOCCC method 31-1998). This method, however, is often considered to be deficient compared to the Jensen method

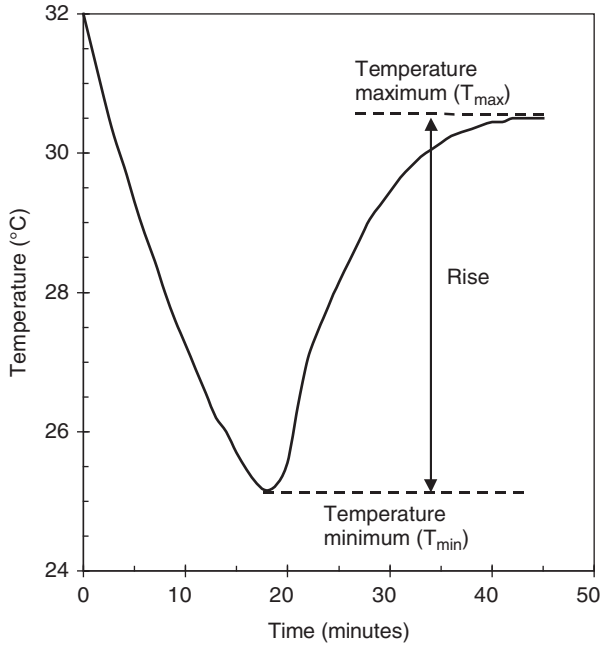

Figure 5.2 Typical Jensen cooling curve of cocoa butter.

because the fats are not stirred. This means that the form in which the fats crystallise in the Shukoff method is closer to the form produced when an untempered cocoa butter is crystallised. The Jensen method, on the other hand, produces the same form of cocoa butter crystals as are produced during tempering. Other ways of measuring crystallisation are by differential scanning calorimetry or by measurement of SFC over time. There are also proprietary methods such as the Barry Callebaut cooling curve (Hanneman, 2000).

Milk fat is a much softer fat than cocoa butter, as indicated in Figure 5.3 in which their SFCs are compared. Both fats vary widely in their properties, depending on their origins (Cullinane *et al*., 1984; MacGibbon and McLennan, 1987; Padley, 1997; Shukla, 1995). Both fats are also fractionated by crystallisation into fractions of different hardness, but only milk fat fractions are readily available commercially (Versteeg *et al*., 1994; Weyland, 1992).

A unique property of cocoa butter is its polymorphism.[3] Although there has been considerable debate about the number of polymorphs that cocoa butter possesses, traditionally, six polymorphs or crystal forms have been thought to exist. These were called Form I through to Form VI by Wille and Lutton (1996). More recent work (van

[3]Polymorphism is the phenomenon of multiple melting points when the fat has several possible crystal packings or polymorphs. For fats, there are three basic polymorphs: α, β′ and β. These can be further subdivided by adding suffixes 2 or 3 to indicate whether the unit cells or the repeat units are two or three fatty-acid chains long. Finally, subscripts are added where there is more than one polymorph of each type, with 1 indicating the highest-melting polymorph.

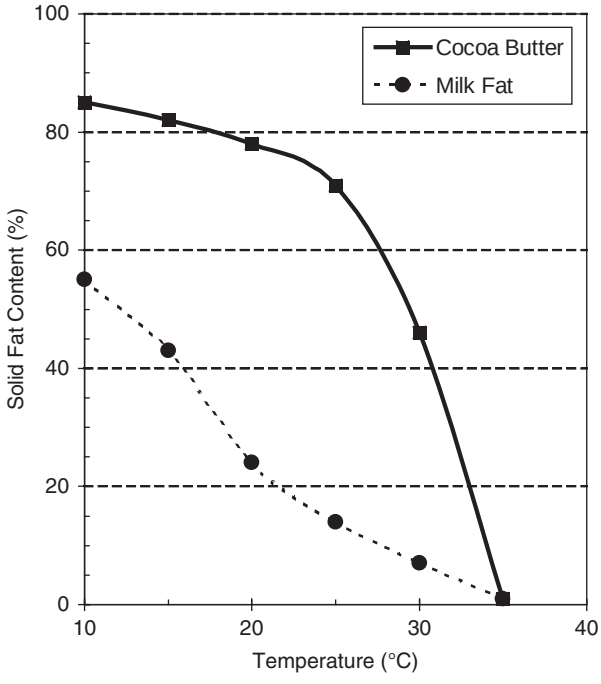

Figure 5.3 Solid fat melting curves of cocoa butter and milk fat.

Malssen *et al*., 1999) has proposed the existence of five forms – a γ form that may have been too unstable to have been identified by Wille and Lutton, an α form that corresponds to Form I from Wille and Lutton, a range of β' forms that correspond to Forms II to IV of Wille and Lutton and two β forms corresponding to Forms V and VI of Wille and Lutton. The debate, however, continues because since the publication of the work of van Malssen *et al*. (1999) a further paper by Fessas *et al*. (2005) uses a combination of DSC and mathematical deconvolution of the peaks to show the existence of six polymorphic forms.

Whatever the real situation, it is true to say that only three forms – form IV (β'-2), form V (β_2-3), form VI (β_1-3) – are important in the commercial production of chocolate. As a result of these more recent studies Form V is now often referred to as β_V and Form VI is referred to as β_{VI}. Form β_V is the characteristic form for chocolate, produced when it is tempered (controlled crystallisation) during production. It may be considered the stable form for practical purposes. The β' form (Form IV) is characteristic of untempered chocolate, and Form β_{VI} is a transformation of Form β_V associated with bloom, the greyish-white discolouration sometimes found on the surface of chocolate (see Section 5.6.1).

The properties of cocoa butter, as with all fats, are determined by its triglyceride composition, which is unusually simple. As shown in Figure 5.4, three triglycerides make up about 80% of the total. These three triglycerides – POP, POSt and StOSt – are themselves so similar that they form a single solid solution and behave

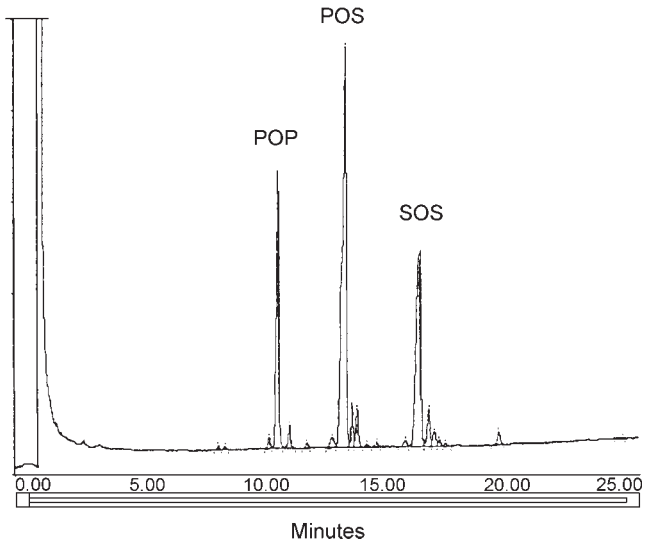

Figure 5.4 Typical triglyceride composition of cocoa butter by high-resolution gas chromatography.

almost like a pure compound, which results in the very sharp melting curve shown in Figure 5.3. In contrast, milk fat is a very complex mixture. Whereas four fatty acids – palmitic, stearic, oleic and linoleic – make up 98% of the cocoa butter fatty acids, milk fat contains at least 12 fatty acids present at more than 1%, ranging from carbon number 4 to 20 (C_4–C_{20}) including several odd carbon numbers not found in vegetable oils. The triglyceride composition is even more complex and hundreds of triglycerides have been identified. The result is a complex mixture with a relatively flat melting curve and simple polymorphism consisting mainly of one polymorph, β' (Timms, 1984).

Since, in milk chocolate, milk fat and cocoa butter are mixed together in the continuous fat phase, the final information we need to understand their functionality is the properties of their mixtures. As would be expected from the SFCs shown in Figure 5.3, when increasing amounts of milk fat are added to cocoa butter the mixtures become softer (i.e. have lower SFCs), at all temperatures. Because the two fats have different stable polymorphs they cannot be expected to mix completely in the solid state (see Section 5.2.6). The phase diagram of mixtures of cocoa butter and milk fat is shown in Figure 5.5. The point to note is that adding milk fat to cocoa butter does not change the β polymorph of cocoa butter until about 50% is added. Since chocolate rarely contains more than 30% milk fat in the fat phase, this means that in practice the properties of the cocoa butter predominate and the effect of the milk fat can be mostly ignored except for its softening effect (Timms, 1980).

5.2.2 Symmetrical SOS-type CBAs: cocoa butter equivalents (CBEs)

The triglyceride composition of cocoa butter was known in the 1950s, which allowed Unilever to develop an alternative fat based on the assumption that if the triglyceride

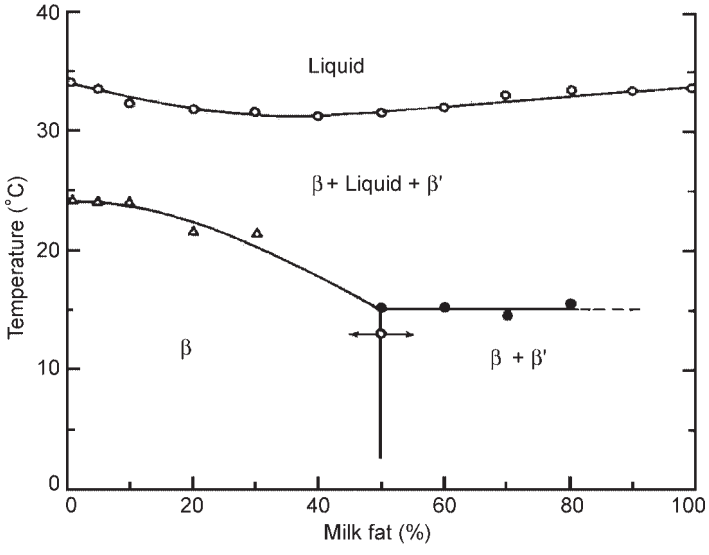

Figure 5.5 Phase diagram of mixtures of cocoa butter and milk fat. *Source:* Timms, 1980. Reproduced with permission of Elsevier.

composition of cocoa butter could be replicated, then its physical properties would be too. The subsequent patent (Unilever, 1956) discloses that the required triglycerides can be obtained from palm oil, illipe, shea and other fats from tropical countries. The patent also discloses the use of solvent fractionation to concentrate the required triglycerides (e.g. POP from palm oil). Such fats were called cocoa butter equivalents (CBEs) as they were substantially equivalent to cocoa butter in all aspects of functionality.

The fractionation of fats by crystallisation and separation of the crystals has been reviewed elsewhere (Timms, 1997). To summarize, the fat is melted and then slowly cooled to produce crystals, which are then separated by some form of filtration. It has been shown that the fundamental efficiency of separation of the triglycerides or triglyceride phases is not affected by the solvent used, although polar solvents do affect the separation of diglycerides from triglycerides (Timms, 1983). Solvents are beneficial in diluting the crystal miscella and lowering the viscosity, thus aiding the mechanical separation of the crystals from the liquid. Partly because of the lack of fundamental effect and partly because of improved mechanical separation techniques, dry (i.e. without solvent), fractionation is now overwhelmingly the preferred technique. Nevertheless, solvent fractionation is still used for the concentration of POP, POSt and StOSt triglycerides because the benefits mentioned are particularly valuable for the scarce and high-cost tropical oil feedstocks. The polar solvent acetone is preferred to hexane because of its effectiveness in removing diglycerides and other polar lipids, which are known to be detrimental to the functionality of chocolate fats (Okawachi *et al*., 1985; Tietz and Hartel, 2000).

The raw materials and processes required to concentrate the desired triglycerides are summarised in Table 5.2. The six raw materials shown are the commonest used

Table 5.2 Raw materials and processing required to produce symmetrical SOS ingredients for cocoa butter equivalent fats (CBEs).

Raw material	Origin	Processing required[a]	Ingredient used in CBE blend	Main triglycerides
Palm oil	Indonesia, Malaysia	Two fractionations[b]	Mid fraction[c]	POP
Shea butter	West Africa (dry tropics)	Degumming and one fractionation	Stearin[d]	StOSt
Illipe butter[e]	Borneo	None	Whole fat	StOSt, POSt
Kokum butter[f]	India	None	Whole fat (stearin[g])	StOSt
Sal fat	India	One fractionation	Stearin (whole fat[h])	StOSt, StOA
Mango kernel fat	India	One fractionation	Stearin	StOSt, POSt

Notes: [a]Additional to refining, bleaching and deodorising.
[b]Fractional crystallisation.
[c]Middle melting fraction.
[d]Stearin is a high melting fraction.
[e]Also called Borneo tallow or Tengkawang fat.
[f]Also called Kokum gurgi fat.
[g]Usually the whole fat is used but where a particularly high-quality component is required, kokum butter can also be fractionated to give a stearin fraction.
[h]Usually the stearin is used but if the sal fat is of especially good quality, the whole fat can also be used.

and are now also the only ones that are allowed for use in chocolate sold within the European Union (European Parliament and Council, 2000). Except for palm oil, the raw materials are all derived from wild or semi-wild trees growing in relatively poor and underdeveloped tropical countries.

Although in Table 5.2 we have shown palm oil as producing a mid-fraction, it should be noted that a wide range of palm mid-fractions is now commercially available, as shown in Figure 5.6, in which they are compared with cocoa butter and milk fat.

As shown in Table 5.3, these various raw materials and their fractions are then blended together to produce a triglyceride composition similar to the composition of cocoa butter. The 'original' CBE consisted of approximately equal parts of a palm mid-fraction and illipe. As can be seen, though it contains about the same total symmetrical triglycerides as cocoa butter, it differs in the proportions of the individual triglycerides. This is partly a question of economics – palm oil is readily available at a moderate price – and partly a question of chemistry – no natural fat contains as much POSt as cocoa butter. Thus, all blends will be deficient in POSt relative to cocoa butter. Later developments, as illustrated by the 'modern' CBE, included shea stearin and other StOSt-rich raw materials, leading to a further diminution in the amount of POSt.

Since the early developments of CBEs there has been an expansion of the types of CBEs available on the market, each of which are then linked to different applications. At one end of the scale there are what are often termed milk fat equivalents (MFEs) or milk fat replacers (MFRs) that are very rich in palm components and are suitable for use in lower milk-fat chocolates. At the other end of the scale are fats that are richer in StOSt than traditional CBEs and are used to enhance the properties of cocoa butter in terms of improving heat resistance or bloom resistance. These fats are known as cocoa butter improvers (or CBIs).

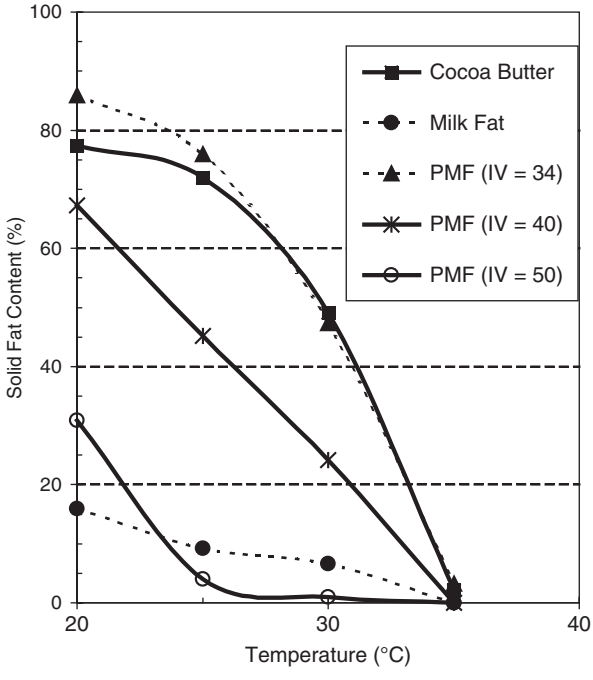

Figure 5.6 Solid fat melting curves of palm mid-fractions (PMFs) compared with those of cocoa butter and milk fat. Note: IV, iodine value.

Table 5.3 Triglyceride compositions of symmetrical SOS-rich CBE components and blends.

	Typical content (%)		
Ingredient fat	POP	POSt	StOSt
Cocoa butter	16	38	23
Palm mid-fraction	57	11	2
Illipe butter	9	29	42
Shea stearin	3	10	63
Original cocoa butter equivalent[a]	33	20	22
Modern cocoa butter equivalent	32	15	28

Note: [a]50% illipe plus 50% palm mid-fraction.

A large amount of information about the symmetrical SOS type of CBA fats and their formulation, especially using palm mid-fractions and illipe, is to be found in two books by Wong Soon (1988, 1991).

5.2.3 High-trans-type CBAs

These fats are produced by the hydrogenation of widely available non-lauric liquid oils such as soybean and rapeseed oils. When used in chocolate recipes, they are often

called cocoa butter replacers (CBRs). They are hydrogenated either singly or blended with palm olein, the liquid fraction from the fractionation of palm oil. Hydrogenation generally takes place with use of a selective nickel catalyst and with limited hydrogen availability in order to ensure a high content of *trans* acids (over 45% and mainly elaidic acid).

The melting profile can be altered by varying the blend proportions of the hydrogenation feedstock and/or the catalyst and conditions used. Despite this, the melting behaviour of *trans*-hardened fats is not generally as steep melting as cocoa butter or the lauric-type alternative fats.

Although these fats are based on C16 and C18 acids, the hydrogenation process gives a different and much more complex arrangement of glyceride composition than that of cocoa butter and, consequently, they can crystallise directly in the β′ form, which is their stable polymorph. This means that they are non-tempering and may be used in a wide range of applications, including compound coatings and as 'structuring' components in softer fat-based confectionery fillings.

The relatively poor melting profile of such products can be improved by fractionation, removing both high-melting and low-melting triglycerides to produce a mid-fraction that has much improved melting characteristics, as shown in Figure 5.7. Because of the complex triglyceride composition of the feed oil, solvent fractionation

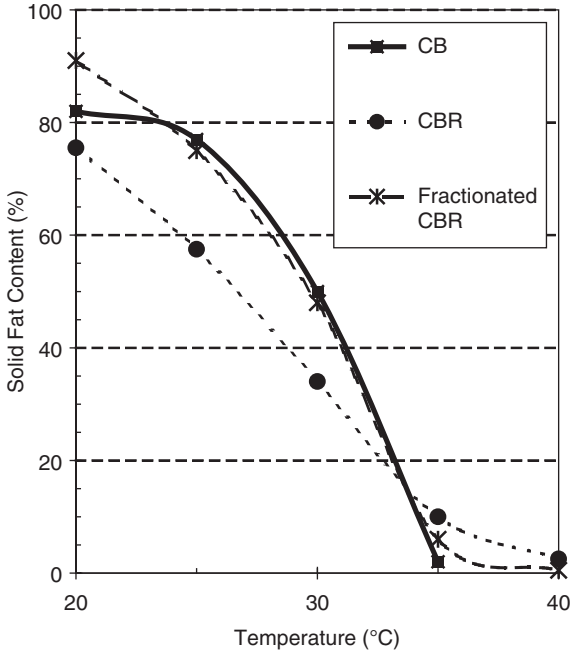

Figure 5.7 Solid fat melting curves of hydrogenated/high-trans alternative fats (AFs) in comparison with cocoa butter. Note: CB, cocoa butter; CBR, hydrogenated but unfractionated cocoa butter replacer; fractionated CBR, hydrogenated and fractionated cocoa butter replacer.

is preferred in order to maximise this benefit (through more efficient separation of the fractions), though recent improvements in dry fractionation technology have enabled reasonable products to be produced.

When used in compound coatings these products generally show good gloss retention, but it has been noted that fats based mainly on C18 acids tend to give a poorer gloss that is lost more rapidly (Padley, 1997). This defect is overcome by incorporating palm olein into the hydrogenation feedstock to introduce C16 acids or by the addition of products such as sorbitan tristearate. The structure of compound coatings containing non-lauric CBRs is such that it is not as brittle as chocolate or coatings based on lauric CBSs (see Section 5.2.5). This makes these fats very suitable for use as the basis of coatings to be enrobed on to large cakes. The malleability of the coating enables the cake to be cut into pieces without the coating shattering.

An interesting aspect of many of these fats is the tendency for the solid fat content to increase during storage at ambient or higher temperatures. This phenomenon is known as post-hardening and is not fully understood (Padley 1997; Wong Soon, 1991). It is a different mechanism from the post-hardening that is seen in cocoa butter-based chocolate. In chocolate, the effect of post-hardening is to increase the SFC at 20°C, giving a harder initial 'bite' to the chocolate, whereas in non-lauric CBR coatings the effect of post-hardening is to increase the SFC at 35°C, resulting in a waxier coating.

5.2.4 Low- or zero-trans non-lauric CBAs

Nutritional studies have shown that *trans* fatty acids can be hypercholesterolaemic and can promote atherosclerosis. The high level of *trans* fatty acids in high-*trans* CBAs is a significant disadvantage at a time when consumer pressure is leading to a trend to reduce the level of *trans* acids in foods generally. This has led oils and fats processors to develop both low-*trans* and zero-*trans* non-lauric CBRs.

Generally speaking, the low-*trans* non-lauric CBRs are often a result of blending existing high-*trans* products with unhydrogenated oils. They typically contain between 5% and 15% *trans* fatty acids (compared with about 50% in many high-*trans* products). While they start to address the issue of *trans*, they do tend to be a compromise. Zero-*trans* CBRs can also be produced by fully hydrogenating liquid oils such as soyabean oil, palm oil or cottonseed oil. The resulting fats are very high melting (typically having melting points ranging from 58°C to 70°C, depending on the base oil used). Ribeiro *et al*. (2013) have, however, used these at low levels (up to 5% w/w) in cocoa butter to enhance the heat resistance of chocolate made with this system. The main issue with these products is that they still need to be labelled 'hydrogenated' and this is, increasingly, a label description that consumers (and many retailers) are avoiding.

In many ways, CBEs can be considered as zero-*trans*, non-lauric, CBAs. They are, though, polymorphic and therefore need to be tempered. One of the major benefits of traditional high-*trans* non-lauric CBRs was that they were β′ stable and did not, therefore, require tempering. In developing zero-*trans* alternatives it was important to retain this β′ stability. It was discovered (Slager *et al*., 2007) that if β-stable POP is mixed with β′-stable PPO, then a product results that is, itself, β′-stable. This is all

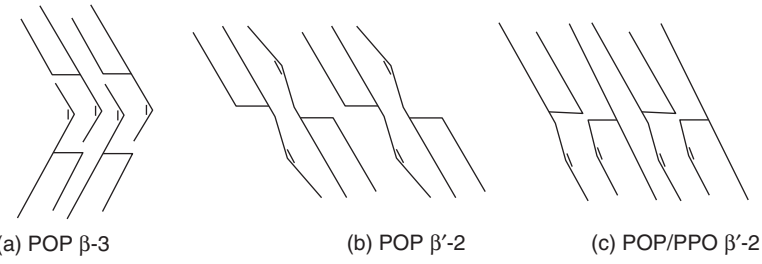

Figure 5.8 Schematic proposed structures of (a) the stable triple chain length β form of POP; (b) the unstable double chain length β′ form of POP; and (c) the double chain length POP/PPO compound. *Source:* Slager *et al*., 2007. Reproduced with permission of Dr Harnish Vergals GmbH.

because of the comparable structures of the two types of triglyceride and, in particular, the position and structure of the double bond in the oleic acid chain. POP generally crystallises in a β-stable triple-chain length structure in which all the fatty acid chains in the 2-position (central position) of the triglyceride molecules line up together. This is important because the main fatty acid in this position is oleic acid which has a single double C=C bond. Wherever there is a double bond in the fatty acid chain, there is a bend in the chain. By ensuring that all the oleic acid chains and, hence, all the double bonds line up, a stable structure (Figure 5.8 (a)) is produced (almost like fitting together a set of spoons).

If POP is crystallised into a β′-2 crystal form, then the oleic acid chains are not adjacent to each other and so a 'looser', less stable crystal structure is formed (Figure 5.8 (b)). When POP and PPO, however, are blended together, the oleic acid on the 2-position of POP and on the 1- and 3-positions of PPO end up next to each other in a stable β′-2 configuration (Figure 5.8 (c)), thus enabling a stable β′ product to be produced that is non-hydrogenated, zero-*trans* and does not require tempering. It is interesting to note also, in this context, that palm mid-fraction generally crystallises in a β′ form despite its high content of POP. If, however, it is seeded with β crystals of palm mid-fraction and sheared, then crystallisation into the β form can be induced (Talbot *et al*., 2009). Indeed, scraping the surface of the fat while it is in the α form can sometimes be enough to induce a transformation into the β form.

5.2.5 Lauric-type CBAs

Lauric-type alternative fats are widely used as confectionery fats. They are typified by the presence of large amounts of lauric (45–55%) and myristic (15–20%) acids. Because of the low melting point of these shorter-chain acids, they have a sharp melting profile and good mouth feel. When used in chocolate recipes, they are often called cocoa butter substitutes (CBSs).

Both palm kernel and coconut oils are soft, with a melting point of 26°C. In order to increase the solid fat content at 20°C to an acceptable level for a confectionery fat, it is common to hydrogenate to reduce or remove the unsaturated acids. A range of different melting point materials can be produced, as shown in Figure 5.9. However,

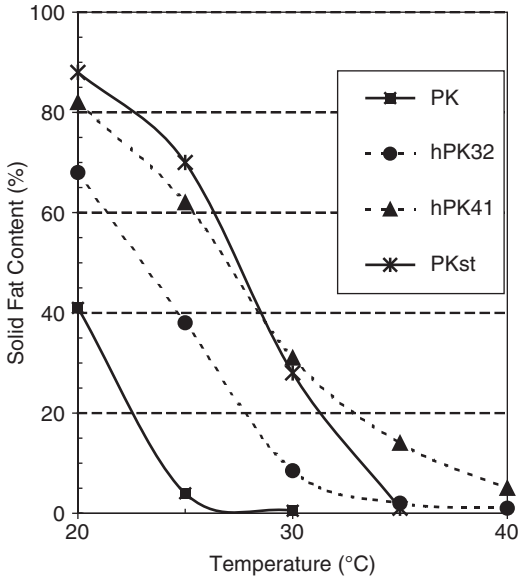

Figure 5.9 Solid fat melting curves of lauric-type alternative fats. Note: PK, palm kernel oil; hPK32, PK hardened to a melting point of 32°C; hPK41, PK hardened to a melting point of 41°C (fully hardened); PKst, palm kernel stearin with an iodine value of about 7.

in palm kernel oil, hydrogenation increases the melting point above 35°C, leading to poor mouth feel and meltdown.

Fractionation is an alternative and preferred method of increasing the SFC at lower temperatures to produce a steeper melting product. Palm kernel oil (rarely coconut oil) is normally dry fractionated and the crystals separated by using high-pressure presses. The stearins produced are very steep melting and have an excellent meltdown, as shown in Figure 5.9. These fractions are often used as such but are sometimes hardened for specific applications, especially in hot climates.

Because of their complex triglyceride composition, lauric-type alternative fats crystallise directly in the β′ form, which is their stable polymorph. This means that, like non-lauric CBRs, they do not require tempering, which is useful in many applications.

5.2.6 Comparison and compatibility

Table 5.4 shows the fatty acid composition of the various alternative fats in comparison with cocoa butter. It can be seen that the cocoa butter equivalents (CBEs) are similar to cocoa butter. The lauric CBS has a totally different composition, with fatty-acid carbon numbers 8–14 predominating, fatty acids that are totally absent from cocoa butter. The non-lauric CBR is composed of the same fatty acids as in cocoa butter but, in the case of the hydrogenated version, it also contains large amounts of trans-unsaturated acids.

Table 5.4 Typical fatty acid compositions (percentage as methyl ester) of the various types of CBA in comparison to cocoa butter.

		CBE		Non-lauric CBR		Lauric CBS	
Fatty acid	Cocoa butter	Low-PMF	High-PMF	Hydrog.	Non-hydrog.[a]	Palm kernel stearin	Hydrog. palm kernel stearin
C8:0	0	0	0	0		2	2
C10:0	0	0	0	0		2	2
C12:0	<0.1	<0.1	<0.1	0		54	54
C14:0	0.1	0.3	0.4	<0.1		22	22
C16:0	26	34	44	23	65[b]	9	9
C18:0	34	29	20	12		2	11
C18:1-*cis*	35	34	33	16	29	7	<0.1
C18:1-*trans*	0	<0.1	<0.1	46	<1	0	0
C18:2	3	2.0	2.4	1	7	1	0
C20:0	1	0.5	0.2	1		<0.1	<0.1

Notes: [a]From (Slager *et al*. 2007).
[b]Quoted as 65% saturates in (Slager *et al*., 2007) but will be predominantly C16:0 and C18:0
PMF, palm mid-fraction.

Cocoa butter contains about two-thirds saturated acids and, by comparison with other fats of similar fatty-acid composition (e.g. tallow and palm stearin), would be expected to have a melting point much higher than 35°C. As we have seen, the reason for its low and sharp melting point is the location of the saturated acids at the 1 and 3 positions of the triglyceride molecule and the unsaturated acids at the 2 position.

Lauric-type alternative fats contain 85–100% saturated fatty acids. Only because the carbon numbers of the main acids are 12 and 14 is the melting point reduced to the organoleptically satisfactory level of 35–40°C.

Hydrogenated non-lauric CBRs contain about two-thirds unsaturated acids. Only by changing the conformation of the double bonds from *cis* to *trans* is it possible to raise the melting point to the required level. Elaidic acid (*trans*-oleic acid) and trielaidin (EEE) have melting points of 45°C and 41°C, approximately the same as the melting points of lauric acid and trilaurin (LLL) (44°C and 46°C, respectively), indicating the similarity that might be expected between the two types of alternative fat.

The newer non-hydrogenated non-lauric CBRs have a fatty acid composition that is very similar to that of cocoa butter, the main difference being in the positional distribution of those fatty acids on the triglyceride molecules.

The isosolid phase diagrams[4] of the three main types of alternative fat are shown in Figures 5.10 (a)–(c) (Gordon *et al*., 1979). The example used in Figure 5.10 (b) is of a hydrogenated non-lauric CBR. Although no equivalent diagram for a zero-*trans*

[4]An isosolid phase diagram is a combination of an isosolid diagram and a conventional phase diagram. The isosolid diagram shows lines of the same SFC, which gives information about melting properties. The phase diagram gives the position of phase boundaries. In particular, we need to know the phase boundaries between different solid phases. These boundaries, separating phases usually of different polymorphs, are superimposed on the isosolid diagram as thick black lines.

non-lauric CBR has been published, it would be expected, for the purposes of defining compatibility between cocoa butter and the CBR to be fairly similar.

For complete compatibility the diagram should be as in Figure 5.10 (a), with a single phase in the single polymorph, as in tempered cocoa butter, and more or less horizontal isosolid lines.

Figure 5.10 (c) shows substantial incompatibility between cocoa butter and the lauric-type CBS, with only small areas on the left-hand and right-hand sides of the diagram where a single solid phase exists. The area on the left-hand side indicates how much lauric CBS can mix with cocoa butter while keeping a single phase with the same properties as cocoa butter. Typically this is a maximum of 5%. The area on the right-hand side indicates how much cocoa butter can mix with lauric CBS while keeping a single phase with the same properties as the lauric CBS. Again, this is about 5%, meaning that the amount of cocoa butter-containing cocoa component that can be used in conjunction with a lauric CBS is extremely limited (see Section 5.4.2.1).

Wang *et al*. (2010) studied the effect of fat composition, particularly the amounts of cocoa butter and milk fat on melting, hardness and bloom formation of compound chocolates based on partially hydrogenated palm kernel olein and fully hydrogenated palm kernel stearin. The addition of cocoa butter or milk fat to hydrogenated palm kernel olein had a small softening effect but nothing compared to the addition of these fats to hydrogenated palm kernel stearin where the addition of 10–15% cocoa butter halved the solid fat content at 25°C. These effects also carried through to the hardness of coatings made from these fats.

Figure 5.10 (b) is similar to Figure 5.10 (c), but the area of single phase on the right-hand side is now significantly larger, indicating that more cocoa butter can dissolve in the non-lauric CBR, enabling up to about 20% cocoa butter to be present in the fat phase without causing significant problems of softening or bloom formation. This allows a much greater amount of fat-containing cocoa component to be used in a non-lauric CBR coating (see Section 5.4.2.2).

The reasons for these variations in compatibility can be understood from the information in Table 5.5. Particularly important in this respect is the chain packing. This is whether the triglycerides pack in a double-chain or a triple-chain configuration. In Figure 5.8 (a), POP is shown packing in a triple-chain configuration, that is, the crystal cell structure is three fatty acid chains long from top to bottom. In Figure 5.8 (b), however, the same molecule is shown in a double-chain configuration with the crystal

Table 5.5 Compatibility of cocoa butter with the different types of CBA.

Fat/CBA type	Chain length[a]	Stable polymorph	Compatibility[b] (%)
Cocoa butter	16 and 18	β-3	Not applicable
Cocoa butter equivalent	16 and 18	β-3	~100
Hydrogenated non-lauric CBR	16 and 18	β′-2	~20
Non-hydrogenated non-lauric CBR	16 and 18	β′-2	~20
Lauric CBS	12 and 14	β′-2	~5

Notes: [a]Of main fatty acids (carbon number).
[b]Maximum percentage of cocoa butter that can be included in the fat phase.

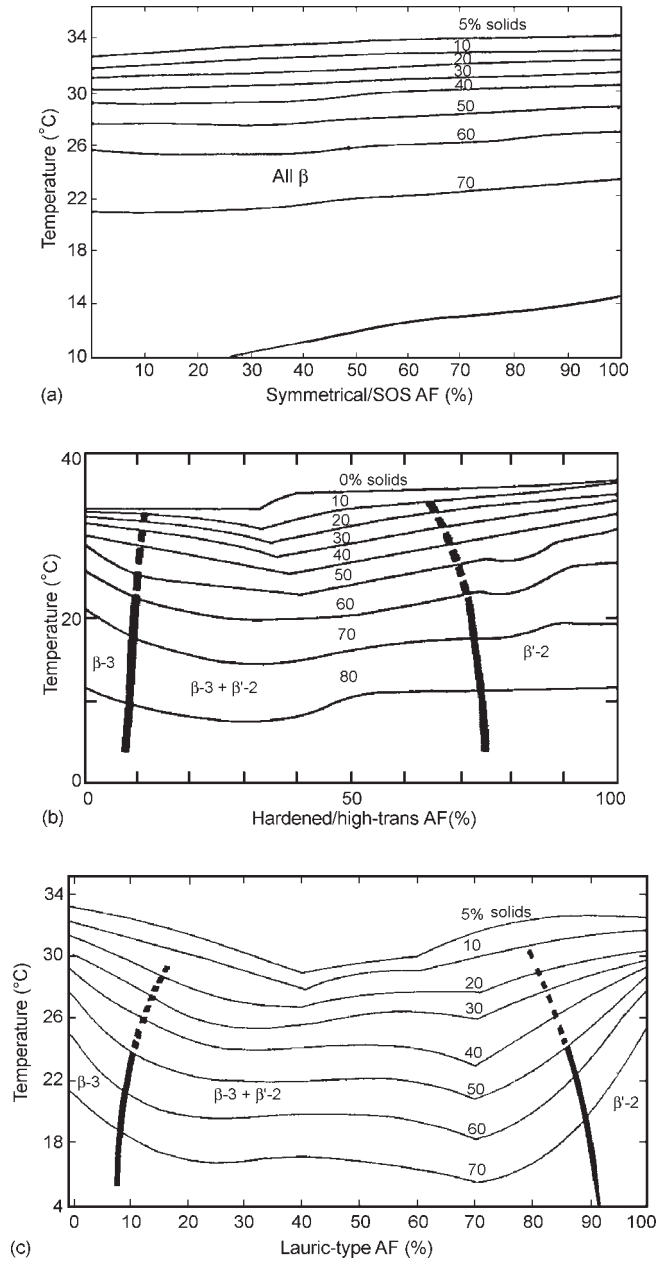

Figure 5.10 Isosolid phase diagrams of mixtures of cocoa butter with the three types of alternative fat (AF) (a) symmetrical/SOS AF compared with cocoa butter; (b) hardened/high-trans AF compared with cocoa butter; (c) lauric-type AF compared with cocoa butter. *Source:* Gordon *et al*., 1979. Reproduced with permission of John Wiley & Sons.

cell structure being only two fatty acid chains long from top to bottom. It can also be seen from Figure 5.8 that triglyceride molecules have a chair-like structure. The number in the column headed 'Stable polymorph' in Table 5.5 indicates the chain length packing in the stable configuration.

Both cocoa butter and symmetrical SOS-rich CBEs have the same stable polymorphic structure. They are both rich in oleic acid in the 2-position which means that they can pack together in a stable configuration similar to that shown in Figure 5.8 (a). Lauric CBS fats, on the other hand, contain much higher levels of saturated fatty acids. These saturated fatty acids have a straight chain structure, unlike the bent oleic acid chains found in cocoa butter and CBEs. This makes it more difficult for these to 'fit' together easily with the usual cocoa butter structure and so it is only when either cocoa butter or a lauric CBS fat greatly predominate that there is any stability. This only occurs when one or other of the fats is present at more than 95%. The non-lauric CBR fats, however, have some fatty acids in common with cocoa butter (this applies, especially, to the newer non-hydrogenated non-lauric CBRs) which allows some of the triglycerides to pack reasonably well with the triglycerides of cocoa butter. This results in some compatibility between the two fats, enabling up to 20% of cocoa butter to be mixed with a non-lauric CBR as shown in the right-hand side of Figure 5.10 (b). The implications of these different levels of compatibility will be shown in Section 5.4, on applications.

5.3 Legislation and regulatory aspects

5.3.1 Legislation

Most countries have felt it necessary to define the composition of chocolate in a prescriptive detail that is not required for most other foods. The reasons for this are many and complex. Like similar legislation for dairy products, although originally designed to protect the consumer, the legislation eventually has tended to protect the producer and inhibit product development. In order to compete more effectively in the marketplace, the dairy industry in most countries has long given up such prescriptive legislation so that milk, butter and yoghurt can have widely varying compositions reflecting consumer preference and desires. In contrast, the chocolate industry has been slow to adapt to the modern philosophy that a government's only job should be to ensure that food is safe and that the consumer should get all the necessary compositional and nutritional information to make an informed choice.

The focus of debate about chocolate legislation has been in the European Union (EU), where the different food legislations of the various member countries have had to be harmonised to bring chocolate into line with the EU Food Labelling Directive and the requirement for free trade between the member states. Contentious issues have concerned the minimum amounts of milk and cocoa components and the use of other vegetable fats besides cocoa butter. For example, northern European countries (the United Kingdom, Ireland and the Scandinavian countries) with traditionally large dairy industries and high milk consumption have tended to prefer milk chocolate with a high

milk content (and therefore necessarily lower cocoa content) than have consumers in countries further south such as France and Italy. Additionally, these northern European countries consume much more chocolate and cocoa products in total.

The history and background to the EU Chocolate Directive (European Parliament and Council, 2000) have been lucidly explained by Eagle (1999). The Directive was adopted by all member states by 3 August 2003 and the details are summarised in Table 5.6. At the time the Directive was adopted there were 15 members of the EU and the biggest change for eight of these members was the opportunity to produce chocolate containing up to 5% of a vegetable fat of the CBE type as well as cocoa butter. Nevertheless, there was also a change for the seven countries that already permitted this option. Only six component vegetable fats (the six given in Table 5.3)

Table 5.6 Summary of composition of chocolate permitted in the European Union as detailed in the Chocolate Directive 2000/36/EC (European Parliament and Council, 2000).

Definition	Requirements[a]
Chocolate	
The product obtained from cocoa products and sugars	Total dry cocoa solids ≥35%
Variations are allowed for vermicelli, flakes, Gianduja or couverture (see below) chocolate	Cocoa butter ≥18% Dry nonfat cocoa solids ≥14%
Chocolate couverture	
Designates the product obtained from cocoa products and sugar	Total dry cocoa solids ≥35% Cocoa butter ≥31% Dry nonfat cocoa solids ≥2.5%
Milk chocolate[b]	
The product obtained from cocoa products, sugars and milk or milk products	Total dry cocoa solids ≥25%
Variations are allowed for vermicelli, flakes, Gianduja or couverture (see below) chocolate	Dry milk solids ≥14% Dry nonfat cocoa solids ≥2.5% Total fat ≥25% Milk fat ≥3.5%
Milk chocolate couverture	
The product obtained from cocoa products, sugars and milk or milk products	Total dry cocoa solids ≥25% Dry milk solids ≥14% Dry nonfat cocoa solids ≥2.5% Total fat ≥31% Milk fat ≥3.5%
Family milk chocolate[b]	
The product obtained from cocoa products, sugar and milk or milk products	Total dry cocoa solids ≥20% Dry milk solids ≥20% Dry nonfat cocoa solids ≥2.5% Total fat ≥25% Milk fat ≥5%
White chocolate	
The product obtained from cocoa butter, milk or milk products and sugar	Cocoa butter ≥20% Dry milk solids ≥14% Milk fat ≥3.5%

Notes: [a]In all products, vegetable fat other than cocoa butter may be used up to a maximum of 5% of the finished product, after deduction of the total weight of any other edible matter used, without reducing the minimum content of cocoa butter or total dry cocoa solids. The vegetable fats allowed are given in Table 5.3.
[b]In the United Kingdom and Ireland, the name 'milk chocolate' may also be used for 'family milk chocolate'.
Source: European Parliament and Council, 2000.

are allowed for use in CBEs. Lauric fats and enzymically processed fats which had previously been used in some chocolates were no longer permitted. Coconut oil may be used only for the manufacture of chocolate for ice cream. This automatically excludes some of the most innovative and functional ingredients developed by the European chocolate fat industry. For example, a process had been developed to produce SOS-rich fats by enzymically combining oils that were rich in oleic acid in the 2 position with palmitic and stearic acids (Bloomer *et al*., 1990; Chang *et al*., 1990; Macrae, 1985; Undurraga *et al*., 2001). This was to ensure a more consistent supply of StOSt and POSt rich fats than could be guaranteed from the traditional sources of shea and illipe. Nevertheless, the fact that CBEs produced in this way cannot be used in EU chocolate has not stopped researchers from developing enzymically produced fats for use as CBEs outside the EU from a variety of base oils. For example, Çiftçi *et al*. (2010) have found that olive pomace oil can be used as a base for CBEs. Olive pomace oil is a low quality oil extracted from olives after all the better-quality oil has been removed. Another development that the EU Directive effectively outlawed was the use of some newly developed anti-bloom fats which contained a proportion of lauric acid.

It should also be noted that the 5% vegetable fat is in addition to the minimum values given for cocoa butter and total dry cocoa solids in Table 5.6. Also the 5% is calculated as 5% of the finished product, after deduction of the total weight of any other edible matter used. In other words, the 5%, like all the other percentage amounts given, refers to the chocolate itself, excluding any fillings, nuts, and so on that may be added.

The situation in the USA is somewhat different. Chocolate is defined under the US Standards of Identity (Federal Register, Title 21, Chapter 163), which covers all chocolate products, including a new standard for 'white chocolate' that was introduced in April 2004. Apart from prescribing minimum levels of milk and cocoa components, the US legislation also does not permit the use of vegetable fats other than cocoa butter. There is, however, a category of product 'milk chocolate and vegetable fat coating' that does allow the use of vegetable fat without any restrictions, though there must be at least 10% total dry cocoa solids and be at least 12% total dry milk solids (Yates, 2009). The majority of companies in the (US) Chocolate Manufacturers Association apparently favour keeping the standards as they are (Seguine, 2000, personal communication) although there has been some lobbying in recent years to include the use of vegetable fat in chocolate.

Other countries have tended to follow the legislation of US or European countries. Thus Canadian legislation is similar to that of the USA and also does not permit the use of vegetable fats other than cocoa butter.

As in Europe the legislation in Australia and New Zealand has been in the process of change. Food standard codes in the two countries have been harmonised and a number of amendments resulted from these changes. The main amendment concerning chocolate is Amendment 55 to Standard 1.1.2 (which lays down definitions for foods that do not have specific compositional requirements elsewhere in the Code). This required chocolate to contain a minimum of 20 wt% of cocoa bean derivatives and a maximum of 5 wt % of edible oils other than cocoa butter or dairy fats (ANZFA, 2001).

Table 5.7 Japanese chocolate compositions.

	Pure chocolate	Pure milk chocolate	Chocolate		Milk chocolate	Quasi-chocolate	Quasi-milk chocolate
Cocoa solids	Min 35%	Min 21%	Min 35%	Min 21%	Min 21%	Min 15%	Min 7%
Cocoa butter	Min 18%	Min 18%	Min 18%	Min 18%	Min 18%	Min 3%	Min 3%
Sucrose	Max 55%	Max 55%					
Milk solids		Min 14%			Min 14%		Min 12.5%
Milk fat		Min 3.5%		Min 3%	Min 3%		Min 2%
Combined milk and cocoa solids				Min 35%			
Other fats						Min 18%	Min 18%
Lecithin	Max 0.5%	Max 0.5%					

Note: Up to 3% water is also permitted in each of these compositions.
Source: http://en.wikipedia.org/wiki/Dark_chocolate (accessed on 3 November 2011).

The situation in Japan is different again. Japan has standards for ranges of chocolate (milk and plain) and for 'quasi-chocolate' (milk and plain) that are summarised in Table 5.7. The standards for 'quasi-chocolate' allow a much larger amount of vegetable fat, other than cocoa butter, than is permitted under European legislation. This relatively liberal legislation has undoubtedly accelerated the development of alternative fat technology in Japan, putting Japanese companies at the forefront of technical developments such as the use of enzymes to synthesise new triglycerides and the development of products such as BOB (l,3-dibehenoyl-*sn*-2-oleoyl-glycerol) fat, which obviates the need for tempering and ensures that chocolate is stable under high ambient temperatures (Hachiya *et al*., 1989a, 1989b).

The Codex Alimentarius Commission has also changed its definitions of chocolate in recent years. The original Codex standard for chocolate was STAN 87-1981. This was recently revised as Codex STAN 97-1981, Rev.1-2003. This revision brings it more into line with the EU legislation in now allowing the use of up to 5% vegetable fat in chocolate (without some of the associated restrictions that are in the EU Directive).

As the reader will have realised, there have been considerable changes in the legislation relating to chocolate in various countries over the past few years. Since legislation is never static, it may be considered that the information presented in this section is a snapshot in time and before developing a new chocolate composition, particularly, say, for a new export market, it is wise to check the current legislation in that market.

5.3.2 Adulteration and its detection

A frequent rationale for objecting to the use of vegetable fats other than cocoa butter in chocolate is that because CBEs are so similar to cocoa butter, they are difficult to detect, allowing the possibility of fraud. There is some justice in this claim, although, on the other side of the coin, the other argument brought against CBEs is that they lower the quality of the chocolate. If this were really so, of course, there would be no problem in detecting adulteration, either in the laboratory or in the marketplace.

In reality, because the triglycerides in cocoa butter and in CBEs are identical, differing only in their relative proportions, and because only 5% of alternative fat is

to be allowed in a total fat content of about 30%, we need to detect a relatively small change in fatty acid or triglyceride composition. There are some other differences between cocoa butter and the alternative fats and their components, principally sterols and their derivatives, but though these may allow qualitative results, they are not capable of quantification. The analytical approaches for identification and determination of CBEs in chocolate have been reviewed (Lipp and Anklam, 1998). A particularly useful method for the detection, but again not quantification, of a CBE in chocolate is to determine sterol degradation products (sterenes) (Crews *et al*., 1997). Sterenes are produced when an oil is bleached, a process that all CBEs but not cocoa butter undergo.

A definitive method for the determination of CBEs in chocolate, including milk chocolate, has been developed (Padley and Timms, 1978, 1980). By using gas chromatography (GC), one can analyse the intact triglycerides on the basis of their carbon number. The method depends on the fact, alluded to above, that no natural fat contains as much POSt (carbon number 52) as cocoa butter and, further, that a plot of carbon number 50 (POP) against carbon number 54 (StOSt) shows all pure cocoa butters to be distributed along a straight line. As a result, precise quantitative predictions about the amount of alternative fat present can be made, including statistical estimates of errors. The method is robust, accurate and rapid. Although there have been some further developments of the method (Fincke, 1982; Young, 1984), it remains essentially the same as when it was first developed.

Both leading up to and since the introduction of the EU Chocolate Directive there was and has been considerable activity in defining better methods to detect the presence of CBEs in cocoa butter. Barcarolo and Anklam (2001) further refined the above-mentioned method of Padley and Timms by plotting the values for C54/C50 and (C54/C50)*C52. With the advent of modern capillary GC columns capable of resolving the individual triglycerides POP, POSt and StOSt, rather than just the triglycerides grouped by carbon number, there has been scope for further improvement in the method (Simoneau *et al*., 1999; 2000; Dionisi *et al*., 2004). Fourier transform infrared (FTIR) spectroscopy and chemometrics have also been used to detect the presence of CBEs as both these fats and cocoa butter have highly reproducible FTIR fingerprints (Goodacre and Anklam, 2001).

However, the validated method accepted by the European Commission Joint Research Centre has been developed by Buchgraber and Androni (2007) which uses high resolution GC to separate out five main triglycerides, POP, POSt, POO, StOSt and SOO to define (by linear regression and partial least squares regression) the levels of milk fat and CBE in a chocolate. This method has now been published as ISO Standard 23275, Parts 1 and 2.

Of the other alternative fats, the hydrogenated non-lauric CBRs and lauric CBSs are easy to detect simply on the basis of their fatty-acid compositions. Since cocoa butter contains neither *trans*-acids nor lauric acid and the non-lauric CBRs and lauric CBSs typically contain at least 45% of either acid, even 1% of either of these fats in cocoa butter would lead to an increase of 0.45% in lauric or *trans*-(elaidic) acid. Such an

amount is easily detectable; in fact, even 0.1% of lauric acid is detectable with ordinary laboratory GC equipment, so that very low levels of lauric fats can be detected. The newer non-hydrogenated non-lauric CBRs contain similar fatty acids to those in cocoa butter but can easily be detected because (a) the ratio of fatty acids is significantly different, and (b) the distribution of these fatty acids on the triglyceride molecule is also different, notably in the ratio of symmetrical SOS to asymmetrical SSO.

5.4 Moulded bar and coating applications

5.4.1 Chocolate

Chocolate is a suspension of cocoa solids and sugar in a continuous fat phase. Where the fat phase consists only of cocoa butter or of cocoa butter and up to 5% CBE, where legislation permits, the resulting product may be labelled 'chocolate'. Where the fat phase contains other alternative fats, the product is designated as a 'compound coating'. Milk chocolate, or milk compound, contains a milk component such as milk powder. So-called 'white' chocolate is basically milk chocolate without any non-fat cocoa solids (i.e. no cocoa liquor or powder is used, only cocoa butter or other vegetable fat).

It is the fat phase that gives chocolate its desirable texture and mouth feel. With milk chocolate, milk fat is added to the basic ingredients and, where legislation allows, an alternative fat (CBE) can be added to improve functionality or reduce cost. As discussed in Section 5.3.1, the allowed ingredients and composition of chocolate vary between countries, and the reader is advised to study the appropriate legislation.

Milk is never added in liquid form, but only as a dry ingredient as described in Section 5.2.1. Milk crumb is produced by mixing condensed milk with sugar and cocoa mass before cooking, drying and milling. It imparts a characteristic 'caramel' flavour to the chocolate and is widely used in the United Kingdom, Australia and the USA. Typical recipes for plain and milk chocolates are given in Table 5.8.

Chocolate production involves mixing cocoa liquor together with some fat. This mixture or paste is then ground between rollers to a particle size of typically 20–30 μm (microns) (Beckett, 2009). This process is known as refining. If the particle size is much lower than this, the chocolate will have a greasy mouth feel; if much higher, it will taste gritty.

Extra fat is then added and the mixture is heated with continuous mixing for a long period (several hours to several days). This process is known as conching and improves the flavour of the product along with its texture and viscosity. Both batch and continuous conches are available.

Because of the polymorphic nature of cocoa butter it must be tempered in order to promote crystallisation in form β_V. The process of tempering involves initially cooling chocolate to promote crystallisation in both unstable β' and stable β_V forms. The chocolate is then warmed to a temperature between the melting points of the two forms to melt the unstable crystals. This used to be a batch process, but is now usually carried out in continuous tempering equipment.

Table 5.8 Chocolate recipes including the use of CBEs.

	Chocolate type		
Ingredient	Basic plain	Basic milk with full cream milk powder	Basic milk with milk crumb
Cocoa mass	40.0	20.0	
Cocoa butter	7.0	12.0	15.0
CBE (vegetable fat)	5.0	5.0	5.0
Full cream milk powder		20.0	
Milk crumb			63.0
Sugar	47.5	42.5	16.5
Lecithin	0.5	0.5	0.5
Total	**100.0**	**100.0**	**100.0**
Fat as percentage of chocolate:			
Cocoa butter	28.2	23.0	19.6
CBE	5.0	5.0	5.0
Milk fat		5.0	5.8
Total fat	**33.2**	**33.0**	**30.4**
Fat as percentage of fat phase:			
Cocoa butter	85.0	70.0	64.5
CBE	15.0	15.0	16.5
Milk fat		15.0	19.1
Total	**100.0**	**100.0**	**100.0**

Note: Percentages are relative to weight (wt%).

5.4.2 Compound chocolate

In some cases the use of real chocolate in confectionery products is not desirable, because of either cost or functionality (e.g. real chocolate is inconveniently brittle for use in ice cream and cakes). Compound chocolates are then often used instead. These can be formulated with either lauric or non-lauric alternative fats and are most frequently used as coatings to enrobe biscuits, cakes, centres or other fillings for snack bars, hence their alternative, commonly-used name of compound coatings.

5.4.2.1 Supercoatings (supercompounds)

It is possible to replace all the added cocoa butter in a chocolate recipe with a CBE. Such a product is commonly known as a supercoating (Talbot, 2009a). The supercoating will require processing in the same manner as chocolate and will be suitable to replace it in most applications. Because, in most countries, the composition falls outside that defined for chocolate, it is not possible to label the product as such. One advantage of supercoatings is to reduce cost, although this will depend on the prevailing price of cocoa butter. Further advantages include increasing or decreasing hardness and viscosity for particular applications. Some supercoating recipes are given in Table 5.9.

5.4.2.2 Compound chocolate with lauric-type alternative fats

Palm kernel stearins have a very steep melting curve not unlike that of cocoa butter and thus have good snap, gloss and eating characteristics. A major disadvantage of

Table 5.9 Supercoating recipes using symmetrical SOS-based CBE fats.

Ingredient	High-milk	Low-milk	Plain
Cocoa mass	10.0	10.0	40.0
CBE	22.0	24.0	12.0
Sugar	45.5	45.5	47.5
Full cream milk powder	22.0	10.0	
Skimmed milk powder		10.0	
Lecithin	0.5	0.5	0.5
Total	**100.0**	**100.0**	**100.0**
Fat as percentage of chocolate:			
Cocoa butter	5.3	5.3	21.2
CBE	22.0	24.0	12.0
Milk fat	5.9	2.7	
Total fat	**33.2**	**32.0**	**33.2**
Fat as percentage of fat phase:			
Cocoa butter	16.0	16.6	63.9
CBE	66.3	75.0	36.1
Milk fat	17.7	8.4	
Total	**100.0**	**100.0**	**100.0**

Note: Percentages are relative to weight (wt%).

lauric fats is that they form strong eutectics with cocoa butter (Figure 5.10 (c)). This means that, in the manufacture of compound chocolate, low-fat (10–12% fat) cocoa powders must be used, making it difficult to achieve a strong cocoa flavour. Even so, if more than about 5% cocoa butter is present in the fat phase, excessive softening and bloom may occur. The use of low-temperature solvent extraction with propane to produce a very low-fat powder with excellent flavour has been described. The resulting powder produced no eutectic softening and a chocolate judged to have a flavour as good as a premium quality plain real chocolate (Trout, 2000).

Typical recipes are shown in Table 5.10. The method of production is similar to that of real chocolate, involving mixing, followed by refining and conching, although the conching time is less. However, the non-tempering nature of these fats means that

Table 5.10 Compound coating recipes using lauric CBS fats.

		Milk		
Ingredient	Dark	1	2	White
Low-fat (10–12%) cocoa powder	14	5	7	
Full cream milk powder		10		
Skimmed milk powder	6	8	19	20
Lauric CBS	32	32	29	32
Sugar	48	45	45	48
Total	**100**	**100**	**100**	**100**
Lecithin	0.2–0.4	0.2–0.4	0.2–0.4	0.2–0.4
Total fat content	33.5	35.2	29.9	32.2
Cocoa butter as percentage of total fat	4.2	1.4	2.3	0
Total cocoa solids	14	5	7	0

Note: Percentages are relative to weight (wt%).

processing is easier and the chocolate can be used instantly for enrobing or moulding. Unlike tempered chocolate, when lauric CBS coatings are used, there are no fat crystals present so the coating has a lower viscosity which can be advantageous in many ways.

Apart from their limited compatibility with cocoa butter, lauric CBRs do also suffer from one other drawback – if they come into contact with water, an active lipase, hydrolysis can occur (see Section 5.6.4). This releases free fatty acids and, as the fats are rich in lauric acid, this is the main one to be produced. Lauric acid is detectable as a soapy off-flavour at levels as low as 0.07%. It is important therefore to keep lauric coatings as dry as possible. The main areas where moisture could come into contact with the coating are (a) at the exit of a cooling tunnel if the temperature at that point is below the dew point allowing condensation to form on the surface or (b) if the coating is handled with damp or sweaty hands. Both of these should be avoided. For the same reason, care must be taken in the selection of milk and cocoa ingredients and to reduce the moisture content of the coating.

5.4.2.3 Compound chocolate with non-lauric CBRs

Hydrogenated, high-trans non-lauric CBRs are often used in place of lauric fats because they are more compatible with cocoa butter. Consequently, cocoa liquor may be used instead of cocoa powder, and this means that products can have a more rounded chocolate flavour. Additionally, because of their compatibility with cocoa butter, the same production line can be used for both real chocolate and for the compound chocolate with only minimal cleaning between runs, without bloom occurring in either the real or the compound chocolate products. Typical recipes are shown in Table 5.11. The method of production is as described for lauric-type compound chocolate.

Table 5.11 Compound chocolate recipes using hydrogenated non-lauric CBRs[a].

	Dark		Milk		White	
Ingredient	1	2	1	2	1	2
Cocoa mass	10.0		10.0			
Low-fat (10–12%) cocoa powder	15.0	20.0		5.0		
Hydrogenated non-lauric CBR	28.0	33.0	28.0	34.0	30.0	35.0
Sugar	46.6	46.6	43.6	43.6	44.6	44.6
Full cream milk powder			6.0		20.0	
Skimmed milk powder			12.0	17.0	5.0	20.0
Lecithin	0.4	0.4	0.4	0.4	0.4	0.4
Total	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**
Total fat content	35.0	35.0	35.2	34.7	35.4	35.2
Cocoa butter as percentage of total fat	20.0	5.7	15.6	1.4	0.0	0.0
Total cocoa solids	25.0	20.0	10.0	5.0	0.0	0.0

Notes: [a]These recipes are also suitable for use with the newer generation of non-hydrogenated non-lauric CBR fats.

Percentages are relative to weight (wt %).

Source: Adapted from Talbot, 2009a. Reproduced with permission of John Wiley & Sons.

5.5 Filling applications

Confectionery fillings vary widely in their nature. Some, such as fondants and liqueurs, are almost free of fat; some, such as caramels and toffees, rely on the presence of some fat for texture and structure; others, such as truffles and pralines, are totally dependent upon the fat phase for hardness, structure, meltdown and many other sensory attributes. Because this is a book about fats, only those filling applications which use fat will be considered here.

One of the distinctions between fat-based fillings and fat-based coatings (such as chocolate) is the lack of any legislative controls on the composition of a filling. As long as it conforms to other food legislation on, for example, hygiene, labelling, use of additives, etc., it is an acceptable part of the product.

5.5.1 Fat-based fillings

Fat-based filling creams arc widely used in confectionery products and biscuits. Applications vary widely from fillings for chocolates such as pralines to the cream fillings used in sandwich-type biscuits. Compositions and the fats used vary correspondingly. Just as it was possible to sub-divide coating fats into various categories, it is equally possible to sub-divide filling fats into the same general categories (though the filling fats will, usually, be softer than the corresponding coating fats).

So, just as there are polymorphic coating fats based on symmetrical SOS types of triglyceride, so there are filling fats also containing significant quantities of these triglycerides. The main differences are that, whereas the coating fats tend to be rich in POSt and StOSt, the filling fats are usually richer in POP and also often contain softer, more unsaturated triglycerides such as POO. They do, though, show some polymorphism and benefit from passing through a tempering process, albeit at lower tempering temperatures than would be used with the corresponding chocolate or CBE coating.

Similarly there are filling fats based on lauric oils such as coconut oil and palm kernel oil. Coconut oil has a long-standing use in these types of product because it imparts a cool-melting effect to the filling. This is because it melts very sharply just above normal ambient temperatures and, as a result, extracts considerable latent heat from the palate, giving a cooling sensation.

Filling fats based on non-lauric, non-polymorphic fats are also commonly used in confectionery fillings. As with coatings, these have been historically based on partially hydrogenated *trans*-containing fats but more recently, filling fats based on palm fractions have been developed (Duurland and Smith, 1995). Both the lauric filling fats and the non-lauric, non-polymorphic filling fats have the advantage over those containing higher levels of SOS triglycerides in that they do not need to be tempered (though the newer non-hydrogenated, non-lauric fillings do benefit from some form of pre-crystallisation before use).

Frequently, the lauric-type or non-lauric, non-polymorphic fats are used for economy and for ease of processing (because they do not require tempering).

Hydrogenated versions of these have the disadvantage of a high *trans* level. A second disadvantage, especially if the product is enrobed with real chocolate, is that, because they are incompatible with cocoa butter, migration from the centre can cause problems with softening and bloom. This problem is even more acute with centres based on lauric-type fats. The issue of fat migration will be discussed in more detail in Section 5.6.2.

The choice of fat to use in fillings is dependent on a number of factors:

- *Texture and mouth feel*. The melting profile of the fat phase of the filling effectively defines the texture of a filling, particularly in terms of its hardness when first bitten into, the way it melts in the mouth and whether or not there is any residual waxiness at the end of melt. In defining the melting profile, it is important to consider all of the fat-contributing ingredients in the filling. If only the added filling fat is considered, then a false impression can often be gained because fillings can often contain ingredients that contribute additional fats to the complete filling recipes. Examples of such ingredients are cocoa mass (which contributes cocoa butter), milk powders or, in shorter shelf-life fillings, butter or dairy cream (which contribute milk fat) and nut pastes (which contribute nut oils).
- *Flavour and flavour release*. The flavour components in a filling are often held within the fat phase and so the rate of flavour release is often dependent on the melting profile of the fat phase. While flavour components can be added to fillings (particularly fruit, coffee, alcohol or mint flavours), flavours are also often inherently present in the added fat-containing ingredients referred to above.
- *Processing*. The issue of tempering or not has already been mentioned but it is important to ensure that if, for example, tempering facilities are not available, that the filling fat system used should be one that is not polymorphic. If a filling that would benefit from tempering is used untempered, then grittiness rather than bloom formation is the main problem that ensues. The fat crystals grow and regrow to a size such that they can be detected on the palate. Other processes that need to be taken into consideration are what might be termed 'downstream' processes. Will the filling be aerated or extruded, for example? Some fat phases are more suitable than others for these processes.
- *Storage and stability*. The issues of bloom formation and fat migration will be discussed in later sections but it is important in defining the type of fat to be used in the filling to ensure that it is as compatible as possible with the fat used in the coating.
- *Labelling and nutrition*. There is increasing pressure on confectionery manufacturers to produce products that are as nutritionally acceptable as possible (while also bearing in mind that much confectionery is indulgent in its nature).

Some filling fats are more appropriate than others to particular types of application. The use of coconut oil as the basis of a cool-melting filling has already been mentioned but this is not the only type of fat to be used in this type of application. Any fat that melts very sharply from a fairly high level of solid fat at 20°C to almost zero at 30°C

will exhibit coolness when used in a filling. To enhance the amount of latent heat removed from the mouth during melting, fillings containing high levels (sometimes up to 50%) of these fats are often used. The coolness can be magnified by the use of other ingredients that have a similar effect, including, for example, dextrose or a mint flavour, both of which can enhance coolness.

Many fillings are deposited into empty chocolate shells. Since the shell has been tempered and cooled to solidify it prior to depositing the filling, it is important to ensure that the shell is not re-melted during deposition of the filling. This means that the fat phase of the filling should be fluid at, say, 30°C. If it is necessary to deposit at higher temperatures than this, there is a great risk of melting the chocolate shell and destroying the temper of the chocolate. The result will be a softer shell that is prone to bloom formation. A further requirement of the fat phase of shell-moulded fillings is that it should be quick to crystallise. This is because as soon as possible after depositing, a 'backing' layer of chocolate is applied to the filled shell to close the product, ensuring that the whole filling is enclosed in chocolate. This 'backing' layer will usually form the base of the end product. It is much easier to apply this layer and to remove any excess if the filling underneath has solidified.

Other fillings can be extruded and then enrobed with chocolate. Here it is less important for the filling to be fluid at 30°C and more important that it is able to withstand higher temperatures without, of course, being waxy. Extruded fillings are 'worked' in a kneader to plasticize them before they pass through an extruder where they are shaped and then cut into lengths for enrobing. There is a significant amount of 'work' in these processes that can melt the fat so the filling needs to be able to withstand this kind of processing without melting unduly. It also needs to withstand the temperature of the coating applied in the enrober without melting.

Fillings are also often aerated either before depositing into shells or before extruding. Here the crystallisation characteristics of the fat phase of the filling are important. If we were to plot the increase in solid fat content against time, the ideal crystallisation curve for an aerated filling would be 'S'-shaped. In other words, it would be initially relatively slow to crystallise in order to allow time for air or gas to be either whipped into the filling or positively injected into the filling. Then, however, it needs to crystallise quite quickly in order to 'hold' the aerated structure in place during subsequent processing.

The use of fillings in biscuits and wafers has already been referred to but here again there are specific requirements that are relevant to the nature of the fat in the cream. First, biscuits and wafers are themselves quite different in texture. Biscuits are hard and solid whereas wafers are much lighter. The nature of the cream fat ought to complement these differences in texture with wafer creams being lighter both in structure and melting characteristics than a corresponding biscuit cream. In both cases, though, the cream has a function that is not found in praline-type fillings – it has to act as a glue to hold the product together. In both biscuits and wafers, therefore, the fat must crystallise sufficiently quickly to hold the two biscuit shells or the wafer blades together without either squeezing out when under pressure of packing or when cutting the large wafer 'books' into fingers.

Table 5.12 Some typical centre filling cream recipes.

Ingredient	Hazelnut praline	Biscuit cream[a]	Cool-melting filling	Bake-stable filling
Dark chocolate	15.0		25.0	
Milk chocolate			25.0	
Low-fat cocoa powder				8.0
Hazelnut paste	15.0			
Full cream milk powder	10.0			
Skimmed milk powder		10.0		
Filling fat	20.0	40.0	49.6	23.0
Sugar	34.6	49.6		40.0
Chopped hazelnuts	5.0			
Maltodextrin				20.0
Cornflour				8.37
Mono-diglycerides				0.23
Lecithin	0.4	0.4	0.4	0.4
Total	**100.0**	**100.0**	**100.0**	**100.0**

Notes: [a]Some or all of the skimmed milk powder in the recipe can be replaced by low-fat cocoa powder to give a chocolate-flavoured biscuit cream.
Flavouring, colour, vanillin and salt are added as required.

Another area of use in the bakery and biscuit industry is of bake-stable fillings. These are fillings that can be injected into a raw biscuit dough or cake batter and then the whole product is baked. The main requirements here is that the filling should (a) stay in place in the product and not migrate during baking, and (b) retain a soft texture in the end product. Oil migration is therefore a big problem in this type of product and fats to structure the filling are commonly used.

Some recipes for a range of typical filling applications are shown in Table 5.12. Production consists of little more than stirring all the ingredients together with the liquid fat, followed by cooling to the depositing temperature, or possibly tempering where necessary.

Sometimes the eutectic interaction between cocoa butter and lauric-type alternative fats can be used to advantage. A mixture of about 65% cocoa butter and 35% lauric-type alternative fat was found to give a filling with very good mouth feel and 'melt-away' characteristics. When the filling was enrobed with real chocolate, bloom occurred within one month, but was still absent after three months when enrobed with a lauric-type CBS compound chocolate (Rahim *et al*., 1998).

5.5.2 Toffees and other sugar confectionery

The main use of fats in sugar confectionery is in toffees, caramel, fudge and nougat. Toffee is an emulsion of fat in a complex aqueous system (Stansell, 1995). There is no definite distinction between caramel and toffee, and the two names may be regarded as synonymous. The main constituents of these products are fat and sugar, and the basic process consists of boiling the ingredients together to dispel water. By heating the ingredients, characteristic flavours develop as a result of the reaction between reducing sugars and milk proteins. This is known as the Maillard reaction.

Traditionally, the fat ingredient used is either AMF or butter. However, butter is preferred because of the contribution made by the non-fat solid components (i.e. milk proteins) to unique flavour development through the Maillard reaction. AMF and butter are frequently replaced by vegetable fat, although there is some loss of flavour because of the absence of milk proteins and the natural milk/butter flavours derived from fatty acids and flavour precursors. The hardness of toffee or caramel is purely dependent on the water content, which depends on the final boiling temperature. In relative terms, the type of vegetable fat is not particularly important. It should, however, be solid at room temperature and be relatively sharp melting as it must be fully liquid at body temperature to avoid an unpleasant mouth feel (Stansell, 1995). Because the system is a mixture of lipid and aqueous phases, an emulsifier is generally used to combine the two phases. Monoglycerides and diglycerides are often used for this. However, some fats contain measurable natural levels of these components and, in some circumstances, can be used as toffee fats with lower levels of added emulsifier than would normally be used.

Hardened palm kernel oil was used for many years but is now often replaced by other fats, with combinations of palm fractions or even palm oil itself being used as a toffee fat. Crystallisation rates can be important especially in the production of caramel fingers in which the boiled caramel is sheeted before passing through a cooling tunnel. On exiting the tunnel the caramel is cut into lengths by a series of rotating blades. These lengths of caramel travel along channels before they are then cross-cut into fingers. If crystallisation is slow, then the long lengths of caramel can flex and become entangled with each other. Further information on toffees, caramel, fudge and nougat may be found in the comprehensive book by Jackson (1995) and in other chapters by Talbot (2006) and Edwards (2009). Some recipes are given in Table 5.13.

5.5.3 Truffles

There are three main types of truffle – American, European and Swiss (Minifie 1989). The American truffle is usually a mixture of dark and milk chocolate, together with milk fat and hardened coconut oil. It has a good shelf-life because it contains virtually no moisture.

Table 5.13 Typical toffee and caramel recipes.

Ingredient	European	Tropical
Granulated sugar	23.5	15.0
Glucose syrup	35.0	43.5
Skimmed sweetened condensed milk	29.5	29.5
Fat	12.0	12.0
Total	**100.0**	**100.0**
Added salt	2.0	2.0

Note: flavouring and water are added as required; percentages are relative to weight (wt %).
Source: Kempas Edible Oil, Johor, Malaysia.

The European truffle contains syrup combined with cocoa powder, milk powder, fat, sugar, glucose syrup and invert sugar. The final truffle is an oil-in-water emulsion adjusted to give a water activity of 0.7 or greater and a syrup phase concentration of greater than 75%. Provided the truffle is manufactured correctly, the shelf-life can be good.

The Swiss truffle is made from dairy cream, dark chocolate and butter. It is made by adding melted chocolate to the boiling mixture of cream and butter. The approximate proportions are 60% chocolate, 10% butter and 30% cream. These truffles have desirable eating qualities but have a shelf-life of only a few days. They tend therefore to be used only by specialist confectioners selling fresh products. The shelf-life of Swiss truffles can be improved by adding alcohol, usually in the form of a liqueur, and by using sweetened condensed milk instead of cream.

In all truffle types, the chocolate can, and often does, contain a CBE type of fat up to the total replacement of all the cocoa butter (see Section 5.4.1 and Table 5.9, relating to supercoatings). It can also be replaced with a mixture of vegetable fat and cocoa liquor or powder. If a CBE is used instead of cocoa butter, the texture and eating characteristics of the product are the same. In fact, by using harder or softer vegetable fats, the consistency of the truffle can be tailored to suit specific applications, thus improving the eating characteristics.

5.6 Problem areas

5.6.1 Bloom

Fat bloom is a common occurrence in the confectionery and biscuit industries. It is caused by a change in crystal morphology after the product is made and is manifested by the appearance of either a white 'frosting' on the surface of the product or a loss of gloss. There are two main causes of bloom: (a) polymorphic change in the fat, from form β_V to form β_{VI}; and (b) migration of fat from fillings or centres to their chocolate coatings. Both types of bloom are frequently seen and, if not controlled, can be a major source of losses and rejection. Bloom problems generally occur because of incorrect processing, use of incompatible fats or poor storage conditions. The rate of formation of both types of bloom is temperature dependent. A chocolate stored at 15°C is unlikely to show bloom within its normal shelf-life. If it is stored at 20°C then it may start to show bloom after a few months, particularly if it is a dark (plain) chocolate. At temperatures above 20°C, however, it is quite likely to bloom within time periods ranging from a few days or weeks (if the storage temperature is 25–30°C) to weeks or months (if the storage temperature is 20–25°C). If the chocolate is stored at an excessively high temperature at which the chocolate melts and is then cooled to, say, about 20–25°C, bloom will form very quickly but this is a different kind of bloom and results from detempering the chocolate and crystallising the cocoa butter initially in a β' form. This then quickly transforms into β_V and results in bloom.

The second type of bloom resulting from fat migration (or, more strictly speaking, oil migration) is also temperature dependent mainly because oil migration itself is

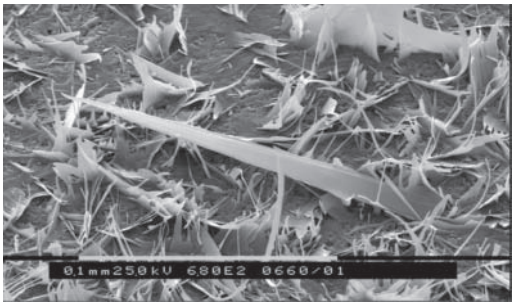

Figure 5.11 Scanning electron micrograph of fat bloom on cocoa butter based chocolate. *Source:* Leatherhead Food International. Reproduced with permission of Leatherhead Food International, Leatherhead, UK.

temperature dependent. In both mechanisms there is an increase in the amount of liquid oil in the chocolate either because the chocolate is melting as the temperature increases or because liquid oil is migrating into the chocolate. This allows the mobility of the triglycerides to increase and also increases the likelihood of cocoa butter dissolving in the liquid oil phase. This is then able to migrate to the surface of the chocolate where it can recrystallise as bloom. Typical bloom resulting from a form β_V to form β_{VI} transition gives long needle-like crystals (Figure 5.11). In model systems in which hazelnut oil was added to cocoa butter, even an addition of 1% hazelnut oil was sufficient to increase the amount of β_{VI} crystals developed in storage compared to cocoa butter with no added oil (Talbot *et al*., 2007).

In a comprehensive series of papers, Ziegleder and co-workers investigated and explained the formation of bloom, especially the bloom in pralines caused by migration of the nut oil from the praline centre into the chocolate shell (Ziegleder and Mikle, 1995a, 1995b, 1995c; Ziegleder and Schwingshandl, 1998; Ziegleder *et al*., 1996a, 1996b). The development of fat bloom in pralines depends particularly on the type of chocolate and the product storage temperature. For milk chocolate, bloom is greatest between 18°C and 22°C; for plain chocolate it is greatest between 18°C and 26°C, with a maximum at 20°C. This maximum at 20°C may be considered surprising since the tendency of plain chocolate to bloom is known to increase over this temperature range. The difference results because migration is the mechanism of bloom formation in a praline. As the temperature rises, there is a balance between an increasing diffusion rate (positive for bloom) and a decreasing crystallisation rate (negative for bloom).

Milk fat has long been known to act as a bloom-retarding agent and small amounts (up to 3%) of milk fat are often added to dark chocolate for that purpose. Milk fat softens the chocolate and would therefore be thought to accelerate rather than inhibit bloom (considering the mechanisms proposed above). However, milk fat with its broad mix of fatty acids contains triglycerides with a mix of short, medium and long chains. Triglycerides of this type have the effect of disrupting the cocoa butter crystal structure and do seem to then have the effect of retarding fat bloom.

Sonwai and Rousseau (2010) have studied the effect of milk fat on bloom resulting from storage at high ambient or fluctuating ambient temperatures. They have shown

that two types of (re)crystallisation take place on storage. There is growth of some existing surface crystals that act as templates for larger bloom crystals and, at the same time amorphous 'cones' solidify and grow with age. When cycled between 26°C and 29°C at 12-hourly intervals for 4 weeks, 2.5% milk fat in chocolate appears to promote the former type of crystallisation while inhibiting the latter type. At a level of 5% of chocolate both types of crystallisation are reduced while, at 7.5%, the degree of inhibition is even greater although the chocolate is then becoming unacceptably soft because of the high level of milk fat.

Some years ago small amounts of hydrogenated high-erucic acid rapeseed oil were used in the same way. These too contained a mix of long (C18) and very long (C22) fatty acids. More recently, other bloom-inhibiting fats with a similar mix of fatty acids have also been developed (Talbot, 1995). These were originally intended for use at a level of 5% in chocolate but because of the basic oils used in their production they are no longer able to be used in that way in chocolate sold in the EU. They can, however, still be used as part of a filling recipe.

Another approach is to add the symmetrical, SOS-type triglyceride BOB, which crystallises directly into the β polymorph (Hachiya *et al*., 1989a, 1989b). Essentially, chocolate containing BOB does not require tempering, so even complete melting does not result in bloom. Chocolate containing BOB is illegal in the EU under the European legislation.

Fat bloom on coatings is not, however, restricted to cocoa butter rich coatings. It can also be found on lauric coatings, particularly if the cocoa butter content of the cocoa components is too high. The type of bloom then produced can be either rich in cocoa butter triglycerides or rich in lauric triglycerides depending on the storage temperature (Smith *et al*., 2004).

As well as these lipid-based solutions to polymorphic change and fat bloom reduction, essential oils such as limonene have been studied. For example, it has been shown (Ray *et al*., 2012) that adding limonene to chocolate enhances the production of lower polymorphic forms in the cocoa butter but then speeds up the transformation to higher forms such as β_{VI} with such forms being produced after only 2–3 weeks at 20°C.

Not all bloom seen on chocolate is fat bloom. Sugar bloom can arise as a result of water condensing on the surface of the chocolate or compound coating. Sugar in the surface layer dissolves in the moisture and then as the moisture evaporates, it recrystallises on the surface to give a layer of bloom. This is easily distinguished from fat bloom in that (a) it does not melt when the chocolate is warmed, and (b) it dissolves easily if a drop of water is placed on it.

5.6.2 Fat migration

Fat migration (or to be more accurate, oil migration) has already been mentioned in the context of fat bloom formation. Bloom formation is not, however, the only problem that occurs as a result of oil migration. Confectionery products are becoming ever more complex and phases of different fats and different hardnesses are often used adjacent to each other to enhance the sensory characteristics of the product. One problem that

can often arise from this is the movement of oils from one phase to another. At its simplest this could be the movement of a nut oil from a praline centre into a chocolate coating. In a slightly more complex form, a chocolate-coated sandwich biscuit consists of three fat-based phases – biscuit, cream, coating – and fats can interchange between each of these. Apart from bloom formation the effects of oil migration are to soften the harder phases into which oil migrates and harden the softer phases from which oil migrates, giving an overall loss in textural differences in the product.

There have been numerous studies into the phenomenon of oil migration. One of the more recent ones was by Lee *et al*. (2010) who used MRI to show migration between two phases of increasing complexity. At its simplest level, peanut oil and cocoa butter were stored together in a model system at 25°C. Over a 28-day period there is a gradual, but slow migration of peanut oil into cocoa butter but two distinct layers were maintained. After 145 days, however, the system was more of a continuous solid than two separate layers. At the next level of complexity, peanut butter was used in place of peanut oil. This behaved completely differently. First, there was a considerable amount of free peanut oil on the surface of the peanut butter after 9 days but this was re-absorbed after 28 days. Second, there was a greater liquid oil intensity at the interface between the peanut butter and the cocoa butter than in the main parts of either phase, suggesting that the material at the interface resembled neither peanut butter nor cocoa butter. At the final level of complexity, chocolate was used in place of cocoa butter. Although there was again pooling and re-absorption of peanut oil on the surface of the peanut butter, the effect at the interface was nothing like that with peanut oil and cocoa butter. It was, in fact, more like the simplest system with just the two oils but with the whole migration process being slower relative to the oils themselves. This study does show the importance of non-fat solids in the oil migration process – the more there are, the slower will be the rate of oil migration, not least because increasing the concentration of non-fat solids decreases the concentration of fat.

While it is very difficult to totally prevent oil migration, there are various strategies that can be used. Some of these relate to the compositions of the coating such as reducing particle size, for example. Some on the face of it are quite obvious: using a thicker chocolate coating, double enrobe with chocolate, increase the ratio of chocolate to filling are all strategies that have been suggested (Ziegler, 2009) and all will give a product with more chocolate to absorb the migrating oil.

In terms of what else can be done, Talbot (2006) proposed three other strategies. The first was to ensure that the fat used in the filling was as compatible as possible with the fat in the coating. It has been mentioned a number of times in this chapter that we can divide both coating and filling fats into three broad groups:

- polymorphic non-lauric fats (such as cocoa butter and CBEs)
- non-polymorphic, non-lauric fats (both hydrogenated and non-hydrogenated)
- lauric fats.

Fats from within the same broad group have the greatest compatibility with each other. At the other end of the scale, lauric fats are the least compatible with both groups of

non-lauric fat. So, if a chocolate coating is being used, then, for compatibility, it is best to use an SOS-rich type of filling fat; if a lauric coating is being used, then, for the same reasons, it is best to use a lauric filling fat. This strategy does not stop oil migration from occurring. All it does is ensure that any softening of the coating that occurs is due only to liquid oil from the filling diluting the harder fat in the coating and that no extra softening due to eutectic formation is taking place. Talbot (2008) showed that there is a demonstrable link between the degree of migration that takes place between a filling and coating, the compatibility of the two fats and the hardness of the chocolate coating as measured by texture analysis.

A second strategy that can be applied to the fat phase of the filling is to use a structuring fat. This is a high-melting triglyceride that, when it crystallises, forms a network that effectively traps the liquid oil in the filling, thus inhibiting movement. It is the type of fat that is used in unsaturated margarines and spreads to give structure to these liquid oil-rich products. It is also the type of fat that is used in chocolate spreads and peanut butters to prevent oil exudation in the jar. To work properly, the filling containing the structuring fat needs to be deposited into the chocolate shell in a fully molten form and then cooled. This allows the network to form. If the filling is sheared in any way during the crystallisation process, then the network breaks up and all that is left are small crystals of structuring fat that do not have the same protective function. Talbot and Slager (2011) evaluated a range of fats added to fillings in this way and found that one of the most effective (at low levels of addition) was the so-called H_2M type of triglyceride (which consists of two saturated fatty acids with chain lengths of 16 and/or 18 carbon atoms (H) and one saturated fatty acid with chain length of 12 and/or 14 carbon atoms (M)). However, at higher levels of addition, this can cause a waxiness. To overcome this, shea stearin can be used instead as a very functional structuring fat either alone or in combination with other fats in the form of a cocoa butter improver (see Section 5.2.2).

In some (limited) applications it is even possible to use a barrier fat between, for example, a filled wafer centre and an outer chocolate coating. The barrier fat needs to have a high solid fat content at the storage temperature yet still be liquid at mouth temperature or slightly above. Suitable fats for this application are cocoa butter improvers and the stearin fraction from cocoa butter itself.

5.6.3 Moisture and alcohol migration

Moisture migration is again a problem that has increased in severity as products have become more complex in their structure, but is more of an issue where some form of cereal-based material is in contact with a water-based component. In the confectionery area an example of this is where caramel is in contact with a wafer or a biscuit. Moisture from the caramel can migrate into the biscuit. The result of this is that the biscuit becomes soft and soggy and the caramel becomes hard and chewy.

Fats can be used as barriers to separate the two phases. Historically these have been hydrogenated fats but it is possible to produce satisfactory moisture barriers from non-hydrogenated bases. They need to have a fairly high level of solid fat because any

moisture that moves through the barrier does so by dissolving in the liquid oil phase of the barrier. It then diffuses through the barrier eventually reaching the 'dry' component phase. The less liquid oil there is, the less moisture can move through the barrier in any given time. Crystallising the fat into flat platelet-like crystals instead of the more common spherulites also helps by increasing tortuosity (the distance the moisture has to move to get from one side of the barrier to the other). This can be achieved by adding waxes to the barrier (Talbot *et al*., 2005).

The most common area where alcohol migration occurs is in liqueur-filled chocolates. There are two types of these products – those with a sugar crust around the liqueur and those without. The problem arises in those products without the sugar crust. The alcohol dissolves sugar from the chocolate shell resulting first in a 'muddy' liqueur as cocoa powder from the chocolate is released and disperses in the liqueur, and eventually in the complete breakdown of the chocolate shell. Linke (1999) has suggested the use of a fat barrier to prevent this but this gives significant problems in terms of production in that the empty shell first has to be sprayed with the barrier and, after filling, the surface of the liqueur has to be sprayed with the barrier before being finally coated with a chocolate backing. A simpler method suggested by Talbot (2009b) is to include 5% cocoa butter improver in the chocolate (where it is allowed). Even this small amount is sufficient to protect the chocolate against attack by the alcohol.

5.6.4 Rancidity

Rancidity arising from oxidation is not usually a problem with chocolate products. Cocoa butter is very stable to oxidation, both because of its low content of polyunsaturated acids and because of its high content of natural antioxidants, which can also protect the other ingredients from oxidation. Similarly, both lauric CBS and hydrogenated, high-*trans* non-lauric CBR are stable to oxidation, though the fractionated products are inferior in this respect because the natural antioxidants present are concentrated into the olein during fractionation. Padley (1994) has reviewed the control of rancidity in confectionery products. A general review of the stability of oils and fats in foods has been published by Kristott (2000).

White chocolate is particularly sensitive to oxidation on exposure to light. If white chocolate is stored in transparent foil, light causes a rancid off-flavour to develop and a loss of the typical yellowish colour. The loss of quality may be reduced by using a nitrogen atmosphere and a high-oxygen-barrier foil, or by using a CBE instead of cocoa butter. CBEs are less sensitive to light because they may contain less or no chlorophyll, the photo-sensitiser for the oxidation (Krug and Ziegleder, 1998a, 1998b).

Hydrolytic (or lipolytic) rancidity, leading to the production of free fatty acids, is only a problem with products containing lauric fats. They are prone to lipase-catalysed rancidity in the presence of low levels of moisture; this is normally described as 'soapy' rancidity because of the characteristic flavour development. It occurs because the low flavour threshold of the short-chain fatty acids (6:0 to 12:0) means that a low level of these are organoleptically detectable. As little as 0.2% of total free fatty acids will cause a detectable flavour. Development of soapy rancidity can be avoided by reducing

moisture and by avoiding microbiological contamination. Lecithin is often added to lauric fats in order to bind any free water and make it unavailable for hydrolysis (Andersen and Roslund, 1987).

Microbiological contamination, usually from poor-quality cocoa powder, can also lead to ketonic rancidity where the flavour compounds are ketones. It is now thought that off-flavours in lauric fats are caused by a combination of ketonic and soapy rancidity (Padley, 1994).

5.7 Nutritional aspects of confectionery fats

Nutritionists, health practitioners, consumers, retailers and the media are increasingly looking at the nutritional content of the food that we consume and are particularly focusing on those areas of diet that are considered to be detrimental to health. In terms of fats in general, this has meant focusing on specific groupings of fats and, in particular, their effects on cholesterol levels in the blood. This is because blood cholesterol level is seen as a marker for risk of cardiovascular diseases (though it has to be said that the link between blood cholesterol levels and cardiovascular disease (CVD) risk is not clear-cut). There are two main types of blood cholesterol: that carried by high-density lipoproteins (HDL cholesterol) and that carried by low-density lipoproteins (LDL cholesterol). In broad terms, HDL cholesterol is considered to be beneficial while LDL cholesterol is considered to be detrimental. *Cis*-mono-unsaturated and *cis*-polyunsaturated fatty acids raise HDL cholesterol levels and lower LDL cholesterol levels and so are considered 'good for you'. *Trans* fatty acids lower HDL cholesterol levels and raise LDL cholesterol levels and so are considered 'bad for you'. This is why so much effort has gone into replacing hydrogenated, *trans*-containing fats with non-hydrogenated alternatives. Saturated fatty acids raise both types of cholesterol levels – the good and the bad and so sit somewhere between *trans* fatty acids and *cis* unsaturated fatty acids (Mensink *et al*., 2003).

The problem with regard to confectionery fats is that these are used in products where some degree of hardness and structure is required (i.e. coatings and, to a lesser extent, fillings). This can only be obtained from either *trans* fatty acids or saturated fatty acids so, inevitably, confectionery products of today contain significant levels of saturated fatty acids. In terms of chocolate and coatings, it is very difficult, if not impossible, to reduce saturated fatty acids to much below about 60% of the fat phase. This is because cocoa butter, milk fat and CBEs all typically contain 60–65% saturated fatty acids. Changing the balance between them does nothing to alter this (Talbot, 2011). Non-lauric CBRs also contain a similar level of saturated fatty acids while lauric CBSs contain much higher levels of saturated fatty acids (up to 99% in the case of fully hydrogenated palm kernel stearin). Mensink *et al*. (2003) found that, while saturated fatty acids as a whole behaved in the way described above, individual saturated fatty acids had different effects, with stearic acid being effectively neutral in its effects on blood cholesterol levels. Cocoa butter and, especially, shea stearin (used in CBEs) contain considerable levels of stearic acid and much work

has been published on the effects of these fats on blood lipids and other CVD risk factors (Sanders *et al*., 2001; Sanders and Berry, 2005; Berry and Sanders, 2005). These studies concluded that stearic acid in cocoa butter resulted in similar blood lipid levels after eating as did a meal containing high-oleic sunflower oil. Stearic acid from shea butter decreases post-meal blood lipid levels. From this work Sanders (2009) concluded that 'chocolate confectionery fats do not have an adverse effect on the lipid profile' and 'are potentially less thrombogenic than high monounsaturated oils such as olive oil and high-oleic sunflower oil'.

5.8 Conclusion

We have seen that a wide variety of fats is available for use in the confectionery industry. The traditional fats – cocoa butter, milk fat and coconut oil – have long since been augmented with a range of alternative fats. Initially, the aim was merely to simulate the properties of the traditional fats, but in recent years the aim has been to improve on them. Improvements that have been achieved include:

- lower cost and improved availability;
- better melting properties;
- resistance to bloom and migration;
- convenience of use (e.g. no need to temper);
- resistance to both oxidative and lipolytic rancidity.

Fat can be seen as the most functional ingredient in both chocolate and sugar confectionery and can be tailor-made for each particular application.

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6
Spreadable products[1]

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6.1 Introduction

6.1.1 Definition of spreads: margarine, low(er) fat spreads and butter

The term 'yellow fat spreads', often just 'spreads', refers to all products that are described as butter, margarine and their low-fat alternatives, the vast majority of which are made mainly from vegetable oils. However, in recent years, two other product groups have emerged – sweet and savoury spreads – and their use in place of yellow fats is so significant that it is appropriate to consider these, albeit briefly, within this chapter. To a lesser extent, flavoured butters are also available but the market for them is relatively small.

In Asia and the Middle East ghee is used instead of butter as a spread on local flour-based hosts such as nan bread in Pakistan and Afghanistan, chapati, and so on in Northern India and pancakes (e.g. thosai) in South India and Sri Lanka. Rice is often also an important host. The vegetable oil alternative is known as vanaspati; both products are discussed in the chapter on culinary fats.

6.1.1.1 Competition between butter and margarine

Butter, which was developed over 5000 years ago, remained unaltered and without serious competition until the invention of margarine by Mège-Mouriès, a French chemist, in 1869. He utilised a mix of beef tallow oleine, with about 10% milk, some water and 0.4% udder tissue as flavour. This patented mix was agitated to produce a cream that was then processed like a butter to obtain margarine, or butterine, as it was known in the UK and the USA respectively in the early days.

[1]The original chapter was written by David J. Robinson and Kanes K. Rajah.

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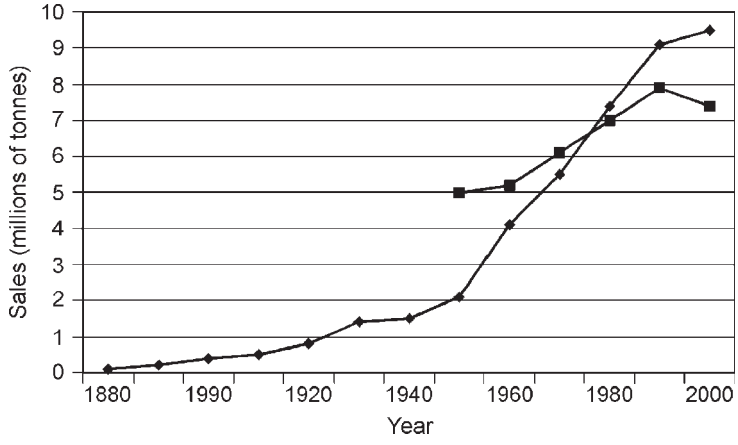


Figure 6.1 World margarine and butter sales. Note: ◆ Margarine, ■ Butter. *Source:* Adapted from Michael Bockisch (1993) with statistics from Oil World [http://www.oilworld.biz/statistics?direct_call=ista&ista=5b9a6b1ef10f6f1e97c7814526266243].

Industrialists rapidly adopted his invention and world consumption grew, overtaking butter in the late 1970s and reaching its zenith, of 9.5 million tons, in the early 1990s. Since then it has levelled off as other spreads and snacking, and probably the lack of innovation in yellow fats, have taken their toll (Figure 6.1). For instance, spreads such as soft cream cheese and chocolate spreads have eroded the yellow fat market. Latterly, the growth of perceived soft 'butter' spreads has further reduced the traditional (minimum 80% fat) 'margarine' market.

Today margarine is fast becoming a generic term for vegetable yellow fat spreads containing less than 80% fat. By 2000, in the USA, the percentage of fat in vegetable yellow fat spreads had dropped to 53% and in Unilever's products in Europe the average fat level dropped to 63% during the same period. In Unilever Europe only 38% of these products remained eligible to be called 'margarine', having over 80% fat.

Numerous on-pack descriptors have replaced the term 'margarine' over the past 20 years. Butter, with over 80% fat, is also fast disappearing as a descriptor, with fat levels falling and butter being replaced by vegetable oils, making them more spreadable and affordable. So we enter the twenty-first century with the descriptor 'margarine', invented in the nineteenth century, almost extinct and another, 'butter', with its origins stretching back over 5000 years following a similar fate.

6.1.1.2 Market and usage considerations

All these spreads are unique in that they are used in conjunction with a 'host', such as bread, biscuits or vegetables. Alternatively, they are used as an ingredient, or aid, in the cooking of meat, cakes, pastry, creams, sauces and other food products. No spread is eaten alone and as such is totally dependent on the market and the properties of the 'host' or destination product. Having said this, the functionality of the spread can significantly improve the attractiveness of the 'host' or destination product and both benefit from mutual innovation.

For example, a spread, such as a margarine or spreadable butter sold in a soft plastic tub will suit softer breads, as often sold in the UK, whereas a harder spread such as butter or margarine sold in a wrapper will be more acceptable on harder breads, such as those made in Germany or France. Also, in markets where the 'host', such as bread, is practically nonexistent, as in China, the market for yellow fats used to be very small but nevertheless it is now growing (Wang *et al*., 2012). Chinese consumers are increasingly adopting a more western lifestyle and matching eating habits which include more vegetable oils and dairy solids in their diet. In the USA, it is traditional for vegetables to be coated with a yellow fat and therefore the 'host' is not always confined to a baked product.

In designing the 'perfect' yellow fat spread it is necessary to consider the multi-functional nature of the product, as often the single pack in the household is used in conjunction with many food products. Any consumer market analysis will show that a single yellow fat is used not only for spreading but typically will be used in the shallow frying of meat, for coating vegetables and for making cakes, pastry and sauces.

Additionally, the taste, colour and texture of the spread will tend to follow the characteristics of the traditional butter sold in that region. Hence, in Sweden and the UK, a high-salted product is preferred, whereas in Holland and Germany lightly salted products are the norm.

Finally, health and nutrition have become an important factor in the yellow fat market and products, with cholesterol-lowering properties, added essential nutrients, such as vitamins and low-calorie products making up a significant proportion of the market.

When designing a product, all these various factors need to be taken into consideration. Some functions will conflict whereas others will be mutually exclusive. A trade-off needs to be made between the essential USP (ultimate selling property) and the other desirable, but not essential, requirements.

6.1.2 Summary of product development

One way to show the history of margarine is on a timeline indicating the years when various product types were introduced together with the enabling process technologies (Figure 6.2). From this it is clear that the first 90 years were characterised by innovation in margarine processes, as well as by considerable oil processing changes, which will not be covered here. The only major product innovation during this period was in 1927 with the adding of vitamins to margarine. This is taken for granted today but without this vital nutritional supplement it is likely that this industry would be much smaller today. In the UK a government committee in 1926 ruled that margarine should not be considered as an effective substitute for butter because of its vitamin deficiency and should certainly not be used by children. It is interesting to note that in the UK today 30% of the daily intake of vitamin D and 15% of vitamin A comes from margarines.

The past 50 years show a significant number of product innovations (Rajah, 2005), with few fundamental process advances (Figure 6.2 (b)). It was only in the early

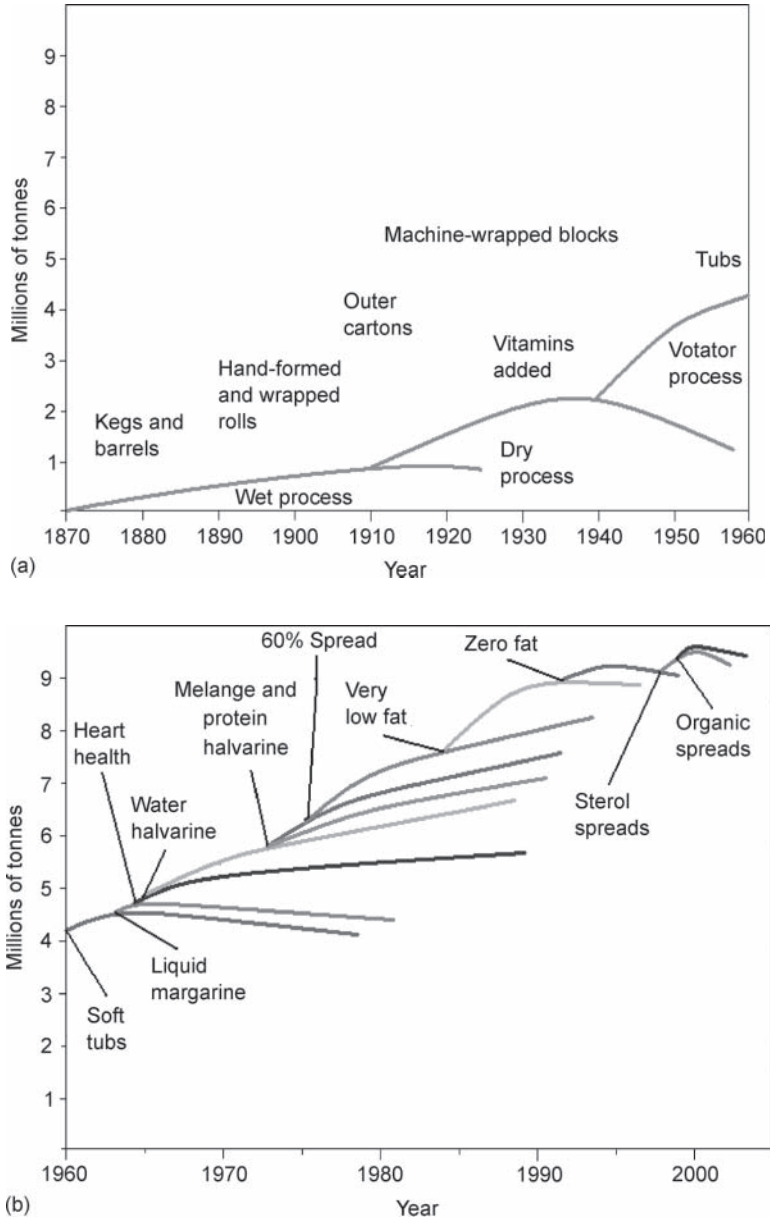


Figure 6.2 Margarine products and processes: (a) 1870–1960; (b) 1960–2000. *Source:* Robinson and Rajah (2002).

1960s that spreadable products sold in tubs were introduced, closely followed by liquid margarine, primarily in the USA. The mid-1960s saw the introduction of tubs of 'heart-health' high-PUFA (polyunsaturated fatty acids) as well as low-calorie halvarine products, with an empty water phase. These products received considerable publicity

in the 1980s with the publication of the COMA (Committee on the Medical Aspects of Food in the UK) report which promoted the reduction of total fat and saturated fatty acid in the diet.

Although milk fat and vegetable fat mixtures, known as melanges, have been used over the years, usually with butter levels below 10%, it was not until the 1970s that an 80% melange, Bregott, with around 75% butter, was marketed in Sweden. Also in Sweden a similarly constituted fat phase is used for a half-fat product, Latt au Lagom. With the benefit of hindsight it is a mystery that similar products took so long to become established in other countries. In the late 1970s the low-protein and high-protein halvarines were introduced with, for the first time in the UK, the use of preservatives.

By the 1980s the fat levels in most traditional brands started to fall, and the ubiquitous 'reduced 60% fat spread' entered our vocabulary. The 20%, very-low-fat, and 'almost-zero-fat' spreads were introduced in the late 1980s and early 1990s.

By the 1990s the market was set for the greening of yellow fats (Rajah, 2006). In 1998, the first significant cholesterol-lowering yellow fat, Benecol, a trademark of Finnish company Raisio Group, was introduced (bene, meaning 'good,' and col for 'cholesterol'), The brand is licensed in more than 30 countries by local food companies such as McNeil Nutritionals in the UK, Ireland, Belgium and the US, Kaiku in Spain, Colanta in Colombia and Kalbe Nutritionals in Indonesia (Food navigator.com, 2008). This was followed in 2000 by Unilever's Proactiv (both Proactiv and Benecol are registered). After 10 years of market decline in volume the market was expected to increase in terms of value, as these products sold at four times the price of equivalent products because of the high price of plant stanols and sterols on which they are based. As of 2013, both brands had grown on the strength of their ability to claim cholesterol-lowering properties to having a range containing Light, Buttery and Olive Spreads. This is being assisted further by the approval received recently for plant stanol esters, the active ingredient used in these products, by the EU's European Food Safety Authority (EFSA) following an application from Raisio Nutrition Ltd, via the Competent Authority of Finland (EFSA, 2012). Notwithstanding this, goats' milk butters which contain lower levels of cholesterol than cows' milk butters are beginning to emerge and starting to sell, with sales of one of the manufacturers, St. Helen's Farm in the UK, reaching £970,000 in 2010. Apparently not all of those who are avoiding cows' milk products like the taste of soya (*The Grocer*, 2010a).

Meanwhile, organic spreads which started to appear on the supermarket shelves during the 1990s in the UK and Sweden are now well established. Both the lack of confidence with governments in dealing with the BSE (bovine spongiform encephalopathy) crisis and the introduction of GMOs (genetically modified organisms), as well as the green agenda of the 1990s, have provided the catalyst for these products to become accepted despite their price premium.

Finally, the debate on butter versus vegetable oils-based spreads has not abated. In 2010, Mr Shyam Kolvekar, an eminent consultant cardiologist from University College London Hospitals, issued a statement through KTB, a public relations company, urging the banning of butter in order to save lives. He maintained that by banning butter and

replacing it with a healthy spread, the average daily saturated fat intake would be reduced by 8 grams, and advised people among other things to switch to olive oil and sunflower oil. In contrast to this, a clinical study by Ramsden *et al*. (2013), published in the *British Medical Journal*, challenged such commonly held beliefs. In evaluating the effectiveness of replacing dietary saturated fat with omega 6 linoleic acid, for the secondary prevention of coronary heart disease and death, the researchers reported that the clinical benefits of the most abundant polyunsaturated fatty acid, omega 6 linoleic acid, have not been established. In addition, an updated meta-analysis of linoleic acid intervention trials showed no evidence of cardiovascular benefit.

6.1.3 Summary of process development

As mentioned earlier, the first 90 years of the industry were characterised by process, rather than product development. Although not covered here, developments in oil processing – particularly hardening, deodorisation and interesterification – greatly influenced the raw materials used and the quality and range of the products manufactured.

6.1.3.1 Unit processes

Mège-Mouriès and the early margarine manufacturers used the same basic unit processes that are in use today – mixing, emulsification, chilling, working and resting – but there the comparison must end, for today's manufacturing process bears little relationship to the open, wet and time- and labour-consuming process at the end of the nineteenth century (Figure 6.3).

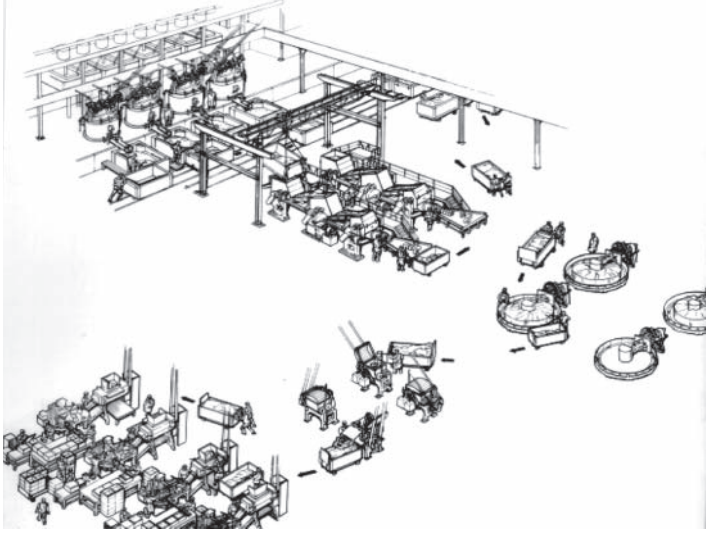


Figure 6.3 Margarine manufacturing in the late nineteenth century: plant layout. *Source:* Anderson and Williams (1965).

6.1.3.2 *Wet chilling*

For a long period of time the mechanical churn drum (Figure 6.4) was used to mix the oil and aqueous ingredients and to create an oil-in-water emulsion. The churn cooled the product through the cooling jacket but also ice was used as an ingredient to aid this process. During this process the emulsion partially inverts to a water-in-oil emulsion.

When the process was complete, the cooled emulsion was flushed out of the churn, sprayed with iced water and poured into open troughs through which cold water flowed. The water and emulsion mix was held in wagons to continue fat crystallisation and separation. The crystallised emulsion was separated from the free water and kneaded in multiplex rollers to start the working process.

The margarine was then stored in wagons for about 24 hours to initiate post-crystallisation, before being transferred to the French rolls. These rolls worked and softened the product further to make it less brittle and easier to spread (Figure 6.5).

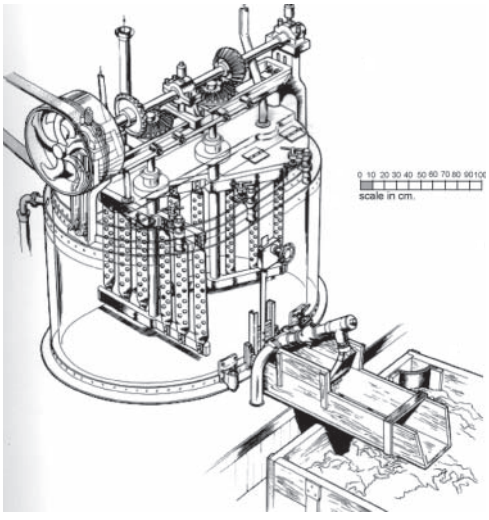


Figure 6.4 Mechanical churn. *Source:* Anderson and Williams (1965).

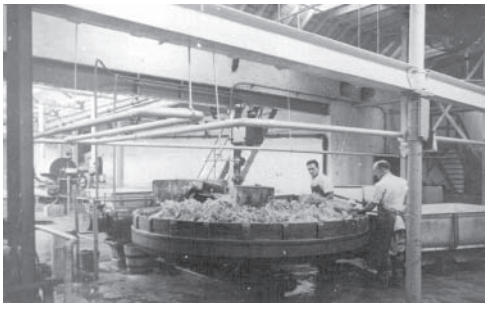


Figure 6.5 French rolls. *Source:* Robinson and Rajah (2002).

Salt and colour were sometimes added in the French rolls or in a kneading blender. Salt and colour were added towards the end of the process to prevent losses and protein precipitation during the wet chilling process. It also allowed small batches of product to be salted and coloured to suit regional tastes. For example, in Wales, it was said they liked to 'chew their salt'; whereas in Kent a very dark colour known as 'double Kent' was required; in Glasgow it was believed the people would eat only pale margarine.

More resting in wagons was required before being packed into kegs, rolls or packets. In total, it took some 60 hours from mixing of the ingredients to the packing of the final product. Estimates suggest that one person was required to produce about 40 tonnes of margarine per year.

6.1.3.3 Open dry chilling

It must have appeared a significant advantage in the 1920s for the wet process to be superseded by the open dry chilling drum (Figure 6.6). The churned emulsion, now of the water-in-oil type, including salt and colour, was passed directly to the feed roll, or trough, on the chilling drum. This was initially chilled internally by brine, but later by ammonia.

The flakes could be held in wagons to continue crystallisation or be fed direct to a complector, which worked the product as well as applying vacuum to remove air. The blocks of product were then stored in wagons to await filling into hopper-fed wrapping machines, developed in the 1920s.

The complete process cut the cycle time in half, to about 30 h, with productivity at about 200 tonnes per person per year.

6.1.3.4 Votator process

In the 1940s a scraped surface heat exchanger was developed to chill margarine. This 'A unit', as it was known, in conjunction with enclosed crystallisers (known as 'C units') and resting tubes (or 'B units') was used to feed product direct to a packing machine (Figure 6.7). For the first time the complete process could be totally enclosed. Surprisingly, this continuous process is still in use today despite a major drawback in that it requires a rework system to accommodate packing machine

Figure 6.6 Chill drum. *Source:* Robinson and Rajah (2002).

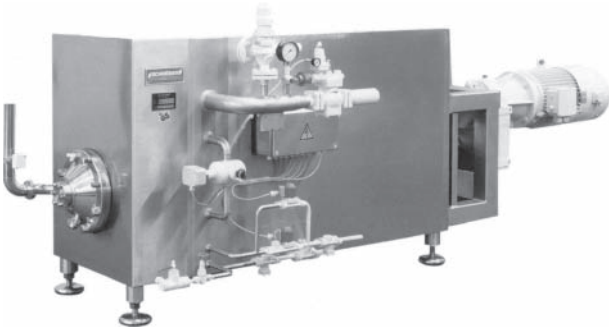


Figure 6.7 A Votator. *Source:* Image by kind permission of Gerstenberg Schröder.

stoppages. Direct-fed packing machines were in operation packing at speeds up to 220 packs per minute; now the figure is 360 tubs per minute.

With little significant change this led the way to today's totally enclosed process, with a total time from mixing to packing of 10 min. Productivity has risen, in larger plants, to 800 tonnes per person per year.

6.1.4 Summary of ingredient development

The ingredients used in traditional margarines can be subdivided into oil-phase ingredients, oil-soluble ingredients and aqueous-phase ingredients.

6.1.4.1 Oil-phase ingredients

Looking behind the products at the raw materials used shows interesting trends in history (Figure 6.8). The first oil to be used was beef tallow, used as the soft fraction, oleine. Tallow was first softened by olive oil, a practice that was quickly abandoned because of the high price of olive oil, in favour of groundnut and cottonseed oil. It has taken over a century for olive oil to reappear under a Mediterranean life-style platform.

Early on, sesame oil was used as a marker in margarine to distinguish it from butter, with the aid of the long-established phytosteryl-acetate colour test. Palm and the lauric oils, coconut and palm kernel were introduced in the early 1900s and still enjoy high usage today. Most of the liquid oils in use today, such as rapeseed, sunflower, maize and soybean oils, were used in the early twentieth century.

The use of whale oil needed to wait for the hardening process to be developed by Normann in 1902, but it was not until the second quarter of the twentieth century that sizeable quantities were used in margarine. By the 1960s public concern and catch restrictions had stopped its use.

Hardened fish oil was used from the 1950s and in some countries was the major oil ingredient until 1993, when worries arising from Willett's *trans* fatty-acid studies and later the sustainable fishing issue cut their use dramatically (Willett *et al*., 1993). This reduction of the raw material supply was closely followed by the BSE crisis, first in the UK and by early 2000 in mainland Europe, which directly limited the use of tallow.

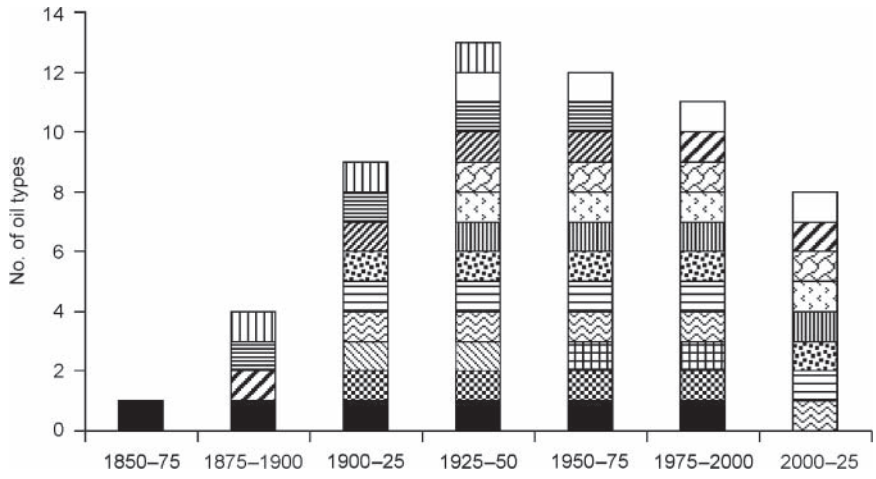


Figure 6.8 Major oil types used in margarine. Note: ■ Tallow, ▩ Lard, ▦ Fish, ▧ Whale, ▨ Palm, ▤ Coconut, ▩ Palm kernel, ▥ Sunflower, ⊡ Soybean, ▨ Rapeseed, ▨ Groundnut, ▨ Olive, ▤ Cottonseed, □ Maize, ▥ Sesame. *Source:* Robinson and Rajah, 2002.

Indirectly, the public questioned the use of all animal fats, so lard has also become unacceptable. Genetically modified oils came under significant public scrutiny in the 1990s, which has limited the use of soybean and maize oil, particularly in Europe.

Fat levels and triglyceride types. Coincident with these changes, the reduction of fat levels and *trans* fatty acids combined with an increase in use of polyunsaturated fats has led to a change in dietary intake from margarine (Figure 6.9). Figure 6.9 shows the UK situation for Unilever's products over a 15-year period, with significantly lower fat and *trans* fatty acid levels and higher PUFA and MUFA (mono-unsaturated fatty acid) levels. Surprisingly SAFA levels have not fallen much, as a percentage of the fat phase, but in total have fallen due to lower fat levels in the products. This position will be similar for most Western countries.

6.1.4.2 Oil-soluble ingredients

The oil-soluble ingredients typically involve the emulsifiers, flavours, colorants and oil-soluble vitamins. An emulsion is created in the margarine by mechanical shearing, originally in the churn but now in the votator, and is in part stabilised by the crystallised fats. However, on storing or temperature cycling, the emulsion will start to break down unless stabilised by an emulsifier. Also, during hot use, such as in shallow frying, a margarine without an emulsifier will spatter. Before the 1900s egg yolk was used as an emulsifier and antispattering agent but was replaced in the 1920s with vegetable lecithin, mainly from soybeans. At about the same time monoglycerides and diglycerides were introduced to stabilise the margarine emulsion at ambient temperatures. To this date these emulsifiers are still in general use.

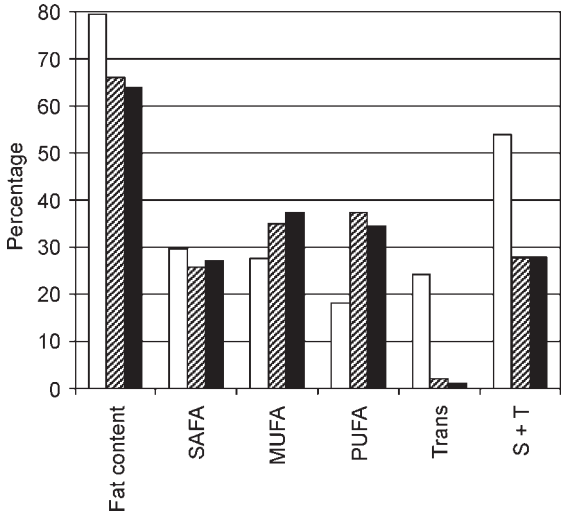


Figure 6.9 Fat content of yellow fats, 1984–2000, as produced by Unilever, UK (in the products Stork, Flora, Olivio and 'I can't believe it's not butter'). Note: SAFA, saturated fatty acid; MUFA, monounsaturated fatty acid; PUFA, polyunsaturated fatty acid; Trans, trans fatty acid; S + T, saturated plus trans fatty acids; the values for SAFA, MUFA, PUFA and Trans are expressed as a percentage of the fat phase only. □ 1984, ▨ 1996, ■ 2000. *Source:* Robinson and Rajah (2002).

Until the 1950s flavouring came from the cultured milk incorporated in the product. Since the 1950s butter flavours have been developed, in particular delta lactones and diacetyl.

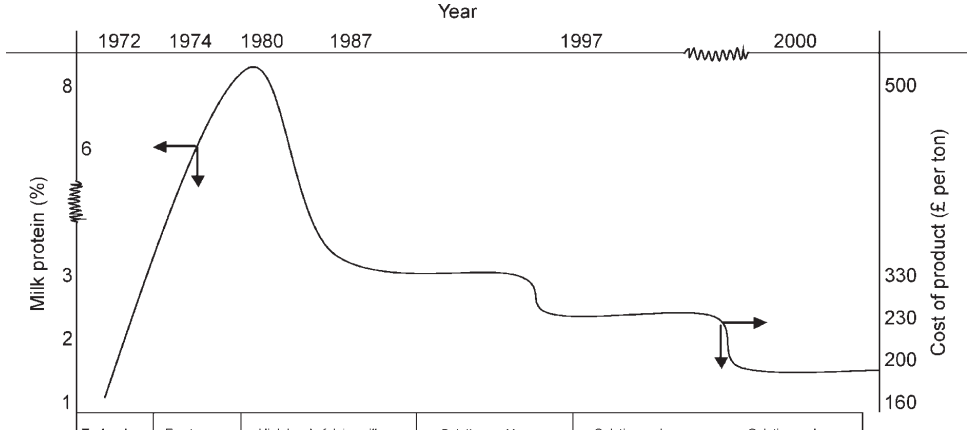
Owing to consumer expectations, colorants have always been an important additive in the manufacture of margarine. A variety of food colours have been available for many years, but the main source has been from the carotenoids in red palm oil and bixin (obtained from the seeds of the annatto tree).

Vitamins were developed in the 1920s and first introduced in margarine in 1927. Vitamins A and D are still used in almost all margarine. Additionally, many margarines contain vitamin E, an antioxidant, which is added to supplement the vitamin E that naturally occurs in crude vegetable oils but is partially lost during deodorisation.

6.1.4.3 Aqueous-phase ingredients

The only major change in the aqueous phase of margarine over the years has been the change from the use of cultured milk to skim milk powder, or whey. This change happened in conjunction with improvements in flavours in the 1950s. Ripening of milk continued up to the 1980s although some plants continued with this process until the end of the twentieth century. The process was both time- and space-consuming, requiring the use of large souring tanks needing up to 30 hours to culture the milk.

More interesting changes have taken place in the aqueous phase of low-fat products (Figure 6.10). Initially, a protein-empty aqueous phase was used in the first halvarines



Technology	Empty aqueous phase (halvarines)	High level of dairy milk proteins in aqueous phase	Gelatine and low level of dairy protein	Gelatine replacer: alginate or alginate/ maltodextrin	Gelatine replacer: modified starch
European commercial product examples	Linnea (Sweden) Outline (UK)	Lätta, Lägom (Swedish Dairies) Primur (Sweden) St. Ivel Gold Unigate, (UK) Delight (UK)	Flora Light (UK) Lätta (Sweden) Lätta (Germany)	Flora Light (UK)	Lätta (Germany)
Process technology	Standard votator line		Inversion processing		

Figure 6.10 Development of Unilever low-fat spreads (40% fat content). *Source:* Robinson and Rajah (2002).

in the 1960s. In the 1970s, high protein levels of dairy-based low-fat spreads such as Latt au Lagom appeared. With the price of milk protein equating to that of milk fat, it was not long before medium-level protein-containing spreads entered the market. Protein levels continued to decline as thickener systems changed from gelatine, to alginate, then to starch during the 1980s and 1990s.

6.1.5 Summary of packaging developments

Margarine was originally packed into kegs or barrels (in the late 1800s). At about the turn of the century it was packed largely in hand-wrapped rolls or bricks. Machine wrapping was introduced in the 1920s. Initially, vegetable parchment was used as the wrapping material, but by the middle of the twentieth century some premium products were upgraded to aluminium foil wrappers. The folded carton was introduced in the USA in 1907 to protect the softer wrapped product usually sold as 'fingers'. This type of pack was, and still is, sold on both sides of the Atlantic for premium softer products.

Tubs were introduced in the late 1950s and the materials and forming processes have changed from waxed card, to thermoformed PVC (polyvinyl chloride), ABS (acrylonitrile butadiene styrene) or polypropylene, to injection-moulded high-density polyethylene and polypropylene, and, latterly, to in-mould labelled polypropylene.

For the best part of the 140-year history of margarine, standard primary pack sizes have been prescribed by law with, depending on the measurement used within a country, packs of 250 g ($^1/_2$ lb), 500 g (1 lb) or 1 kg (2 lb) being the most common. In recent years unit pricing (price per kilogramme or pound stated on shelf, or pack) has been introduced, which has overcome the main reason for standard ranges, namely, consumer price confusion. As such, a growing number of countries no longer prescribe a standard range of packs.

Primary packs were hand packed into wooden boxes until replaced by cardboard, around the 1940s. Secondary packaging machines were introduced in the middle of the 1990s and the American box as well as the simple cardboard tray, usually followed by shrink or stretch wrapping, were being mechanically packed on the larger lines by the 1970s. In the 1990s more sophisticated secondary packs consisting of trays with reinforced corners were being formed on-line by robotic packing machinery.

Throughout the second half of the twentieth century the pallet was used as tertiary packaging, in common with most other industries. For about 30 years the display pallet has also been used, particularly in countries where ambient distribution is still used, such as Germany. In Sweden the display pallet, or cage, has been in use in the chilled cabinet for many years. This form of tertiary packaging enables the primary packs to be merchandised within the shop without the need to unbox the product.

6.2 Legislation

Almost from the start, the margarine industry was subject to what can be viewed as discriminatory regulations brought about by strong political activity from the dairy

lobby. Margarine was seen to be produced by ‘big business’, whereas butter was made predominately on a large number of small farms.

Past regulations have played a significant part in the development of the product and its packaging. Regulations proposed that margarine must

- be colourless (with colour capsules provided for the consumer to add at home);
- be coloured (pink, brown or blue!);
- be sold only in cubic packs;
- be sold in a separate area from butter;
- have a red band printed on the pack;
- have sesame and starch tracers;
- have a lead seal closure;
- be made in quantities set by legal production quotas.

Apart from setting adverse taxes, governments have been obsessed with preventing the product being mixed with butter or from being coloured, or packed, as butter. Although blue margarine was never sold, a cubic pack with the warning red band was.

In the USA, capsules of colorant were sold with the colourless margarine to allow consumers to ‘mix their own’. In fact, even in the 1980s in Wisconsin, a dairy state, colour capsules were still sold. Unbelievably, in 1885, the clash between the butter and margarine lobbies led to the dissolution of the Danish parliament.

The very regulations that made butter so secure also restricted butter to such a narrow definition that the dairy industry locked itself into a single product. The flexibility of the margarine regulations with regard to ingredients and processes – provided milk fat was not used – enabled margarine to thrive at the expense of the dairy industry, at least until the latter part of the twentieth century.

In the 1970s, developments in Sweden with Breggott and Latt au Lagom started to push butter into the melange area. But it was the introduction of the single unifying EU Yellow Fats Spreads regulation in 1994 that legally freed up the use of milk and edible fats, at varying fat levels. The dairy industry at last had the legal flexibility to exploit the advantages of butter, this time not only as a raw material but with brand names perceived by the consumer to be ‘butter’.

6.2.1 EU regulations

The initial European regulations for spreadable fats were laid down in 1994 (Council Regulations [EC] No. 2991/94) but were subsequently modified by five regulations between 1997 and 1999 (EC Regulations No. 577/97, No. 1278/97, No. 2181/97, No. 623/98, and No. 568/99). The most recent modification is offered by Commission Regulation (EC) No. 445/2007. These regulations apply to products made from three fat groups, namely, ‘milk fats’, ‘fats’, and ‘fats composed of plant and/or animal products’. Hence butter, margarine and melanges are all covered within one set of regulations.

In principle, the regulation applies to yellow fats with a fat content between 10% and 90% by weight. The fat content must be at least two-thirds of the dry matter, excluding salt. The products must remain solid at room temperature and be suitable for use as spreads and be intended for human consumption. The sales descriptions of the products are set out in Table 6.1.

Table 6.1 Fat groups: description and product category.

Sales description	Product category[a]
Milk fats[b]	
Butter	Milk-fat content not less than 80% but less than 90%; maximum water content of 16%; maximum dry nonfat milk-material content of 2%
Three-quarter-fat butter	Milk-fat content of not less than 60% but not more than 62%
Half-fat butter	Milk-fat content not less than 39% but not more than 41%
Dairy spread (*x*% fat)	Milk-fat content: less than 39% more than 41% but less than 60% more than 62% but less than 80%
Fats[c]	
Margarine	Obtained from vegetable and/or animal fats with a fat content of not less than 80% but less than 90%
Three-quarter-fat margarine	Obtained from vegetable and/or animal fats with a fat content of not less than 60% but not more than 62%
Half-fat margarine	Obtained from vegetable and/or animal fats with a fat content of not less than 39% but not more than 41%
Fat spreads (*x*% fat)	Obtained from vegetable and/or animal fats with fat content: less than 39% more than 41% but less than 60% more than 62% but less than 80%
Fats composed of plant and/or animal products[d]	
Blend	Obtained from a mixture of vegetable and/or animal fats with a fat content of not less than 80% but less than 90%
Three-quarter-fat blend	Obtained from a mixture of vegetable and/or animal fats with a fat content of not less than 60% but not more than 62%
Half-fat blend	Obtained from a mixture of vegetable and/or animal fats with a fat content of not less than 39% but not more than 41%
Blended spread (*x*% fat)	Obtained from a mixture of vegetable and/or animal fats with fat content: less than 39% more than 41% but less than 60% more than 62% but less than 80%

Notes: [a]Including a description of the category with an indication of the percentage fat content by weight.
[b]Products in the form of a solid, malleable emulsion, principally of the water-in-oil type, derived exclusively from milk and/or certain milk products, for which the fat is the essential constituent of value. However, other substances necessary for their manufacture may be added, provided those substances are not used for the purpose of replacing, either in whole or in part, any milk constituents.
[c]Products in the form of a solid, malleable emulsion, principally of the water-in-oil type, derived from solid and/or liquid vegetable and/or animal fats suitable for human consumption, with a milk-fat content of not more than 3% of the fat content.
[d]Products in the form of a solid, malleable emulsion, principally of the water-in-oil type, derived from solid and/or liquid vegetable and/or animal fats suitable for human consumption, with a milk-fat content of between 10% and 80% of the total fat content.

6.2.2 US regulations

The US Federal regulations for butter and margarine are contained in separate documents. Additionally, there are laws governing margarine in many of the individual States. The standards for margarine-type products apply to all substances, mixtures and compounds known as margarine and to all substances, mixtures and compounds that have a consistency similar to that of butter. These products may contain any edible oils and fats other than milk if made in imitation or semblance of butter.

The term 'spread' is the commonly used term for lower-fat margarine, but there is no Federal standard for spread. 'Diet margarine' is a name applied to a product with 40% fat made like a margarine except for the lower fat content. Again, there is no Federal standard or definition.

The composition of margarine is defined by two Federal standards, one for vegetable products, administered by the Food and Drug Administration (FDA), and one for products containing animal fats, administered by the US Department of Agriculture (USDA). The FDA standard, which applies to the majority of margarine, defines margarine as 'food in plastic form or liquid emulsion containing not less than 80% fat'. There is no maximum to the milk fat that can be used. It is obligatory to add vitamin A, but not vitamin D. However, if vitamin D is added, it must be at a prescribed minimum level. Addition of vitamin E is not permitted.

6.2.3 Codex standards

There are four separate standards covering margarine (Codex Standard 32–1981 [Rev. 1–1989]), minarine (Codex Standard 135–1981 [Rev. 1–1989]), butter (Codex Standard A-1-1971 [Rev. 1–1999]) and Codex Standard 256 – 2007. Essentially the margarine standard applies to 'a food in the form of a plastic or fluid emulsion, which is mainly of the type water/oil, produced principally from edible fats and oils, which are not derived from milk'. The margarine must contain a minimum fat content of 80% and a maximum water content of 16%. Vitamins A, D and E are permitted as well as other ingredients including milk or milk products, salt, sugars, suitable edible proteins, colours, flavours, emulsifiers, preservatives, antioxidants, antioxidant synergists, acidity regulators and antifoaming agents.

Minarine has a similar product description to margarine but requires a fat content between 39% to 41%. Also, the water content must not be less than 50%. It has a similar ingredient list to margarine, although gelatine, natural starches and thickening/stabilising agents can be used.

Butter is described as a fatty product derived exclusively from milk and/or products obtained from milk, principally in the form of an emulsion of the type water-in-oil. It must contain a minimum of 80% milk fat and a maximum of 16% water and a maximum of nonfat milk solids of 2%. The only additives that can be used are salt, starter cultures, potable water, prescribed colorants and acidity regulators.

6.3 Emulsion technology

6.3.1 Properties of emulsions

Andersen and Williams' (1965) book on margarine manufacture was generally accepted as the most important treatise on the subject at that time. The 1980s saw a number of major developments coming through which were well documented by Hoffman (1989) and soon after by Rajah (1992 and 1999), with Moran (1994) reporting comprehensively and with particular emphasis on the preparation of lower-fat emulsions. Robinson and Rajah (2002) and Mortensen (2009) have offered recent updates on the production of yellow fats and spreads.

The book on buttermaking by McDowall (1953) was the first in-depth coverage of the subject. Important updates have followed, most notably by Munro (1986), Jebsen (1994), and Ranjith and Rajah (2001) and more recently by Keogh (2006) and Wilbey (2009).

Smiddy, Kelly and Huppertz (2009) have discussed recent updates on the manufacture of cream and of butter.

6.3.1.1 Texture, plasticity and consistency

The crystallisation of fat in emulsions is discussed comprehensively in Chapter 1. However, the report by Ghosh and Rousseau (2011) on fat crystals and water-in-oil emulsion stability, and the effect of minor components and additives on the crystallisation of fat as discussed by Smith *et al*. (2011) offer some additional background here.

As a result of such processing, spreads take the form of viscoelastic materials, the physical properties typically being measurable by elasticity, viscosity and work softening. These properties are also discussed in terms of the physical quality of the emulsion (i.e. texture, plasticity and consistency; De Man *et al*., 1976). Texture, plasticity and consistency are equally important because they encapsulate those aspects of product benefit sought by the consumer in food applications. For instance, texture is primarily used to describe the state of the emulsion structure, and can range from smooth to floury, grainy, granular, or sandy to coarse and lumpy. The dispersed phase coalescence mechanisms have been compared in different table spreads (Rousseau *et al*., 2009). The dispersed phase destabilisation in table spread has also been reported (Rousseau *et al*., 2003).

Very close to this is the aspect of consistency, a temperature-dependent property. It describes a smooth, even plastic, state, varying from soft, medium, firm and tough to hard and brittle. Since it is possible to encounter smooth as well as grainy and coarse plastic products, plasticity is associated with both these terms.

Plasticity remains distinct from the other two terms because it describes the ability of a fat or emulsion to retain its shape under slight pressure, such as that encountered

during rolling, mixing or spreading. Three conditions must apply for a fat system to be considered plastic:

- Two phases must be present, one of which must be a solid and the other preferably a liquid or clearly behaving as a liquid.
- The solid phase must be finely dispersed to enable the entire mass to be effectively held together by internal cohesive forces. The particle size of the solids must be small enough for the force of gravity on each to be negligible in relation to the adhesion of the particle to the mass. Equally, the interstitial spaces must also be small enough to prevent the liquid phase seeping from the material.
- Mass flow must be facilitated. Flow behaviour is usually described with reference to Newtonian, Bingham and pseudo-plastic materials. Liquid oils are typically Newtonian but crystallised emulsions behave as pseudoplastic materials. In accordance with Bingham's (1922) concept of plasticity, flow is achieved by ensuring the proportion of the phases present are such that the solid particles remain small enough to prevent obstruction or to engage in the formation of a rigidly interlocking crystalline structure.

Melting and solidification or solid–liquid and liquid–solid phase changes are among the most important of physical properties of all fats, including milk fat (Patton and Jensen, 1975; Sonntag, 1979). They are determined by the glyceride composition, that is by the amount and type of fatty acids present, the triacylglycerols in which they occur, including their position and rate of occurrence, and polymorphic form (Table 6.2). Larsson (1966) reported that complex triacylglycerol mixtures such as margarine exhibit four polymorphic crystal forms – α, β', β_2, and β'_1 in increasing order of stability.

In rheological terms, plastic fats possess a yield stress and hence a yield value (Lupi *et al*., 2011). This measure can be used to distinguish between the consistency of butter, margarine and low-fat spreads by studying the alterations in yield value following work softening (mechanical working). After normal work softening, those substances with a high degree of secondary bonds display comparatively higher structural hardness relative to those with a mainly primary bonded structure. Recovery for the primary bonded group is generally limited to achieving a degree of hardness, but not the original values, unless of course standard procedures are adopted for recrystallisation.

Haighton (1965) found that there is a correlation between lower degrees of work softening with plastic fats and high degrees with brittle fats. He also reported on a number of values for different fats (Haighton, 1959).

Table 6.2 Plastic behaviour of spreads.

Crystal property	Behaviour or performance
Amount	Solid:liquid ratio
Melting point of crystals	Melting point of fat
Geometry	Melting behaviour, consistency, etc.
Mixed crystals	Fat stability
Flocculation to form networks	Firmness

6.3.1.2 *Spreadability*

The term 'spreadability' is often used in connection with the solid state of table spreads. It is connected with consistency, texture and shear but is also influenced by the material on which the fat is spread (i.e. the host). These properties are not only important for their physical effect but also for their physiological and psychological effect on flavour and general palatability (Table 6.3). These effects are primarily determined by glyceride composition, state of emulsion and type of crystallisation of the fat.

Spreadability can be measured by testing the strength of the structure of spreads. A number of common methods are available. Cone penetrometry is a routine test based on the determination of the yield value. Mortensen and Danmark (1982) have reported on the use of the yield strength to determine the spreadability of butter. Moran (1994) has reviewed a number of techniques: extrusion method, cutting or sectility method, oil exudation, microscopy, sizing of emulsions and electrical conductance.

6.3.1.3 *Emulsion quality*

A stable emulsion state is important to the quality of the spread. Fundamental to this is the water droplet size. Typically, an 80% fat margarine would contain 95% water droplets in the diameter range 1–5 μm, 4% between 5–10 μm and 1% around 20 μm. It is estimated that when the water droplet diameter is 3 μm, and given that 1 g of margarine contains 16% water, there will be 10–20 million droplets. It is known that bacteria will grow to a length of 15 μm and so it is imperative to keep the diameter of the water droplets below this. However, with the development of lower-fat spreads there is a consequent increase in water content. The water droplet size can increase to 80 μm and therefore the shelf-life of such products is affected. To overcome this, preservatives are often added, particularly to very low-fat spreads, while factory hygiene standards and microbiological quality of raw materials have also to be monitored closely and maintained at an optimum level.

The functional benefits of a fine emulsion are as follows (Andersen and Williams, 1965):

- It contributes towards the plasticity of the product.
- It improves the shelf-life of the product by making it more resistant to bacterial attack (in a small droplet, a bacterium cannot multiply and soon dies).
- Added flavours are best perceived when in the aqueous phase because it is held that only water can wet the tastebuds; nevertheless, some good oil-soluble flavours are also available (Figure 6.11).

Table 6.3 Performance expected of spreads at specified temperatures.

Temperature (°C)	Performance
0–10	Spreadability from the cold or from the fridge
20–30	Butter, margarine or pastry fats for baking (e.g. pastry products) must retain their plastic character during the early stages of baking
30–35	Organoleptic property or eating quality (i.e. complete melt is required for sandwich spreads but a higher melting property is expected in fats for meat pies)

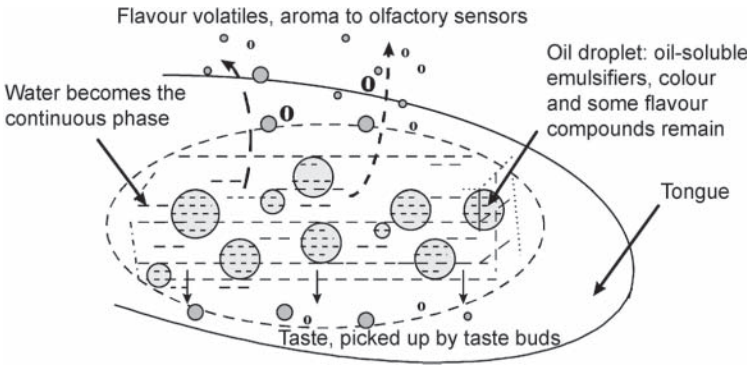


Figure 6.11 Phase inversion of a water-in-oil emulsion and organoleptic quality. Phase inversion is caused by the combined effect of an increase in moisture level from saliva, an increase in temperature to that of the mouth (typically 37.8°C) and mechanical action from mastication. These factors weaken the fat crystal structure, allowing water to become the continuous phase, thereby releasing the flavour compounds held within that phase. *Source:* Robinson and Rajah (2002).

However, it should be noted that too fine a dispersion can also mask the flavour of the margarine. Equally, such an emulsion could also be absorbed without being broken on the palate and therefore never really be tasted.

The measurement of butter quality still remains largely a manual process, undertaken by butter graders. The following factors are taken into consideration when grading and assessing the suitability of the butter for retailing as a spread:

- flavour and aroma;
- body and texture;
- colour, appearance, finish and salt content;
- absence of free moisture.

Those that fall outside the specification for free moisture may be processed into anhydrous milk fat (butter oil). However, if the moisture level is either much lower than the legal maximum allowed of 16% (e.g. below 15%) or exceeds it, the batch is likely to be blended in with other batches of butter to reach a level as close to 16% as possible. Similar action could also be taken when the salt level falls outside the required limit. However, if the product fails in terms of free moisture, poor texture or flavour, it is more than likely to be processed into butter oil. If there are slight flavour defects, it could still satisfy the specification for ghee. For instance, a well-developed butter flavour is considered a rancid product in many Western countries. However, it is a much desired product in the Middle East and Far East as a spread and fat base both for sweet confections and for savoury preparations.

6.3.2 Emulsifiers and hydrophilic–lipophilic balance values

The crystallisation of fat contributes a solid crystal network to stabilise the emulsion. However, this alone is insufficient to reduce the interfacial tension at the interface of

the two fluids (i.e. water and oil). Emulsifiers are necessary to overcome this problem (Young and Wassell, 2008). The most widely used products are the monoacylglycerols and diacylglycerols, both fulfilling this function by providing the base materials for emulsifiers that are used in water-in-oil emulsions (e.g. margarines). Monoacylglycerols and diacylglycerols of low HLB (hydrophilic–lipophilic balance) numbers help to stabilise the water-in-oil emulsions in margarine. Distilled monoglycerides are used for reduced-fat spreads.

Spreadable butter that is manufactured by emulsifying vegetable oils into the cream prior to churning requires additional emulsifiers because the natural emulsifiers, the phospholipids from the milk-fat globule membrane, are reduced as a result of the blending. A detailed treatment of emulsifiers is available in Chapter 7.

6.3.3 Stabilisers

Oil-in-water emulsions such as milk and mayonnaise are stabilised by milk proteins such as casein and lactalbumin, vegetable protein derived from, for example, soybeans, and proteins and lecithin from egg yolk (Hoffman, 1989). Equally, when low-fat water-in-oil spreads, typically below 40% fat, are to be stabilised, similar ingredients are used, including starches and gelatine. A more recent study by Okamura *et al*. (2011) reported on the influence of emulsifiers in W/O low fat spreads for fat crystallisation.

6.3.4 Preservatives and microbiological stability

Reduced shelf-life of spreads can be caused either by microbiological or by chemical processes.

6.3.4.1 Microbiological rancidity

Yeast, bacteria or mould cause microbiological rancidity (Charteris, 2007). Their activity leads to the hydrolytic decomposition of fats and sometimes the splitting of the proteins in the water phase, with either event resulting in unpleasant taste and odour. Hence prevention of microbiological activity is important. Since microorganisms cannot usually grow in fat, it follows that it takes place in the water droplets and on the surface of yellow fat spreads. A number of additives and procedures can be used to address the problem.

- *Preservatives*. Benzoates or sorbates are added to the water phase, and benzoic acid or sorbic acid are added to the fat phase, to prevent the growth of microorganisms. Usually, the decomposition of fats as a result of microbiological activity will result in an increase in its acid value, from below 0.1% in a neutral oil to 0.3%–1.0%, which is considered too high. It should be noted that addition of sorbic acid or benzoic acid may cause the acid value to increase by 0.5–1.0% without any decomposition of the fats having taken place. Dosage rates depend on the composition of the water phase and the degree of contamination. Typical rates are 0.1–0.2%, calculated on the finished margarine. Preservatives are more effective at a pH of 4.0–4.5 than at a pH of 5.5–6.0.

- *Salt*. Sufficient addition of salt to the water phase should stop the growth of microorganisms, but this is dependent on the type of microorganism. In normal margarine recipes, a 1% addition of salt will prevent the growth of many microorganisms, but the addition of 2% will stop most. However, equally, in some instances small quantities of salt, (i.e. 0.1–0.2%), may even support the growth of microorganisms. It is maintained that it is the actual percentage of salt within the water phase that is important and not the salt content of the overall margarine. A 1% addition in a margarine containing 16% water should result in 6% in the water phase with 2% addition naturally leading to 12% in the water phase.
- *pH in the water phase*. A low pH, of 4.0–4.5, retards the growth of microorganisms whereas a high pH, 5.5–6.0, furthers growth.
- *Starch*. Microorganisms can thrive in the conditions created by the presences of starches but they can also be adversely affected.
- *Pasteurisation*. The process described for cream pasteurisation (see Section 6.3.5) applies here. Pasteurisation of the aqueous phase or the liquid emulsion will improve shelf-life stability.
- *Fat blend*. Some fats are more prone to hydrolytic activity by microorganisms than others (e.g. the lauric oils, mainly coconut oil and palm kernel oil, which develop a soapy taste).
- *Temperature*. Low storage temperatures, of 5–10°C for butter and margarine is recommended. Most microorganisms thrive at 20–30°C.

6.3.5 Emulsion preparation

A stable emulsion is a fine dispersion of one immiscible liquid in another. For butter-making the following procedures are carried out (Jebsen, 1994).

- *Separation*: cream (an oil-in-water emulsion) is concentrated to an optimal fat level of 38–42% by expelling a considerable amount of water (as skimmed milk) through centrifugal separation. With use of modern separators, the fat level in the skimmed milk may be as low as 0.05%. Milk-fat globule diameter varies from 1 μm to 10 μm. Those below 1 μm are lost in the skimmed milk, and 10% of those between 2–3 μm microns are also lost in this way.
- *Pasterisation*: heat treatment destroys many microorganisms and enzymes. Hence, a typical pasteurisation treatment of 95°C (203°F) for 15 s is often used.
- *Deodorisation*: dairy herds feeding on fresh pasture (e.g. in New Zealand) sometimes graze on weeds and shrubs. Some varieties of these weeds and shrubs impart such strong flavours that can carry through to the milk fat during biosysnthesis. In other instances, oils and high-fat fluids readily pick up aromas from the environment. Deodorisation removes these unwanted aromas and flavour taints. A vacreator is used for this purpose. Cream is heated to 95–98°C (203–208°F) through direct steam injection, which strips out and removes the aromas in the outgoing vapours. This is a severe treatment which leads to more

fat loss in the buttermilk. The cream is then cooled to 5–8°C (41–46°F) to crystallise the fat and to inhibit the growth of microorganisms.

- *Cream treatment*: this takes place in cream ripening tanks. Crystallisation technology for fat in cream differs from that of milk fat. Milk fat has a tendency to become supercooled (i.e. cooling to below its melting point without crystallisation or solidification having taken place). At this point, further subcooling cannot follow, but once crystallisation is triggered it does not abate until crystallisation is evident in the entire mass. With cream, however, crystallisation must be triggered for every single fat globule. Consequently, crystallisation of cream is time-dependent, and typically takes a minimum of 2 h at 8°C (46°F) (Berntsen, 2001). Sufficient crystallisation will minimise fat loss in the buttermilk and lead to obtain good consistency in butter. However, cream churned directly from the cooling section of the pasteuriser will result in fat loss between 50 to 100% higher than that which had been held and 'ripened' over time. If fat loss is the only criteria, then deep cooling alone would suffice but this will inevitably also contribute towards a very hard butter.
- *Cream temperature treatment*: the temperature treatment varies with the type of butter to be produced (i.e. whether it is lactic or sweet cream butter). For instance, lactic butters are preferred in Scandinavia and in most Western European countries, whereas sweet cream butter is more popular in the United Kingdom, the Republic of Ireland and New Zealand.
- *Lactic butter*: butter from cultured cream (pH 4.7–4.8) is held in a jacketed cream-ripening tank. Considerations of volume of cream to heat-transfer surface (heating/cooling area) suggest that tank volumes should not exceed 30 000 l. Tight control of temperature is also required. This allows the culture added to promote fermentation of the cream to form lactic acid and the desired flavours. Equally, the type of fat in the cream will influence the choice of cooling profile to be used. Hence the final selection is a compromise between the two. For fermented winter cream (i.e. for low-iodine-value fats (more saturated fatty acids)), the temperature cycle often used is 8°C to 19°C to 16°C. For fermented summer cream (i.e. high-iodine-value fats (relatively higher levels of unsaturated fatty acids)), the profile is 19°C to 16°C to 8°C. There may be local variations in the temperature profile used (Berntsen, 2001)
- *Sweet cream butter*: although the temperature treatment of sweet cream can be carried out in the same tanks as for lactic cream, it is often in much larger silos. For winter sweet cream (low-iodine-value fats), the temperature profile is typically 18–21°C then 14–16°C followed by 8–10°C before churning.

The important aspects of process change that take place during churning are (Jebsen, 1994; Ranjith and Rajah, 2001):

- The emulsifiers, particularly the milk-fat globule membrane, which stabilise the original oil-in-water emulsions, are inactivated by aeration.

- Phase inversion results, and the oil becomes the continuous phase (i.e. the water-in-oil emulsion found in butter). However, the butter emulsion is complex. Unlike margarine emulsions it will contain some oil-in-water droplets, arising from still-intact milk-fat globules. Hence, butter is a mixed emulsion. The free fat (continuous phase) acts as a lubricant. If the amount of lubricant is insufficient, the consistency of the butter is likely to be 'short' or 'brittle'. Rapid cooling of cream results in fast crystallisation and this leads to the creation of many small crystals with a large total surface area. These crystals can bind much of the liquid (noncrystallised) fat; that is, the fat is retained within the globule and thereby the amount of fat available to form the continuous fat phase is reduced, with the consequence that the butter will be hard. Conversely, with slow cooling of the cream, large crystals, with total individual surface area far exceeding that of the small crystals obtained from rapid crystallisation, will form, thereby squeezing out a larger portion of noncrystallised liquid fat from the globules. This forms a more distinct and larger continuous fat phase and hence a relatively softer butter. Therefore, for a more plastic and spreadable butter there needs to be a distinct and dominant continuous fat phase. It is noted that Kerrygold Lighter Softer, launched in May 2009 as a healthier spread with reduced fat and salt, is unlike other spreadable butters as it does not use vegetable oil to soften it. Instead, it is reported that they use a heating and cooling process (*The Grocer*, 2010b).
- Butter consistency is affected by the melting point of the milk fat and the size and composition of the fat crystals.

For the manufacture of margarine and low-fat spreads, the following stages are of primary importance:

- preparation of the water phase;
- preparation of the fat phase;
- emulsion preparation;
- chilling, crystallisation and kneading;
- packing or filling.

6.4 Process technology

6.4.1 Current yellow fat range

The current market for yellow fat spreads is summarised in Table 6.4. Higher-fat-content spreads such as those from Denmark based on omega-3-rich nonhydrogenated fish oil have been prepared with up to 95% fat. Equally, concentrated butter (up to 97% fat) is available in Europe as beurre cuisine (cooking butter), at a part-subsidised price, strictly for domestic consumption. If required, this butter can be emulsified further, with addition of water and mechanical working with a domestic blender, into

Table 6.4 Spreads in the market: yellow fats.

Percentage of fat				
80–82[a]	55–75[b]	39–41[c]	20–25[c]	0–5[c]
Butter and recombined butter lactic sweet cream (unsalted, slightly salted and salted varieties) Other butters: savoury additives (e.g. garlic, chives); sweet additives (e.g. brandy butter)	Butter with 60% fat Clotted cream Dairy blends Vegetable oil blends	Butter with 40% fat Dairy blends Vegetable oil blends	Mainly vegetable oil blends	Vegetable oils Nonfat varieties (e.g. mimetics such as globulised egg or whey protein, sucrose polyester)
Margarine unsalted slightly salted salted	Mainly slightly salted and salted varieties	Only slightly salted and salted varieties	Only slightly salted and salted varieties	Only slightly salted and salted varieties

Notes: [a]Both groups of products are available in spreadable or packet (stick) form. Pourable margarine is also available.
[b]All groups are available mainly in spreadable form.
[c]All groups are available in spreadable form only.

a spread. In Italy, bread is eaten dipped into fresh virgin olive oil (100% liquid oil). Ghee (99.8%) and vanaspati (100%) are also used on appropriate hosts which, in some cultures, include bread.

6.4.2 Scraped-surface cooling

6.4.2.1 Drum

This is no longer used as a commercial route for producing spreads and so will not be considered here. The most well-known system is the Diacooler, manufactured by Gersternberg and Agger (Denmark).

6.4.2.2 Tubular action

The schemes available for producing butter or butter–vegetable oil spreads with use of scraped-surface cooling and mechanical working are as follows:

- Phase inversion of high-fat cream. Three pathways are available:
- creams of with greater than 75% fat undergo phase inversion and are then cooled and texturised mechanically, following one of two routes: in the Alfa Laval, Alfa, New Way and Meleshin process, the cream is destabilised during cooling and mechanical working; in contrast, in the Creamery Package and Cherry Burrell (Gold ‘n’ Flow) process, phase inversion takes place before the cooling and working stage.
- 60% fat, phase inversion to 60% butter.

- 40% fat, phase inversion to 40% butter (although this is claimed to be feasible, it is necessary to ensure that, without additives, the water droplet size will not be too large and cause either microbiological or emulsion breakdown).
- Ammix process: cream is added to anhydrous milk fat (AMF) to produce 80% butter. The Ammix process, developed in New Zealand, claims to improve on earlier processes. In principle, a proportion of the cream from the same batch is converted to AMF. The two phases are brought together and scraped-surface cooling and pin working are used to convert an emulsion of the AMF, cream and brine into butter (Rajah, 1992).
- Pacillac process: a mixture of butter and vegetable oils produces 80%-fat or lower-fat spreads.
- Pacillac process: butter and milk protein serum are mixed to produce 60%-fat and 40%-fat butter.
- AMF (or a substitute with milk-fat fractions for spreadable butter (Deffense, 1987, 1993)) is added to milk solids to produce 80%-fat or lower-fat-content butter by using a butter recombination process (Munro, 1982).
- AMF, vegetable oils/fats and milk solids are mixed to produce 80%-fat butter blends.

Today, some of the well-known scraped surface equipment manufacturers and associated branded technology have been consolidated under SPX Gerstenberg Schröder (GS Nexus, Perfector and Kombinator technology) and Waukesha Cherry Burrell (Votator II®), TMCI Chemtech (Series 2 and Series 4 Chemetator), with Phropines Manufacturing still remaining independent (Phrocessor and Phrotator, with two further models to handle palm oil-based products and higher pressure ratings).

A typical plant manufacturing margarine, shortening and yellow fat spreads will feature the following:

- Holding or mixing tanks: to enable minimum holding times, small batch sizes are used.
- Automated load cell batch control: this ensures maximum weight accuracy.
- Digitalised control system interfaced with computer-driven programs: this facilitates repeatability, record tracking and advanced stock or plant performance monitoring.
- Pumps: typically variable-speed triplex piston pumps fitted with a hygienic pulsation damper in order to achieve a constant flow, free of pressure variation, are used. This feature is particularly important in 100% fat products where compressed gas injection and entrainment are required (e.g. aerated shortenings). Pressure pulsations result in coagulated bubbles appearing as streaks in the final product.
- A pasteurisation unit for emulsions: scraped-surface heat exchangers (SSHXs) are also being used for pasteurisation of low-fat emulsions containing large amounts of emulsifiers and stabilisers. This treatment is carried out at about 80°C.

The use of SSHXs prevent 'burn' of the milk proteins (i.e. caseinates) and of starches used in the formulations; consequently fouling of the pasteurisation surfaces are avoided. Cooling to 40°C is then completed in tubular coolers.

- Aerating unit: this is a gas injection system capable of sparging compressed gas (usually nitrogen) into the fat and is required for the purpose of creaming or whitening fats or to add body (volume) and/or soften the fat. The injection probe is typically manufactured from sintered stainless steel in order to ensure a very fine dispersion of gas, a significant technological improvement over the earlier crude orifice-type injection system. Typically, the injection system is located before entry into the first SSHX.
- Inverter: this phase inverts an oil-in-water emulsion into a water-in-oil emulsion.
- Scraped surface units (also referred to as A units): the development of crystals and crystallisation take place in these units.
- Working section units (also referred to as B units): the fat passes into a worker unit and undergoes further crystal development and growth while at the same also being physically broken and worked to aid texturisation. The worker unit is designed as a tubular structure with a central rotor shaft containing an arrangement (in some systems a semihelical arrangement) of pins that intermesh with static pins on the tube surface. The pins on the rotor shaft are removable in some systems (e.g. Phrotex), therefore offering the opportunity to reduce shear when all other conditions of temperature and pressure are adjusted to aid crystal development.
- Resting section or tube (also referred to as C units): this unit is required for packet or stick-type spreads and for higher melting pastry margarines and fats.
- A range of stainless steel piping and holding and melting facilities for reworking leftover blends and fats.

The principle underlying the operation of an SSHX remains unchanged, but the technology has been revised to account for market needs. For instance, in the 1960s SSHXs were rated up to about 40 bar g pressure, and these coped adequately with the margarine and shortening manufacture of the day. Many were also driven by gear pumps. However, with increased use of higher melting fats, units capable of 100–160 bar g pressure are now standard. To overcome the inherent problems of slip in gear pumps, triplex piston pumps have been introduced.

Four schematics are presented (courtesy of Chris James Consultants and Propines Manufacturing) (Figures 6.12–6.15). Three show the principles of plants producing tub margarines, pastry margarines and reduced fat spreads. The fourth schematic shows the typical full layout of a modern plant producing yellow fat spreads.

1. FS1S022C – Tub/cake margarine
2. FS1S021C – Pastry margarine
3. FS1S029C – Reduced fat spreads
4. FS2S205A – Flow sheet for pastry margarine and shortening.

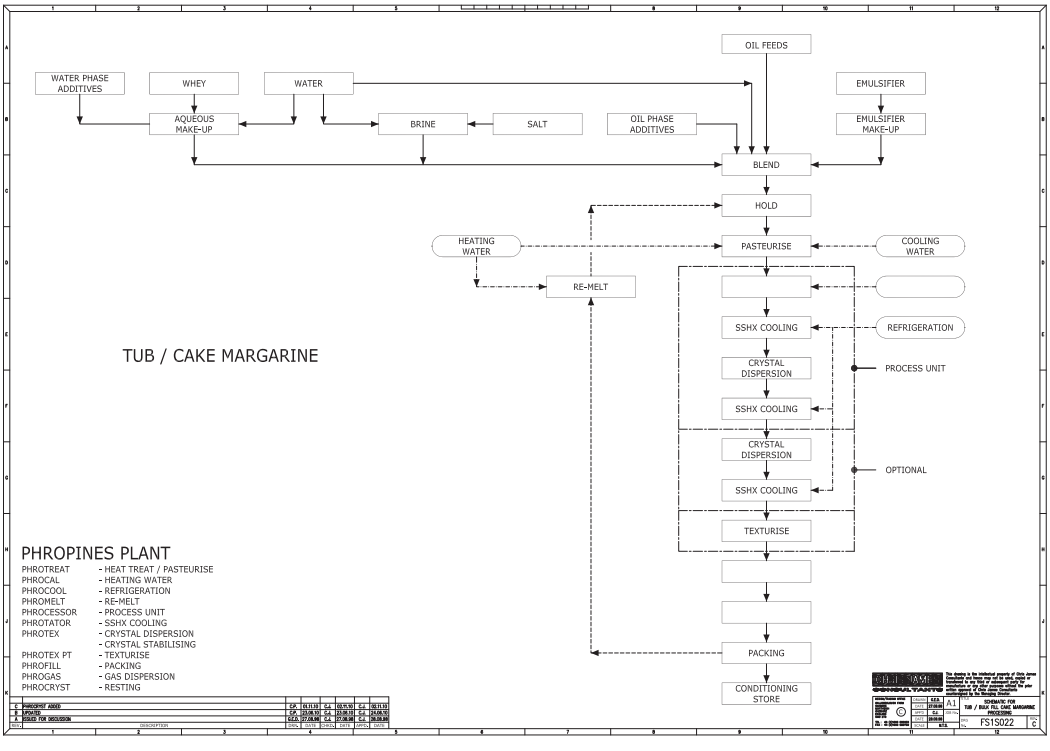


Figure 6.12 FS1S022C – Tub/cake margarine. *Source:* Courtesy of Chris James Consultants and Propines Manufacturing.

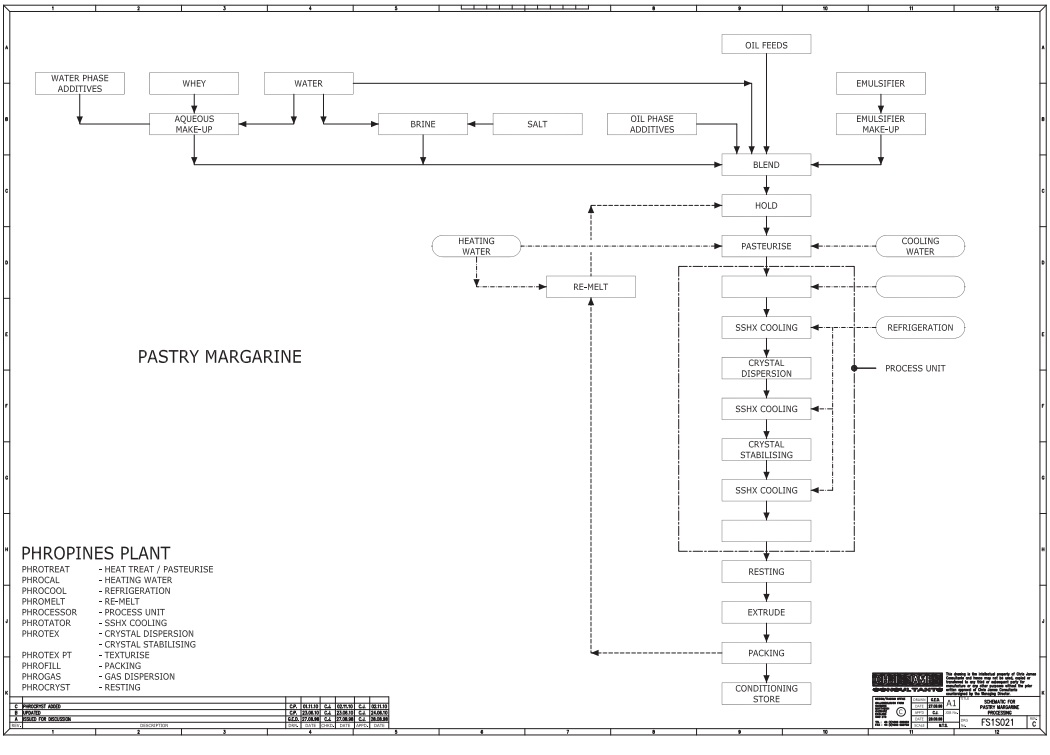


Figure 6.13 FS1S021C – Pastry margarine. *Source:* Courtesy of Chris James Consultants and Propines Manufacturing.

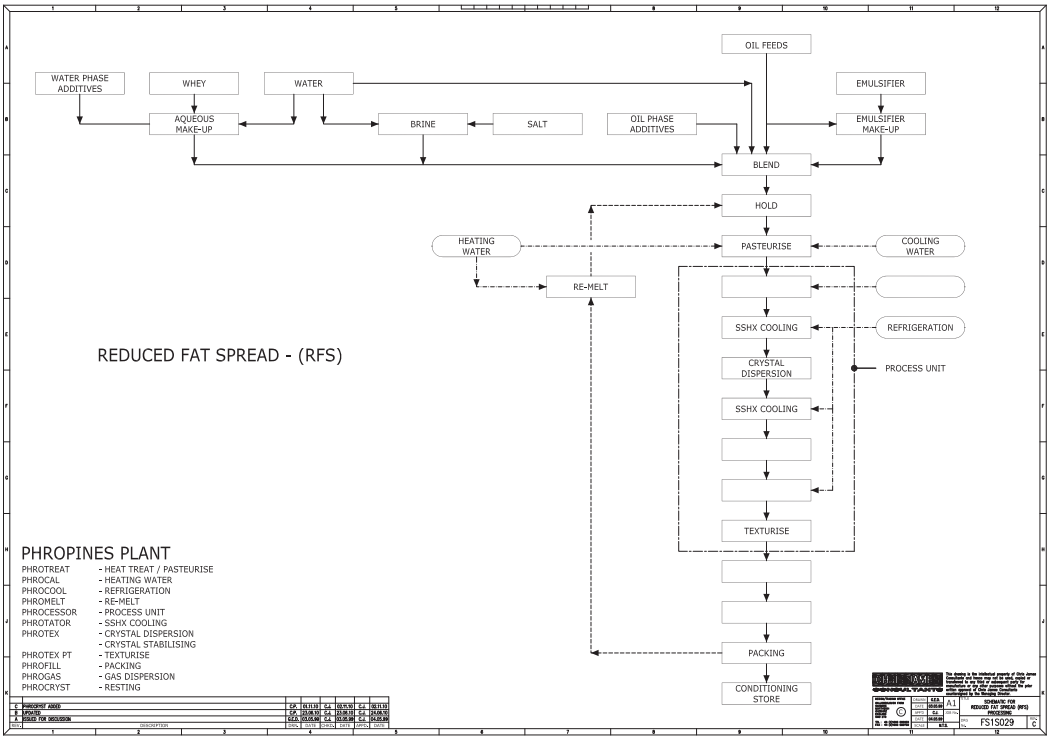


Figure 6.14 FS1S029C – Reduced fat spreads. *Source:* Courtesy of Chris James Consultants and Propines Manufacturing.

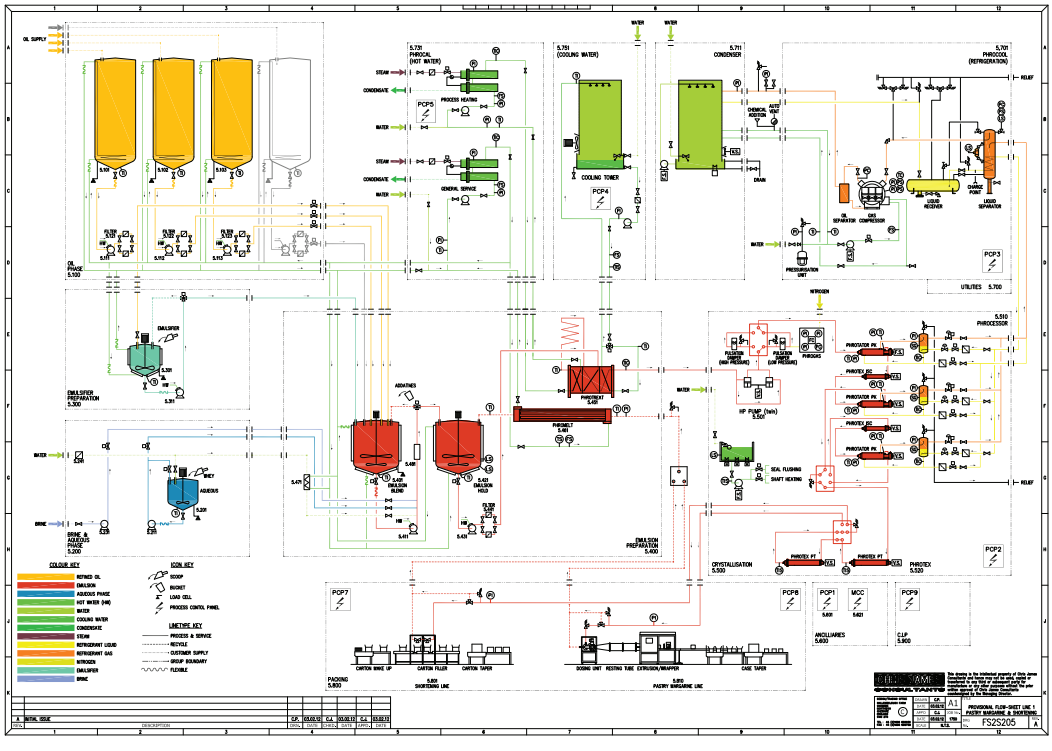


Figure 6.15 FS2S205A – Flow sheet for pastry margarine and shortening. *Source:* Courtesy of Chris James Consultants and Propines Manufacturing.

Most SSHX units are constructed of high-yield carbon steel tube and hard chromium plated on a nickel base giving maximum heat exchange capability within a high-pressure cylinder. A number of blade arrangements are available. Typically, the Phrotators are fitted with a balanced 2 mm cut-away 'floating' blades of a design that promotes turbulence, and hence further heat exchange, at the rear of the blade tip. The Perfectors may be fitted with a 'sword' knife system consisting of long heavy stainless steel holders with inserted replaceable plastic blades. The knives are mounted on the knife rotors so that they are movable at their fixing points. At high rotation speed, the blades or knives are pressed against the tube surface mainly by centrifugal force. Towards the end of the crystallisation process, a low rotation speed may be used, the blades or knives now being pressed against the tube mainly by product pressure. The blades or knives are fitted onto temperature-controlled rotor shafts. Close control of the rotor temperature is achieved through the flow of tempered water (close to the temperature of the fat) in the annular space between the rotor shaft and an inner tube.

Manufacturers offer two-bladed or three-bladed shafts at the periphery. It is often argued that three-bladed shafts offer 'a balanced pressure stress reaction at the shaft and so resist the promotion of stress-related shaft vibration, always a potential with high viscosity products such as puff pastry fats'. However, the high level of engineering evident in both systems appears to mitigate against this argument.

Eccentric shafts (BP 842,310) were developed by the Chemetron Corporation (Votator Division). They are claimed to provide more intensive cooling for high melting bakery margarines as well as a certain amount of kneading and a compressive action similar to that provided by the roller, table and helical worm treatment in the older type of plant. Most of the SSHX units available today have the rotor in a central position.

SSHXs also contain an annular space. The annular space is the area between the centre shaft and the inner wall of the SSHX. The distance between the shaft and wall is important for crystallisation. A small annular space contributes to a high degree of crystallisation; important, for example, in puff pastry production, whereas larger dimensions cause less shear and therefore may be important for low-fat (high-moisture) products. Typically, the annular space between the rotor shaft and the tube surface is 8–20 mm.

The rotor speed is also of importance. The frequency at which surface scraping (or cutting speed) takes place determines the types of crystals being formed and worked. The conditions will therefore be set based on the product being processed. Two factors contribute towards achieving the best results: the rotor speed (typical range, 300–700 rpm) and the number of blades fitted at the periphery. To aid in the control of rotor speed manufacturers offer variable speed or fixed-speed drives (most offer two-speed drives).

6.4.3 Churning technology

6.4.3.1 Batch process

The development of the butter churn pre-dates the 1900s. They consisted primarily of a wooden barrel that rotates on its horizontal axis. These barrels were fitted with internal side baffles that lift and drop the cream to create the necessary working action.

6.4.3.2 Continuous process

Significant changes took place in the 1930s, when continuous butter-making techniques and processes were developed (McDowall, 1953). Details have been described by Jebsen (1994). Several process techniques are now available to produce spreadable butter:

Butter is subject to seasonality effects. In many Western countries cattle feeding practices are dictated by the season (i.e. cows graze during the milder spring and summer months and are on solid feed during winter). Hence, selection of milk (and therefore cream) from cows fed only on fresh pasture, which leads to higher levels of unsaturated fatty acids in the milk fat, will result in a relatively softer butter. Typically, in the UK, summer butter churned from Friesian cows' milk has N_{20} values of 13–18% solids (solid fat content (SFC)) compared with 18–22% for winter butter. Irish butter is typically 13–16% solids. Supermarkets sell these butters packed in tubs, adding further to the perception of a more spreadable butter relative to what is perceived to be normal butter.

Monobutter is produced from the milk of lactating cows fed a diet rich in full-fat rapeseed (in excess of 20% of diet) or soybean in a concentrated mixture. The milk produced has an altered fatty-acid content in the milk fat (Charteris, 1991). This change improves the physical and nutritional properties of butter such that the high stearic acid (C18 : 0) content from the oilseeds is desaturated in the gut wall and mammary gland to oleic acid (C18 : 1). This is subsequently secreted into the milk. Murphy *et al*. (1990) found that, typically, the palmitic acid (C16 : 0) level is reduced and the oleic acid is increased. Consequently, the SFC at 10°C is reduced from 40–45% (characteristic of Irish butter) to 30–32%, making the butter spreadable from the fridge.

Other techniques consist of:

- whipping: this consists of aerating with nitrogen;
- work softening: mechanical working of the butter;
- temperature treatment (Alnarp treatment): this involves temperature cycling of cream prior to churning;
- addition of fractionated milk fats to the cream;
- addition of vegetable oils (e.g. Bregott development; see Figure 6.16);
- addition of vegetable-oils-based cream (artificial cream).

Moran (1991) elegantly encapsulated the variations in the manner of adding vegetable oil by identifying three inventions that best describe them:

- British Patent (1968): this involves addition of liquid oil to dairy cream, emulsification prior to ripening and churning, up to 30% of the fat phase being nondairy
- European Patent (1984): this involves addition of liquid oil and partially hydrogenated bean oil to dairy cream, emulsification prior to pasteurisation, ripening and churning, the final fat phase containing at least 35% nondairy fat
- European Patent (1985): crystallisable vegetable cream is prepared separately and blended in with a dairy cream; the mixture is churned with liquid vegetable oil; the final fat phase contains 50% or more nondairy fat.

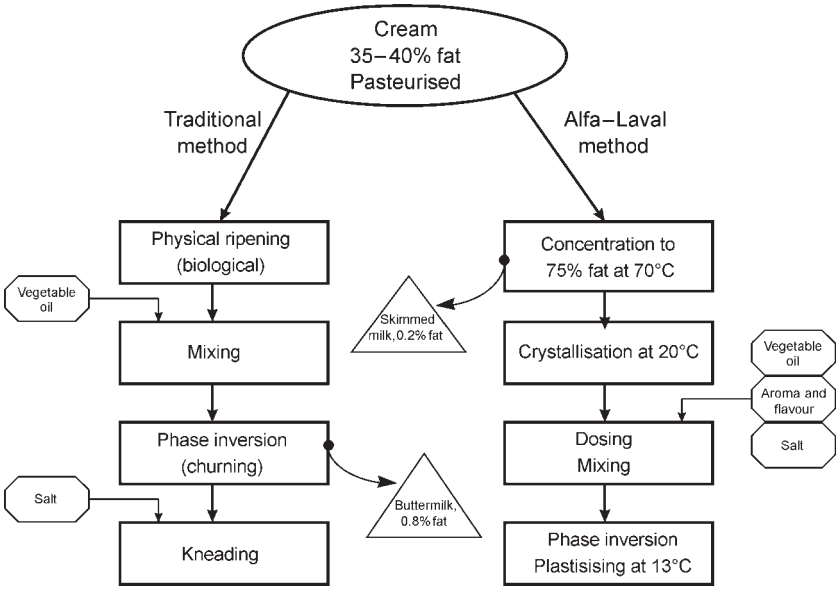


Figure 6.16 Bregott manufacture; percentages are the solid fat content.

One drawback of these processes is that the buttermilk will contain vegetable oils. Since authentic buttermilk or buttermilk powder is a premium-priced food ingredient in its own right, this may restrict its application. To overcome this, another route is now available (Studer, 1990): butter is produced from the churn. Fresh or stored butter is then softened and re-emulsified with a serum rich in dairy protein (i.e. caseinates) and vegetable oils to produce a spreadable 80% fat product. Equally, with the absence of vegetable oils 60% and 40% fat butter can be produced. The re-emulsified blend is crystallised in a closed tubular chiller (scraped-surface cooling) and is mechanically worked before packing. These lower-fat butters are also more spreadable compared with the freshly churned 80% butter.

6.4.4 Storage conditions

It is good practice to store butter in tightly sealed, polymer-lined cartons. If the product is partially used, then the container should be resealed without removing the balance of product from its original polymer lining and should be stored in a humidity-controlled (80–85%) room. Typically, good-quality bulk butter can be stored up to four months when refrigerated (0–3°C; 32–38°F), or up to one year when frozen (−23°C to −29°C; −10°F to −20°F). In Europe, butter stored frozen in EU intervention stores have been found to be of satisfactory quality after two years.

When thawing, or ‘conditioning’ as it is sometimes referred to by butter traders in Europe, it is important to remove butter cartons (boxes) from tightly stacked pallets and to distribute them around a temperature-controlled room with good ventilation and

good air circulation. The cartons should also be moved occasionally, to ensure that all sides of each carton are thawed slowly and evenly. Humidity should be controlled and not exceed 20%; room temperature should not exceed 21°C and preferably be at 16–18°C (60–65°F). Under these conditions, typically, a 25 kg block (Europe) or 68 lb block (USA) will take 4–5 days to thaw to 0–3°C (32–38°F).

With respect to spreads, the results reported by Pothiraj *et al*. (2012) could be useful when assessing the melting and texture properties during ageing. Lin *et al*. (2008) looked at the effect of oil phase transition on freeze/thaw-induced demulsification of water-in-oil emulsions.

6.5 Yellow fat blends

6.5.1 Trans-fatty-acid-free oil blends

Margarines with low or no *trans* fatty acids are now an important part of the shopping basket in many developed economies. Consumer preference for low-*trans*-fatty-acid products has focused attention on the C18 : 1 and C18 : 2 *cis–trans* isomers (Menaa *et al*., 2013; Piller, 2011). These are normally absent in vegetable oils while milk fat has about 5% occuring naturally. However, during the hydrogenation reaction the *cis–cis* isomers convert to the *cis–trans* form. This is dependent on the process conditions and the catalyst used and can result in large amounts of the latter being formed.

However, the interesterification reaction does not progress in this direction and is therefore often the preferred route when low-*trans*-fatty-acid hardstock is required (MPOB, 2001; Teah *et al*., 1994). In 1996, a collaborative research project between the Palm Oil Research Institute of Malaysia (PORIM), now part of the Malaysian Palm Oil Board (MPOB), and the Joint Stocks Society Soyuzmargarinprom, Russia, found that formulations based largely on palm oil can be used to produce low-*trans*-fatty-acid table and industrial margarines with properties matching those of equivalent conventional Russian products. PORIM based its formulation on interesterified (IE) palm products, whereas the Russian products were formulated based on hydrogenated sunflower oil (HSFO). The margarine based on the PORIM formulation had a *trans*-fatty-acid content of less than 1% compared with 14.1% in the conventional Russian product (see Table 6.5 and Figure 6.17).

More recently, Berger and Idris (2005) also considered the formulation of zero-trans acid shortenings and margarine and other food fats with products of the oil palm.

6.5.2 Some properties of butter

A comparison of UK summer and milk fats is provided in Table 6.6.

6.5.3 Oils high in lauric and palmitic fatty acids

These are palm kernel and coconut oils, and palm oil, respectively. The amount of palm oil used in the fat blend for good-quality soft table-margarine is 30%, but up to 40%

Table 6.5 Low-*trans*-fatty-acid margarine formulations for the Russian market (MPOB, 2001).

	Solid fat content (%)	
Temperature (°C)	Russian formulation[a]	PORIM formulation[b]
5	44.5	43.2
10	34.9	33.3
15	22.9	21.0
20	13.9	14.2
25	6.4	6.5
30	2.5	2.5
35	trace	trace
37	0.0	trace
40	0.0	0.0
Total trans fatty acids (%)	14.1	<4.1

Notes: [a]Russian formulation: HSFO : PO : SFO = 36 : 44 : 20; slip melting point, 32.7°C.
[b]PORIM formulation: IE(Poo : PKO) : SBO = 80IE(75 : 25) : 20; slip melting point, 31.5°C.
Note: HSFO, hydrogenated sunflower oil; IE, interesterified; PKO, palm kernel oil; PO, palm oil; POO, palm olein; SBO, soybean oil; SFO, sunflower oil.
Source: MPOB (2001). Reproduced with permission from the Malaysian Palm Oil Board.

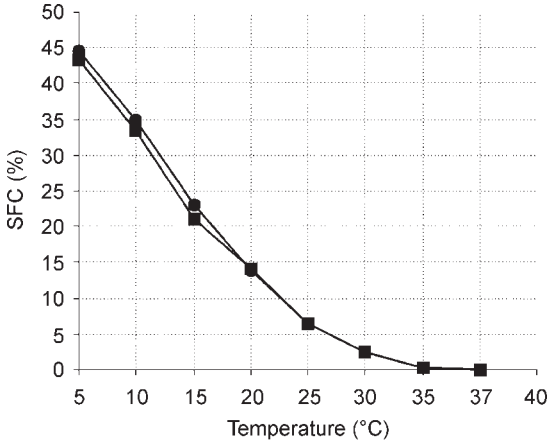


Figure 6.17 Solid fat content (SFC) of low-trans-fatty-acid table-margarine for the Russian market. For details of the formulations, see Table 6.5. Notes: —●— Russian formulation, —■— PORIM formulation. *Source:* MPOB (2001). Reproduced with permission from the Malaysian Palm Oil Board.

can be used without significant difference. Up to 60% palm olein is recommended but palm stearin should not be more than 10% of the fat phase (MPOB, 2001). However, up to 50% of palm oil can be used in the fat phase of packet margarine, while a 100% blend of palm oil and its derivatives can be used in tropical margarines (Table 6.7).

The physicochemical characteristics of palm-based oil blends for the production of reduced fat spreads has also been reported (Lida and Ali, 1998).

High levels of palm oil inclusion can lead to product quality problems (i.e. slow cooling and post-hardening, both caused by the glyceride composition and high

Table 6.6 Properties of UK summer and winter milk fats.

Properties	Summer	Winter
Flavour	Rich in flavour precursors	Lower flavour level
Typical colour (carotene, ppm)	6–8	4–6
Vitamins	Rich in vitamins A and E	Relatively lower levels of vitamins A and E
Oxidative stability	Relatively more stable	Stable
Degree of unsaturation	Increase in unsaturated fatty acids	Increase in saturated fatty acids
Typical melting point range (°C)	28–32	30–35
Solid fat content (N_{20}, %)	13–17	18–22

Source: Robinson and Rajah (2002).

Table 6.7 Typical formulations (as percentages) of soft margarines consisting of oils high in lauric, palmitic, oleic, linoleic and linolenic fatty acids.

	Blend				
Oil[a]	A	B	C	D	E
Palm oil (C16 : 0, 40.9–47.5 wt%)	30	0	50	0	0
Palm olein (C16 : 0, 38.2–42.9 wt%)	0	25	0	22	0
Palm stearin (C16 : 0, 49.8–68.1 wt%)	0	0	0	0	0
Palm kernal oil (C12 : 0)	15	0	0	0	0
Palm kernal olein (C12 : 0)	0	0	10	0	0
Hydrogenated palm oil (42°C)	0	25	5	20	0
Canola oil[b] (C18 : 1)	55	0	0	0	50
Soybean oil[b] (C18 : 2, C18 : 3)	0	0	35	0	0
Sunflower oil[b] (C18 : 2, C18 : 3)	0	50	0	58	0
Interesterified palm stearin and palm kernel olein	0	0	0	0	50

Note: [a]Figures in parentheses give the fatty-acid composition and the percentage of methyl esters.
[b]These soft oils are interchangeable and can replace each other without significant changes to product texture.
Source: MPOB (2001). Reproduced with permission from the Malaysian Palm Oil Board.

levels of partial glycerides). These problems can be overcome by close control during scraped-surface cooling and working. The main solutions to problems involve increasing the residence time and the amount of agitation and operating at lower temperatures and higher pressure. Alternatively, hydrogenated or interesterified palm oil or palm kernel oil can be used. These fats crystallise at much faster rates than standard palm oil, and so increasing their ratios in the blend can be useful (MPOB, 2001).

6.5.4 Long-chain fatty acids

There are found in fish oils. Typical usage of fish oil in margarine formulations is in the hydrogenated form, normally at a melting point of at least 30°C–32°C. This is because oxidation of specific long-chain fatty acids in these oils causes an objectionable fishy taste and smell. Hydrogenation eliminates the tetraene, pentaene and hexaene fatty acids and significantly reduces the levels of trienes, thereby resolving the problem. However, these are also the fatty acids of the omega-3 (ω-3) group, specifically the long-chain polyunsaturated fatty acids (LCPUFA), eicosapentaenoic acid

(EPA, C20 : 5) and docosahexaenoic acid (DHA, C22 : 6), which are understood to impart health benefits. The hydrogenation reaction reduces much of the unsaturation in these fatty acids and, consequently, they lose their beneficial biological effects. Therefore, although, worldwide, fish stocks are depleted and hydrogenated fish oils are no longer used in many countries, the use of unhydrogenated fish oil is still being considered for margarine manufacture. A typical formulation used consists of 20% unhydrogenated fish oil, 25% hydrogenated palm oil and 55% soyabean oil (there forming 95% of the total margarine).

6.6 Flavoured butters

The premium quality flavoured butters sector is still relatively small but growing. In 2010, this sector was worth £5 million in the UK alone (*The Grocer*, 2010a). The major butter producers have not weighed into this business except for Lurpak which was one of the first to experiment in this sector by launching a garlic-infused butter in 2003. French high end butter brand Isigny Sainte Mère launched a sampling pack of three products in December 2009 infused with French-grown mushrooms – truffles, ceps and morels. However, much of this market is being left to the smaller players, an example of which is the speciality food producer Enrich Your Food, based in Somerset, UK. They make butters with seasonal flavours, such as roasted garlic, wholegrain mustard, spiced honey, lime and chilli, and Somerset cider brandy.

6.7 Non-yellow fat range

A number of products are evident and are challenging the dominance of yellow spreads. Changes in lifestyle, health concerns and heavy media campaigns by manufacturers are contributing towards important structural changes in the spreads market towards more savoury and sweet spreads. Equally, the substantial growth witnessed in the sandwich market has also opened up the market for oil-in-water spreads such as mayonnaise, which is used in a variety of ways including as a mix with chopped vegetables (e.g. in coleslaw) or with chopped ham and sweet corn, etc., for sandwich fillings.

Examples of sweet spreads are:

- chocolate spreads (e.g. Nutella® and similar products);
- fruit-based spreads (e.g. Brown and Brummel and similar products in the USA, i.e. fresh fruit in yellow fat);
- coconut cream jam (Kaya) from Malaysia, Singapore and Indonesia;
- low-fat or no-fat spreads (e.g. lemon curd, jam, marmalade, etc.).

Examples of savoury spreads are:

- Philadelphia cheese and similar products (not only in Europe and the USA but also in many countries in the Southern hemisphere);

- peanut butter (significant in the USA and gaining an important market share in Europe and the Far East);
- low-fat or no-fat spreads (e.g. Marmite®, which is a yeast extract popular in the UK).

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7

Emulsifiers and stabilisers[1]

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7.1 Introduction

Fats are important structural components of many food materials, and successful control of their ultimate functionality usually requires advocacy of a mulitidisciplinary approach (Wassell *et al*., 2010; Wassell and Young, 2007), as well as stringent control of levels of *trans* fats and not least saturates (Young and Wassell, 2008a). Within food systems, fats interact with the other component parts predominantly at the interface between two distinct phases, of which three are important in foods:

- liquid–liquid (emulsions)
- air–liquid (foams)
- solid–liquid (dispersions).

Thus, it is crucial to control the physical nature of such interfaces to produce successful, high-quality food products. This is achieved through adroit use of emulsifiers and stabilisers, which may be intergral components of an ingredient (e.g. egg yolk from eggs) or individually (e.g. monoglyceride).

The Food and Drug Administration (FDA), and European Union EU have defined these ingredients as follows (Table 7.1).

Emulsifiers are generally relatively small molecules (molecular weight less than 1000 Da), whereas stabilisers and thickeners are typically biopolymers such as hydrocolloids and proteins. Several books are available that cover the use of these types material in detail (Akoh and Min, 2002; Gunstone, 2008; Hassenhuettl and Hartel, 2008; Phillips and Williams, 2009).

[1]The original chapter was written by Clyde E. Stauffer.

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Table 7.1 Definitions of emulsifiers, emulsifying salts, stabilisers, thickeners and surface active agents from the FDA, and EU.

Substance	EU	FDA
Emulsifiers	Substances which make it possible to form or maintain a homogeneous mixture of two or more immiscible phases such as oil and water in a food stuff	Substance which modify surface tension in the component phase of an emulsion to establish a uniform dispersion or emulsion
Emulsifying salts	Substances which convert proteins contained in cheese into a dispersed form and thereby bring about homogeneous distribution of fat and other components	
Stabilisers	Substances which make it possible to maintain the physico-chemical state of a foodstuff; stabilisers include substances which enable the maintenance of a homogeneous dispersion of two or more immiscible substances in a foodstuff, substances which can stabilise, retain or intensify an existing colour of a foodstuff and substances which increase the binding capacity of the food, including the formation of cross-links between proteins enabling the binding of food pieces into re-constituted food	Substances used to produce viscous solutions or dispersion, to impart body, improve consistency, or stabilise emulsions, including suspending and bodying agents, setting agents, jellying agents, and bulking agents, etc.
Thickeners	Substances which increase the viscosity of a foodstuff	
Surface active agents	Foaming agents: substances which make it possible to form a homogeneous dispersion of a gaseous phase in a liquid or solid food stuff. Anti-foaming agents: substances which prevent or reduce foaming.	Substances used to modify surface properties of liquid food components for a variety of effects, other than emulsifiers, but including solubilising agents, dispersants, detergents, wetting agents, redhyration enhancers, whipping agents, foaming agents, and defoaming agents, etc.

Source: Data from the FDA and EU.

7.2 Surface activity

7.2.1 Surfactants

A surfactant, or emulsifier, is a molecule, or moiety, that migrates to interfaces between two physical phases and is concentrated in the interfacial region rather than in the bulk. As such, surfactants are amphiphilic in nature, with the lipophilic, or hydrophobic, part of the molecule preferring to be in a lipid, nonpolar, environment and the hydrophilic part preferring to be in an aqueous, polar, environment in, say, an oil and water mixture. The thermodynamic free energy of the system is at a minimum when the lipophilic part is in the oil, or air, phase and the hydrophilic part is in water. The

emulsifier concentrates at the oil/water interface, thus reducing the free energy of the interface or interfacial tension (γ) compared to the absence of the emulsifier.

Emulsifiers are therefore used within food systems to decrease the surface tension of dispersions, emulsions, foams and suspensions, where stabilisation of the two phase products is required. Such uses can include stabilisation of water in oil (W/O) emulsions, such as margarine; or stabilisation of oil in water (O/W) emulsions, such as mayonnaise or ice cream; or improving the crumb structure or volume of baked goods such as bread or cakes.

Lipid-based emulsifiers can be anionic, cationic, nonionic or zwitterionic in character, but all have a long-chain fatty acid tail. In the food industry the predominant types are nonionic, anionic or zwitterionic, examples being monoacylglycerols, fatty acids and lecithin respectively. Nonionic surfactants are relatively insensitive to pH and salt concentration whereas the functionality of the anionic and cationic types can be markedly influenced by pH and ionic strength. Cationic emulsifiers are not used since they are toxic.

7.2.2 Surface and interfacial tension

The surface tension of a solution of a surfactant is lower than that of the pure solvent. Surface tension is, roughly, a linear function of the natural log, (ln), of the surfactant concentration up to the critical micelle concentration (cmc) (Figure 7.1). Above the cmc the thermodynamic activity of the surfactant does not increase with the addition of more surfactant, and the surface tension remains constant.

Application of energy, mixing, increases the amount of interface, and can be thought of in terms of an oil and water mix in a flask. Gentle shaking of the flask results in few large droplets with little addition to the interfacial area; whereas vigorous shaking creates many small droplets and considerable increase in the interfacial area. This now gives the system a higher total free energy. This free energy is due to the presence of

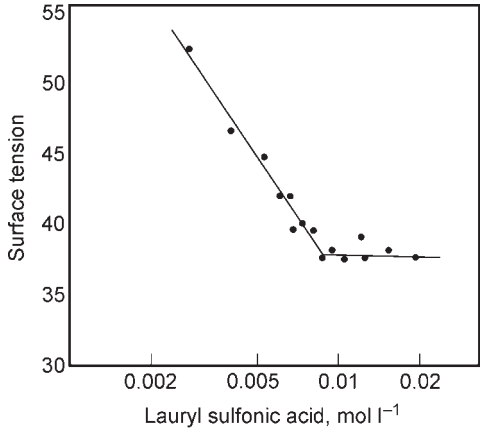

Figure 7.1 Surface tension of lauryl sulfonic acid solutions.

the interface, and is expressed in milli-Newtons per metre (mN m^{-1}). It is referred to as interfacial tension or surface tension, and these terms are synonymous.

Hence, it would appear that a larger number of droplets would be advantageous. Indeed, decreasing the droplet size and increasing the droplet size distribution influences the bulk physicochemical, organoleptic (McClements, 2004) and therefore psychophysical properties of the emulsion, for example, stability, texture, taste, appearance, and perception thereof. However, in order to reduce the emulsion droplet size, one has to exert enough disruptive force such that one overcomes the interfacial forces which hold the droplet together! This force is termed the Laplace Pressure, and is given in Equation 7.1.

$$\Delta P_L = \frac{4\gamma}{d} \tag{7.1}$$

where ΔP_L is the Laplace Pressure acting across the interface, γ is the interfacial tension between the oil and the water, and d is the droplet diameter.

The implications of Equation (7.1) indicate that the internal pressure of small bubbles is greater than that of large bubbles, which has practical consequences in aerated food systems. In cake batter, a well-homogenised emulsion system, the small air bubbles will, over time, decrease in number, while the larger bubbles increase. Thus, the cake batter becomes unstable over time, which in ultimate consequence could give the final baked cake a poorer, less even crumb structure, and a corresponding loss of volume. However, this migration of air has little impact on the bowl-lickers that are out there, since it occurs over longer timescales! The migration of the gas is due to its dissolution into the aqueous phase because of higher pressures, and it then enters the larger bubbles – areas of lower internal pressures. Similar effects are expected in other foods where the continuous phase may act as a conduit for gases dissolved from within the bubble. The same pressure differential applies to a dispersed condensed phase (e.g. oil droplets in water) but has no practical consequences for food systems.

7.3 Interface formation

7.3.1 Division of internal phase

In practical terms, interfaces are formed simply by mixing oil and water, but this simple bipartite co-existence is insufficient to form the basis of stable emulsions. For stable emulsion formation, work must be done to break the two-phase system into droplets, usually by mechanical mixing such that the average droplet diameter ranges from 1–100 μm. Stirring such an oil water mixture first of all forms droplets, which are further distorted into cylinders and finally to smaller droplets, where the deformation is in line with the shear field (Figure 7.2). The stirring process continues until the droplet size cannot become smaller, that is, cannot be further subdivided.

At large droplet diameters, the shear forces of mixing or homogenisation are greater than interfacial tension forces, the droplets are distorted, and subdivision occurs.

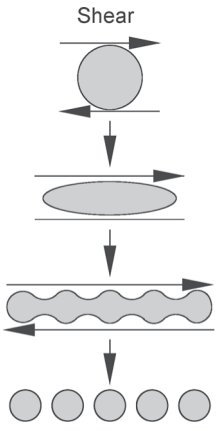

Figure 7.2 Breakage of cylinders of liquid into smaller droplets, under shear.

Droplet radius further decreases until the interfacial tension forces balance, or exceed shear forces, and further division stops. When the amount of mixing energy is constant and γ, from Equation 7.1, is changed by adding emulsifier, it is found that the average oil droplet diameter parallels γ, that is, as more emulsifier is added, γ decreases and so does average droplet size. If γ is unchanged but mixing energy is increased, the droplet size is also decreased due to the change in the balance of shear and interfacial forces, allowing cylindrical distortion of smaller droplets. Equipment design that enhances shear is more effective at dividing droplets – as in homogenisers.

7.3.2 Emulsion formation

Emulsion formation can either be single step or multi-step depending on the nature of the emulsion in question, which can take into consideration aspects of starting materials, and end properties of the product (McClements, 2002). It is also often necessary to dissolve the various component parts in their respective soluble phases before mixing takes place, that is, oil-soluble in oil, and water-soluble in water. Upon vigorous mixing of this system without added emulsifier, droplets will form, but as soon as mixing is stopped, the droplets will contact, coalesce and phase separation will quickly occur. Adding an emulsifier to the system changes this outcome. When mixing stops, one phase has become continuous, while the other remains dispersed, or discontinous. The nature of the emulsion is determined by the emulsifier. As a general rule, the continuous phase is the one in which the emulsifier is soluble.

The physical step of mixing, or homogenisation usually occurs in two stages (Figure 7.2): the first being referred to as a primary homogenisation step; and this is basically the initial droplet formation. Then the secondary homogenisation reduces the droplet size to their final value. A range of homogenisers are available, such as high speed blenders, colloid mills, high pressure valve homogenisers, ultrasonic homogenisers, membrane homogenisers and microfluidisation (McClements, 2002).

7.3.3 Foams

Foams are stable dispersions of gases within liquids, and are constructed by whipping the aqueous solution in the presence of the emulsifier, or foaming agent. Proteins, for example, egg white, stabilise the bubble formation by creating flexible cohesive films around the air bubbles. Air is first entrapped by the whipping action and thereafter the air bubbles are elongated and subdivided into smaller bubbles, under similar mechanics described in Section 7.3.1 for liquid internal phases. The impact of the whipping process causes the protein to be adsorbed at the interface followed by a partial unfolding, which in turn reduces the interfacial tension. Air's non-polar nature concentrates the emulsifier at the water–air interface so that the hydrophobic tail extends into the gas phase. The reduction in interfacial tension then facilitates the formation of new interfaces and increases the number of stabilised air bubbles. Foams collapse due to a similar course of events to that described in the cake batter above, that is, large air bubbles begin to grow at the expense of small ones, in a process termed disproportionation.

7.3.4 Wetting

Wetting is the ability of a substance to spread over a surface, and is a useful property of some emulsifiers. Good wettability can enhance the spreading of chocolate, the dispersion of dry mixes in liquids, or the incorporation of dietary fibres in dressings. It can be thought of in terms of drop behaviour when placed on a given surface. Take mercury on glass; here the mercury will form a droplet where the contact angle is greater than $\pi/2$, that is, it does not wet the surface. Oil on the same glass surface will ultimately spread completely out, complete wetting, and the contact angle will decrease with time to zero. Water on the same glass surface, will spread out only partially, and have a contact angle between 0 and $\pi/2$ (Starov *et al.*, 2007). This is schematically represented in Figure 7.3.

The contact angle, θ, is determined by the surface tension at the three interfaces involved: the solid, the liquid and the air, or similar. The angle θ can then be defined

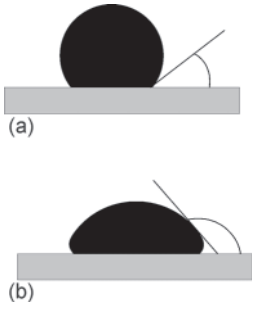

Figure 7.3 Contact angle θ at the liquid–solid–air juncture of (a) nonspreading ($\theta < 90^{\circ}$) and (b) spreading ($\theta > 90^{\circ}$) liquid drops.

as follows:

$$\cos\theta = \frac{(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} \tag{7.2}$$

where S relates to the solid, V relates to the vapour, and L relates to the liquid. From this, the spreading coefficient (Miller and Neogi, 2008) can be defined:

$$S_{L/S} = \gamma_{SV} - \gamma_{SL} - \gamma_{LV} \tag{7.3}$$

when $S_{L/S}$ is greater than 0, the surface is wetted, and the liquid spreads out over the surface in question. When $S_{L/S}$ is less than 0, then the surface is not wetted and the liquid remains in a droplet form on top of the surface. Efficient wetting agents therefore minimise the surface tension of the air–liquid and solid–liquid interfaces while leaving the air–solid surface tension unchanged. This situation arises when dry powder, for example, custard or lycopodium powder, is added to water, that is, the powder spreads out over the water's surface. Addition of a surfactant, or emulsifier, for example, sodium dodecyl sulphate, lowers the air–liquid and solid–liquid interfacial tensions and enhances mixing and dispersibility. In the absence of the surfactant, the contact angle at many of the powder particle surfaces is greater than 90° and the powder, with its entrapped air, floats on the top of the water.

For chocolate, the liquid continuous phase is lipid-based, and the solid dispersed phase consists of finely ground cocoa particles and sugar crystals. The addition of an emulsifier, CITREM, PGPR (polyglycerol polyricinoleate), or lecithin, aids the wetting of the solid particles by oil, by concomitant lowering of γ_{SL}. Any unwetted solid particles tend to adhere to each other, or flocculate, forming a matrix which decreases the flow characteristics of the coating, and thereby decreases its spreadability. Wetting by oil disrupts this matrix, lowering the apparent viscosity of the heterogeneous mass as well as giving a smoother mouth feel to the final product.

7.4 Stabilisation

Emulsion stability is somewhat of an anomalous statement since they are, in thermodynamic terms, inherently unstable systems! Hence, the emulsifier has another role to that described earlier of emulsion formation; it must also secure the stability of the emulsion – at least for the required lifetime of the given emulsion. Therefore, emulsion stability can be better thought of as the ability of the emulsion to resist change to its established properties with respect to time. Hence, the main requirement is to 'equip' the emulsion with the ability to resist coalescence, whereby small oil droplets or gas pockets migrate and merge into larger droplets or gas pockets, leading to emulsion breakdown and foam breakage respectively. Focusing on interfacial crystallisation of fats in W/O emulsions Wassell *et al*. (2012) explained these interactions of fats with food emulsifiers to indicate the conditions necessary for structured stable emulsions.

7.4.1 Creaming and sedimentation

Creaming or sedimentation(Spyropoulos *et al*., 2011) occurs when the dispersed phase of an emulsion is lighter or heavier respectively than the continuous phase and the dispersion remains quiescent for a period of time. The rate at which the particles rise or sink is given by Stokes's law:

$$v = \frac{2gr^2(\rho_1 - \rho_2)}{9\eta} \tag{7.4}$$

where v is the rate of creaming or sedimentation, g is the gravitational constant, r is the droplet radius, ρ_1 and ρ_2 are the densities of the oil and water phase, respectively, and η is the viscosity of the water phase.

The implications of Stokes's equation can be seen by examining oil droplets in an O/W emulsion. They float to the surface because the density of vegetable oil is about 0.91 g ml^{-1}, 0.09 g ml^{-1} less than that of water, and the rate at which they rise depends on the diameter of the droplet. Hence, a drop having a 1 μm diameter rises at a rate of 4 cm day^{-1}, and one with 10 μm diameter rises at 4 m day^{-1}. Therefore, it is obvious that reducing the average droplet size reduces the rate of creaming. Fat globules in raw milk have an average diameter of 3–4 μm, but can be as high as 10 μm and after homogenisation the average diameter is 0.5 μm. Similarly, after homogenisation, the droplet size distribution is more uniform. In raw milk, the average flotation rate is 36 cm day^{-1}, and in homogenised milk the rate is 1 cm day^{-1}. The process of creaming brings the oil droplets closer together, and coalescence occurs if contact is not prevented. A simple creamed layer of stabilised oil droplets is readily redispersed by inverting the container a few times – but is no more stable unless efforts are made to hinder the coalescence process.

Sedimentation occurs when the dispersed phase is denser than the continuous phase. The most common food example of this is in salad dressings containing solid particles of spices and vegetables. Hydrocolloids such as pectin, xanthan or xanthan/guar mixtures (Sworn, 2009) are added to increase the viscosity of the water phase, which then holds the dispersed particles in suspension throughout the dressing for the shelf-life of the product.

7.4.2 Flocculation and coalescence

The droplets within an emulsion are dynamic entities within that bulk emulsion, and as such are in constant motion, being affected by all of the following forces, gravitational, thermal and mechanical – though not necessarily simultaneously. Through this motion the droplet will be in collision with other droplets in the system, which will result in one of two conditions; either (1) the droplets will aggregate and come together, or (2) the droplets will remain separate entities, and will not aggregate. The result of this is defined by the relative nature of the attractive or repulsive forces between the droplets. Hence, we have a situation where the droplets will either flocculate, that is,

come together but retain their droplet form, or coalesce, that is, the droplets come together and merge to form a larger droplet.

The capability of two droplets to aggregate is affected by two parameters related to the droplet collisions: (1) collision frequency; and (2) collision efficiency. Collision frequency (Dickinson, 1992), naturally, refers to number of droplet collisions occurring within a given unit volume over a given time; and collision efficiency refers to those collisions that either lead to aggregation through flocculation, or through coalescence. An inefficient collision leaves the droplet in it pre-collision state. Thus, any outside factor, for example, mechanical stirring, that increases the collision frequency will in turn likely increase the collision efficency and as such play a de-stabilising role on the emulsion.

Creaming and flocculation are closely related, in that one affects the other. In cases of low droplet concentration, creaming rate actually increases since the effective size of the particles (droplets) is increased. This is governed by Stokes's law equation, given above. However, for high droplet concentrations the rate of creaming is retarded due to the entrapment of droplets within the networked matrix of the aggregated emulsion droplets.

Extensive coalescence results in a phenomenon called *oiling out*, which basically means there is the formation of a free layer of oil on the surface of the system. This aggregation of the droplets leading to larger droplets occurs quickly in unprotected emulsions, and is a primary mechanism of emulsions reverting to their most thermodynamically stable state, that is, two phases. This is because coalescence acts to reduce the surface area of the oil and thereby reduce the surface energy, making the two-phase state thermodynamically more attractive. Addition of an emulsifier protects the oil droplets, thereby making them largely resistant to droplet–droplet collisions under static conditions, and therefore for a given collision frequency will lower the collision efficiency. Mechanical forces, however, will alter this status quo and can induce coalescence again.

7.4.3 Droplet–droplet interactions

As seen above, collision efficiency is dependent on the outcome of the collision, which is itself dependent on the nature of the forces between the colliding particles, or droplets. If the droplets are attracted to each other, that is, if the droplet–droplet attractive forces are high, the collision is likely to lead to coalescence or aggregation. If the droplet–droplet forces are repulsive, the collision is unlikely to be effective, and hence the droplet or particle will remain as it is. Basically the entire nature of the collision outcome hinges on the sum of the free energy of the attractive and repulsive forces; which are split up into different categories: van der Waals, hydrophobic, short range, and electrostatic.

Van der Waals forces occurring between emulsion droplets are always attractive, and the interaction potential is related to the radius of the droplets which are separated by some distance. The strength of the van der Waals interaction increases with droplet size. Compared to other interactive forces, van der Waals forces are considered long

range due to their strength decreasing with the reciprocal of the droplet separation, and tend to be over-estimated because of the imprecise nature of the Hamaker constant.

Hydrophobic interactions can be summarised as being fairly strong and can be long range in nature, and therefore play important roles in stabilising food emulsions (Nylander *et al*., 2008). As a consequence of the emulsion droplets not always being fully covered by the emulsifier, nonpolar functional groups may be exposed to the aqueous phase, which then give rise to hydrophobic interaction between these nonpolar groups at the water surface.

Electrostatic interactions will only occur between electrically charged droplets; and in food systems, charged droplets are usually of the same charge, that is, they will repel each other. The result of this charge is that the droplet will begin to attract counterions towards itself from the bulk solution and repel other charges of like sign. This results in the creation of a layer near the surface with a net charge. As the number of the surface charges increases, so too does the repulsive nature of the droplet and thus protection against aggregation. Increasing droplet size would similarly increase the electrostatic interaction strength. However, screening of the electrical charge between the droplets by counterion attraction decreases the electrical double layer thickness. Thus, emulsions stabilised by proteins are open to sensitivity towards the effects of pH or salt concentration changes due to the subsequent changes these two factors would have on the surface energy and ionic strength respectively.

Short range forces occur when two droplets approach each other closely enough such that their interfacial layers begin to interact. No precise predictive model of these interactions exists, which include steric interactions, hydration, and are dependent on packing, shape, conformation, etc. However, the short range forces tend to be repulsive, increase significantly as the interfacial layers begin to overlap and therefore play a strong role in the overall interaction make-up. This whole section about the different droplet–droplet interactions can be summarised in the following general equation for free energy:

$$\Delta G(s) = \Delta G_{VDW}(s) + \Delta G_{Hyd}(s) + \Delta G_{Elec}(s) + \Delta G_{Short}(s) \qquad (7.5)$$

where $\Delta G(s)$ is the sum of the attractive and repulsive energies, $\Delta G_{VDW}(s)$ is the van der Waals free energy, $\Delta G_{Hyd}(s)$ is the hydrophobic free energy, ΔG_{Elec} (s) is the electrostatic free energy, and ΔG_{Short} (s) is the short range free energy.

7.4.4 Viscosity and gelation

Addition of hydrocolloids to the emulsion alters the viscosity of the system, raising it to levels above the original value. This increase in viscosity, as indicated by Stokes's law, retards either the processes of creaming or sedimentation. Another option is to add the hydrocolloid at concentrations or conditions such that it gels. This can either be in the classical sense of a solid gel where the system is prevented from flowing, or it can be in terms of a 'fluid gel', as in salad dressings, where the xanthan gum provides a very distinct gel that suspends the droplets and the spice particles until

it is required to flow. Upon tipping the flask, enough force is applied to make the system pourable and the salad dressing flows out. Cease pouring and the xanthan will recover its structure through thixotropy to hold the remaining spice particles and emulsion droplets in suspension again. The action of the gel therefore creates a gelled matrix which physically prevents the dispersed elements from creaming, sedimenting or coalescing.

7.5 Food emulsifiers

7.5.1 Monoglycerides

The generic term, monoglycerides, is used commercially to define a range of products produced typically by interesterification (Wassell and Young, 2007) of oils or fats with glycerol in a process known as glycerolysis. Monoglycerides have been the emulsifier of choice for the margarine industry since 1920, where both in the USA and the EU regions its use is extensive (Young and Wassell, 2008b).

Monoglycerides produced by the glycerolysis technique without further purification are usually termed mono-diglycerides, and concentrated monoglycerides are referred to as distilled monoglycerides. Commercial monoglycerides usually contain between 45–55% monoacylglycerides, 38–45% diacylglycerides, and 8–12% triacylglycerides plus traces of unreacted glycerol and free fatty acids. When these are utilised in the cake margarine applications and cake batters (Table 7.2), they have the effect of ensuring improved crumb structure and stability of the cake (Young and Wassell, 2008b).

7.5.2 Monoglyceride derivatives

There are four main derivatives of the monoglyceride family of emulsifiers: ACETEM, LACTEM, DATEM, and CITREM. These arise out of the principle that the free hydroxyl groups on the monoglycerides can be esterified with organic acids,

Table 7.2 Different emulsifier combinations for cake margarines together with guideline dosages.

Application	Emulsifier combination	Dosage
Cake margarine	Polyglycerol ester + fully saturated distilled monoglyceride	0.5–1.0% + 0.2–0.5%
	Lactic acid ester + fully saturated distilled monoglyceride	0.5–1.0% + 0.2–0.5%
	Propylene glycol ester + fully saturated distilled monoglyceride	0.5–1.0% + 0.2–0.5%
Cream margarine whipped with granulated sugar	Fully saturated distilled monoglyceride + polyglycerol ester	0.1–0.2% + 0.5–.0%
	Fully saturated distilled monoglyceride + lactic acid esters or polyglycerol ester	0.1–0.2% + 0.5–1.0%
Cake margarine with sugar syrup	Unsaturated distilled monoglyceride	0.5–1.0%

resulting in monoglycerides with modified hydrophilic/lipophilic properties. The previously mentioned derivatives are made using acetic, lactic, diacetyl tartartic and citric acids respectively.

- *ACETEM*. Acetylated monoglycerides vary in their degree of acetylation from 50–90%, forming either monoacetylated or diacetylated monoglycerides, where the surplus free acetic acid is removed under distillation. Palmitic and stearic acids are the most common fatty acids in ACETEMs and produce primarily plastic products, whereas liquid types are based on the unsaturated oils of oleic acid. The partially acetylated monoglycerides are lipophilic and non-ionic in nature, with low polarity and possess α tending properties. Contrary to this, the fully acetylated monoglycerides possess no surface activity, are not thought of as emulsifiers and are classed as speciality fats.
- *LACTEM*. Lactylated monoglycerides are made by direct esterification of glycerol, fatty acids and 15–35% lactic acid, where the usual raw materials comprise of saturated monoglycerides or fatty acids. Care must be taken to remove the water-soluble components such as esters of glycerol and lactic acid, since these give rise to unpleasant off flavours. A number of different commercially available LACTEMs are available, but the most common fatty acid sources are palmitic and stearic; and these are considered to possess low polar, non-ionic, α tending properties.
- *DATEM*. Diacetyl tartaric acid esters of monoglycerides are one of the most hydrophilic monoglyceride derivatives, whose composition can vary widely with respect to the degree of esterified tartaric acid. US regulations from the Food Chemicals Codex allow 17–20% of these, whereas in the EU a much wider range of between 10–40% is allowed. DATEMs are anionic-active emulsifiers due to the free carboxyl group, and therefore are sensitive to changes in pH in aqueous solutions. However, their anionic nature makes them reactive towards the proteins frequently used in the food industry – particularly within the bakery industries.
- *CITREM*. Citric acid ester of monoglycerides is an esterification of monoglycerides in the presence of citric acid (12–20%). The final CITREM can be neutralised with alkali, and can form either sodium or potassium salts, improving water dispersibility, and functionality in emulsions. CITREM structure is complex due to acyl-migration during esterification. CITREMS are water-dispersible anionic emulsifers.

The structure and chemical formulae of the above emulsifier variations of monoglycerides are given in Figure 7.4.

A range of emulsifiers can also be produced by esterification of polyols, for example, condensed glycerol, propylene glycol, sorbitol/sorbitan or lactic acids with fatty acids. Polyglycerol esters of fatty acids (PGE) are produced at elevated temperatures in the presence of an alkaline catalyst, where the polymerisation process is a chain condensation, which produces a number of different polyglycerols from diglycerol to

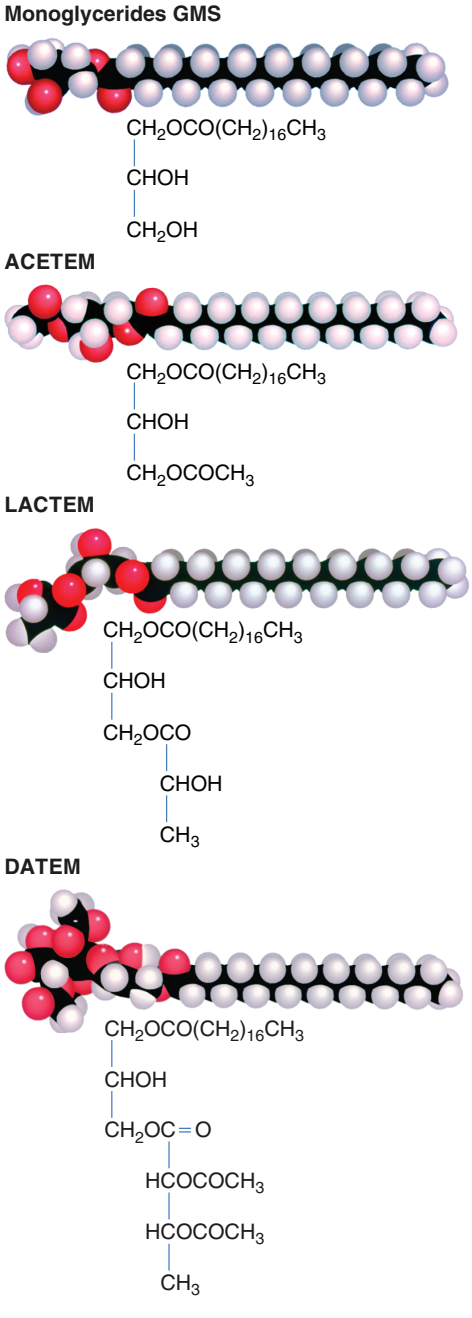

Figure 7.4 Chemical structure and molecular models of glycerol monostearate (GMS) and the main component of organic acid derivatives of monoglycerides. *Source:* DuPont Nutrition and Health. Reproduced with permission of DuPont Nutrition and Health.

decaglycerol. The polymerised glycerol can now be esterified with the fatty acids of choice, usually palmitic and stearic, which forms an equilibrium mixture of polyglycerol esters. This is done with the aim of optimising the monoacyl ester content, but di-, tri- and tetra-acyl esters may still be present due to the high number of free OH groups in polyglycerols. Hence, the composition of polyglycerol esters is extremely complex with a large number of positional isomers and compounds with various degrees of polymerisation and esterification being possible.

Concentrated diglycerol monoacyl esters; which are hydrophilic, non-ionic emulsifiers with improved properties over the standard polyglycerol esters, can be produced by esterifying purified diglycerol with fatty acids. A molecular distillation follows, which then concentrates the monoacyl esters.

7.5.3 Polyol esters of fatty acids

Propylene glycol esters of fatty acid (PGMS) made from the esterification of propylene glycol with fatty acids yield an equilibrium mixture of monoacyl or diacyl esters in the ratio of 55% to 45% resepectively. PGMS can be concentrated under similar molecular distillation techniques used for monoglycerides. These distilled PGMS contain a minimum of 90% monoacyl esters and are usually based on a 1:1 mix of palmitic and stearic fatty acids. PGMS are known to be oil-soluble, non-ionic and low polar in property and are often used in conjunction with monoglycerides.

Sorbitan esters of fatty acids (SMS, STS) derive from dehydration of sorbitol followed by esterification with palmitic and stearic acid blends. Depending on the molar ratio between sorbitan and fatty acids, either sorbitan mono acyl esters (SMS) or sorbitan triacyl esters (STS) are the main component of the final product. The composition of the commercial sorbitan esters are manifold, and contain mixures of 1,4-, 1,5-, and 2,5-sorbitans as well as iso-sorbide in the form of monoacyl, diacyl, and triacyl fatty acid esters.

SMS is a non-ionic, water-dispersible emulsifier, whereas STS is an oil-soluble emulsifier predominantly used as a fat crystal modifier in fat-based systems (e.g. chocolate, Weyland and Hartel, 2008) due to its crystalline compatibility with triglycerides, see Figure 7.5.

Polyglycerol polyricinoleate (PGPR) is made by reacting polyglycerol with castor oil fatty acids under vacuum, where 90% of the castor oil is composed of Ricinoleic acid. The resultant material is an essentially odourless, colourless, free-flowing liquid, which is used extensively in the confectionery industry within chocolate as a flow modifier. It is also known as a water scavenger (Garti and Yano, 2001), and as such is successfully applied to the chocolate used in dip coating of ice cream sticks.

7.5.4 Lactic acid esters of fatty acids

Lactic acid esters of fatty acids (SSL, CSL) are made by esterification of lactic acid with 1:1 blends of palmitic and stearic acids in the presence of sodium or calcium hydroxides. Thus, the sodium or calcium salts of stearyol lactylates, fatty acids salts

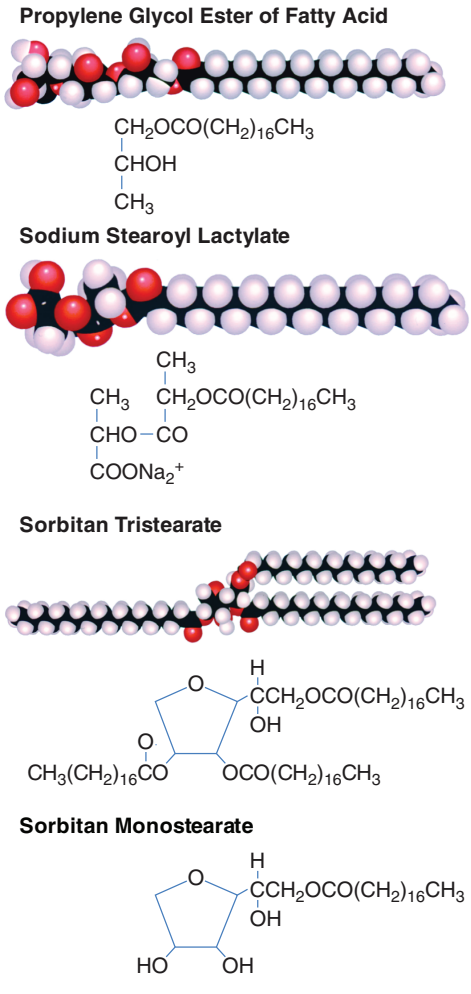

Figure 7.5 Chemical structure and molecular models of selected polyol esters of fatty acids. *Source:* DuPont Nutrition and Health. Reproduced with permission of DuPont Nutrition and Health.

and free fatty acids are produced. Lactic acid esters easily polymerise to form lactoyl-lactic or polylactic acids, giving rise to a variety of lactylated compounds. SSL is a versatile, anionic, water-dispersible emulsifier, which is more frequently used than the less water-dispersible but oil-soluble CSL.

7.5.5 Lecithin

Commercially, lecithin is extracted from soybeans or sunflower seeds by solvent extraction, which contains approximately 65% acetone insoluble phosphatides and 35% soybean oil. Surface activity comes from the phosphatidyl group, which is hydrophilic and the two fatty acid chains which are of course lipophilic. There are

three main phosphatidyl groups: phosphatidylethanolamine, phosphatidylcholine, and phosphatidylinositol. These fatty acid chains can either be saturated in nature, that is, palmitic or stearic, or unsaturated, that is, oleic or linoleic. Increased aqueous dispersibility is achieved by treating the crude lecithin with concentrations of hydrogen peroxide higher than 1.5%, which forms hydroxylated lecithin. Hydroxylated lecithins are most effective emulsifiers in oil-in-water emulsions. Ethanol fractionation of the lecithin separates the phosphatidyl groups into ethanol soluble and insoluble fractions. The ethanol soluble fraction, phosphatidylcholine, is effective at stabilising oil-in-water emulsions, and can be further purified to give a material that is routinely used as egg yolk replacer. The ethanol insoluble fraction, phosphatidylinositol, works effectively to promote and stabilise water-in-oil emulsions. Lecithin predominantly finds a use in the chocolate industry where it regulates the rheological yield properties of the chocolate. In this case the hydrophilic head groups align with the sugar crystals and the fatty acids groups with the fat continuous phase of the cocoa butter fats.

7.6 The hydrophilic–lipophilic balance

Emulsifiers, due to their amphiphilic nature, possess a functional duality within their chemical structure, and the balance between their hydrophobic and hydrophilic characteristics can determine how the emulsifier will function in a given emulsion. This can be expressed as a semi-empirical concept known as the hydophilic-lipophilic balance (HLB), introduced by Griffin (1949). It works by essentially characterising the relative solubilities of the oil-soluble and the water-soluble moeties of the emulsifier. The HLB value is assigned based on the chemical structure of the emulsifier, that is, an emulsifier with a high HLB has a high ratio of hydrophilic groups compared to lipophilic groups, and vice versa.

Initially the mode of calculation of the HLB value relied upon a knowledge of the individual type and number of the hydrophobic and hydrophilic groups, or it could be determined through cloud point experiments. However, Davies (1957) developed a method for calculating the HLB based on the sum of hydrophobic and hydrophilic group values (Table 7.3) that can be expressed as:

$$\text{HLB value} = \sum(\text{hydrophilic values}) - \sum(\text{lipophilic values}) + 7 \qquad (7.6)$$

This semi-empirical equation has its roots in thermodynamics, where the sums of the values given in Table 7.3 correspond well to the free energy changes in the relative hydrophilic and hydrophobic regions of the emulsifier during micelle formation (McClements, 2002). It is generally found that the calculated and experimentally determined HLB values vary by no more than a few tenths.

The HLB value therefore allows characterisation of the emulsifier, providing sagacity in predicting what type of emulsion will be formed. Generally, emulsifiers with low HLB values are more hydrophobic, that is, they preferentially dissolve in the oil phase

Table 7.3 Hydrophilic–lipophilic balance (HLB) functional group numbers.

	Groups number
Hydrophilic groups	
SO_4Na	38.7
—COOK	21.1
—COONa	19.1
Sulfonate	*c*.11
$—N(CH_3)_3$	9.4
Ester	
sorbitan ring	6.8
Other	2.4
—COOH	1.9
—OH:	
sorbitan ring	0.5
Other	1.9
$—(CH_2—CH_2—O)\}$	0.33
Lipophilic groups	
—CH—	0.475
$—CH_2—$	0.475
$—CH_3$	0.475
—CH—	0.475

and therefore would be recommended to stabilise water-in-oil emulsions. They will typically have HLB values in the range of 4–6. An emulsifier with an intermediate HLB value of 6–8 has no preference for either the oil or water phase, and can be thought of as good wetting agents. Emulsifiers with high HLB values of 8–18 prefer the aqueous phase, and are predominantly hydrophilic in nature. Hence, they will be used to stabilise oil-in-water emulsions.

McClements (2002) reports that the value of the HLB can also be used to predict the relative stability of the emulsion produced. Emulsion droplets stabilised by emulsifiers which have extreme high, low, or intermediate HLB values are prone to coalescence. This is due to the extremes of the HLB scale giving the emulsifier low surface activity and therefore poor ability to protect the droplet. Those with the intermediate HLB values provide poor stability due to the surface tension around the drop being very low, such that remarkably little collision energy is required to result in a successful collision, that is, to expediate coalescence.

Hence, for water-in-oil emulsions, maximum stability is obtained with HLB values between 3 and 5, and for oil-in-water emulsions HLB values between 10 and 12, and this is attributed to sufficient surface activity being present to cover the surface of the droplets, but not catastrophically to lower the surface tension to increase collision efficiency.

As described above, there is tremendous advantageous information to be gleaned from the HLB concept, calculating HLB values for a blend of emulsifiers, and tables of experimentally determined HLB value are available (Table 7.4). However, it also singularly neglects other important factors, for example, effects of molecular weight,

Table 7.4 Experimental hydrophilic–lipophilic balance (HLB) values for food emulsifiers.

Emulsifier	HLB value
Sodium lauryl sulfate	40
Sodium stearoyl lactylate	22
Potassium oleate	20
Sucrose monoester	20
Sodium oleate	18
Polysorbate 60	15
Polysorbate 80	15
Decaglycerol monooleate	14
Decaglycerol monostearate	13
Ethoxylated monoglyceride	13
Decaglycerol dioleate	12
Polysorbate 65	11
Hexaglycerol dioleate	9
Decaglyerol hexaoleate	7
Triglycerol monostearate	7
Glycerol monolaurate	7
Sorbitan monostearate	5.9
Sucrose triester	5
Propylene glycol monolaurate	4.5
Propylene glycol monostearate	3.4
Glycerol monostearate	3.8
Sorbitan tristearate	2.1

temperature changes, or solvent conditions. It remains difficult to determine HLB values for common food emulsfiers, for example, phopholipids, and no information can be deduced from them about crystallisation properties of monoglycerides or their modified derivatives (Bergenståhl, 2008). However, the HLB concept remains a well-established and useful tool to provide initial insight into the likely performance of emulsifiers or emulsifier blends.

7.7 Hydrocolloid stabilisers and thickeners

7.7.1 Hydrocolloids

The term hydrocolloids refers to a wide range of molecules with an equally wide range of functions that are used predominantly to thicken, stabilise, and in some cases emulsify systems, widely within the food industry. They can be extracted from plant materials, such as pectin, guar, locust bean gum (LBG), seaweeds; such as alginate, carrageenan, or as bacterial products, for example, xanthan (de Vries 2004, Sworn, 2004). They are typically of high molecular weight and all dissolve in water, either under hot or cold conditions to form viscous aqueous solutions or gels. In their component form, hydrocolloids are constructed of monosaccharides which are glycosodically linked through water elimination (Al-Assaf and Phillips, 2009). Typical concentration levels for the hydrocollods lie between 0.05 to 1.0% depending on the

Table 7.5 Commercial hydrocolloids and their principal function.

Hydrocolloid	Principal function
Agar	Gelling agent
Alginate	Gelling agent
Gum Arabic	Emulsifier
Carrageenan	Gelling agent
Carboxymethyl cellulose	Thickener
Hydroxyproylcellulose	Thickener and Emulsifier
Methycellulose	Thickener, Emulsifier and Gelling agent
Gelatin	Gelling agent
Guar gum	Thickener
Karaya	Thickener
Locust bean gum	Thickener
Pectin	Gelling agent
Pectin (low ester)	Gelling agent
Propylene Glycol Alginate	Emulsifier and Foad stabiliser
Starch	Thickener and gelling agent
Starch (modified)	Thickener and gelling agent
Tragacanth	Thickener
Xanthan gum	Thickener

nature of the hydrocolloid in question and the functionality required. The principal individual property of the main commercial hydrocolloids is given in Table 7.5.

Hydrocolloid functionality is, in essence, linked to solubility. The generally good solubility of the hydrocolloids is due to the many hydroxyl groups present on the molecules, but is influenced by nature of the monosaccharides units themselves. Hence, neutral hydrocolloids are less soluble than those containing uronic acid groups (Al-Assaf and Phillips, 2009). Once dissolved, the hydrocolloids will adopt different conformations, anything from spherical, random coil, to rigid rod, depending on their monosaccharide make-up, inter-sugar linkages, or associative interactions of intra or intermolecular nature.

Hydrocolloids basically consist of long polysaccharide main chains with numerous side branches of sugars or oligosaccharides. Frequently, the sugar units include carboxylic acids, for example, d-guluronic, d-mannuronic or d-galacturonic acid, e.g. alginate and pectin. In a few instances, sulphate esters provide an anionic character, e.g. carrageenan. Many different saccharides are found in gums, including the hexoses; d-glucose, d-mannose and d-galactose, as well as the pentoses l-arabinose, d-xylose and l-rhamnose. The highly branched structure contributes to water solubility, and the anionic hydrocolloids, pectin and alginate often form gels in the presence of cations such as Ca^{2+} (Braccini and Pérez, 2001; Grant *et al*., 1973; Siew *et al*., 2005).

Low viscosity hydrocolloids such as gum arabic are used in many industries where they provide emulsification in beverages by coating the oil droplets present with arabinogalactan protein complex (Al-Assaf and Phillips, 2009). Similarly, gum arabic can be used as a protective agent for flavour oils by forming a protective layer at the oil-in-water interface and subsequent spray drying results in encapsulated flavour particles.

Hydrocolloids of medium viscosity, 100–1400cP at 1% aqueous solution, propylene glycol alginate and xanthan being examples, are used to impart body and viscosity to the system. They can have emulsifying properties themselves, and one of the most common food applications is dressings where they ensure a stable system that pours easily but simultaneously clings well to the salad in question (Al-Assaf and Phillips, 2009; Sworn, 2009).

High viscosity hydrocolloids, for example, guar, LBG are primarily used as thickeners and stabilisers where they significantly increase the viscosity of the aqueous phase of the food product. At lower dosages than for true thickening, they can have a positive effect through water binding on controlling syneresis. By causing such significant viscosity increases, they can also be utilised in generating mouth feel characteristics that are sought after in low-fat products – particularly dressings and sauces (Williams, 2006).

The gel-forming hydrocolloids, for example, pectin, alginate, carrageenan, etc., are primarily used where the food system requires a solid or semi-solid texture, such as in jams, jellies, fruit fillings (Lynenskjold *et al*., 2008; Young *et al*., 2003). These hydrocolloids are also said to impart freeze–thaw stability to many products. The ingredient statement for many frozen whipped toppings and ice creams include one or more of the hydrocolloids listed here, particularly carrageenan, pectin or alginate.

7.7.2 Modified starch

Starch is principally obtained from corn and potatoes for commercial purposes, but can also be obtained from tapioca, rice and sago. It consistes of two molecular types: amylose, a linear α 1-4 linked glucopyranose chain with little branching and a molecular weight of around 10^5 to 10^6; and amylopectin which has the same linear α 1-4 linkages, but also significant branching at the α 1-6 position and a typical molecular weight of 10^7 to 10^8 (Williams, 2006).

Starch is insoluble in water at room temperature, but, upon heating, the starch granules swell and ultimately burst, which releases amylose as a viscous paste at a specific temperature depending on the starch. This temperature is typically called the gelatinisation temperature, though more accurately it could be referred to as the pasting temperature, and for most starches is around 60–67°C. Upon cooling, the gelatinised starch retrogrades where the amylose self-associates and gelation occurs. Modification through chemical means changes the properties of the starch and therefore alters the applications where it can be used in the food industry. Such modification is usually applied to starch, since due to native starch's tendency to retrogradation, it is undesirable for the food industry.

Modified starch can include treatments to produce hydroxyproyl starch, starch phosphates, oxidised starch and cross-linked starch. Cross-linked starch is treated so that bonds are formed between glucose residues between adjacent chains. The act of cross-linking raises the gelatinisation temperature, but also stabilises the resultant gel towards effects of temperature, low pH and shear, where the degree of stability is governed by the degree of cross-linking. Such treatment is useful for low pH applications where

starch is required, for example, dressings (Phillips and Williams, 2009; Williams, 2006) where the starch is pre-cooked before the pH is lowered. Hydroxypropyl starch and starch phosphates usually have lower gelatinisation tempertures compared to native starch and also are more susceptible to shear, but due to the modification are less likely to undergo retrogradation upon cooling.

7.7.3 Cellulose derivatives

Obtained commercially from trees and cotton, cellulose in its native form is composed of linear chains of β 1-4 linked glucopyronose units, which associate into a number of crystalline structures. Cellulose is the most abundant hydrocolloid, and in its native form is insoluble in water. However, through modification, usually etherification of the reactive hydroxyl groups on the glucose residues, it can be made water-soluble. The most common derivatives used within the food industry are carboxymethyl cellulose (CMC), methyl cellulose (MC), and hydroxymethyl cellulose (HPMC).

CMC is the most popular of the cellulose derivatives in food, and is readily soluble in water, giving viscous solutions, and because of its anionic nature is best suited to higher pH applications. It is predominantly used in dairy products, bakery products and frozen or ready-to-eat meals. HPMC and MC are nonioinic in character, and gel through association of the hydrophobic methyl or hydroxypropylmethyl moieties. Their main application is as water binders and shape retention agents on products that are heated, for example, fish burgers, and reconstituted vegetables.

7.8 Applications

7.8.1 Margarine and dairy products

7.8.1.1 Margarine

The margarine industry uses predominantly monoglyceride esters securing a fine stable water-in-oil emulsion, which in turn gives the margarine an even homogeneous character with good functional and microbiologically durable attributes (Young and Wassell, 2008b). Over and above this property, the monoglycerides can prevent syneresis in aerated systems and hydrated systems, while facilitating the incorporation of other ingredients into the fat phase. Specifically, LACTEM-based emulsifiers will act on the margarine to impart functionality more in the final product which the margarine is incorporated into, as opposed to the margarine itself. They reduce the whipping time required for cake batters or creams, and can increase the degree of overrun which can be achieved, as well as improving subsequent foam stiffness. Furthermore, transcending into the baked product, use of LACTEM-based emulsifiers can boost the crumb firmness in the given cake.

The CITREM-based emulsifiers are a primary source of lecithin replacements, and will allow the fat fraction and solids fraction of a cake batter to become efficiently mixed and integrated, with the beneficial consequence that the system is homogeneous and easy to handle. Confining the CITREM properties to the margarine itself, they

make excellent anti-spatter agents for use in frying margarines, where they are active in controlling and regulating the water droplet size and distribution, together with the concomitant reduction in interfacial tension. Hence, the water within the system will still turn to steam, but will not 'explode' as it can escape under significantly more controlled conditions.

Recent trends have been to remove the *trans* fats from margarines of all types; table, industrial and puff pastry (Wassell and Young, 2007). For table margarines the use of a β' tending oil or fat source is beneficial, thus making palm oil one of the sources of choice (Berger and Idris, 2005; Wassell and Young, 2007). Combining different amounts of palm stearin and palm olein, it is possible to formulate a suitable *trans*-free table margarine which possesses the optimal Solid Fat Content (SFC) profile to make the margarine both stable and spreadable (Yusof *et al*., 1998). Industrial margarines call for firmer characteristics and therefore require fat blends with up to 40% palm olein and 10% palm strearin, with the remainder being rapeseed oil (Yusof *et al*., 1998). Palm kernel oil has been recognised as giving beneficial qualities to industrial margarines used within the baking industry, where its short chain lauric content provides excellent creaming properties in cake batters (Podmore, 2002; Wassell, Chapter 2 in this volume; Yusof and Dian, 1995). Puff pastry margarine, requiring the firmest structure, calls for blends which are in the order of 10% palm oil and 90% palm stearin, or 20% palm kernel oil and 80% palm stearin (Yusof *et al*., 1998).

7.8.1.2 Butter

The production of butter is arguably the oldest form of preserving the fat components of milk, where the fat droplets in milk are encased in, and stabilised by, a protein membrane. The bulk of the fat required for butter lies in the cream fraction, and has to be separated from the milk bulk either by gravitational or centrifugal means (Hettinga, 2005). Essentially all fat globules larger than ~0.8 μm can be removed by modern separation techniques, and as such carry most of the milkfat over, ready for churning. Churning of the cream is a phase inversion process, that is, the transformation of an O/W emulsion into a W/O emulsion. The fat globules are forced together, some degree of membrane removal occurs, likely as a result of increased collision efficiency through mechanical forces rather than interfacial energetics, and the fat coalesces. This process continues until the fat forms a discrete mass with some entrained aqueous phase. Knowing the fat content of the cream and its subsequent control is essential in estimating yields and smooth operational procedures. Numerous tests are available, although the Babcock test, dating from 1890, is most prevalent. The temperature of churning, between 4.4 to 12.8°C is an important processing parameter. Fat globule coalescence, usually requiring about 45 minutes, occurs via the liquid phase, but the solid fat stabilises the mass and keeps the entrained aqueous droplets separate. The SFC profile of milk fat varies with the season, higher in the winter, and lower in the summer, and the churning operation must take this into account. If the milk fat is too hard, the protein membrane does not desorb sufficiently to allow coalescence; if

it is too soft, the aqueous phase and air, about 3–5% of the total mass by volume, is not incorporated. The proper water and air content is important for the flavour and the spreadability of the butter, and can be controlled largely by working the butter to ensure the uniformity and desirability of the butter's texture.

7.8.1.3 Whipped cream

Cream can be effectively whipped if it contains a minimum of 30% fat, and is held at cool, that is, refigerated temperatures beforehand. Whipping the cream generates a foam in which the air bubbles are stabilised by agglomerated fat globules. At the early stages of mixing, air is incorporated into the cream and divided into large bubbles. Fat globules then concentrate at the air–water interface and stabilise the air bubble. Simultaneously fat globules in the aqueous phase agglomerate, partly through membrane–membrane interactions and partly through binding of membrane protein to milk proteins. The fat globules must not however, coalesce. Thorough cooling of the cream solidifies the fat and prevents coalescence; if the cream is too warm, no stable foam will be formed and one may find a more butter-like substance in one's bowl!

The majority of air incorporation occurs during the first stage of mixing, before any significant viscosity has developed, and additional mixing simply shears and subdivides the air bubbles further. The new air–water interface area is stabilised by more of the fat globule agglomerates from the aqueous phase. Increased viscosity is attributable to two factors: an increase in the number of bubbles, and continued agglomeration of fat globules to form a network throughout the system. As viscosity slowly builds, the shear stress on the air bubbles increases, contributing to further subdivision; and the whipped cream rapidly becomes stiff. If the bowl is overfilled, it takes longer to effect fat agglomeration and hence longer to reach the internal shear stress that contributes to completion of whipping.

The stabilisation of the whipped cream, based on the controlled de-stabilisation of the emulsion is therefore achieved by partially coalesced but relatively intact fat globules which adsorb at the air–water interface (Euston, 2008). Thus, the main function of emulsifiers in a whippable system is to provide the controlled de-stabilisation correlated to the crystallinity of the fat phase and a reduction of the protein-load and surface film viscosity. Through this function, the addition of emulsifiers to whippable systems can increase the amount of overrun, that is, amount of air incorporated per unit volume of material than would be the case otherwise.

A 50:50 mixture of polysorbate 60 (the monostearate) and polysorbate 65 (the tristearate), used at 0.5% concentration, gives whipped cream with an overrun of about 200%. Polysorbate 80 (the monooleate) in place of polysorbate 60 gives much lower overrun but softer whipped cream (Min and Thomas, 1977). Studies using monoglycerides and two derivatives (the citric and the lactic acid esters) at 0.2% levels have also been reported (Sogo and Kako, 1989). Monoglycerides alone gave poor results, a blend of citric acid ester plus monoglyceride gave good results, and lactylated monoglyceride produced very stiff foams with a high overrun.

7.8.1.4 Non-dairy whipped topping

Whipped toppings of a non-dairy nature are stabilised by crystalline fat at the air bubble interface, and extensive studies have been carried out into the mechanics of structure formation within whipped toppings (Barfod and Krog, 1987; Bucheim *et al*., 1985; Euston, 2008; Krog *et al*., 1986). The fat must have the proper SFC profile so that the optimal amount of solid fat is present to stabilise the air bubbles. Similarly, the emulsifier must interact with the protein coating the fat so as to produce the necessary degree of controlled desorption of the protein layer. Finally, the emulsion is frequently spray-dried then reconstituted with cold water before whipping. The emulsifier, protein and any other ingredients, for example, sugar, flavours, maltodextrins, etc., must rehydrate properly to give an emulsion that is whippable.

Fragments of the fat present in spray-dried topping powders have been shown to exist in the supercooled state (Barfod and Krog, 1987). They show structural changes when they are reconstituted in aqueous systems at low temperature, thereby heavily influencing the subsequent foam structure and overall whipping traits. The emulsion now becomes somewhat unstable due to spontaneous recrystallisation of these supercooled fat fractions, and this de-stabilisation can be attributed largely to, first of all, the temperature-dependent protein desorption from the surface, and, second, the ensuing coalescence. Collectively, then, this increases the potential for the supercooled fat fraction to crystallise due to the enhanced number nucleation sites (Bucheim *et al*., 1985), and therefore ultimately providing stability to the topping.

A basic whipped topping powder formula is: 25% partially hydrogenated fat and 5% emulsifier, mixed and melted together; 15% maltodextrin and 5% sodium caseinate, dissolved in the water; and 50% water. The two phases are mixed and homogenised, then spray-dried. The emulsion is stabilised by the combined effects of the emulsifier and protein, as outlined above. The powder is held at 5°C for an hour to solidify most of the fat, and stored at temperatures below 20°C. For whipping, the powder is dispersed into an equal weight of cold water, where agitation intitiates many of the same events that occur during whipping of dairy cream, that is, fat globule agglomeration, partial desorption of protein from the fat–water interface, air incorporation, stabilised by fat globules, and air subdivision leading to formation of a stable foam.

The best results are obtained with partially hydrogenated lauric fats (coconut, palm kernel) plus partially hydrogenated vegetable oils (soybean, sunflower). Crystallisation concurrent with protein desorption is necessary for proper agglomeration, and concentration of the fat at the air–water interface leads to air bubble stabilisation. This phenomenon appears connected to shorter-chain C_{12} fatty acids; it is observed with lauric fats but not if the fat phase contains solely the C_{18} vegetable oils. A partially hydrogenated C_{18} fat, exhibiting no supercooling phenomenon, gives a poor whipped topping; and a partially hydrogenated C_{12} fat with a low melting point, translating to little or no fat crystal formation at the temperature of the mixture being whipped, also gives poor results (Barfod *et al*., 1989).

α-tending emulsifiers, such as propylene glycol monostearate or lactylated monostearin, have been used with good success in whipped toppings. Polysorbate 60 (the

monostearate derivative) is frequently used in commercial nondairy whipped toppings, as has glycerol latopalmitate (GLP) (Westerbeck and Prins, 1991). A common characteristic is that both types form a rather thick layer at the fat–water interface, a multilayer of emulsifier by the α-tending emulsifiers, or a layer of adsorbed water held by the polyoxyethylene chain of Polysorbate 60. These properties promote partial protein desorption required, yet maintain a 'sticky' surface on each fat globule, enhancing agglomeration.

7.8.1.5 Ice cream

Ice cream is a complex food structure, but is basically a foam and an emulsion! It contains ice crystals, and a nonfrozen aqueous phase (Euston, 2008). However, that said, the basic interfacial phenomena occurring during ice cream manufacture are similar to those occurring in whipping (Berger, 1997; Krog *et al*., 1989). The aim is the subdivision of air bubbles, with stabilisation by adsorbed fat globules (Clarke, 2005). However, in this case the temperature regime is quite different, so one would expect differences in details of the types of emulsifiers that produce the best product.

The initial ice cream emulsion is aged for 4–24 h at approximately 5°C. This is an important step. During the aging, partial desorption of the fat globule membrane takes place and the globules agglomerate (Barfod *et al*., 1991). Desorption is aided by the presence of emulsifiers, and also gives the resultant ice cream improved meltdown resistance, a smoother body and texture (Euston, 2008). During agitation and freezing the fat globules collect at the air–water interface and stabilise the air bubbles. Studies have shown that increasing the degree of desorption, by the addition of a monoglyceride, gives a 'drier' ice cream (Arbuckle, 1986), with smaller average air-bubble diameter.

The emulsifiers commonly used in ice cream manufacture are glycerol monostearate (GMS) and polysorbates, which destabilise the emulsion by displacing protein from the fat-droplet surface (Zhang and Goff, 2005). Different emulsifiers have been shown to have different efficacy as regards the order of coalescence such that glycerol monooleate (GMO) > glycerol monopalmitate (GMP) > glycerol monostearate (GMS), an effect attributed to the ability of the emulsifiers to displace protein from the interface, and the morphology of the fat crystals in the emulsion droplets (Davies *et al*., 2000, 2001).

Hydrocolloids, such as guar, LBG, carrageenan, or alginate, are also frequently used in ice cream mixes (Sworn, 2004). They help prevent shrinkage due to temperature changes, wheying off, control ice crystal growth, and can also aid in shape retention during melting.

7.8.1.6 Coffee whiteners

Cream substitutes and coffee whiteners have existed for around 50 years (Abrahamson *et al*., 1988), and serve a number of functions: they whiten the coffee, reduce the bitter taste, flavour the coffee, and provide body (Sims, 1989).

Coffee whiteners are usually spray-dried powders with a typical formulation where the contents are expressed as percentage terms of the powder; maltodextrin, 62; fat, 30;

sodium caseinate, 4; monoglycerides, ~1.5; dipotassium phosphate, 1.5; tartaric esters of monoglyceride, 0.5; flavour, 1000 ppm; water, 1.5 (Si, 1991). The emulsifiers are added to the fat, the other materials are dissolved in water and an emulsion of the two phases is homogenised and spray-dried. The powder is tempered at a cool temperature to solidify the fat and avoid clumping. The fat for coffee whitener usually has a melting point around 42°C–45°C and has a rather steep SFC profile.

The emulsifier used serves two purposes: it facilitates formation of fine fat globules, around 1 μm in diameter during homogenisation and, in conjunction with the protein, prevents feathering, a process whereby the emulsion breaks and the fat oils out when the whitener is dissolved in the coffee. The protein aids emulsification of the fat, and can stabilise the protein layer when the whitener is added to the coffee. The protein layer can be destabilised by calcium ions and organic acids in the coffee, and the dipotassium phosphate counteracts this tendency. SSL can also be utilised and this is likely to be due to its ability to complex with the sodium caseinate (Leo and Betscher, 1971).

7.8.2 Baking

The largest user of food emulsifiers of all types is the baking industry, accounting for an estimated 50% of food surfactant consumption (Kamel and Ponte, 1993; Knightly, 1996; Krog, 1981; Wassell, 2006). The largest single usage category is that of monoglycerides for antistaling purposes (Jønsson and Tørnæs, 1987; Knightly, 1999). The next largest category is dough strengtheners (Stauffer, 1990), followed by cake emulsifiers (Wootton *et al*., 1967) and icings.

7.8.2.1 Antistaling

Monoglycerides retard bread staling, experienced as increased crumb firmness, by complexing with gelatinised starch. This slows the rate at which the starch retrogrades or recrystallises (Knightly, 1996; Krog *et al*., 1989; Stauffer, 1990). The monoglyceride interacts primarily with the free, soluble amylose in the dough, thus increasing the natural content of the amylose-lipid complex. When more than 1% monoglyceride is added, all free amylose is bound and an increased interaction with the amylopectin fraction takes place, which reduces the degree of retrogradation – and hence contributes positively to antistaling (Krog *et al*., 1989). The lipid–starch complex forms with any straight-chain aliphatic compound such as stearic acid (Krog, 1971), and antistaling properties are observed with a variety of such surfactants. Besides the structural requirement of the linear aliphatic chain, it also appears the surfactant must exist in the lamellar mesophase in the dough to function effectively as a starch-complexing agent (Krog, 1975; Krog and Jensen, 1975). Thus, the hydrated GMS product, because it is already in the lamellar mesophase form, is considered by many to be a more effective antistaling agent. However, comparative studies using all three commercial types of monoglycerides for bakeries (plastic monoglycerides and diglycerides, hydrated hard

monoglycerides, and soft distilled monoglycerides) have shown that on an equal α-monoglyceride basis all three forms are equally effective at retarding the development of crumb firmness.

7.8.2.2 Dough strengthening

Dough strengtheners enhance the ability of a proofed loaf to withstand mechanical shock, and increase the extent of ovenspring during baking and hence increase final loaf volume. The most widely used surfactants for this purpose are SSL and DATEM, although EMG and polysorbate 60 also show positive results in published test reports. The emulsifiers interact with gluten, strengthening the homogeneous dough network. Theories exist to explain the dough strengthening process, but generally, the effective dough strengthening emulsifiers are able to form aqueous films with a lamellar structure at the interface between the gluten strands and the starch, while being specifically bound to the gluten (Carlsson, 1981). Furthermore, it appears that the best stabilisation occurs when the air cells are surrounded exclusively by either lipids or proteins. However, if lipid and protein are both present, they tend to disrupt each other and stabilisation is decreased.

7.8.2.3 Cake emulsifiers

Successful manufacture of good quality cakes requires dispersal of air into the batter and retention of these bubbles until the starch has swollen and the cake structure is set. In other words, the creaming and emulsifying capacity are critical parameters. Good creaming is required since it contributes to the final cake's baked volume and emulsification since it controls and regulates moisture uptake (Wassell and Young, 2007; Young and Wassell, 2008b).

Thus, a good cake shortening must create a stable emulsion, able to withstand the rigours of the beating and baking process, whie also providing good creaming power. Creaming power is related to the amount of air that can be incorporated into the fat/sugar mixture during aeration (Idris *et al*., 1989). Monoglyceride shortenings allow optimal subdivision of the air droplets, begetting smaller droplets which are more efficiently retained, and provide for more uniform nucleation for leavening gases during baking.

The effectiveness of α-tending emulsifiers stems not from their lowering of interfacial tension, but rather their ability to form a solid film at the oil–water interface, preventing the lipid phase from de-stabilising the protein-stabilised foam during the cake batter mixing. There is a defined relationship between temperature and the minimum bulk concentration of the emulsifier that produces a film; the minimum concentration increases as the emperature increases. The addition of a second surfactant enhances the film formation, for example, a mixture of PGMS/stearic acid (80/20) is a stronger film-former than pure PGMS at the same weight concentration.

For shortenings of the nonliquid type, β' tending fat crystals are favourable, which are able to tangently orientate at the air/fat or fat/moisture interface (Idris *et al*., 1989). The use of α-tending emulsifiers, for example, PGMS combined with a fully saturated

monoglyceride in liquid oils, allows maintenance of a physical film round the oil droplet (Wassell, 2006).

7.8.2.4 Icings

A basic icing is formed by creaming the fat with sugar, and then adding flavour and egg whites (Orthoefer, 2008), and whipping the mixture to incorporate air. Milk or water can be added if further moisture is required. Commercial bakeries are more likely to use shortening rather than butter, which can contain 2–3% of α monoglyceride in the shortening. This provides the necessary emulsification to enhance air incorporation. PS60 can be added to aid in the aeration function, the use of this high HLB emulsifier produces a smooth and stable icing. The appearance of the icing can be enhanced by PGME addition to the shortening, which will result in icings with both excellent gloss and gloss retention (Orthoefer, 2008). High levels of monoglyceride make for less stable icing due to loss of air and subsequent collapse. Low viscosity and hydrated hydrocolloids such as gum arabic can also enhance the stability of such icings and toppings (Al-Assaf and Phillips, 2009).

7.8.3 Coatings

Confectionery coatings are used to enrobe products, and are generally centred on fat-based formulations in their melted form and then allowed to set. The variety of food products enrobed is large: nuts, nougats, flavoured gels, cakes, doughnuts, cookies, sugar wafers, ice cream bars, fruit pieces, indeed almost anything the manufacturer thinks will be enhanced by the addition of the flavour and texture of the coating.

Coatings comprise a solid phase dispersed in a continuous fat phase. The most common solids are cocoa, sugar and milk solids. The coating fat should be rather hard at room temperature so that it does not soften or melt during storage and handling, but it must have a melting point close to body temperature so that it does not leave a waxy mouth feel. The most common emulsifiers for these chocolate-based coatings are PGPR, lecithin, and CITREM examples, where their main function is to control the flow properties (Weyland and Hartel, 2008).

Enrobing involves passing the piece through a curtain, or ‘waterfall’, of melted coating. The thickness of the covering is governed by the viscosity and yield value of the liquid coating. Several factors influence these rheological properties: fat content – increasing the amount of fat lowers the yield value; fineness – more conching, reducing particle size, increases the viscosity and yield value; moisture – interacting with sugar and cocoa solids increases yield value; emulsifiers – the addition of lecithin, PGPR or CITREM modifies both properties.

The shear stress on the coating, as it is pumped to the ‘waterfall’, is above the yield value, and when coating first falls on the piece being enrobed, its flow is governed by viscosity. As the layer of coating thins, due to drainage, the shear stress falls below the yield value and further drainage stops. Decreasing either factor leads to a thinner layer of coating on the enrobed piece.

Lecithin decreases coating viscosity, probably via the 'wetting' mechanism discussed in Section 7.3.4. It is added to the coating at a level of 0.5–1% of the total weight. PGPR, used at 0.1–0.4% of total weight, markedly decreases yield value but has no effect on viscosity. These two emulsifiers have complementary effects and can be used together to achieve the desired thickness of coating on the enrobed piece. Alternatively, one single emulsifier, a CITREM type can be used in the dosage range of 0.3 to 0.6% which can alter both viscosity and yield value of the coating. Hence, this CITREM gets the name, CITREM 2 in 1.

7.8.4 Dressings and sauces

7.8.4.1 Pourable salad dressings

Salad dressing oil is a vegetable oil, usually winterised to prevent development of cloudiness, arising from crystallisation of high melting triglycerides during refrigeration. An anticrystallisation agent can be added to increase the length of time before such cloudiness can develop. Crystal inhibitors deposit on the face of the growing fat microcrystals and interfere with the further deposition of fat molecules. Two compounds specifically approved for this use are oxystearin and polyglycerol esters. Several emulsifiers, in addition to polyglycerol esters, also inhibit crystal formation, among those are sucrose esters, glucose esters and sorbitan tristearate.

The viscosity of a simple emulsion of 35% oil in water is almost that of water. For many dressings a higher viscosity is desired so that the dressing does not drain quickly from the salad collecting in the bottom of the salad bowl, or alternatively suspending spices and finely cut herb particles. Hydrocolloids can be used at concentrations between 0.05–0.3% to give the desired viscosity, and include xanthan, propylene glycol alginate, starch derivatives and cellulose derivatives (Sworn, 2004). The main property demanded of the hydrocolloid, besides giving the desired viscosity, is that it must be stable in an acidic environment, since hydrolysis at low pH decreases viscosity.

Microcrystalline cellulose may be used at 1–2% concentration, increasing viscosity by decreasing the amount of continuous (water) phase in the formulation. It is most often seen in dressings that contain tomato products, where it gives a smooth texture and imparts a certain degree of thixotropy to the mixture so that the dressing clings to the surface of the salad.

7.8.4.2 Spoonable salad dressings

Spoonable dressings are yield stress fluids, i.e. if they are exposed to a stress below that required to produce flow, they behave as a solid. Above the yield value, the dressing begins to flow, and behave as a fluid. The yield value of spoonable dressings and of mayonnaise is an important factor in the consumer perception of product quality.

Starch is a key component, providing the desired structure as well as a creamy texture in the finished product. The modified starch most often used is a highly cross-linked, stabilised waxy maize starch. Waxy maize is essentially 100% amylopectin

cross-linked with sodium trimetaphosphate. The starch requires rather high temperatures for gelatinisation, and sets into a soft gel on cooling. The cross-linked starch is stable against hydrolysis in the low-pH environment of the finished dressing; without this stability, the starch gel softens during storage. Treating starch with propylene epoxide, to give hydroxypropyl starch, produces a starch where the recrystallisaton of the side chains is inhibited. This creates and maintains a creamy texture in the finished dressing during storage, particularly if the dressing is held at refrigerator temperatures or even frozen.

Spoonable salad dressing is made in two stages. First, vegetable oil is emulsified with egg yolk and some of the water and vinegar. The egg yolk lipoproteins are the surface active materials that stabilise this emulsion, which is rather coarse. Hence, although the egg yolks are critical to the stability of the emulsion, egg yolks in themselves are not particularly good emulsifiers. Their surface active parts are lecithin and cholesterol which exist in a ratio of around 6.7:1. However, if the lecithin/cholesterol ratio is low, below 8:1, this may be enough to invert the emulsion to a water-in-oil type. Hence, mustard is usually added to stabilise the system (Becher, 2001; Narsimhan and Wang, 2008).

Mayonnaise is an O/W emulsion, stabilised by the lipoprotein components of egg yolk, with the legal minimum for oil content being 65%, although most commercial products contain 77–82% oil. Liquid egg yolk (45% solids) is the emulsifier, at 5.3–5.8% of total formula weight, and sometimes whole eggs (25% solids) are substituted to give a stiffer product. This is due to the denaturation of egg albumin at the interface forming a matrix in the aqueous phase, increasing the yield stress of the product.

Oil is the internal phase in the emulsion. If all the droplets are spherical, incompressible, and have the same diameter, the maximum volume percentage of oil is 74.05%. If the droplets differ in diameter, then small droplets can fill in the spaces between larger drops. This is the case with mayonnaise, otherwise the emulsion would invert to a water-in-oil emulsion when the oil volume percentage exceeds 74%.

This ‘filling in the spaces’ also has a major effect on the rheological characteristics of the product. Mayonnaise is a yield stress fluid, where the yield value is related to the amount of internal (oil) phase in excess of the 74% (by volume) theoretical limit. Thus, a mayonnaise with the legal minimum of 65% oil by weight has a very low yield value and is seen as too ‘thin’ by users. Mayonnaise with 80–84% oil by weight has a high yield value and is seen as dry or rubbery by home consumers, although it is preferred for institutional use because it does not soak into bread in sandwiches or soften and flow over salads.

7.8.4.3 Sauces

Many different condiments and cooking ingredients can be considered as sauces. Some of the most common are: ketchup; ‘Tex-Mex’ salsas, chilli sauce and taco sauce; barbecue sauce; steak sauce (e.g. Worcestershire sauce); and numerous flavoured sauces meant for use on sandwiches. Consumer acceptance of these items depends, in large

Table 7.6 Regulatory status of emulsifiers[2,3,4].

Emulsifier	USA[a]	EU[b]
Monoglycerides and diglycerides (GRAS)	21 CFR 184.1505	E 471
Succinyl monoglyceride	21 CFR 172.830	
Acetylated monoglyceride	21 CFR 172.828	E 472a
Lactylated monoglyceride	21 CFR 172.852	E 472b
Monoglyceride citrate	21 CFR 172.832	E 472c
Monoglyceride phosphate (GRAS)[1] * Regulation no longer exists. May be investigated by searching the Federal Register.		
Diacetyl-tartrate ester of monoglyceride (GRAS)	21 CFR 184.1101	E 472e
Stearyl monoglyceride citrate	21 CFR 172.755	E 472f
Polyoxyethylene monoglyceride	21 CFR 172.834	
Polyoxyethylene (8) stearate		
Propylene glycol monoester	21 CFR 172.856	E 477
Lactylated propylene glycol monoester	21 CFR 172.850	
Sodium and potassium salts of fatty acids	21 CFR 172.863	E 470
Sorbitan monostearate	21 CFR 172.842	E 491
Sorbitan tristearate (GRAS)	Sa[c]	E 492
Polysorbate 60	21 CFR 172.836	E 435
Polysorbate 65	21 CFR 172.838	E 436
Polysorbate 80	21 CFR 172.840	E 433
Calcium stearoyl-2-lactylate	21 CFR 172.844	E 482
Sodium stearoyl lactylate	21 CFR 172.846	E 481
Stearoyl lactylic acid	21 CFR 172.848	
Stearyl tartrate		E 483
Stearoyl propylene glycol hydrogen succinate (succistearin)	21 CFR 172.765	
Sodium stearyl fumarate	21 CFR 172.826	
Sodium lauryl sulphate	21 CFR 172.822	
Dioctyl sodium sulphosuccinate	21 CFR 172.810	
Polyglycerol fatty acid esters	21 CFR 172.854	E 475
Polyricinoleate (GRAS) (For polyglycerol polyricinoleate there is a GRAS notice for this ingredient: http://www.fda.gov/Food /FoodIngredientsPackaging/GenerallyRecognizedasSafeGRAS /GRASListings/ucm165937.htm)	Sa (GRAS Notice No. 266)	E 476
Sucrose fatty acid esters	21 CFR 172.859	E 473
Sucrose glycerides		E 474
Lecithin (GRAS)	21 CFR 184.1400	E 322
Hydroxylated lecithin	21 CFR 172.814	E 322
Oxystearin	21 CFR 172.818	
Triethyl citrate (GRAS)	21 CFR 184.1911	

Notes: [a]US code of Food Regulations, Title 21.

[ab]European Parliament and Council Directive No.95/2/EC–(20 February 1995) and amendments.

[bc]Self-affirmed GRAS.

GRAS: generally recognized as safe; blank spaces indicate the specified emulsifier is not listed in the jurisdiction concerned.

[1]The references to the Code of Federal Regulations (CFR) Title 21 were found here: http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?sid=c7a75c5bad2566718b7c68d6def84f4candc=ecfrandtpl=/ecfrbrowse/Title21/21cfrv3_02.tpl

[2]If an ingredient is not listed in the CFR, then it may be permitted for use by a GRAS determination made by an individual with the option of notifying FDA through the GRAS notice procedure. I think one of the ingredients on the list is covered by a GRAS notice, for which I listed the notice number and link where it may be found. The link to GRAS notices are here: http://www.accessdata.fda.gov/scripts/fcn/fcnNavigation.cfm?rpt=grasListinganddisplayAll=true

[3]All of the changes to the US column were made based on data accessed electronically on Sept. 18, 2009.

[4]This link lists most ingredients/additives along with their CFR references:
http://www.accessdata.fda.gov/scripts
/fcn/fcnNavigation.cfm?rpt=eafusListinganddisplayAll=true.

part, on their rheological characteristics. The sauce must spread easily, and therefore have relatively low viscosity, but concomitantly remain where it is put, and therefore have sufficient yield value. The values of viscosity and yield stress value can be modified by the inclusion of various hydrocolloid thickeners to the formulation. Xanthan gum and carboxymethyl cellulose are popular viscosity increasers, while microcrystalline cellulose and carrageenan are popular for increasing yield value (cling).

7.9 Regulatory aspects

Emulsifiers are recognised ingredients which impart function to foods and, as such, their use is regulated by most governments. In the USA they are approved by the Food and Drug Administration in one of three categories – approved additives, generally recognised as safe (GRAS) materials, or affirmed as GRAS compounds – and are listed in Code of Federal Regulations, Title 21. In Europe, the European Union issues European Parliament and Council Directives that list food additives authorised for use in human foodstuffs.

Most of the emulsifiers commonly used in foods are listed in Table 7.6. Blank spaces indicate that the particular emulsifier is not listed by that jurisdiction. Table 7.6 is aimed only as a guide to the regulations. Many emulsifiers are approved for only certain kinds of food products, and often the allowable amount is limited. Before embarking on a large-scale product development project, the actual regulations concerning the emulsifiers to be used should be consulted to make sure that the final product meets all the regulatory guidelines.

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8

Food safety and quality issues of dairy fats

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8.1 Introduction

The origin of food safety in the form of Hazard Analysis and Critical Control Point (HACCP) began during 1959–1960. During that period food safety and quality systems followed a procedure where only end products were being tested to assure their suitability for human consumption. However, when technicians were assessing whether all necessary protection was in place to contain *Salmonella* infection in food destined for the US National Aeronautics and Space Administration (NASA), it was realised that the procedures operating at that time were inadequate to ensure the safety of food for the astronauts and a preventative system was required instead. The responsibility for the development of the appropriate systems and safety protocol to ensure the production of safe foods was given to the Pillsbury Company in the US who were to work alongside NASA on this project.

The initial study into food safety highlighted the hazard analysis procedures and later linked them to critical control points, which initiated the abbreviation HACCP, which is known to the food industry world over. Publication of the NASA food safety procedures was documented in the early 1970s.

8.1.1 Codex Alimentarius

In 1963, the Food and Agriculture Organization (FAO) and the World Health Organisation (WHO) of the United Nations created the Codex Alimentarius Commission to develop food standards, guidelines and related codes of practice under the Food Standard Programme (Codex Alimentarius Commission, 1995). In 1991, Food Trade

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recommended to the FAO/WHO that the Codex Alimentarius Commission (CAC) should incorporate risk assessment principles into its decision-making process (WHO/FAO 2006). Since then the CAC, FAO and WHO have convened a number of expert consultations to provide advice to Codex and member countries on practical approaches to the application of risk analysis to food standard issues. The outcome of that work, together with the progress made with work related to developing a systematic framework for applying principles and guidelines for food safety risk analysis propelled a structured protocol for safe production of foods. The food safety system became an essential item for all food producers worldwide and the FAO/WHO were cited in the Codex in 1985. In 1993, the European regulation cited the system and detailed its use in food production.

8.1.2 The European Food Safety Authority (EFSA)

The European Food Safety Authority (EFSA) was established by the European Parliament in 2002 following a series of food scares such as BSE, dioxime, which undermined consumer confidence in the safety of the food chain. EFSA is an independent European agency and the EU budget allocates funds for its activities. It is governed by an independent Management Board whose members are appointed to act in the public interest and do not represent any government, organisation or sector.

EFSA's role is to assess and communicate all risks associated with the food chain and provide independent scientific advice on existing and emerging food safety issues (Deluyker and Silano, 2012). Their communication activities aim to provide appropriate, consistent, accurate and timely solutions and information based on risk assessments and scientific work to stakeholders and the public at large.

8.1.3 The importance of the HACCP in food production

This food safety system identifies where hazards might occur in the food production process and puts in place stringent measures to prevent the hazard from occurring. Its procedure strictly monitors and controls each step in the food process so that the chances of a hazard occurring are minimised or eliminated. The control parameters include potential hazards related to microbiological, chemical and physical contaminants, and that reduces food-borne hazards, leading to strengthening the public health protection.

The incidence of food contamination from chemical residues such as pesticides and antibiotics has been reduced and is almost non-existent. Those related to microbiological contaminants are causing concern in food production due to *Salmonella*, *E. coli* 0157H7, *Listeria*, *Campilobacter* and *Clostridium botulinum*.

Having a food safety system in place and managed properly will boost the confidence of the customers, maximise product safety, improve the professional image of the company and lift the standard of operation.

8.1.4 Food safety standards

All food businesses are obliged to supply safe, legal and quality products to their consumers. The sixth issue of the Global Standard for Food Safety commenced on the 1st January 2012, which was originally developed and introduced by the British Retail Consortium (BRC) in 1998. This is a certification scheme that provides a framework to produce safe, legal and quality food and is recognised by many retailers, food service companies and manufacturers across the world. Food businesses are certified after completion of a satisfactory audit by an auditor employed by an accredited third-party certification body approved by the BRC. The standard requires facilities to have senior management commitment, a fully implemented risk-based HACCP system, a documented quality management system and effective prerequisite systems to control the product, process, personnel and facilities (British Retail Consortium, 2011).

8.2 Food-borne disease: the problem

Food safety and food-borne diseases are issues of universal concern. Unsafe food has been a human health problem since history was first recorded, and many food safety problems encountered today are not new. Governments throughout the world are intensifying their efforts to improve the safety of the food supply. Food-borne diseases are a widespread public health problem and a significant cause of reduced economic productivity. They impair the national economy and development, because of both direct and indirect costs, as well as having serious implications for food export and tourism (WHO, 2006). Food-borne disease is classified as any disease from microbiological origin caused by, or thought to be caused by, the consumption of contaminated food or water (*CDR Review*, 1995).

Food-borne disease is a widespread global issue which is difficult to estimate and the true scale of the problem is unknown. However, effective control of food-borne disease must be based on information evaluated regarding food-borne hazards and the incidence of food-borne disease. It has been reported that in 2005 alone 1.8 million people died from diarrhoeal disease. A great proportion of these cases can be attributed to contamination of food and drinking water (WHO, 2007). It is estimated that 5.5 million people (1 in 10 people) in the UK apparently suffer from food-borne illnesses (Foodlink, 2002).

8.2.1 Microbiology of milk and milk products

Milk is an invaluable source of human nutrition, and yet provides favourable physical environments for the multiplication of microorganisms. Milk is an animal product subjected to different processes throughout its production and, therefore, can result in contamination by a wide spectrum of microbial types (Gilmour and Rowe, 1990).

Milk provides an excellent culture medium for the growth of pathogenic microorganisms, such as *Salmonella* spp., *Staphylococcus aureus, Listeria monocytogenes, Campylobacter* spp., *Yersinia enterocolitica*, and *Bacillus subtilis*. Two major pathogens that are becoming increasingly important in the dairy industry are *Bacillus cereus* and Vero cytotoxin-producing *Escherichia coli* – VTEC O157 (Neaves and Langridge, 1998).

Milk from the udder of a healthy cow contains very few organisms (no more than about 300/ml), and these are of no danger to the consumer. Milk is contaminated generally by post-production handling procedures including milking equipment and the general hygiene of the operatives (Ranjith and Wijewardene, 2006). The microbial contamination during production, collection, and handling will be reflected in the initial micro-flora in milk that is monitored immediately after production.

Milk can be contaminated with faeces during its production and unpasteurised dairy products host the main risk. Cheese produced from unpasteurised milk has caused illness after VTEC O157 subsisted through the cheese-making process. Recontaminations after pasteurisation and failures in pasteurisation can also contribute to outbreaks in the dairy industry (Veterinary Surveillance Strategy, 2006).

8.2.2 Magnitude and nature of milk-borne disease outbreaks

The dairy industry is a semi-intensive animal farming industry in the UK that accounts for 19% of the UK agricultural production. It is the single largest agricultural sector at £2.7 billion, with an annual production of 13.5 billion litres of milk (UK Dairy Industry, 2007).

Milk is a highly nutritious food that also supports the growth of both pathogenic and spoilage organisms. Outbreaks of milk-borne disease date from the outset of the dairy industry. Several outbreaks of food poisoning attributed to milk and milk products were reported in the UK before the Second World War (i.e. diphtheria, scarlet fever, tuberculosis, and typhoid fever) before heat treatment was invented, and therefore those outbreaks were inevitably linked to consumption of raw milk (Ryser, 2001).

The importance of a variety of etiological agents in milk-borne disease has changed significantly and drastically over time, with the practice of the pasteurisation of milk. It is stated that the number and size of the outbreaks have decreased with the impact of increased pasteurisation of milk (Ryser, 2001).

The major milk-borne outbreaks reported in the UK are salmonellosis, campylobacteriosis, yersiniosis, listeriosis, staphylococcal food poisoning, etc. However, most of these outbreaks were associated with recontamination of heat-treated milk products. Outbreaks of milk-borne salmonellosis and campylobacter enteritis were contained to a reasonable extent in England and Wales throughout the 1970s and early 1980s (Sharp, 1992).

The Milk Special Designation Amendment Regulations 1985 banned the sale of untreated cow's milk in canteens, shops, supermarkets and other retail outlets in England and Wales, but continued to permit sales direct from dairy farms in rural areas. More stringent microbiological standards were introduced in 1990, including the requirement of carrying the warning 'This milk has not been heat-treated and

may contain organisms harmful to health' on the untreated milk being sold in retail outlets (Sharp, 1992).

The Dairy Products (Hygiene) Regulations 1995 (as amended in accordance with European Commission obligations) implement the legislative provisions in England and Wales and establish hygiene rules for the production, wrapping, storage and transport of milk and milk products.

Milk-borne outbreaks accounted for less than 1% of all general outbreaks of infectious intestinal disease in England and Wales in 1992–1996. The new regulations came into force on 1st January 2006 which replaced the Dairy Products (Hygiene) Regulations 1995, as amended, that apply to all premises used in the production of raw milk for human consumption (Dairy Hygiene Inspections, 2007).

At present, the dairy industry is proud of the fact that very few outbreaks (less than 3.5% of general outbreaks) have been attributed to dairy products (Neaves, 2007, personal communication) following the implementation of improved sanitary practices, and advances in milk handling and animal husbandry practices.

8.2.3 Food-borne disease outbreak surveillance

An incident of food-borne illness refers to either an outbreak or a sporadic case (Sockett *et al*., 1993). An outbreak is an incident in which two or more people, thought to have a common exposure, experience a similar illness or proven infection and at least one of them is ill (HPA, 2003).

A general outbreak is an outbreak affecting members of more than one private residence or residents of an institution, whereas a family outbreak affects members of a single house residence (McLauchlin and Little, 2007). A sporadic case is a single case which has not apparently been associated with other cases, or carriers, in the same period of time (*CDR Review*, 1995).

Surveillance is the ongoing systematic collection, analysis and interpretation of outcome-specific data, closely integrated with the timely dissemination of these data to those responsible for disease control and prevention.

The general outbreak surveillance was initiated in England and Wales by the Public Health Laboratory Service (PHLS) in 1992. The data of the setting in which the outbreak occurred, the mode of transmission, the causative organism, and the details of the laboratory and epidemiological investigations were collated using a standardised structured questionnaire (McLauchlin *et al*., 2007).

Under the Public Health (Control of Disease) Act 1984, all doctors and general practitioners (GPs) have a statutory duty to notify the Consultant in Communicable Disease Control (CCDC) of food poisoning. The CCDC works for the Health Protection Agency (HPA, previously called the PHLS) and thus is called the Consultant in Health Protection.

Data on laboratory confirmed cases of food-borne disease have been produced in England and Wales by the HPA. Reports are compiled via electronic reporting to a central database at the HPA Centre for Infections (CfI) in London (McLauchlin *et al*., 2007).

The outbreak data are used to identify routes of transmission, the trends of the pathogens, the trends in food vehicles, new pathogens and vehicles of infections, the impact of the outbreak in different settings, and the impact of specific interventions (McLauchlin and Little, 2007). Food-borne disease surveillance is integrated with food monitoring data along the entire feed-food chain (WHO, 2002).

8.2.4 Surveillance of milk-borne disease outbreaks

The HPA-CfI has received 56 *Salmonella enteritidis* serotype *montevideo* isolates, which reflects a significant national increase in reported *S. montevideo* infections in England and Wales during the period of March to July 2006. The HPA-CfI has attempted to contact all cases and detailed food histories have been obtained from 15 cases where 13 (87%) of the cases were associated with seven chocolate products made by one of the biggest chocolate companies in Britain (*CDR Weekly*, 2006).

Twenty-seven milk-borne outbreaks of infectious intestinal disease were reported to the Communicable Disease Surveillance Centre (CDSC) during the period of 1 January 1992 to 31 December 2000. These outbreaks represented a fraction (2%), of all outbreaks of food-borne origin (no. = 1774) reported to the CDSC, but they were characterised by significant morbidity. They also found that unpasteurised milk (52%) was the most commonly reported transmission medium for infection in milk-borne outbreaks. The milk sold as pasteurised accounted for the majority of the rest (37%). *Salmonella spp*. (37%), VTEC O157 (33%) and *Campylobacter* (26%) were the most commonly detected pathogens, and most outbreaks were linked to farms (67%). This report further highlights the importance of VTEC O157 as a milk-borne pathogen and the continued role of unpasteurised milk in human disease (Gillespie *et al*., 2003).

The number of reported outbreaks associated with milk and dairy products declined in the period 1987–89 (annual average 8 incidents) compared with the period 1981–86 (annual average 16 incidents). Unpasteurised milk accounted for half of all incidents recorded during the period 1987–1989. Despite an overall improvement in the quality of milk, 8 incidents were due to unpasteurised milk. Three outbreaks associated with the consumption of heat-treated milk occurred in 1987 (2) and 1989 (1), due to campylobacter infection, and accounted for 45% of cases. Seven incidents recorded were due to dairy products other than milk. Three were due to cheese, including two where unpasteurised milk was known to have been used (Sockett, 1991).

Thirty-two outbreaks (11 in 1983 and 21 in 1984) were associated with the consumption of milk and dairy products and it is stated that at least 714 people were reported as suffering in England and Wales. Twenty-seven of the outbreaks were attributed to raw milk, two to contaminated pasteurised milk and one each to cheese, cream and ice-cream where twenty-two were due to *Salmonella*, seven due to *Campylobacter* and one each to *Staphylococcus aureus, Yersinia enterocolitica* and *Streptococcus zooepidemicus*. Two sporadic cases of *Corynebacterium ulcerans* infection associated with raw milk were also reported. It also highlighted that there were eight deaths, all associated with the *S. zooepidemicus* outbreak. The research suggested the urgent need to enforce the pasteurisation of milk and dairy products in England and Wales to control milk-borne outbreaks affecting rural communities (Barrett, 1986).

There were 233 reported outbreaks of communicable disease attributed to milk and dairy products affecting nearly 10,000 people in England and Wales during 1951–80, of whom four died. Tuberculosis and brucellosis have been controlled, but milk-borne outbreaks of *Salmonella* and *Campylobacter enteritis* due to raw or defectively pasteurised milk are common and may be increasing in number. It is suggested that universal heat treatment of milk is an effective preventive measure and the fact that untreated milk is still allowed to be sold in England and Wales is thoroughly regretted (Galbraith *et al*. 1982).

8.2.5 Control of food-borne diseases

The prevention of food-borne disease depends on careful food production, handling of raw materials and finished products, and preparation of finished foods. Hazards can be introduced at any stage from production to consumption. Various technologies are available to prevent food-borne illnesses. Monitoring and control strategies are systematically applied to food production to prevent food-borne illnesses. The Hazard Analysis Critical Control Point (HACCP) system is a much more effective and efficient science-based food safety management system than traditional end product testing and visual inspection practices. The use in HACCP systems in food production, processing, distribution and preparation is the best-known systematic approach to ensure food safety (Altekruse *et al*., 1997).

The HPA, the Food Standards Agency (FSA), and the Department of Health are the main local authorities involved in the detection, investigation and management of food-borne outbreaks.

The knowledge gained from intensive outbreak investigations provides a quantitative estimate of food-borne risk that can serve as a benchmark for developing risk assessment models and calculations so that this may prevent more cases happening in the future.

The surveillance of food-borne disease is the basis for the formulation of national strategies to reduce the health and social burden of food-borne disease. Detailed and accurate knowledge about the nature and levels of food-borne diseases are prerequisites for action to lower these levels. The present lack of reliable data on food-borne disease in the UK and elsewhere is a major obstacle for evidence-based interventions (WHO, 2002).

8.2.6 Safety of milk and milk products

The control of microbiological hazards in the dairy industry is necessary to ensure the food safety and quality of milk and milk products. A sound prerequisite programme and HACCP system together will assure the safety and quality of milk and milk products. EC Regulation 852/2004 requires that dairy operators should apply the HACCP principles to ensure the safety of their products (Code of Practice, 2006). Pasteurisation is the main critical control point in ensuring the safety of milk and milk products. The hygiene regulation effective from the 1st of January 2006 will provide the necessary prerequisites for the application of HACCP to pasteurisation process (the High

Temperature Short Time – HTST method). Pasteurisation has been defined in Regulation 2074/2005 as a treatment involving (1) a high temperature for a short time (at least 72°C for 15 seconds); (2) a low temperature for a long time (at least 63°C for 30 minutes); or (3) any other combination of time–temperature conditions to obtain an equivalent effect, such that the products show, where applicable, a negative reaction to an alkaline phosphatase test immediately after such treatment (Wijewardene, 2008).

8.3 Food safety and quality issues of dairy fats

Food-borne illness continues to pose a serious public health problem globally. The continued growth of new food-borne pathogens and related food-borne outbreaks has been the reason for the remarkable media alertness and hence an increased demand for safer food by the public. As a result, it is clear that government regulatory authorities around the world are striving to introduce more stringent regulations for food safety.

The Hazard Analysis and Critical Control Point (HACCP) system is the most effective way to ensure the safety of food and the safety of the operations in food industry. HACCP pinpoints the things that can go wrong and sets out preventive measures. The HACCP concept originated in the early 1960s to ensure the microbiological safety of the food used by the astronauts in the US manned space programme, and it was then launched publicly in the 1970s. Since then, the HACCP system gradually developed, though in the mid to late 1980s the HACCP was systematised into a more organised approach. The HACCP was based on the engineering concept of failure, mode and effect analysis (FMEA) which focuses at what could potentially go wrong at each and every stage in an operation together with possible causes and likely effects, and then sets effective control measures for them (Mortimore and Wallace, 1998).

The HACCP concept was accredited by the Food and Agriculture Organization of the United Nations and the World Health Organization (FAO/WHO) in 1983 as an effective way of controlling food-borne disease, and they advised that the HACCP must be put in place of traditional end product testing (Mayes and Mortimore, 2001). The FAO/WHO also support the continuous development of national policies to improve food safety and quality to protect the consumers' health and to foster the national economy.

The Codes and Guidelines for the Application of the HACCP system were adopted by the FAO/WHO Codex Alimentarius Commission in 1993. All the relevant Codes of Hygienic Practices including the Codex Code on General Principles of Food Hygiene were amended to include recommendations for the application of the Codex HACCP Principles and Guidelines. These Guidelines play a vital role in the international harmonisation of the application of the Codex system.

Following the successful conclusion of the GATT Uruguay Round of Multilateral Trade Negotiations in April 1994, the Codex Standards, the guidelines (including the Guidelines for the Application of HACCP system) and the recommendations constitute the reference for food safety requirements in international trade.

Improvements in the protection of public health depends on the advancement of food safety, therefore governments, the food industry and consumers have a communal responsibility to adopt the best practices to control food safety hazards. Other than adopting and monitoring compliance with national food legislation, the governments should actively promote food safety measures through the adoption of food safety management systems such as the HACCP. It is fair to state that the advancement of HACCP system provides interdependent benefits to the governments, including safer food, therefore increased public health protection, increased confidence by national consumers and tourists and hence an increase trade which ensures the economic growth and national development (FAO/WHO, 2006).

All foods including milk and milk products have the potential to cause food-borne illness. Dairy animals may carry human pathogens. Such pathogens present in milk may increase the risk of causing food-borne illness. It is important that control measures are applied during both primary production and processing to minimise or prevent the microbiological, chemical or physical contamination of milk. In addition, special attention should be given during the processing of different milk products so that inadvertent cross-contamination does not occur, including with respect to ingredients that may contain allergenic substances.

8.3.1 Approach to risk assessment and the HACCP

There are well-documented guidelines for food manufacturers to follow and develop a specific system to ensure a high level of food safety in the manufacturing process. Any food safety system must monitor the whole food chain which includes the agrarian origin, transportation, storage, industrial processing, handling by the consumer and the environment. Risk assessment and the HACCP are constituents of the overall risk analysis process which includes risk management and risk communication. The approach to implementation of HACCP starts with good manufacturing practices (GMP) and good hygienic practices (GHP) and culminates in microbiological criteria. GMP is an essential part of the HACCP identified as a prerequisite.

In the early development period of food safety the emphasis on the prerequisite requirement appeared to take low priority, and took up maybe less than 25% of the total content of the HACCP implementation programme. This is an important stage now and it probably takes up about 40% of the total programme content. It is widely recognised that GHPs form the basis of an integral part of food safety. The prerequisite programme provides the basic environmental and operating conditions that are necessary for the production of safe, wholesome food.

The prerequisite is not limited to specific programmes and based on the type of foods in question it varies, and the following are some aspects commonly included in the majority of manufacturing processes:

- *Facilities*. Is the establishment located in a suitable place and maintained to sanitary design principles? Is it arranged for linear product flow and traffic-controlled to minimise cross-contamination from raw to cooked materials?

- *Supplier control*. All materials supplied for food use must ensure that suppliers have in place GMP and food safety programmes and carry a continuing guarantee.
- *Specifications*. There should be written specifications for all ingredients, products and packaging materials.
- *Production equipment*. All production equipment should comply with sanitary design principles and preventive maintenance and calibration schedules should be established and documented.
- *Cleaning and sanitation*. All procedures for cleaning and sanitising the equipment should be written and followed. A master sanitation schedule should be in place.
- *Personal hygiene*. All employees and other persons who enter the manufacturing plant should follow the requirements for personal hygiene.
- *Training*. All employees should receive documented training in personal hygiene, GMP, safety and sanitation procedures, personal safety, and their role in the HACCP programme.
- *Chemical control*. Documented procedures must be in place to assure the segregation and proper use of non-food chemicals in the plant. These include cleaning chemicals, fumigants, and pesticides or baits used in and around the plant.
- *Receiving, storage and shipping*. All raw materials and products should be stored under sanitary conditions and the proper environmental conditions such as temperature and humidity to assure their safety and wholesomeness.
- *Traceability and recall*. All raw materials and products should be lot-coded and a recall system should be in place so that rapid and complete traces and recalls can be done if a product retrieval is necessary.
- *Pest control*. Effective pest control programmes should be in place.

Other parameters that may be included in the prerequisite programme are quality assurance procedures, operating procedures for sanitation, product formulations and recipes, glass control, procedures for receiving, storage and shipping, labelling and employee food and ingredient handling practices.

8.3.1.1 Sanitary standard operating procedures (SSOP)

It is also necessary to have documentation prepared for sanitary standard operating procedures (SSOP) applicable to the food business. Here the procedure is documented indicating daily actions to prevent direct contamination or adulteration of the product. The following points are considered:

- Preparation of food contact surfaces, equipment and utensils.
- Frequency of SSOP for each procedure.
- Employee's responsibility for implementing and maintaining the procedures.
- Record keeping on a daily basis and include updates and corrective actions taken.

- The documents are signed and dated by a responsible person with overall authority.

8.4 Implementing the HACCP

The sequence in the initial steps when implementing food safety system in food production is given in Figure 8.1.

After the initial six steps the most important stage is to determine the critical control points (step 7) in the manufacturing process. To help with this task a procedure is illustrated in Figure 8.2. The questions should be answered in sequence.

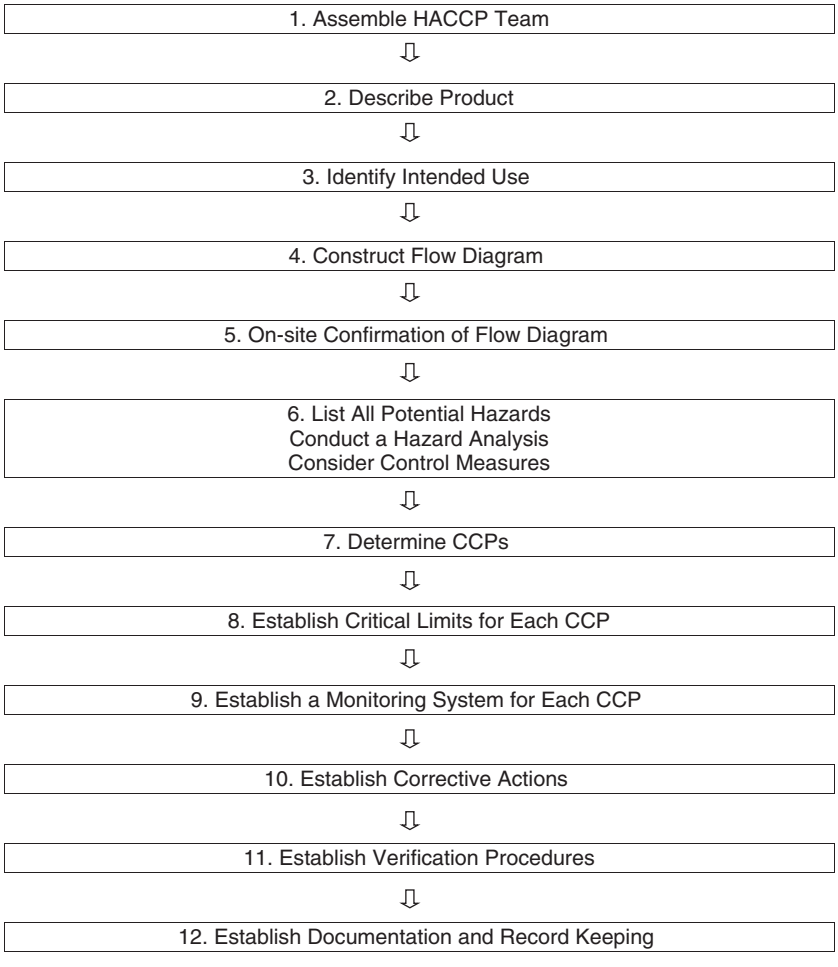

Figure 8.1 Logical Sequence for Application of the HACCP. *Source:* Codex, 1995. Reproduced with permission of Food and Agriculture Organization of the United Nations.

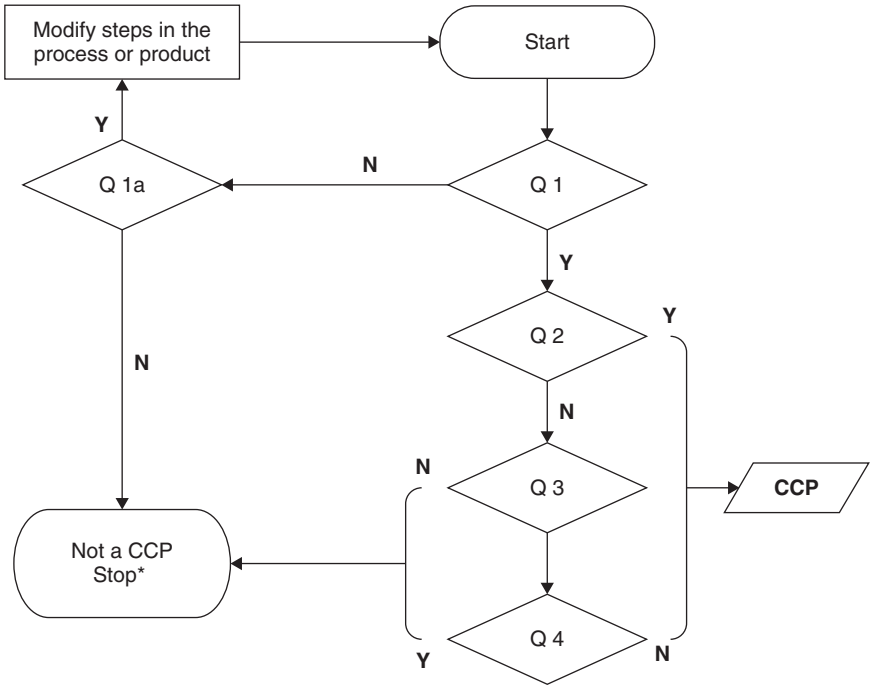

Figure 8.2 Example of a decision tree to identify CCPs. *Source:* Codex, 1995. Reproduced with permission of Food and Agriculture Organization of the United Nations.

The HACCP team is formed mainly of those who are key managers or supervisors on the site/organisation capable of developing the food safety system for the intended production line. The required expertise may not be available on site/organisation, in which case advice should be obtained from other sources, such as trade and industry associations, independent experts, regulatory authorities and food safety literature and guidance documents.

8.4.1 Areas concerning food safety

The HACCP team must identify every danger area that is a potential threat to the intended food manufacturing process. Some examples of the possible dangers threatening food production are as follows:

- *Biological hazards*. This may be due to macrobiological (e.g. poisonous insects) or microbiological (bacterial infections, e.g. Salmonella, Campylobacter) and virus infections (e.g. hepatitis).
- *Parasites*. Due to nematodes and other worms.
- *Chemical contaminants*. From herbicides, pest control baits, allergens, toxic metals, nitrites, nitrates, polychlorinated biphenyls and dioxins.

- *Bacterial poisoning*. Presence of natural toxins even when the organism has been removed (e.g. Botulism, Staphyloccocine and other toxins).
- *Physical hazards*. Broken glass, metal, stones, bone chips, wood, pests or broken plastic.
- *Radioactive contaminants*. Raw material from areas affected by a radioactive leak or fall-out.
- *Unsuitable processing conditions*. Very high temperature cooking/frying where dangerous intermediate chemicals are formed (e.g. acrylamid in French fries).
- *Wrong concentrations of ingredients*. Excess supply of vitamins, trace elements, lack of dietary fibres.

It is possible that one or many of these hazards are associated with prepared foods and should be thoroughly investigated for possible threats from them at each stage of production. Many hazard issues can be controlled effectively as part of GMP on the premises.

Food safety is shared by everyone involved with food production to consumption, including growers, processors, regulators, distributors, retailers and consumers. The government usually provides an enabling institutional and regulatory environment for food control. The extent to which the government is involved directly in food safety varies in different countries but it is normal to have dedicated scientific institutes, agencies, industry organisations, analytical laboratories, food regulatory departments and others collaborating to develop food safety systems.

In various risk categories the approach varies towards controlling them. For example, the chemical hazards such as food additives, residues from crop pesticides and veterinary drugs have been given zero risks as tolerance for food applications. However, for microbiological hazards, the tolerable limits may be given as guides to keep the levels down rather than to eliminate them entirely as they are present everywhere in the normal food production environment. The exception to this is the aseptic packing environment where a sterile area in the packing environment is a must for the long shelf-life production of foods. In the production of fresh foods it is required to eliminate all pathogens and other toxin-producing microorganisms to ensure the safety of the foods.

Hazards known to have less significance before may regain prominence in modern foods, for example, acrylamide residues in baked and fried starchy foods and *Campylobacter* in poultry. Others previously not being identified have also gained worldwide importance, such as a mutant protein, technically called a ‘prion’ that causes ‘mad cow disease’ or bovine spongiform encephalitis (BSE). Food safety is a fundamental public health concern and to achieve safe foods has become a major challenge to all involved from the raw material suppliers to the retailers and the consumer. New technologies such as the genetic modification of agricultural crops have raised further food safety concerns that require assessment and management and adequate risk communication.

8.5 Food safety and quality in dairy production

As described in Section 8.4.1, this section highlights some of the risk areas in food manufacture. However, it is also required to start from the environment or the premises and gradually work your way into the production plants and processes. The areas under consideration would include the following:

- The environment is suitable and free of any nearby sources of contaminants such as harmful foreign materials, pests, weeds, flooding and stagnant water, birds, tainting substances, etc.
- Building to ensure the design, construction and sanitation comply with production guidelines.
- Food handling equipment is appropriately designed, installed, maintained and complies with sanitary requirements.
- Movement of raw and finished products are streamlined and do not cross at any stage to cause cross-contamination.

The details of the full HACCP system development and implementation are beyond the scope of this chapter but the emphasis here would be to highlight the basic steps in the food safety of some dairy product manufacture.

All major food manufacturers globally have adapted HACCP systems for all their manufacturing procedures and now more and smaller food producers are also implementing basic food safety practices to comply with regulatory requirements. Once a system is in places the aim is to improve consumer protection by regularly tidying up all the possible weak areas and raising the standard of food production.

Small businesses may find it difficult to address the national and international legislations covering food quality/safety. In most cases the slow progress in implementing the HACCP is due to lack of technical expertise and economic constraints necessary for compliance with stringent legislation. The HACCP ensures the safety, whereas the ISO 9001system is focused on ensuring the quality.

The HACCP system should be developed based on individual products' characteristics, specifically to reflect the manufacturing techniques, storage, distribution and consumption method. In the development of a HACCP programme, the work commences after forming the HACCP team who are experts from various fields in the food industry. The team initially understand the details of the product manufacture by establishing a process flow chart. Using the process flow chart and the decision tree (Figure 8.1 and Figure 8.2), the team establish the CCPs in the process. This information finally produces the control chart for the manufacture of the product which indicates the CCPs, monitoring points and corrective actions for the management. A case study of selected dairy product manufacture is given in Sections 8.5.1 to 8.5.4. Some of the information for the flow charts is derived from Bylund (1995) and Varnam and Sutherland (1994).

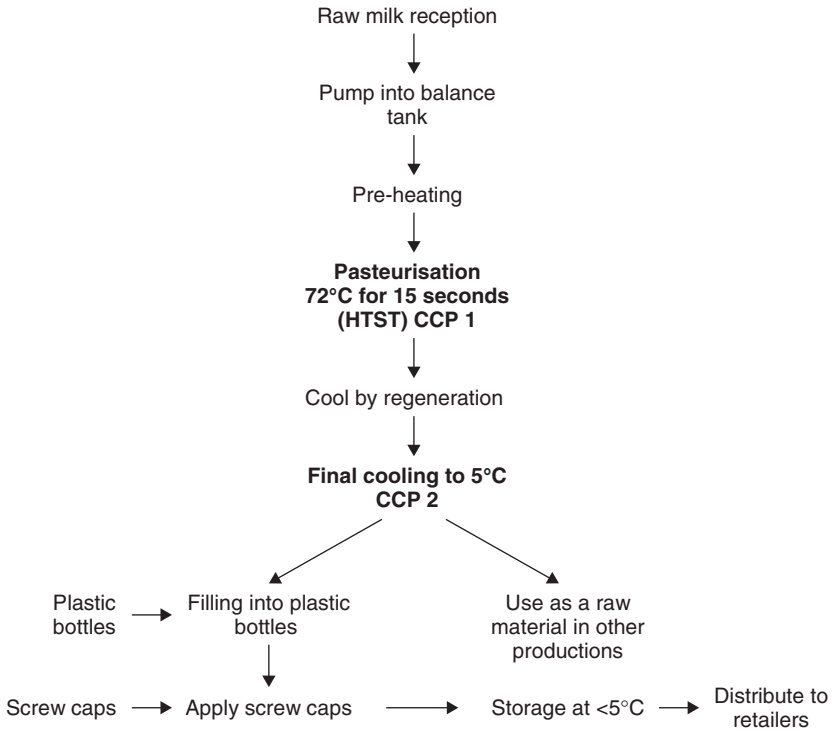

Figure 8.3 The HACCP flow chart for milk pasteurisation.

8.5.1 Pasteurised milk

The stages in the pasteurisation process of milk are given in Figure 8.3 and Tables 8.1 and 8.2 show the hazard analysis and CCP identification in the pasteurisation process and the HACCP control chart.

8.5.2 Cheese

The stages in the process of the manufacture of cheese are presented in Figure 8.4. Tables 8.3 and 8.4 show the hazard analysis and CCP identification in the pasteurisation process and the HACCP control chart for cheese.

8.5.3 Yogurt

The stages in the manufacture of yogurt are given in Figure 8.5, and Tables 8.5 and 8.6 show the hazard analysis and CCP identification in the pasteurisation process and the HACCP control chart.

Table 8.1 Pasteurisation of milk: Hazard analysis and CCP identification for raw materials and process steps.

Raw material/ Process step	Hazard	Control measures	Significant hazard	Q1	Q1a	Q2	Q3	Q4	CCP	Justification
Milk	Survival of vegetative pathogens	Effective pasteurisation	No	Yes		Yes	No		No	Product will be pasteurised
Plastic bottles and screw caps	No hazard identified			No					No	Food grade material, Supplier Quality Assurance (SQA)
Mains water	No hazard identified			No					No	No contact with the product, only use as a cooling medium
Milk reception	No hazard identified								No	Vegetative pathogens destroyed by pasteurisation Food hygiene practices are observed – prerequisite programme.
Pump to balance tank	No hazard identified								No	Food hygiene and equipment maintenance in place – prerequisite programmes
Pre-heating by regeneration	Vegetative pathogens	Time/ temperature control/ Pasteurise at later stage	No	Yes		No	Yes	Yes	No	Vegetative pathogens destroyed by pasteurisation
Pasteurisation	**Survival of vegetative pathogens; *Mycobacterium tuberculosis***	**Effective pasteurisation Correct temperature/ time combination 72°C for 15 seconds**	**Yes**	**Yes**		**Yes**			**Yes**	**No subsequent step to remove hazard**
Cooling by regeneration	Inadequate cooling	Effective cooling Control of time/ temperature	No	Yes		No	Yes	Yes	No	Commissioning of the plant ensured the 95% regeneration and this step follows a subsequent cooling step
Final cooling by chilled water	**Growth of surviving spore forming pathogens due to inadequate cooling**	**Effective cooling Correct temperature of the product maintained at (5°C)**	**Yes**	**Yes**		**Yes**			**Yes**	**Control the quality and limit the growth rates of pathogenic and spoilage microbes**

Manual filling	*St. aureus* transfer from operator's hands	Effective hand washing	No	No	Food hygiene practices are observed
Apply caps	*St. aureus* transfer from operator's hands	Effective hand washing	No	No	Food hygiene practices are observed
Storage and distribute to retailers	No hazard Identified	Correct temperature in store $<5^{\circ}C$		No	Food hygiene and equipment maintenance in place – prerequisite programmes
Use as a raw material in other products	No hazard identified			No	Subsequent steps of other manufacturing processes will destroy the vegetative pathogens

Raw material control decision tree questions

Q1 Is there a hazard associated with this raw material?

Q2 Are you or the customer going to process this hazard out of the product?

Q3 Is there a cross-contamination risk to the facility or to the products which will not be controlled?

Process step decision tree questions

Q1 Do control measures exist? Q1a. Is control at this step necessary for safety?

Q2 Is the step specifically designed to eliminate or reduce the likely occurrence of a hazard to an unacceptable level?

Q3 Could contamination with identified hazard(s) occur in excess of acceptable level(s) or could these increase to unacceptable levels?

Q4 Will a subsequent step eliminate identified hazards or reduce the likely occurrence of a hazard to acceptable level(s)?

Table 8.2 Pasteurisation of milk: HACCP control chart.

Process stage	Hazard	Control Measures	CCP No.	Specifications/ Critical Limits	Monitoring			Corrective actions	
					Procedure	Frequency	Responsibility	Procedure	Responsibility
Pasteurisation	Survival of vegetative pathogens; *Mycobacterium tuberculosis*	Correct effective heat process 72°C for 15 seconds	CCP1	Temperature/ Time combination 72°C for 15 seconds	Calibrated heat exchanger chart recorder Visual check and sign off	Every 6 months Every 30 minutes	Instrument Calibration Company Operator	Undertaking of the doubtful batches Interrupt functioning and repair the heat exchanger	Operator Contract Engineering Manager
Final cooling by chilled water	Growth of surviving spore forming pathogens due to inadequate cooling	Control of effective cooling rate, Temperature of the product is maintained below 5°C	CCP2	Cooling at or below 5°C	Preventive maintenance of the Glycol Chiller Visual check of the digital recorder	Every 6 months Every 30 minutes	Contract Refrigeration Company Operator	Rejection of the doubtful batches Interrupt functioning and repair the Glycol Chiller	Operator Contract Engineering Manager

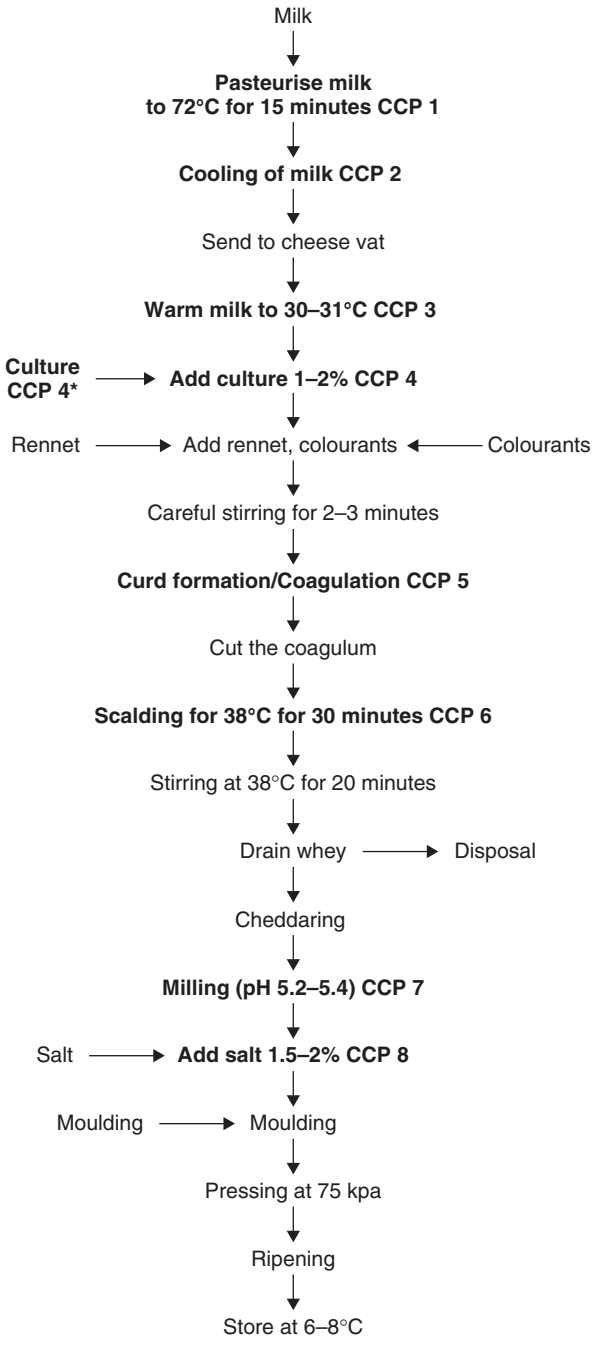

Figure 8.4 The HACCP flow chart for cheese manufacture.

Table 8.3 Manufacture of cheese: Hazard analysis and CCP identification for raw materials and process steps.

Raw material/ Process step	Hazard	Control measures	Significant hazard	Q1	Q1a	Q2	Q3	Q4	CCP	Justification
Milk	Survival of vegetative pathogens	Effective pasteurisation	No	Yes		Yes	No		No	Vegetative pathogens destroyed by pasteurisation
Culture	**Growth of vegetative pathogens**	**Qualified culture supply**	**Yes**	**Yes**		**No**			**Yes**	**No unqualified cultures be used Supplier Quality Assurance (SQA)**
Rennet	No hazard identified			No					No	Supplier Quality Assurance (SQA)
Colorants	No hazard identified			No					No	Supplier Quality Assurance (SQA)
Salt	No hazard identified			No					No	Supplier Quality Assurance (SQA)
Moulds	No hazard identified			No					No	Food grade material, Supplier Quality Assurance (SQA)
Pasteurisation	**Survival of vegetative pathogens; *Mycobacterium tuberculosis***	**Effective pasteurisation Correct temperature/ time combination 72°C for 15 seconds**	**Yes**	**Yes**		**Yes**			**Yes**	**No subsequent step to remove hazard**
Cooling	**Growth of surviving spore forming pathogens due to inadequate cooling**	**Effective cooling Correct temperature of the product maintained at (5°C)**	**Yes**	**Yes**		**Yes**			**Yes**	**Control the quality and limit the growth rates of pathogenic and spoilage microbes**
Send to cheese vat	No hazard identified								No	Food hygiene and equipment maintenance in place – prerequisite programmes
Warm milk to 30–31°C	**Microbial contamination**	**Proper temperature setting at 30–31°C**	**Yes**	**Yes**		**No**	**Yes**	**No**	**Yes**	**Proper temperature setting is critical**
Add culture 1–2%	**Microbial contamination**	**Proper additional rate of 1–2%**	**Yes**	**Yes**		**No**	**Yes**	**No**	**Yes**	**Correct additional rate is critical**
Add rennet, colorants	No hazard identified								No	Food hygiene practices
Careful stirring for 2–3 minutes	No hazard identified								No	Food hygiene and equipment maintenance in place – prerequisite programmes
Curd formation	**Microbial contamination**	**Proper temperature/ time setting and recording Temperature/ time is set at 30°C for 30 minutes**	**Yes**	**Yes**		**No**	**Yes**	**No**	**Yes**	**Proper coagulation temperature and time is critical**
Cut the curd	No hazard identified								No	Food hygiene and equipment maintenance in place – prerequisite programmes
Scalding for 38°C for 30 minutes	**Microbial contamination**	**Proper time/temperature setting 38°C for 30 minutes**	**Yes**	**Yes**		**No**	**Yes**	**No**	**Yes**	**The growth of acid-producing bacteria is limited by the heat, thus acidification of the curd**

Stirring for 20 minutes	No hazard identified								No	Food hygiene and equipment maintenance in place – prerequisite programmes
Drain whey	No hazard identified								No	Food hygiene and equipment maintenance in place – prerequisite programmes
Cheddaring	Microbiological contamination	Constantly monitor pH during cheddaring	Yes	Yes	No	Yes	Yes	No	Food hygiene and equipment maintenance in place – prerequisite programmes
Milling	**Microbial contamination**	**More cheddaring time Control the pH (5.2–5.4)**	**Yes**	**Yes**	**No**	**Yes**	**No**	**Yes**	**Proper pH before milling is critical**
Add salt 1.5–2%	**Microbial contamination**	**Correct level of salt, 1.5–2% Correct mixing during salting**	**Yes**	**Yes**	**Yes**			**Yes**	**Moisture content is optimum at 39%**
Moulding	No hazard identified							No	Food hygiene and equipment maintenance in place – prerequisite programmes
Pressing (75 kpa)	No hazard identified							No	Proper whey drainage setting Food hygiene and equipment maintenance prerequisite programmes
Ripening	No hazard identified							No	Proper storage condition setting – prerequisite programmes
Store at 6–8°C	No hazard identified							No	Proper storage condition setting – prerequisite programmes

Raw material control decision tree questions

Q1 Is there a hazard associated with this raw material?

Q2 Are you or the customer going to process this hazard out of the product?

Q3 Is there a cross-contamination risk to the facility or to the products which will not be controlled?

Process step decision tree questions

Q1 Do control measures exist? Q1a. Is control at this step necessary for safety?

Q2 Is the step specifically designed to eliminate or reduce the likely occurrence of a hazard to an unacceptable level?

Q3 Could contamination with identified hazard(s) occur in excess of acceptable level(s) or could these increase to unacceptable levels?

Q4 Will a subsequent step eliminate identified hazards or reduce the likely occurrence of a hazard to acceptable level(s)?

Table 8.4 Manufacture of cheese: HACCP control chart.

Process stage	Hazard	Control Measures	CCP No.	Specifications/ Critical Limits	Monitoring			Corrective actions	
					Procedure	Frequency	Responsibility	Procedure	Responsibility
Pasteurisation	Survival of vegetative pathogens; *Mycobacterium tuberculosis*	Correct effective heat process 72°C for 15 seconds	CCP1	Temperature/ Time combination 72°C for 15 seconds	Calibrated heat exchanger chart recorder Visual check and sign off	Every 6 months Each batch	Instrument Calibration Company Operator	Undertaking of the doubtful batches Interrupt functioning and repair the heat exchanger	Operator Contract Engineering Manager
Cooling	Growth of surviving spore forming pathogens due to inadequate cooling	Control of effective cooling rate, Temperature of the product is maintained below 5°C	CCP2	Cooling at or below 5°C	Preventive maintenance of the Glycol Chiller Visual check of the digital recorder	Every 6 months Each batch	Contract Refrigeration Company Operator	Rejection of the doubtful batches Interrupt functioning and repair the Glycol Chiller	Operator Contract Engineering Manager
Warm milk to 30–31°C	Microbial contamination	Proper temperature setting at 30–31°C	CCP3	Warm milk to 30–31°C	Check thermometer Record keeping	Each batch Each batch	Operator Operator	Adjust the heater to change temperature	Operator
Add culture	Microbial contamination	Proper additional rate Agitate properly	CCP4	Proper additional rate of 1–2%	Check the additional rate of the culture Check the rate of the agitator Record keeping	Each batch Each batch Each batch	Operator Operator Operator	Apply more testing on pH Adjust agitator rate	Operator Operator
Curd formation	Microbial contamination	Proper temperature/ time setting and recording	CCP5	Temperature/ time is set at 30°C for 30 minutes	Check the time and temperature Record keeping	Each batch Each batch	Operator Operator	Reject product Operator training	Operator

Scalding	Microbial contamination	Proper time/ temperature setting	CCP6	Temperature/ time set at 38°C for 30 minutes	Check the temperature and the time Record keeping	Each batch Each batch	Operator Operator	Adjust the heater to change temperature	Operator
Milling	Microbial contamination	More cheddaring time Control the pH	CCP7	pH measured at 5.2–5.4	Constantly monitor pH during cheddaring	Each batch	Operator	Apply more testing on pH Reject product	Operator Operator
Add salt	Microbial contamination	Correct level of salt, Correct mixing during salting	CCP8	Salt % = 1.5–2%	Records and testing	Each batch	Operator	Incorrectly salted curd must not be allowed to progress	Operator
Culture	Microbiological contamination	Qualified starter supply	CCP4*	No unqualified material be used	Apply supply quality assurance (SQA)	Each supply	Quality Assurance Department (QA)	Change supplier	QA

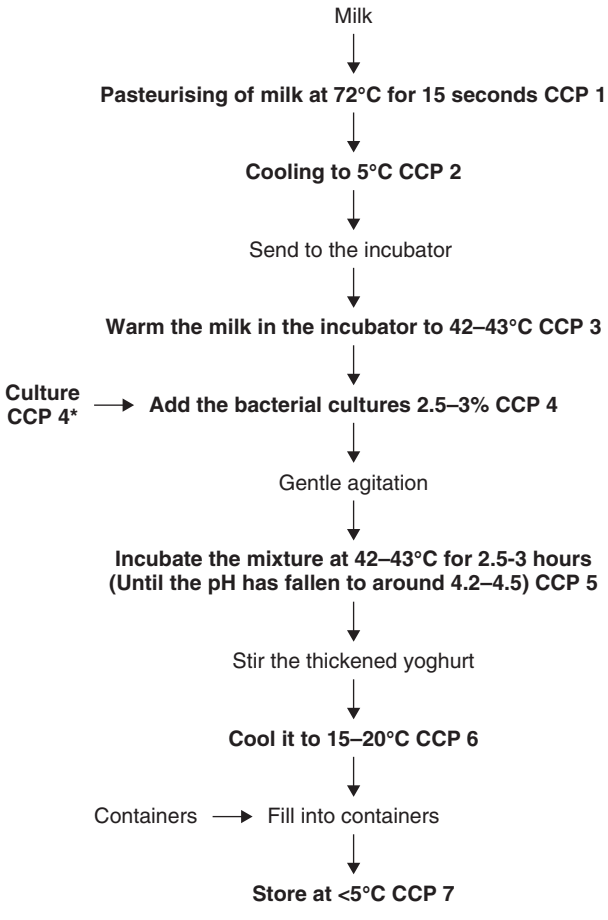

Figure 8.5 The HACCP flow chart for yogurt manufacture.

8.5.4 Cream/Butter

The milk separation process for the manufacture of cream and butter is given in Figure 8.6, and Tables 8.7 and 8.8 show the hazard analysis and CCP identification steps and the HACCP control chart.

Raw cream after separation is pasteurised and aged for butter making as shown in Figure 8.7 and Tables 8.9 and 8.10 show the hazard analysis and CCP identification steps and the HACCP control chart.

Table 8.5 Manufacture of yogurt: Hazard analysis and CCP identification for raw materials and process steps.

Raw material/ Process step	Hazard	Control measures	Significant hazard	Q1	Q1a	Q2	Q3	Q4	CCP	Justification
Milk	Survival of vegetative pathogens	Effective pasteurisation	No	Yes		Yes	No		No	Vegetative pathogens destroyed by pasteurisation
Culture	**Growth of vegetative pathogens**	**Qualified culture supply**	**Yes**	**Yes**		**No**			**Yes**	**No unqualified cultures be used Supplier Quality Assurance (SQA)**
Containers	No hazard identified			No					No	Food grade material, Supplier Quality Assurance (SQA)
Pasteurising	**Survival of vegetative pathogens; *Mycobacterium tuberculosis***	**Effective pasteurisation Correct temperature/ time combination 72°C for 15 seconds**	**Yes**	**Yes**		**Yes**			**Yes**	**No subsequent step to remove hazard**
Cooling	**Growth of surviving spore forming pathogens due to inadequate cooling**	**Effective cooling Correct temperature of the product maintained at (5°C)**	**Yes**	**Yes**		**Yes**			**Yes**	**Control the quality and limit the growth rates of pathogenic and spoilage microbes**
Send to the incubator	No hazard identified								No	Food hygiene and equipment maintenance in place – prerequisite programmes
Warm milk in the incubator to 42–43°C	**Microbial contamination**	**Proper temperature setting at 42–43°C**	**Yes**	**Yes**		**No**	**Yes**	**No**	**Yes**	**Proper temperature setting is critical**
Add culture 2.5–3%	**Microbial contamination**	**Proper additional rate of 2.5–3%**	**Yes**	**Yes**		**No**	**Yes**	**No**	**Yes**	**Correct additional rate is critical**
Gentle agitation	No hazard identified								No	Food hygiene and equipment maintenance in place – prerequisite programmes
Incubate the mixture	**Microbial contamination**	**42–43°C for 2.5–3 hours Until the pH has fallen to around 4.2–4.5**	**Yes**	**Yes**		**No**	**Yes**	**No**	**Yes**	**Proper incubation temperature and time is critical**
Stir the thickened yoghurt	No hazard identified								No	Food hygiene, equipment maintenance prerequisite programmes

(*continued overleaf*)

Table 8.5 (*Continued*)

Raw material/ Process step	Hazard	Control measures	Significant hazard	Q1	Q1a	Q2	Q3	Q4	CCP	Justification
Cool to 15–20°C	**Microbial contamination**	**Carefully control cooling to 15–20°C**	**Yes**	**Yes**		**Yes**			**Yes**	**Too rapid cooling rate leads to syneresis** **Cooling will control the further increase in acidity**
Fill into containers	No hazard identified								No	Food hygiene, equipment maintenance prerequisite programmes
Storage at <5°C	**Microbial contamination**	**Effective cooling to <5°C**	**Yes**	**Yes**		**Yes**			**Yes**	**Proper temperature setting of the storage is critical**

Process step decision tree questions

Q1 Do control measures exist? Q1a. Is control at this step necessary for safety?

Q2 Is the step specifically designed to eliminate or reduce the likely occurrence of a hazard to an unacceptable level?

Q3 Could contamination with identified hazard(s) occur in excess of acceptable level(s) or could these increase to unacceptable levels?

Q4 Will a subsequent step eliminate identified hazards or reduce the likely occurrence of a hazard to acceptable level(s)?

Raw material control decision tree questions

Q1 Is there a hazard associated with this raw material?

Q2 Are you or the customer going to process this hazard out of the product?

Q3 Is there a cross-contamination risk to the facility or to the products which will not be controlled?

Table 8.6 Manufacture of yogurt: the HACCP control chart.

Process stage	Hazard	Control Measures	CCP No.	Specifications/ Critical Limits	Monitoring			Corrective actions	
					Procedure	Frequency	Responsibility	Procedure	Responsibility
Pasteurisation	Survival of vegetative pathogens; *Mycobacterium tuberculosis*	Correct effective heat process 72°C for 15 seconds	CCP1	Temperature/ Time combination 72°C for 15 seconds	Calibrated heat exchanger chart recorder Visual check and sign off	Every 6 months Each batch	Instrument Calibration Company Operator	Undertaking of the doubtful batches Interrupt functioning and repair the heat exchanger	Operator Contract Engineering Manager
Cooling	Growth of surviving spore forming pathogens due to inadequate cooling	Control of effective cooling rate, Temperature of the product is maintained below 5°C	CCP2	Cooling below 5°C	Preventive maintenance of the Glycol Chiller Visual check of the digital recorder	Every 6 months Each batch	Contract Refrigeration Company Operator	Rejection of the doubtful batches Interrupt functioning and repair the Glycol Chiller	Operator Contract Engineering Manager
Warm milk to 42–43°C	Microbial contamination	Proper temperature setting at 42–43°C	CCP3	Warm milk to 42–43°C	Check thermometer Record keeping	Each batch Each batch	Operator Operator	Adjust the heater to change temperature	Operator
Add culture	Microbial contamination	Proper additional rate Agitate properly	CCP4	Proper additional rate of 2.5–3%	Check the additional rate of the culture Check the rate of the agitator Record keeping	Each batch Each batch Each batch	Operator Operator Operator	Reject product Adjust agitator rate	Operator Operator
Incubate the mixture	Microbial contamination	Proper temperature/ time combination	CCP5	42–43°C for 2.5–3 hours Until the pH has fallen to around 4.2–4.5	Check the time/ temperature Record keeping	Each batch Each batch	Operator Operator	Apply more testing on pH	Operator
Cool to 15–20°C	Microbial contamination	Carefully control cooling to 15–20°C	CCP6	Cooling to 15–20°C	Check the temperature Record keeping	Each batch Each batch	Operator Operator	Rejection of doubtful lot	Operator
Storage at <5°C	Microbial contamination	Maintain temperature <5°C Proper temperature setting of the storage is critical	CCP7	Maintain temperature <5°C	Check temperature Record keeping	Each batch Each batch	Operator Operator	Rejection of the doubtful lot Proper maintenance of the chilled storage	Operator Contracted Engineer
Culture	Microbiological contamination	Qualified starter supply	CCP4*	No unqualified material be used	Apply supply quality assurance (SQA)	Each supply	Quality Assurance Department (QA)	Change supplier	QA

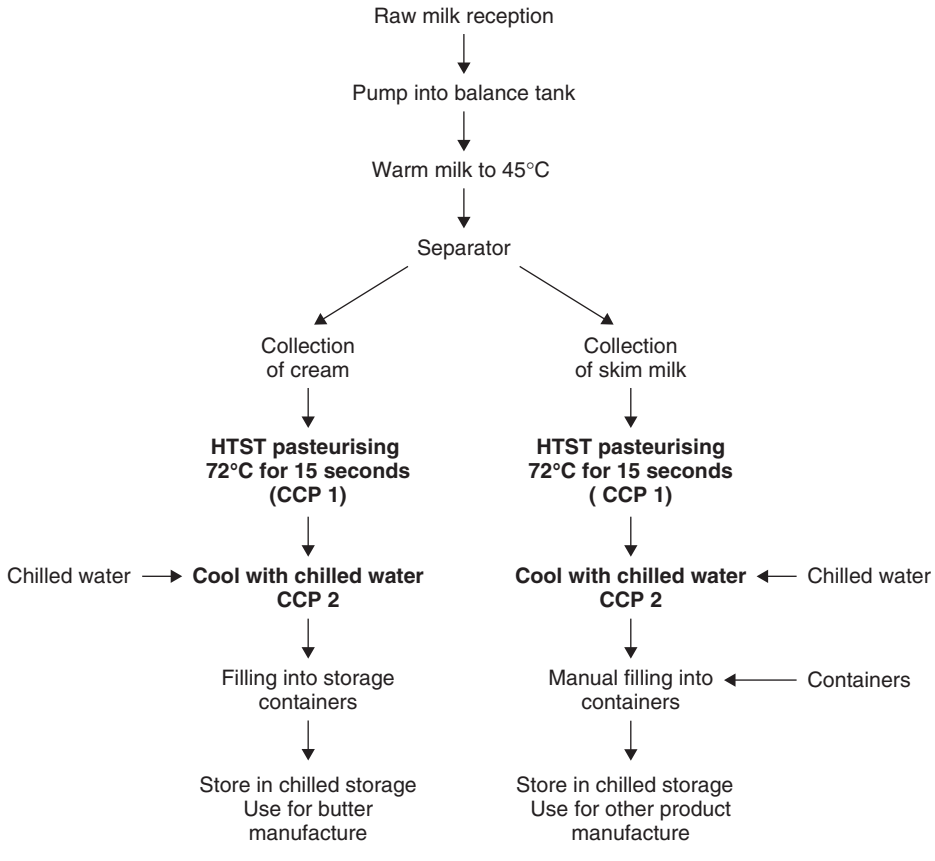

Figure 8.6 The HACCP flow chart for milk separation.

8.6 Future trends

It is evident that recent investigations into chemical residues and natural contaminants in foods have increased awareness across the food manufacturing sector as well as the consumer. The need for practical and rapid control of these contaminants requires new techniques to facilitate detection for risk assessment in the HACCP programme. Many quarters of the food industry are active in the search for effective control techniques for their food manufacturing steps especially when such commodities are exported to other countries.

Table 8.7 Separation of milk: Hazard analysis and CCP identification for raw materials and process steps.

Raw material/ Process step	Hazard	Control measures	Significant hazard	Q1	Q1a	Q2	Q3	Q4	CCP	Justification
Milk	Survival of vegetative pathogens	Effective pasteurisation	No	Yes		Yes	No		No	Product will be pasteurised
Containers	No hazard identified			No					No	Food grade material, Supplier Quality Assurance (SQA)
Mains water	No hazard identified			No					No	No contact with the product, only use as a cooling medium
Milk reception	No hazard identified								No	Vegetative pathogens destroyed by pasteurisation Food hygiene practices are observed – prerequisite programme.
Pump to balance tank	No hazard identified								No	Food hygiene and equipment maintenance in place – prerequisite programmes
Warm milk to 45°C	Vegetative pathogens	Time/ Temperature control/ Pasteurise at later stage	No	Yes		No	Yes	Yes	No	Vegetative pathogens destroyed by pasteurisation
Collection of cream, Collection of skim milk	No hazard identified								No	Food hygiene and equipment maintenance in place – prerequisite programmes
Pasteurising (both cream and skim milk)	**Survival of vegetative pathogens;** ***Mycobacterium tuberculosis***	**Effective pasteurisation Correct temperature/ time combination 72°C for 15 seconds**	**Yes**	**Yes**		**Yes**			**Yes**	**No subsequent step to remove hazard**
Cool with chilled water (both cream and skim milk)	**Growth of surviving spore forming pathogens due to inadequate cooling**	**Effective cooling Correct temperature of the product maintained at (5°C)**	**Yes**	**Yes**		**Yes**			**Yes**	**Control the quality and limit the growth rates of pathogenic and spoilage microbes**
Manual handling of final cream by operatives (both cream and skim milk)	*St. aureus* transfer from operator's hands	Effective hand washing	No						No	Food hygiene practices – prerequisite programmes

(*continued overleaf*)

Table 8.7 (*Continued*)

Raw material/ Process step	Hazard	Control measures	Significant hazard	Q1	Q1a	Q2	Q3	Q4	CCP	Justification
Store in chilled storage in the dairy (both cream and skim milk)	No hazard identified								No	Food hygiene, equipment maintenance – prerequisite programmes
Use in butter and/or other product manufacture	No hazard identified								No	Subsequent steps of other manufacturing processes will destroy the vegetative pathogens

Raw material control decision tree questions

Q1 Is there a hazard associated with this raw material?

Q2 Are you or the customer going to process this hazard out of the product?

Q3 Is there a cross-contamination risk to the facility or to the products which will not be controlled?

Process step decision tree questions

Q1 Do control measures exist? Q1a. Is control at this step necessary for safety?

Q2 Is the step specifically designed to eliminate or reduce the likely occurrence of a hazard to an unacceptable level?

Q3 Could contamination with identified hazard(s) occur in excess of acceptable level(s) or could these increase to unacceptable levels?

Q4 Will a subsequent step eliminate identified hazards or reduce the likely occurrence of a hazard to acceptable level(s)?

Table 8.8 Separation of milk: HACCP control chart.

Process stage	Hazard	Control Measures	CCP No.	Specifications/ Critical Limits	Monitoring			Corrective actions	
					Procedure	Frequency	Responsibility	Procedure	Responsibility
Batch pasteurisation (Both cream and skim milk)	Survival of vegetative pathogens; *Mycobacterium tuberculosis*	Correct effective heat process 72°C for 15 seconds	CCP1	Temperature/ Time combination 72 °C for 15 seconds	Calibrated heat exchanger chart recorder	Every 6 months	Instrument Calibration Company	Undertaking of the doubtful batches	Operator
					Visual check and sign off	Each batch	Operator	Interrupt functioning and repair the heat exchanger	Contract Engineering Manager
Cooling with chilled water (Both cream and skim milk)	Growth of surviving spore forming pathogens due to inadequate cooling	Control of effective cooling rate, Temperature of the product is maintained below 5°C	CCP2	Cooling at or below 5°C	Preventive maintenance of the Glycol Chiller	Every 6 months	Contract Refrigeration Company	Rejection of the doubtful batches	Operator
					Visual check of the digital recorder	Each batch	Operator	Interrupt functioning and repair the Glycol Chiller	Contract Engineering Manager

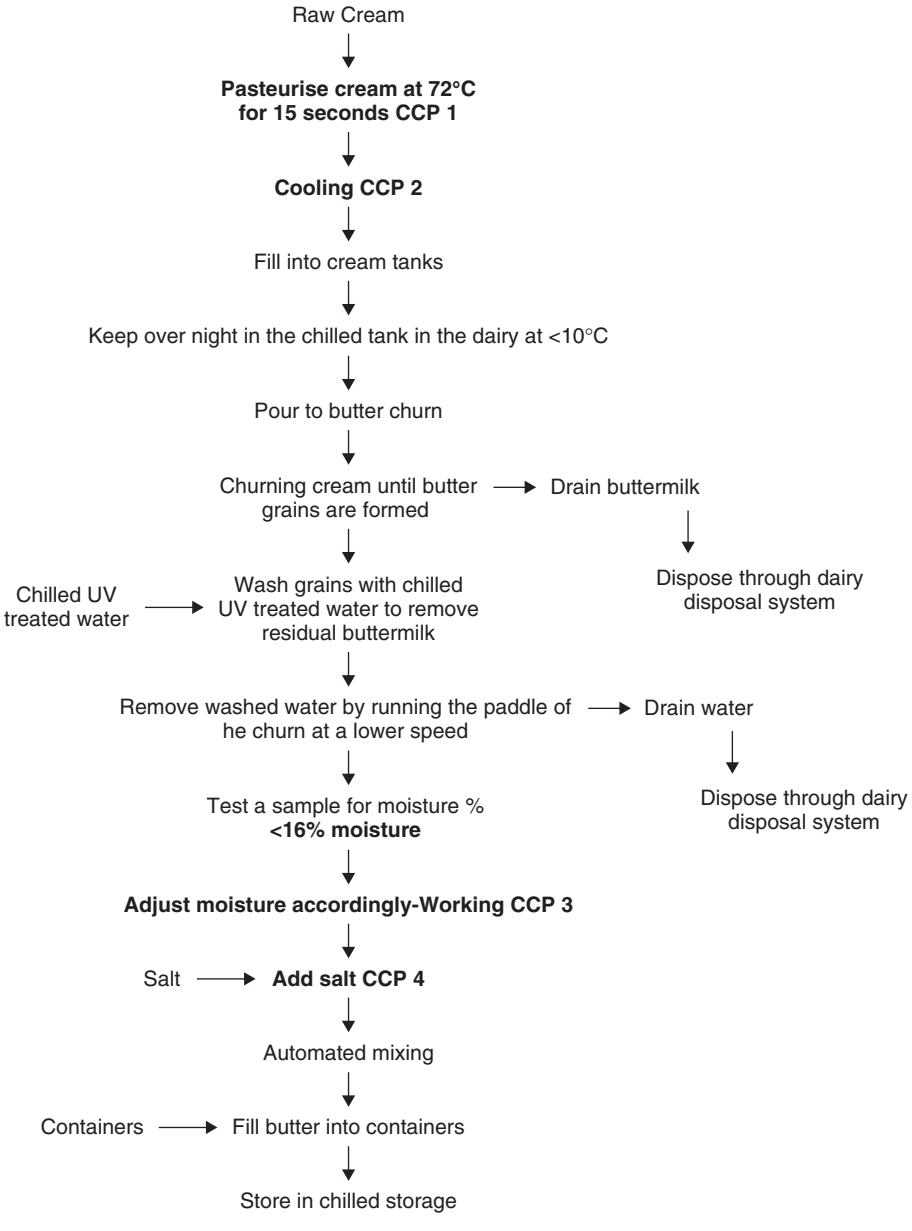

Figure 8.7 The HACCP flow chart for butter manufacture.

Table 8.9 Manufacture of butter: Hazard analysis and CCP identification for raw materials and process steps.

Raw material/ Process step	Hazard	Control measures	Significant hazard	Q1	Q1a	Q2	Q3	Q4	CCP	Justification
Cream	Survival of vegetative pathogens	Effective pasteurisation	No	Yes		Yes	No		No	Cream will be pasteurised
Containers	No hazard identified			No					No	Food grade material, Supplier Quality Assurance (SQA)
UV treated water	No hazard identified			No					No	Supplier Quality Assurance (SQA)
Salt	No hazard identified			No					No	Supplier Quality Assurance (SQA)
Pasteurising	**Survival of vegetative pathogens; *Mycobacterium tuberculosis***	**Effective pasteurisation Correct temperature/ time combination 63°C for 30 minutes**	**Yes**	**Yes**		**Yes**			**Yes**	**No subsequent step to remove hazard**
Cooling	**Growth of surviving spore forming pathogens due to inadequate cooling**	**Effective cooling Correct temperature of the product maintained at (5°C)**	**Yes**	**Yes**		**Yes**			**Yes**	**Control the quality and limit the growth rates of pathogenic and spoilage microbes**
Fill into containers	*St. aureus* transfer from operator's hands	Effective hand washing	No						No	Food hygiene practices – prerequisite programmes
Keep over night in the chilled tank in the dairy at <10°C	No hazard identified								No	Food hygiene, equipment maintenance – prerequisite programmes
Pour to butter churn	No hazard identified								No	Food hygiene and equipment maintenance in place – prerequisite programmes
Churning cream until butter grains are formed	No hazard identified								No	Food hygiene and equipment maintenance in place – prerequisite programmes
Drain buttermilk	No hazard identified								No	Correct draining procedures – prerequisite programmes
Disposal of buttermilk	No hazard identified								No	Correct disposal procedures – prerequisite programmes
Wash grains with chilled UV treated water to remove residual buttermilk (Repeated)	No hazard identified								No	Washing helps to remove buttermilk and consolidate the butter

(*continued overleaf*)

Table 8.9 (*Continued*)

Raw material/ Process step	Hazard	Control measures	Significant hazard	Q1	Q1a	Q2	Q3	Q4	CCP	Justification
Remove washed water by running the paddle of the churn at a lower speed									No	Food hygiene and equipment maintenance in place – prerequisite programmes
Test a sample for moisture %	No hazard identified								No	Correct test procedures, and functioning equipments used
Adjust moisture accordingly – Working	**Growth of vegetative pathogens**	**16%**	**Yes**	**Yes**		**Yes**			**Yes**	**Butter must meet correct legal requirements for moisture level**
Add salt	**Survival of vegetative pathogens**	**2%**	**Yes**	**Yes**		**Yes**			**Yes**	**No subsequent step to remove hazard**
Automated mixing	No hazard identified								No	Food hygiene and equipment maintenance in place – prerequisite programmes
Fill butter into containers	No hazard identified								No	Food hygiene practices – prerequisite programmes
Store in chilled storage	No hazard identified								No	Food hygiene and equipment maintenance in place – prerequisite programmes

Raw material control decision tree questions
Q1 Is there a hazard associated with this raw material?
Q2 Are you or the customer going to process this hazard out of the product?
Q3 Is there a cross-contamination risk to the facility or to the products which will not be controlled?

Process step decision tree questions
Q1 Do control measures exist? Q1a. Is control at this step necessary for safety?
Q2 Is the step specifically designed to eliminate or reduce the likely occurrence of a hazard to an unacceptable level?
Q3 Could contamination with identified hazard(s) occur in excess of acceptable level(s) or could these increase to unacceptable levels?
Q4 Will a subsequent step eliminate identified hazards or reduce the likely occurrence of a hazard to acceptable level(s)?

Table 8.10 Manufacture of butter: the HACCP control chart.

Process stage	Hazard	Control Measures	CCP No.	Specifications/ Critical Limits	Monitoring			Corrective actions	
					Procedure	Frequency	Responsibility	Procedure	Responsibility
Pasteurisation	Survival of vegetative pathogens; *Mycobacterium tuberculosis*	Correct effective heat process 72°C for 15s	CCP1	Temperature/ Time combination 72 °C for 15s	Calibrated heat exchanger chart recorder Visual check and sign off	Every 6 months Every batch	Instrument Calibration Company Operator	Undertaking of the doubtful batches Interrupt functioning and repair the heat exchanger	Operator Contract Engineering Manager
Cooling	Growth of surviving spore forming pathogens due to inadequate cooling	Control of effective cooling rate, Temperature of the product is maintained below 5°C	CCP2	Cooling at or below 5°C	Preventive maintenance of the Glycol Chiller Visual check of the digital recorder	Every 6 months Every batch	Contract Refrigeration Company Operator	Rejection of the doubtful batches Interrupt functioning and repair the Glycol Chiller	Operator Contract Engineering Manager
Adjust moisture accordingly	Growth of vegetative pathogens	16%	CCP3	16% moisture	Test for moisture by dry weight method	Every batch	Operator	Repeat on working if the moisture level is higher than legal level Or add UV treated water if moisture level is below the legal level	Operator
Add salt	Survival of vegetative pathogens	Correct level of salt Correct mixing during salting	CCP4	2% salt	Records and testing	Every batch	Operator	Incorrectly salted product must not be allowed to progress	Operator

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9

Culinary fats: solid and liquid frying oils and speciality oils[1]

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9.1 Introduction

The use of hot and cold oils in food preparation has been known for thousands of years, in fact there are reports that frying was used in the Mediterranean as long ago as 1000 bc. The oils and fats can be of animal or vegetable origin, depending on geographical and historical factors. The oil or fat used influences the flavour and texture of the food. This is particularly relevant in fried food where, though reaction flavours from proteins and carbohydrates account for much of the flavour, the condition of the oil used to fry the food also has an influence on flavour. A crisp outer texture is a characteristic of most fried foods, caused by rapid surface dehydration, which again has an influence on flavour perception.

There are two main types of frying, namely shallow and deep fat frying. Shallow frying uses a little oil in relatively flat cooking utensils, the food usually being immersed; whereas deep fat frying completely immerses the product. Deep fat frying of food has gained enormously in popularity because of its speed, operational simplicity and ability to supply a desirable flavour, golden colour and crisp texture to the food.

The physical and chemical stresses placed on a frying fat during the deep fat frying process are highly complex, leading to the oil decomposing thermally and oxidatively to form a wide variety of volatile and nonvolatile decomposition products, which ultimately alter the nutritive and functional properties of the oil or fat. The way in which these changes take place has been the subject of considerable research.

[1]The original chapter was written by John Podmore.

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The importance of ghee and vanaspati in Asia requires detailed consideration, as these are major culinary fats in a number of countries – principally India and Pakistan.

Developments in the purification of oils have made available salad oils and cooking oils that are both clear and bland. When these are used for shallow frying, the fat or oil not only acts to prevent the food sticking to the pan but also contributes to the mouth feel and texture of the food.

There has been a developing interest in 'speciality oils' which often are used in their natural state to retain their full colour and flavour. They are used in a range of culinary applications to impart flavour, colour and an oily sheen to the food.

This chapter will consider the attributes required of these oils and fats for use in food preparation.

9.2 Salad and cooking oils

Salad oils and cooking oils can be either fully liquid at room temperature, solid or semisolid; the more liquid the oil, the more unsaturated fats it contains; however, this will result in it being more prone to oxidation. Examples of liquid oils are soybean, sunflower, rapeseed, groundnut, corn, cottonseed and olive oil. Examples of solid and semisolid oils are lard, tallow, palm oil, palm oil fractions, coconut oil and palm kernel oil. In addition to these are oils which have been modified from their original state, such as hydrogenated oils. The hydrogenation process will change the fatty acid profile of the oils and decrease the level of unsaturation, therefore making the oils more stable and less susceptible to oxidative attack. In addition to the enhanced stability, a more preferable melting profile for the specific application can be attained. The downside of hydrogenation, however, is the occurrence of *trans* fatty acids, which appear to have an even greater detrimental health effect than saturated fats (Menaa *et al*., 2013; SACN 2007; Stender and Dyerberg, 2003; 2006; 2009; Wassell *et al*., 2010).

Traditionally, in northern Europe cooking oils were derived from domestic animals, so that lard, tallow and butter were popular; in Mediterranean countries, Asia and Africa liquid oils were more popular. There is a similar story in North America; tallow was popular in the early part of the twentieth century but it has now been largely replaced by vegetable oils such as soybean, cottonseed, sunflower and corn oils.

There has now been a significant shift in the composition of salad oils and cooking oils as a result of the greater global movement of people and an increased interest in nutrition and health issues, which highlight the relationship between saturated fatty acids and cardiovascular disease. Thus cooking and salad oils are almost exclusively vegetable oils.

Cooking oils can be used in the natural state or after processing. The majority of cooking oil is now used as processed oil. Oils used in the natural state tend to be those oils found in the speciality sector of the market, where the natural taste and flavour of the oils are beneficial and not detrimental to the taste and flavour of the final product.

Ghee and vanaspati represent a specific type of cooking oil traditionally used in Asia, though liquid vegetable oils are also used extensively in Asian cooking.

Modern salad and cooking oils are purified by refining and deodorisation to give a clear, bland, stable and 'low-coloured' oil. The distinction between salad oils and cooking oils is the difference in their oxidative stability, with cooking oils being used for frying and so needing to be more stable at elevated temperatures. Also, the term 'salad oil' is applied to those oils that remain clear at refrigerator temperatures. The criteria for clarity at refrigerator temperature are defined by the cold test described in AOCS (cc 11–53) (1981).

Oils that are likely to deposit crystals or waxes after prolonged storage at 0°C are subjected to a winterisation process. This is a modified fractionation process that crystallises high melting triacylglycerols and waxes so that they can be filtered off in order to meet the salad oil criteria. The separation was originally seen in refined cottonseed oil (which separated after storage in cold weather, allowing a clear, liquid oil layer to be separated off), today's oil refiners can achieve the same effects by using chilling and or the use of centrifuges. Sunflower oil and corn oil contain high levels of natural waxes and so need dewaxing before they meet the salad oil criteria, whereas soybean oil and low-erucic-acid rapeseed oil both naturally conform to the requirements of the cold test. Cottonseed oil, because of its high content of higher melting palmitic acid, requires winterisation in order to be certified as a salad oil. Groundnut oil, because of the noncrystallinity of the high melting fraction, cannot be made to conform to the salad oil standards. One oil that has gained prominence, particularly in Asian countries, is rice bran oil (Dassanayake *et al*., 2009; Lerma-Garcia *et al*., 2009). This requires winterising to remove saturated tryglycerides and the 2–6% waxes that occur in the oil. Owing to the presence of relatively high levels of unsaponifiables containing sterols and orzyganols, rice bran oil has excellent oxidative stability.

Salad oils and cooking oils are interchangeable when the criterion of good oxidative stability is achieved and when clarity at refrigeration is maintained. This has been achieved with oils such as soybean and rapeseed oil. These could be lightly hydrogenated (i.e. the iodine value is reduced by approximately 20 units), which reduces the linolenic acid content by more than half and so improves the oxidative stability. The oil must be then winterised to remove the solid triglycerides created in the hydrogenation (Figures 9.1(a) and (b)]. This process provides an oil that has all the characteristics necessary for use in salads and deep fat frying. Where the use is limited to deep fat frying, then the hydrogenated oil can be processed into a pourable slurry.

The oxidative stability of salad and cooking oils is heavily influenced by the degree of unsaturation, particularly by the linolenic acid content as well as the levels of natural antioxidants such as tocopherols, sterols and phospholipids. Other factors affecting quality are the initial quality of the crude oil, processing and handling, and conditions of transport and storage.

The shelf-life of oils can be extended because of antioxidants which are naturally present within the oils; these contribute to the total overall antioxidant capacity of the oil. Such components include tocopherols, polyphenols, carotenes, and various sterols. For salad oils the shelf-life can be extended by the addition of further antioxidants; these could be synthetic antioxidants such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) propyl gallates and tertiary

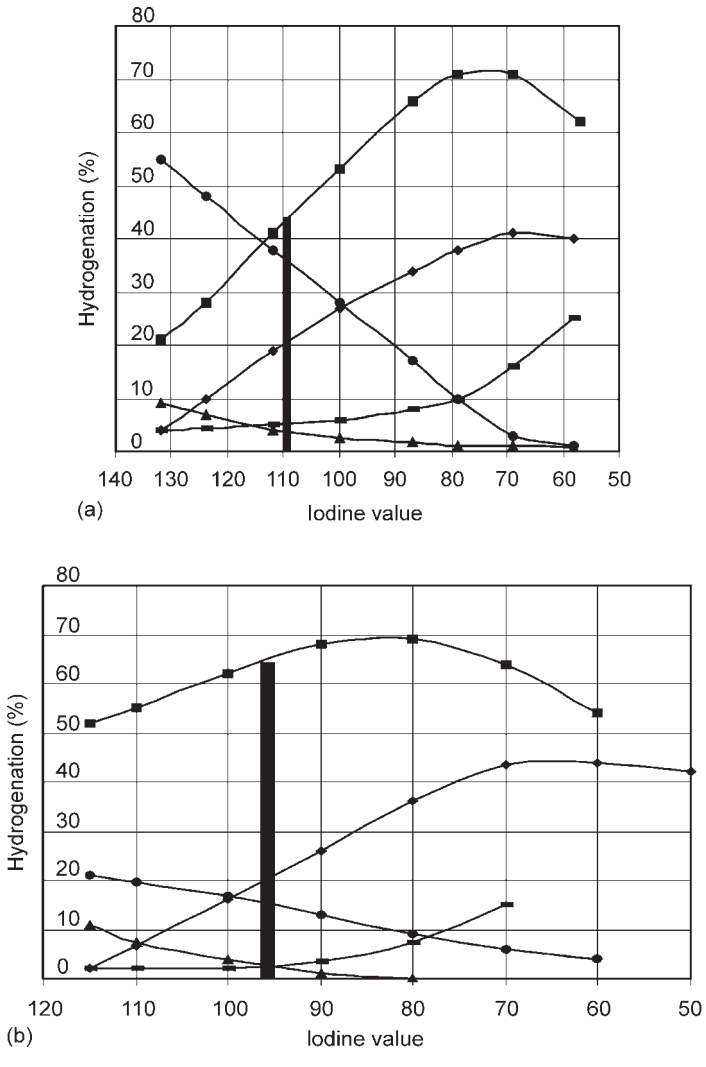

Figure 9.1 Hydrogenation of (a) soybean oil and (b) rapeseed oil. The solid vertical line indicates the point at which the reduction in linolenic acid is maximised and the increase in saturated and *trans* fatty acids is minimised. Notes: C18:0; C18:1; C18:2; C18:3; *trans*.

butylhydroquinone (TBHQ). Or else, with the increasing trend of trying to move towards natural ingredients where possible, the antioxidants could be a natural variety such as rosemary or green tea extracts, tocopherols, ascorbyl palmitate and squalene. These antioxidants will help to secure longer shelf-life by slowing down the oxidative degradation during storage. During the frying process, however, the natural antioxidant systems of the oilseeds will be destroyed, therefore the addition of antioxidants is even more essential. Work has been shown that the life of the

frying oil can be prolonged with an antioxidant addition as free radical scavenging properties help keep the quality and properties such as colour of the oil (Amarowicz, 2009; Gwo *et al*., 1985).

Salad oils, as the name implies, are used as dressings for salads. They can either be added directly at the table or they can be used in the preparation of, for example, French dressing, which is basically oil, vinegar and spices. Salad dressings, either as mayonnaise or as salad cream, are oil-in-water emulsions, they can be thickened by the use of gums and hydrocolloids and are emulsified by the use of egg yolk and emulsifiers. Sauces of the hollandaise and béarnaise variety represent another use of salad and cooking oils. These sauces contain about 30% oil and are designed for dressing hot food in order to add succulence and flavour. Though oils are used in sauces of this kind, butter is favoured in these recipes as it contributes a special richness and flavour, but it does not have the potential health benefits the oils could impart.

Olive oil has always been considered the outstanding salad oil, though it is considered as a speciality oil when used in gourmet cooking. However, its use has grown considerably in Western societies in recent years, with the benefits of the Mediterranean diet becoming more apparent. The Mediterranean countries, unlike other sectors of Europe, embrace the use of oil and use it extensively in their cooking and for applying to their salads, and yet their levels of cardiovascular disease are among the lowest in the world. It was shown that the cholesterol-lowering effect of mono-unsaturated fatty acids compared with saturated fatty acids is similar to that of polyunsaturated fatty acids, but obviously with a greater resistance to oxidation. The increased appearance of olive oil on supermarket shelves suggests it can be dealt with as a salad oil although it is also used for shallow frying.

Table 9.1 shows the composition of olive fruit; however, the oil content can vary in the range 15–30%. Table 9.1 also shows how widely the fatty-acid composition can vary, being affected by region, climate, fruit variety and maturity at the time of

Table 9.1 Composition of olives and olive oil.

	Percentage
Olive fruit:	
Moisture	50.0
Protein	1.6
Oil	22.0
Carbohydrate	19.1
Cellulose	5.8
Ash	1.5
Olive oil:[a]	
Oleic acid	55–83
Linoleic acid	3.5–21
Palmitic acid	7.5–20
Stearic acid	0.5–5

Note: [a]Fatty-acid composition; there are also traces of myristic, palmitoleic, heptadecanoic, heptadecenoic, linolenic, arachidic, behenic lignoceric and eicosenoic acid.

harvest. For example, Spanish, Italian and Greek olive oils are generally low in linoleic acid and high in oleic acid content, whereas Tunisian olive oils are high in linoleic and palmitic acids and lower in oleic acid content.

Though nutritional concerns have helped to drive up the usage of olive oil, consumers traditionally have selected it for its unique and distinctive flavour, which is altered by regional and climatic conditions. There has been a considerable volume of work published on the flavour components of olive oil and how they are varied by the maturity of the fruit at the time of harvesting and the variety of the fruit. Major flavour components have been shown to be hexenal, *cis*-3-hexenal, *trans*-2-hexenal, hexanol, *cis*-3-hexenol and 2-hexenol and the corresponding esters.

Regional differences in flavour are well known; for example, Spanish olive oil has a strong 'peppery' note, Greek oils are thought to be 'grassy', and Italian olive oil is 'fruity'. There are then variants of these basic flavour characteristics. In the modern marketplace, unless an olive oil is sold as being specific to a particular region, it will usually be a blend of oils of various varieties of olive and from various regions. This enables the supplier to ensure a more consistent flavour.

Olive oil is sold in a number of grades, each of which has a strict definition and chemical specification. Olive oil is obtained by crushing the fruit and pressing the resulting paste. The yield from the pressing is a mixture of oil and water. This mixture is then separated centrifugally.

The first pressing of the olive paste gives 'virgin' oil, which is then graded on acidity and flavour. The criteria for defining olive oil quality have now been strictly regularised, particularly in the European Union. The grades are defined in EC Regulation 2568/91 and its amendments (1991).

The grades can be defined as follows:

- extra virgin olive oil: this is the premium grade and must have an acidity less than 1% and a flavour of closely defined character
- virgin olive oil: in this grade the acidity can be up to 2% but flavour criteria are as described above
- ordinary virgin olive oil: this oil must have an 'acceptable flavour' and a maximum acidity of 3.3%
- lampante virgin olive oil: this is the lowest grade, with a poor flavour and usually with an acidity of greater than 3.3%.

Other grades of olive oil are based on olive pomace oil. After pressing there is a 3–8% residue of oil in the pulp. This is solvent extracted to give crude olive pomace oil. Crude pomace oil and lampante oil are usually refined and deodorised if used in edible products.

The grades of oil usually found in the retail market are as follows:

- extra virgin olive oil and virgin olive oil, sold in the quality described above
- ordinary olive oil (this is a blend of virgin olive oil and olive oil refined and deodorised to have an acidity less than 0.5%; the proportions of each oil are

varied in order to give the desired flavour intensity, colour and acidity, though the flavour of this oil will always be milder than that of virgin olive oil);
- olive pomace oil (this is a blend of virgin oil and refined solvent-extracted pomace oil), similar in appearance and flavour to olive oil.

The health benefits have been exploited in spreads that contain olive oil, yet the high commodity price and the very distinctive flavour of olive have meant that olive spreads usually only contain a portion of olive along with the usual soft oils. However, as people's exposure and knowledge of the benefits of olive increase, the taste of olive has now become more acceptable, leading to higher levels being added. There are available some cooking and salad oils which are blends of sunflower oil and olive oil, as well as of rapeseed oil and olive oil. There are mildly flavoured but have a mix of the nutritionally acceptable mono-unsaturated and polyunsaturated fatty acids.

Olive oil is used widely as a culinary salad oil. The oil can be 'drizzled' onto salad and vegetables and used in the cooking of classic Mediterranean and Asian dishes, particularly where vegetables are being cooked. In Indian cooking, olive oil is often flavoured with garlic when used in cooking; for example, in Goa it is used to cook beef roulade. It is possible to purchase in retail outlets olive oil flavoured with a variety of herbs and spices.

9.3 Frying fats

There are two major methods of frying: shallow (pan) frying and deep fat frying. The two frying methods put entirely different demands on the fat used. In shallow frying the oil or fat is generally used only once so that its resistance to break down during frying is unimportant; in deep fat frying the reuse of the frying fat and its effect on fat quality are of the greatest importance.

9.3.1 Shallow (pan) frying

In the case of pan frying, the fat or oil used is present mainly to prevent the food sticking to the pan while it is being cooked by the heat applied. This frying method has been popular for hundreds of years and is a quick method of food preparation. During the frying, the food surface absorbs some of the heated fat. This may transfer distinctive flavours to the food and improves the palatability, giving the food an oily surface.

Solid fats based on lard, tallow and palm oil have been used extensively in shallow frying but have been largely replaced by liquid vegetable cooking oils, and this is due to healthier nutritional aspects as well as the fact that more solid fats can leave a waxy taste in the mouth because of their higher melting properties. Where distinctive odours and flavours are required, then butter and margarine can be used, as well as speciality oils. The presence of water in butter and margarine causes spattering. Spattering occurs when water droplets coalesce and sink to the bottom of a hot frying pan where they

evaporate with an explosive action, although in the case of margarine, the presence of certain emulsifiers can alleviate the effect. The presence of milk solids gives the fried food colour and flavour; however, it can also cause the food to stick to the pan. There are also available flavoured oils and liquid margarines designed for use in frying and griddling, and these are gaining in popularity.

Consideration of shallow frying would not be complete without noting the contribution of the Chinese, who have used both shallow and deep frying in food preparation for many centuries. Stir-frying (Hom, 1990) is a highly popular method of preparing many Chinese dishes and is done in a wok. This is a conical shaped pan that is set on top of a brazier so that heat can be spread over the whole surface. This means large amounts of food can be cooked rapidly by stir frying, as the food always returns to the hottest part of the wok after stirring. Woks are also used for deep fat frying, for which they are very efficient in that they provide depth of oil with relatively small amounts of oil so that heating and temperature maintenance are easy.

In Chinese cuisine, the oil most favoured is groundnut oil because of its mild pleasant flavour of roasted peanuts. A range of other oils are used, including corn oil, rapeseed oil, cottonseed oil, soybean oil and sunflower oil. Sesame oil is occasionally used for stir frying; however, its principal use is as a condiment because of its strong and distinctive aroma and flavour.

9.3.2 Deep fat frying

Deep fat frying has become one of the most important methods of food preparation. It is used domestically and in the food service, snack and baking industries. The frying fat plays such a unique role in the frying process that frying has become the focus of an enormous volume of research, such that the reactions taking place during the frying of food are now more clearly understood so that food quality is better maintained and nutritional standards improved.

There is no ideal frying fat suitable for all frying applications. Factors such as the process used, the food being fried, storage, shelf-life of the finished product, nutritional value of the fat and cost impact on frying fat selection all matter. In the process, the frying temperature and turnover have a major impact on the maintenance of quality during use, and whether the process is batch or continuous has an effect on the fat used. The product to be fried also influences the frying fat to be used, as the oil affects the surface texture of the food, its flavour and the shelf-life, the oil removed from the product being fried can also influence the keeping properties of the frying fat.

The cost of a frying fat is very important in commercial operation, not only in terms of purchase price, but also cost in use. Resistance to degradation and hence to increased rates of absorption may be required, justifying the use of a highly priced hydrogenated fat, specialist fractions or trait-enhanced oils to ensure longer frying life. Hydrogenated fats reduce the degree of unsaturation; hence they improve the stability of the oil as previously discussed. A palm olein fraction has the advantage of being more liquid than standard palm, but with a similar fatty acid profile; hence not too high in unsaturates and so being fairly resistant to oxidation. This palm olein

could in theory be further fractioned, giving an even more liquid product, with an iodine value in the 60s as opposed to the 50s. Trait-enhanced oils are oils which have been selectively bred to improve their fatty acid profile. Examples are liquid rape and sunflower seed oils, which through the process have lower levels of the more susceptible to oxidation unsaturates. Hence varieties such as mid or high oleic sunflower and high oleic rapeseed are becoming more commonly seen frying media, and a great deal of research into the benefits of these oils is being carried out (Warner and Gupta, 2005). As the names imply, the levels of oleic acid have been increased, but it is the lower levels of linoenic and linoelic acids which are key to their stability.

The selection of frying media is now becoming heavily influenced by nutritional issues. The findings that high intakes of saturated and *trans* fatty acids are implicated in arterial and cardiovascular disorders, and that mono-unsaturated and polyunsaturated fatty acid are beneficial, have placed an increasing emphasis on the use of natural more highly unsaturated oils and away from solids and hydrogenated fats. However, it has also been shown that heating unsaturated oil at high temperatures will result in the double bonds breaking down to form short chain aldehydes. These are not beneficial to the body, attributing to arthrosclerosis and interfering with endothelial function. Balancing nutritional and health requirements with those of cost and thermal stability has become a major task for suppliers.

9.3.2.1 The chemistry of frying fats

Deep fat frying is a heat-transfer process in which food is cooked and dried and in which the heat-transfer medium – the oil – is absorbed by the food particles. The reactions taking place in this process are shown in Figure 9.2, and the physical and chemical changes taking place are shown in Table 9.2. These changes are caused by hydrolysis, oxidation and polymerisation. The degradation products, both volatile and non-volatile, affect the physical properties of the medium.

The thermal degradation of frying oil is complex, with many variables. Oil, food and process variables are shown in Table 9.3. These are the factors that affect the hydrolysis, oxidation and polymerisation processes and the frying oil deterioration; thus the management of these factors controls the rate of degradation of frying oil. For example, it is preferred that fresh oil of good quality is used; that is, oil with no prior oxidation and with low levels of polyunsaturation. These features are shown in the basic specification given in Table 9.4.

Table 9.2 Effects of physical and chemical reactions during deep fat frying.

Physical changes:
increased viscosity, colour and foaming
decreased smoke-point
Chemical changes:
increased free fatty acids, carbonyl compounds and high molecular weight products, for example polar compounds
decreased unsaturation, flavour quality and nutritive value (e.g. from essential fatty acids)

Source: Warner (1998). Reproduced with permission of Taylor and Francis.

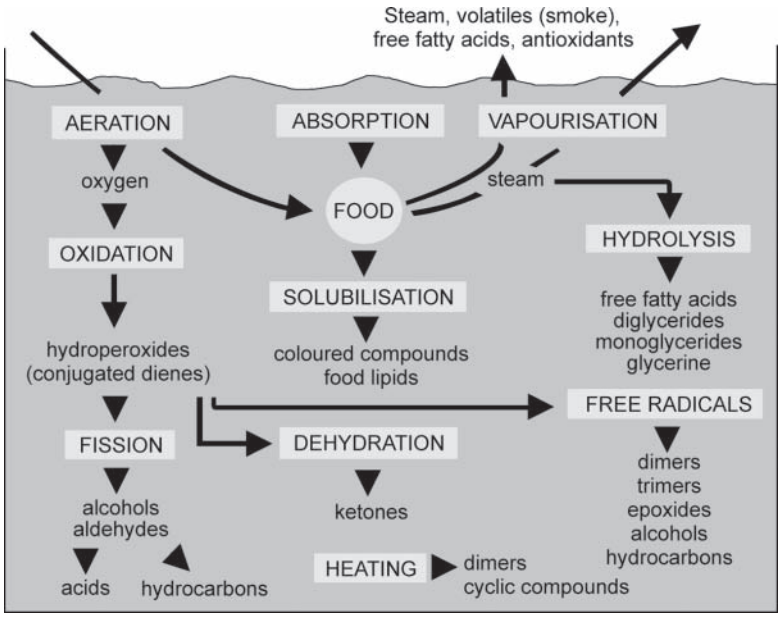

Figure 9.2 Changes occurring during deep fat frying.

Table 9.3 Factors affecting frying oil degradation.

Oil or food factors:
Unsaturation of fatty acids
Type of oil
Type of food
Metals in oil, food or frying equipment
Initial oil quality
Degradation products in oil
Antioxidants
Antifoam additives
Process factors:
Oil temperature
Frying time
Aeration or oxygen absorption
Frying equipment
Continuous or intermittent heating or frying
Frying rate
Heat transfer
Turnover rate;[a] addition of makeup oil
Filtering of oil or fryer cleaning

[a]Turnover is the ratio of the volumetric capacity of the fryer to the rate at which fresh frying oil is added to replenish the fryer.

Table 9.4 Basic specification for frying fat.

Criterion	Specification
Colour	Light
Taste	Bland
Flavour	Bland
Free fatty acids (wt %)	0.1[a]
Peroxide value (meq O_2 kg^{-1})[c]	1[a]
Smoke-point (°C)	220[b]
Moisture (%)	0.1[a]
Linolenic acid (%)	2[a]
Melting point	To fit the application

Notes: [a]Maximum.
[b]Minimum.
[c]meq O_2 kg^{-1}, milliequivalents of oxygen per kilogram of oil.
Source: Brinkmann (2000). Reproduced with permission of John Wiley and Sons.

The rate and extent of degradation can be controlled by management of frying conditions, such as temperature, time, exposure to oxygen, filtration and turnover. Intermittent frying and heating have been found to increase the rate of oil degradation compared with continuous heating (Perkins and Van Akkeren, 1965).

Turnover has always been seen as critical to maintaining frying oil quality, where turnover is the ratio of the fryer's volumetric capacity to the rate at which fresh frying oil is added to replenish the fryer (Banks, 1996). It can be seen that the higher the turnover, and so the greater the replenishment with fresh oil, the more the frying oil is maintained in its best condition. Where the turnover is slower, it is impossible to avoid discarding used frying fat in order to maintain quality. Low turnover leads to the accumulation of degradation products in the frying oil and their eventual incorporation in the fried food – an area of concern in nutritional and flavour terms.

The many thermal and oxidative reactions involving oil, protein, carbohydrates and minor food constituents that take place during frying leading to the development of volatile and non-volatile degradation products have been the subject of much research (Figure 9.3).

During the frying process the volatile degradation products are in part responsible for flavour being formed in the oil or food particle. The degradation products can be detrimental to the oil and food as well as making the flavour more attractive. The non-volatile degradation products shown in Table 9.5 are likely to promote further degradation of the oil, which in turn affects the long-term flavour stability of the fried food.

The breakdown of frying fats in use is believed to follow a distinct pattern of degradation. Blumenthal has developed a 'frying oil quality curve', describing the stages the frying oil passes through during use, (Figure 9.4) (Blumenthal and Stiers, 1991). The various stages are quantified in Table 9.6 for a mixed-use fast-food service fryer.

The measurement of the quality indicators of used frying fats has been the subject of considerable investigation and has been reviewed by Gertz (2000), who looked at physical and chemical parameters. The control of quality in the production of fried food

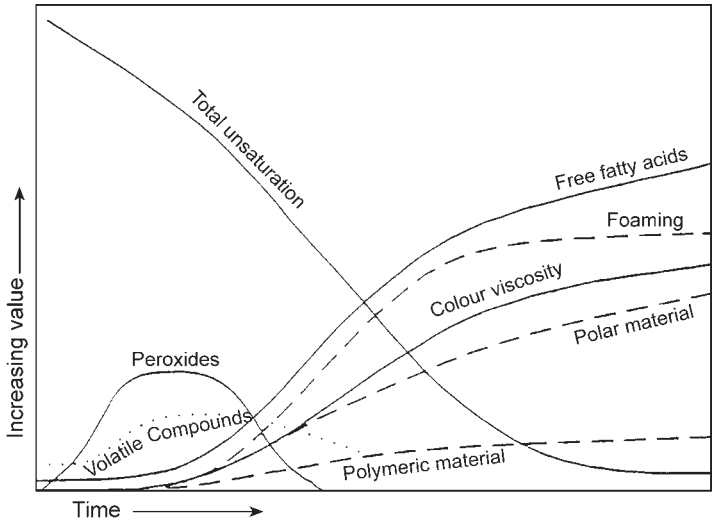

Figure 9.3 Changes in volatile and nonvolatile decomposition products during the frying process. *Source:* Warner (1998). Reproduced with permission of Taylor and Francis.

Table 9.5 Volatile and non-volatile degradation products from frying oil.

Nonvolatile products	Volatile products
Monoglycerols	Hydrocarbons
Diglycerols	Ketones
Oxidised triacylglycerols	Aldehydes
Triacylglycerol dimers	Alcohols
Triacylglycerol trimers	Esters
Triacylglycerol polymers	Lactones
Free fatty acids	

Source: Warner (1998). Reproduced with permission of Taylor and Francis.

is an area of great concern as the achievement of consistent quality with good control of cost is very important to the fryer. Quality control tests need to be simple, easy to carry out and preferably avoid the use of chemicals. This area of research continues to evolve, it is possible from varyingly complex analytical tests in the laboratory to give parameters and levels at which a frying oil is judged to be no longer acceptable. This point of unacceptability has led many European countries to bring in legislation to reinforce this cut-off (Sanchez-Muniz, 2006). For instance it could be necessarily to discard oil when the altered part of the oil (this includes polar compounds, thermally oxidised and hydrolysed compounds) reaches more than 25% of the total oil, or else if the amount of oligomers is over 10%. These tests can be determined relatively easily in the laboratory, for instance, the determination of polar compounds is achieved by silica column chromatography, however, these tests can be time-consuming and costly. The ideal is to correlate these values to a device which could be used safely, with

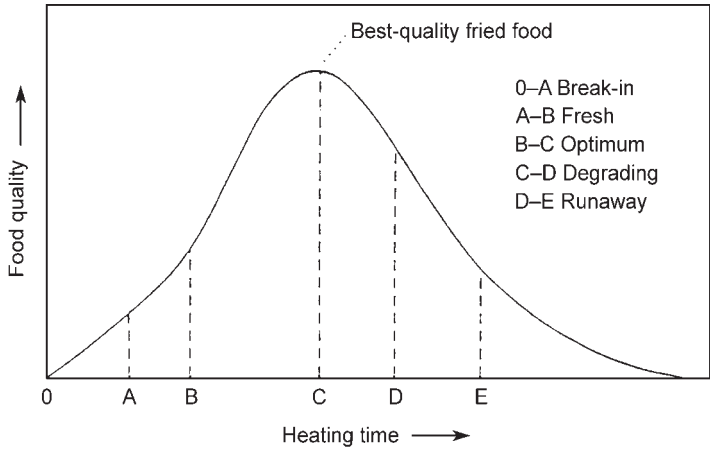

Figure 9.4 Frying oil quality curve showing the five phases that a frying oil passes through during the degradation process. *Source:* Blumenthal and Stiers (1991). Reproduced with permission of Elsevier.

Table 9.6 Effects of oil quality on the characteristics of fried potato strips.

Oil quality	Characteristics of fried potato strips
'Break-in'	White, raw interior; no rich potato odour; surface not crisp
Fresh	Slight darkening of surface; some crust formation; interior not fully cooked
Optimum	Golden brown; oily surface; fully cooked centre (ringing gel); rich potato odour
Degraded	Oily surface; darkening and spotting of surface; surface hardening; excess oil; centre not fully cooked
'Runaway'	Excessively oily (greasy); dark and hardened surface; walls beginning to collapse; centre hollow

Source: Blumenthal and Stiers (1991). Reproduced with permission of Elsevier.

minimal training, and at no compromise to the product safely of quality at the fryer. Some examples include colour indictor strips to determine FFA and probes to measure polar compounds, achieved by measuring the change in dielectric constant of the oil.

9.3.3 Selection of frying media

Although the basic selection requirements are the same irrespective of the specific application, as shown in Table 9.4, the type of fryer and operational demands will always affect the choice. Table 9.7 lists those features that are of greatest interest when a frying medium is being selected. The major areas of deep fat frying will be considered individually.

9.3.3.1 Fast-food-service frying

In fast-food restaurants the rate of turnover in the fryer is of the order of 25%–30%, which is the result of relatively low fat absorption and periods of fryer 'idling'. The low turnover and necessity to fry a range of food types mean that used frying fat has to be discarded frequently. The timing of the point when the fat is discarded is

Table 9.7 Features to be considered when selecting a frying fat.

No contribution of off flavours to the food
Long frying life to make the operation economical
Ability to produce an appetising, golden brown, nongreasy surface on the food during its fry life
Resistance to excessive smoking after continued use
Ability to produce food with good taste and texture
Resistance to gumming (polymer formation)
Resistance to rancidity
Uniform in quality
Ease of use, including form and packaging

important economically and in terms of food quality. Discarding fat too early means unnecessarily high frying fat costs and too late means poor-quality food; additional pressures are the smell generated from the degrading oil and the potential fire risk, as the FFA builds and the smoke and flash points reduce.

Many restaurants either have a fixed period for discard or fix the weight of food fried before discard; otherwise the restaurants use parameters such as colour, evidence of smoking, condition of the fried food and evidence of foaming. None of these approaches is completely satisfactory as they lack objectivity and accuracy and so can lead to variable food quality. The search for a quick and easy test for quality is still continuing, as discussed earlier (Section 9.3.2.1).

Fats used in food-service applications used to be solid plasticised fats of animal and/or vegetable origin; for example, in the USA blends of tallow and cottonseed oil were very popular, and in Europe palm oil was widely used. Hydrogenated vegetable oils such as soybean or rapeseed oil were also popular, with the oil hydrogenated to a slip melting point of $30^{\circ}C-34^{\circ}C$ to ensure the virtual elimination of linolenic acid content. Where fast-food service was of a lighter duty then liquid vegetable oils were popular, such as soybean, rapeseed, corn and cottonseed oil. Increasingly the trend has been to move away from any partially hydrogenated blends, due to the *trans* issues and use the most nutritionally favourable, yet stable blends possible. These could potentially incorporate the use of fully saturated (hence low *trans*) fats in the blend mix.

Liquid vegetable oils increased in popularity when the effectiveness of dimethyl polysiloxane, an antifoaming agent, was demonstrated to reduce the oxidative breakdown of frying oils when added at as little as 1 ppm . Frying stability has been found to increase by three to ten times compared with original frying stability, as studied under laboratory-controlled conditions (O'Brien, 1998). Work by Freeman *et al.* (1973), demonstrated dimethyl polysiloxane acts to stabilise the frying oil by providing a monomolecular layer at the oil surface, however, it could be argued that the benefits are greater when there are infrequent frying cycles (Marquez-Ruiz, 2004). The formation of this mono-layer, it has been suggested, could act to increase the FFA content, as the water is trapped and unable to escape, and so starts the hydrolysis reaction. A further disadvantage of DMPS is that an addition of too much can actually promote foaming; this is particularly worth bearing in mind due to the high viscosity of the

product, and care should be taken that high dosing does not occur as the DMPS builds up on the sides and bottom of storage vessels, agitation is therefore essential.

As stated earlier, the presence of natural antioxidants is also found to extend the frying life of a vegetable oil; therefore, refining processes are being modified to maximize the residual levels of tocopherols in vegetable oils and in some cases losses of tocopherol as a result of refining are made up by additions to the refined edible oil of natural or synthetic tocopherol.

Gertz *et al*. (2000), using a newly developed test to give the OSET index (oxidative stability at elevated temperature), have shown the influence of sterols, sesame oil, rosemary extract and other naturally occurring substances on the stability of frying oil at high temperatures. In the same study, experiments with other natural and synthetic antioxidants demonstrated that ascorbyl palmitate increased the oxidative stability of the oil (Gwo, 1985).

It is now possible for fast-food-service restaurants to use a very wide range of frying oils, and those selected are governed by economic and nutritional issues. A higher polyunsaturation in an oil or blend of oils, particularly linolenic acid, has been shown to give a shorter frying than oils with lower levels of polyunsaturation. The introduction of opaque liquid shortening followed from this consideration. Brush hydrogenated soybean oil and rapeseed oil, where the iodine value is reduced by, say, 20 units, shows a reduction in both linolenic and linoleic acids, with only a small increase in the amount of saturated and *trans* fatty acids (see Figure 9.1). A clear, more stable, oil can be produced by 'winterisation'. Alternatively, the addition of a small proportion of fully hydrogenated oil followed by chilling produces an opaque pourable slurry. In products of this type, with the addition of dimethyl polysiloxane, an acceptable frying life can be obtained even in heavy-duty applications. As with the other applications above, increasing pressure to move to zero hydrogenated fats has seen an increased used of the palm fractions and the trait-enhanced oils. Due to cost implications these can be blended with liquid and solid fats to give an acceptable frying medium.

9.3.3.2 Industrial snack-food frying

In this case, products such as potato crisps (chips), tortilla chips and puffed snacks are fried and packaged for consumption, with a shelf-life of several months after manufacture. The frying oil used is crucial to the quality of the fried snack; hence the process is highly controlled.

The frying oil becomes a major component of the snack after the hot oil has first dehydrated the particle to concentrate the flavours. Fried snacks have a very high proportion of absorbed fat, in the order of 30–45%, so that the fat has an influence not only on the turnover of the fryer but also on the finish of the snack. A snack will have an oilier or brighter surface with a frying oil that is liquid at room temperature compared with one where the oil is solid at room temperature, giving a duller and greyer product. Additionally there is always the risk that a more solid fat could give some mouth feel to the final product due to its higher melting point.

In modern production plants, liquid oils or blends are used under tight control to minimise degradation in the frying oil in order to ensure an adequate shelf-life for the product. In some cases, to ensure a good shelf-life, phenolic antioxidants such as BHA, BHT and TBHQ are introduced, giving some carry-through protection for the snack food (Buck, 1981).

Oils that are popular in this application are cottonseed oil, palm olein, rapeseed oil and groundnut oil. These oils are often used as blends. Palm oil is used but is usually blended with liquid vegetable oil in order to ensure the oil is liquid at room temperature. Once again pressure to lower saturates and go for nonhydrogenated has opened up the option of using fractionated oils and trait-enhanced oils and blends. Trait-enhanced oils because of their liquid properties and additional stability potential have found a good niche within this market, and their use has even been advertised on the front of some packets of crisps in the UK.

Another option which has been used for snack frying is the use of red palm olein. This is palm olein which due to adjusted processing conditions still contains higher amounts of its naturally occurring beta carotene. This has an advantage in that is will help impart in the products a good final colour.

9.3.3.3 Bakery frying fat application

The major fried bakery product is the doughnut, although there are also fried pies and pastries. The fact that these products often have a coating as a finish (e.g. sugar or icing) places a constraint on the frying medium that can be used; thus, the frying fat as well as being a heat-transfer medium becomes a major ingredient of the product and must act as a binder for any added coating.

Frying fats that are solid at room temperature are preferred in this application. Hydrogenated liquid oils with a slip melting point of between 33°C and 40°C have been used. Palm and palm fractions and hydrogenated lard have also been used.

In selecting the particular melting characteristics a balance has to be struck between achieving a good appearance (i.e. no visible layer of fat, as such a layer could give a waxy mouth feel) and enough solid fat to ensure good sugar pickup. Finally, the solid fat content at body temperature must not be so high as to impair the eating quality. A profile of bakery frying fats is given in Table 9.8.

9.4 Oils for roasting nuts

Many varieties of nuts are now available as snack foods, the major example being peanuts. When nuts are roasted in oil, the surface is dehydrated and there is browning and the nut texture and appearance are changed. The nuts have a low moisture (about 5%) and high oil content and thus very little frying medium is absorbed, giving an extremely low turnover. Hence oil with good oxidative stability is required. The preferred oils in this application are coconut oil and hydrogenated palm kernel oil, which have little unsaturation and which, because of the high content of short-chain and medium-chain fatty acids, have a low melting point.

Table 9.8 Typical solid fat index (SFI) profiles of bakery frying shortening.

Solid fat index			
Temperature (°C)	Solids (%)	Characteristic affected	Solid–liquid relationship effect
10.0	33–38 21–26	Shelf-life	The correct solids content will create a moisture barrier, keeping moisture inside the doughnut
21.1	21–26	Appearance	Too high an SFI value leaves a visible layer of fat on the doughnut, which provides a waxy mouth feel and can promote flaking of the sugar coating; too low an SFI content will leave the crust oily, which can promote oil soakage of the sugar
26.7 33.3	19–21 12–17	Sugar pickup	The correct ratio of hard to soft fractions in the frying shortening composition will help ensure proper sugar pickup; too high an SFI results in decreased sugar adherence; too low an SFI results in increased sugar disappearance
40.0	7–12	Eating quality	SFI content of doughnut frying shortening at temperatures above body temperature have a direct effect upon eating quality; SFI values above 12% at 40°C may cause a waxy, unpleasant, mouth feel

Source: O'Brien (1998). Reproduced with permission of Taylor and Francis.

9.5 Ghee

Ghee is clarified crystallised butter from buffalo's or cow's milk. It is the most common form in which butterfat is used in India and other countries of the Far East. Ghee manufacture in India is still a home industry (Ganguli and Jain, 1973). However, increasing industrialisation and growth of the urban population have led to the establishment of factories using both batch and continuous processes. Anhydrous butterfat is also widely sold as ghee.

Ghee is traditionally made from the boiled and cooled milk of the cow or buffalo by allowing it to set overnight after addition of a starter culture. The curd that is formed is then churned to butter prior to clarification at high temperature (100–120°C) to remove the water. This is the *desi* method and it is claimed that it gives the best flavour characteristic because during the moisture removal there is interaction between the fat and the fermented residue of the nonfat solids.

In factory manufacture the process is simplified, with the use of cream or sweet cream butter. Heat is applied to either the butter or the cream in open-jacketed vessels to remove the moisture through agitation. A prestratification method can also be used where after initial heating of the butter the bottom layer is discarded before the remainder is heated to the desired temperature.

The continuous method is based on pumping cream or butter through a steam-heated scraped-surface heat exchanger. The superheated cream or butter is passed into a flash

evaporator, where the moisture is separated from the liquid fat. This process goes through multiple stages to remove the moisture completely.

The processes are selected on the basis of yield and energy efficiency as well as achieving the desired flavour, colour and shelf-life. The quality of the ghee depends on the quality of the milk, cream, the curd or butter and the temperature of clarification. The lower temperature of 110°C gives a mild flavour, whereas a temperature of 120°C gives a stronger and more 'cooked' flavour.

9.5.1 Ghee attributes and quality

Ghee has a shelf-life of up to eight months in tropical temperatures. This high stability is attributed to the low moisture and high phospholipid content. It is thought that amino acids in the fat phase from the phospholipid–protein complex form during culturing and cooking.

The highly characteristic flavour of ghee is generated mainly during the boiling-down process, where there is an interaction between protein and lactose. A range of ketones, alcohols, hydrocarbons and lactones have been identified as contributing to the flavour (Achaya, 1997).

The flavour, texture and colour have long served to characterise ghee, so they can also be used as indicators of its quality. Where the manufacture of ghee is still a cottage industry, using the *desi* method, flavour and texture are the only criteria used to judge quality. A nutty, lightly cooked aroma and flavour are generally prized. The texture can vary from granular to smooth and, in some cases, even show a tendency to separate out a liquid portion. These textural differences are fixed by local tradition; for example, a granular texture with no separation is preferred in India, whereas in Pakistan the product is favoured when it has larger, softer granules dispersed in a supernatant liquid.

In the industrial manufacture of ghee considerable effort has gone into providing a product of greater uniformity and extended shelf-life. The quality of ghee depends heavily on the milk, which in turn depends on the animal feed, the season and the health of the animals. For example, winter ghee has been shown to have a high acidity, melting point and grain size, and milk from animals fed on cottonseed gives ghee that increases in acidity less quickly, but that also leads to a product of lower melting point. Where the ghee preparation is by way of cream *dahi* or butter, the quality of these products also influences the quality of the ghee. Further, the method of preparation and temperature of clarification have an influence. These factors determine the physiochemical features of ghee. Typical analytical characteristics of cow and buffalo ghee are shown in Table 9.9.

The quality of ghee (Sharma, 1981) is generally measured analytically by parameters such as acid value, peroxide value, flavour and shelf-life. Bacteriological quality is assured by reducing the moisture content to less than 0.3%.

The free fatty acid content of ghee varies with the method of preparation. Thus, in ghee prepared from ripened cream or butter, the free fatty acid is in the range of 0.34–0.40% whereas in unripened cream or butter it is 0.23–0.28%. The peroxide

Table 9.9 Typical analytical characteristics of cow and buffalo ghee.

	Buffalo	Cow
% Solid fat °C		
10	51·9	53·4
15	37·5	38·6
20	23·1	22·6
25	16·3	15·7
30	10·8	7·9
35	4·0	3·2
40	NIL	NIL
Slip point (°C)	29·9	33·4
IV	28·4	34·9
Lovibond colour (5 · 25 in cell)	2 · 5R 24 · 0Y	4 · 3R 44 · 0Y
% Moisture	0 · 3 max.	0 · 3 max.
% Free fatty acid		
Ripened milk	0 · 34–0 · 40	
Unripened milk	0 · 23–0 · 28	
Unsap. (mg/100)	390	450

Source: Based on data from Sharma (1981).

value is a less valuable indicator of quality than either free fatty acid content or flavour, and though in the fresh product it should be low, in the stored product it varies considerably, particularly near the point where rancidity is detectable organoleptically.

The flavour of fresh ghee is greatly influenced by the temperature of clarification. Ghee prepared at 120°C has a distinctive 'cooked' flavour, whereas that prepared at 140°C has a 'burnt' flavour. The temperature of clarification also influences off-flavour development; product clarified at 110°C retains its flavour longer than that clarified at 120°C. The flavour of ghee is also dependent on the method of preparation. Ripening of the cream or butter is always considered to give an improved flavour, and ghee from *desi* butter is believed to be the best, having a 'nutty' flavour with a 'cooked' or 'caramelised' aroma.

It has been found that the keeping quality of *desi* ghee is better than that of direct cream or creamery butter ghee; longer heating has been found to improve the oxidative stability of ghee because of the liberation of phospholipids into the fatty matter. As well as organoleptic changes, ghee undergoes textural changes in storage. When filled into containers crystallisation occurs with the formation of solid, semisolid and liquid layers. Below 20°C ghee has a small-grained and compact texture. Storage temperatures of 28–29°C lead to a well-defined granular texture, though cooling to this too rapidly can give rise to a granular settled portion, a liquid oil portion and a floating hard flake, each layer having different chemical characteristics. At higher temperatures the texture becomes looser and a liquid oil layer then becomes evident. At 34°C the product is fully liquid.

The consumer's perception of quality is based on flavour, texture and colour, as these three indicate quality and purity. A uniform granular structure, with a white or off-white colour is expected. The flavour should be characteristic, with *desi* ghee the most popular.

Anhydrous milk fat, in spite of its more bland flavour, is now being supplied as ghee. The anhydrous milk fat is prepared at temperatures of 80°C, so it has a greater moisture content, but less protein.

9.5.2 Uses of ghee

Traditionally, ghee was the major culinary fat in the Middle and Far East and was used in a wide range of foods. It was used in the shallow frying of vegetables. In India it was used in curries, paratas and dosais. Certain foods such as puris and samosas were deep fried in ghee. Basting chicken and pilau with ghee imparts a distinctive and characteristic flavour. Certain recipes demand that the ghee be a solid. Finally, ghee is used as a spread in molten or semimolten form for chappatis or partially malted and mixed rice. A small proportion of the ghee produced is used in confectionery and to cook sweetmeats based on cereals, milk solids and fruit.

Changing culinary practices combined with the increasing popularity of vanaspati and liquid vegetable oils have meant that ghee consumption is declining. For example, less than 8% of households in India consume ghee (GCMMF, 1993).

Ghee is now used more in high-quality cooking. For example, pulses are flavoured with ghee, which is the equivalent of cooking them in butter. Ghee is also used in combination with vanaspati in order to enhance the flavour of the vanaspati. Cooking in ghee has a certain amount of status attached to it, rather like cooking in butter. However, the vast majority of recipes for dishes from the Indian subcontinent and Middle East call for the use of liquid vegetable oil or vanaspati.

9.6 Vanaspati

Vanaspati or vegetable ghee is a substitute for natural ghee and has been based traditionally on hydrogenated vegetable oils. In India the economic situation caused the demand for animal fats to exceed production, resulting in a price increase so that the product was put beyond the reach of the general population.

Vanaspati was first imported into India from the Netherlands after the First World War as a substitute for ghee for the bulk users such as restaurants and sweetmeat manufacturers. In 1930, production started in India, and 10 years after, these imports ceased. The volumes produced have increased since that time, with a significant jump during the Second World War, when vanaspati was approved as a cooking fat for the armed forces.

The development of vanaspati in the marketplace has been controlled by the Vegetable Oil Products Control Order (1942) which regulates manufacture and control standards. Some of the important parameters are:

- moisture content, maximum 0.25%
- slip melting point, 31–41°C
- free fatty acid (asoleic), maximum 0.25%

- unsaponifiable matter, maximum 2.0%
- nickel content, maximum 1.5 ppm.

Colour and flavour are not permitted. The addition of refined sesame oil is mandatory. Vitamin A is a required additive at 25 IU; vitamin D addition is optional.

The oils permitted for use in vanaspati are under regular review and include soybean oil, cottonseed oil, rapeseed oil, sunflower oil, maize oil, palm oil, palm olein, rice bran oil, mahua fat, nigerseed oil, watermelon seed oil, sal fat (to a maximum 10%) and sesame oil (used mainly as a marker). Recently included have been solvent-extracted expeller cake oils such as mustard–rapeseed, groundnut and sesame oil. Groundnut oil, on which the early vanaspati was developed, is no longer permitted to be used because of the demand for its use as a direct edible oil.

As vanaspati was exclusively made from hydrogenated oils, a considerable amount of work had been done on the hydrogenation conditions to be applied and how they are varied for the individual oils. Selective hydrogenation conditions were applied, which led to steep melting curves and the generation of high levels of *trans* fatty acids. The high level of *trans* fatty acids was felt to assist in the generation of the desired granular texture associated with ghee. It has been shown that as the hardened oil cools to 50°C, the triacylglycerols containing '*trans*' fatty acids in the liquid phase nucleate to initiate crystallisation with heat evolved, which is controlled by external cooling. Photomicrographs of vanaspati show the presence of large granules made up of radially arranged needle-like crystals. This crystal network, though containing large saturated triacyl glycerol crystals causing the granularity, can trap the liquid phase to prevent separation at ambient temperature.

Vanaspati is no different to any other oils and fats application in that lower, if not zero *trans* solutions are being sought. This has led to extensive work, with blends such as 50/50 palm stearine and ricebran oil being suggested (Mayamol, 2004), this particular blend showing melting and cooling characteristics similar to commercial hydrogenated vanaspati. The palm stearine helps to give the desirable gritty, granular texture due to its particular polymorphic crystallinity, this crystallinity being confirmed by X-ray diffraction.

Vanaspati is expected to be similar in texture and colour to natural ghee and achieve at least the same shelf-life. It is obviously not possible for the product to have the same flavour as natural ghee; however, there is now a growing acceptance of the product and in some countries flavours may be added to make a vanaspati even more similar to ghee. The culinary uses of vegetable ghee are equivalent to those of ghee, it being used in a range of basted and fried dishes. The improved oxidative stability of vanaspati compared with ghee and its higher melting point give it a wider application in confectionery.

In those countries where vanaspati has become the major culinary fat (Johnson and Saikia, 2009), there is now a call for a fat product for commercial baking to make products such as puff pastry and patties. Shortening products are made as described elsewhere in this book (see Chapter 2 of this volume) and typically use the same oils as used in vanaspati, though they are hydrogenated under processing conditions

different from those used for vanaspati to give different melting curves and melting points in order to give the plastic characteristics desired for the given shortening. The shortenings are designed for use in a wide range of products such as crisp cookies, wafers and cream biscuits.

9.7 Speciality oils

Speciality oils are usually vegetable derived. The oils are sourced from minor crops, of which in some cases the oil content of the seed may be very low and so are available only in small quantities and are hence of high value. The special flavours and odours of these oils are the key attributes for their purchase. The market for speciality oils is growing as they are perceived as being nutritionally healthy; the fatty acid compositions of some of the oils provide components which are not present in the usual commodity oils and fats. Most are liquid oils so have a high degree of unsaturation and hence low levels of saturates. This is believed to be beneficial in helping to prevent cardiovascular disease; the unsaturates can also contribute to the intake of essential n-3 and n-6 fatty acids which the human body is incapable of synthesising. Also, there is a growing interest in the consumption of exotic foods, which require the use of these characteristically flavoured oils. Many of the speciality oils are not refined, in order to ensure that the distinctive flavour and colour characteristics are maintained. These requirements can cause significant problems, especially with consistency in quality with such minor crops.

Speciality oils are extracted mainly by cold pressing, and the use of solvents is avoided. Some speciality nuts and seeds are roasted prior to extraction in order to develop the desired flavours (e.g. toasted sesame oil). A potential issue with cold pressed oils concerns people with food allergies. Usual refining of the oil will remove any traces of protein, and hence the oils should pose no problems to people with allergies, but cold pressed/untreated oils will in all likeness contain protein and so could cause a reaction. This is applicable to oil derived from nuts, peanuts, sesame seed and soya in particular.

There are an enormous number of nuts and seeds that can provide oils for food, pharmaceutical or cosmetic purposes. Some examples are as follows:

- apricot kernel oil
- blackcurrant oil
- cherry kernel oil
- macadamia nut oil
- meadowfoam oil
- borage oil
- passion fruit oil
- pistachio nut oil
- flaxseed oil
- safflower seed oil.

The major oils currently found on supermarket shelves are:

- groundnut oil
- grapeseed oil
- sesame seed oil
- walnut oil
- avocado oil
- almond oil
- hazelnut oil.

Olive oil can also be considered to be speciality oil and constitutes a major member of this group of oils. The use of olive oil in cooking in countries with cooler climates has expanded significantly in recent years because of the highly characteristic flavour and the claimed nutritional benefits

The grades and applications of olive oil are discussed in Section 9.2 as a salad and cooking oil; however, the variations in colour and flavour are such it is now possible to purchase olive oils that are both specific to a variety of the fruit and to the growing area – making the oil highly specialist.

Table 9.10 shows the fatty-acid composition of some of the speciality oils. It can be seen that they generally contain high levels of unsaturated fatty acids, which in some cases leads to poor oxidative stability.

The speciality oils that are used in food applications are used almost exclusively for their flavour. However, where the oil's nutritional attributes are thought to be beneficial, the oil can be refined by the usual processes, though the flavours and odours will be diminished, the nutritional contribution will still be valid. Those of major interest are discussed below.

9.7.1 Almond oil

This is an oil with a sweet aromatic odour and flavour. It is popular in fish cookery and for use in some bakery products.

9.7.2 Groundnut oil

Although this oil at one period in Europe had the status of a commodity oil and in some parts of the world is still a major culinary oil, its use has declined as it is a premium oil. The concerns of peanut allergies have also been a factor in its popularity; though the risk is greatest in cold pressed oils due to the presence of protein, the fully refined oils would still have to be labelled as allergens despite the fact that the protein will almost certainly be absent. In its unrefined state it is used as a speciality oil, giving a distinctive 'nutty' flavour to food. The absence of linolenic acid in groundnut oil provides it with greater oxidative stability compared with other speciality vegetable oils.

Groundnut oil is used extensively as both a shallow-frying and deep-frying medium (Pattee, 2005). As mentioned earlier, it is a particular favourite in Chinese cooking

Table 9.10 Data on speciality oils.

Oil	Plant name	Iodine value	Fatty acid (% wt)												
			C16:0	C16:1	C18:0	C18:1	C18:2	C18:3a	C18:3g	C20:0	C20:1	C22:0	C22:1	C24:0	Other
Almond	*Prunus amygdalus*	98–105	4–9	0.8[a]	0–3	60–80	17–30	–	–	–	–	–	–	–	–
Apricot kernel	*Prunus armenica*	98–112	3–8	1.0[a]	0–2	56–70	21–33	1.0[a]	–	–	–	–	–	–	–
Avocado	*Persia gratissima*	80–95	10–20	3–10.5	0–1.5	56–75	8–16	0–2	–	–	–	–	–	–	–
Borage	*Borago officinalis*	140–155	9–13	0.6[a]	3–5	10–20	34–42	0.4[a]	18–25	0–1	2–6	–	1–3.5	–	0.5–3.5[b]
Cherry kernel	*Prunus avium*	110–130	5.5–10	1.0[a]	1.5–3	23–39	40–48	1.0[a]	–	2[a]	0.6[a]	0.5[a]	–	–	1–13[c]
Corn (maize)	*Zea mays*	103–131	9–14	0.5[a]	0.5–4	24–42	34–62	2.0[a]	–	–	–	–	–	–	–
Evening prmrose	*Oenthera blennis*	145–165	5.5–7	–	1–3	7–18	60–75	0.3[a]	7.5–11	–	1.0[a]	–	0.2[a]	–	–
Flaxseed (Linseed)*	*Linum usitatissimum*	179**	5.3	–	4.1	20.2	12.7	53.3		–	–	–	–	–	–
Gold of pleasure	*Camelina sativa*	145–165	3–8	–	2–5	12–26	15–24	30–40	–	0–2	9–17	–	0–4	–	–
Grapeseed	*Vitis vinefera*	125–145	5–11	–	3–6	12–28	58–81	1.0[a]	–	–	–	–	–	–	–
Hazelnut	*Corylus americana*	87–102	4–10	–	1–4	70–84	9–19	1.5[a]	–	1.0[a]	–	–	–	–	–
High oleic sunflower	*Helianthus annus*	80–90	3–5	–	3–5	77–84	4–15	1.0[a]	–	–	–	2.0[a]	–	–	–
Macadamia	*Macadamia ternifolia*	–	7–10	16–24	2–45	54–65	1–3.5	–	–	1.5–3	1.5–3	1.0[a]	–	–	0–1[d]
Meadowfoam	*Limnanthes alba*	90–102	1[a]	–	0.5[a]	4[a]	4[a]	–	–	–	60–65	–	2–4[e]	–	15–23[f]
Olive oil	*Olea europaea*	80–88	7–20	3.5[a]	0.5–5	55–83	3.5–21	0.9[a]	–	0.5[a]	0.2[a]	0.2[a]	0.1[a]	0.2[a]	–
Passion flower	*Passiflora Incarnata*	132–145	8–12	0.3[a]	1.5–3	12–18	65–75	1.0[a]	–	–	–	–	–	–	–
Peach kernel	*Prunus persica*	98–115	2–8	1.0[a]	0.5–2.5	54–67	23–35	0.8[a]	–	0.5[a]	–	–	–	–	–
Pistachio	*Pistachia minor*	90–120	9–20	0–2	1–3	40–60	28–38	2.0[a]	–	–	–	–	–	–	–
Pumpkin seed	*Curcurbita peppo*	110–130	6–13	–	5–8	20–41	44–57	2.0[a]	–	–	–	–	–	–	–
Safflower	*Carthamuc tinctorius*	138–150	2–10	–	1–10	7–42	55–81	1.0[a]	–	–	–	–	–	–	–
Sesame	*Sesamum indicum*	103–118	7–12	–	3.5–6	35–50	35–50	1.0[a]	–	–	–	–	–	–	–
Toasted sesame	*Sesamum indicum*	103–118	7–12	–	3.5–6	35–50	35–50	1.0[a]	–	–	–	–	–	–	–
Walnut	*Junglans* spp.	145–155	5–10	–	2–6	15–36	40–65	0.5–15	–	1.0[a]	–	–	–	–	–
Wheatgerm	*Triticum vulgare*	115–140	11–21	0.5[a]	0.5–4	15–26	49–60	2–10	–	0.2[a]	2.0[a]	–	–	–	–

Notes: –Zero.
[a]Maximum.
[b]C24:1.
[c]C18:3 isomers.
[d]C14:0.
[e]Delta-5 isomer.
[f]C22:2
*From USDA national nutrient database, **calculated.

due to its pleasant subtle flavour. The fact that at low temperatures the higher melting triglycerides deposit in a gelatinous form limits its use in sauces and mayonnaise, as at low temperatures these separate.

9.7.3 Hazelnut oil

Though hazelnuts are grown mainly in Turkey, Italy and Spain, the major producer of the oil is France, where it is used as a salad oil. Hazelnut oil is sold both in a refined and an unrefined state, with the more strongly flavoured unrefined oil being more popular. The near equivalence of this oil to olive oil in terms of mono-unsaturated fatty acid content means that hazelnut oil has some of the same nutritional attractions; in fact, these attributes have meant that adulteration of more expensive extra virgin olive oil with hazelnut oil has been a dilemma for many years, similarities in their fatty acid and sterol compositions making detection very difficult to detect (Jee, 2002).

9.7.4 Sesame seed oil

Before extraction of the oil, the seeds are usually toasted to intensify the flavour of the oil. The extracted toasted oil is dark brown and has a very strong bitter 'nutty' flavour and odour. Unrefined sesame oil is used extensively in Oriental foods and is frequently added to stir-fry dishes in Chinese cookery to give a characteristic flavour. The unrefined oil is generally not used for cooking but for flavouring.

The refined oil, which is straw yellow in colour with a mild 'nutty' taste and exceptional oxidative stability, is commonly used for frying, roasting, stewing meat, fish and vegetables. Foods fried in sesame oil (e.g. snack foods) have been found to have an excellent shelf-life (Maiti *et al*., 1988).

Sesame oil and groundnut oil are used interchangeably in Asian countries as frying oils, and sesame oil is often used as a replacement for olive oil. Sesame oil is a prized oil and so attracts a high price, which has led to the development of blends with oils such as groundnut, cottonseed and rapeseed oils; these are cheaper and the blend retains some of the attributes of the sesame oil.

The great advantage of sesame oil as a frying oil is its great oxidative stability, which is greater than would be expected from the tocopherol content. The unsaponifiable matter (see Table 9.11) includes sesamol and phytosterols not found in other vegetable oils. The remarkable oxidative stability of the crude oil is now attributed to the presence of the endogenous phenolic antioxidants, sesamin, sesamolin and sesamol. A review by Deshpande *et al*. (1996) suggests sesamol is generated by various processes from sesamolin to the active antioxidant. Refining and deodorising of sesame oil reduce any released sesamol, lowering the oxidation stability of the refined and deodorised oil (Kikugawa *et al*., 1983).

The fatty-acid composition of sesame oil is predominantly oleic and linoleic acid present in nearly equal amounts, making it an attractive oil from a nutritional and health viewpoint.

Table 9.11 Codex Standards of the Food and Agricultural Organisations and the World Health Organisation for fatty acid composition and characteristics of sesame oil.

	Range
Fatty acid (%):	
C < 14	<0.1
C14:0	<0.5
C16:0	7.0–12.0
C16:1	<0.5
C18:0	3.5–6.0
C18:1	35.0–50.0
C18:2	35.0–50.0
C18:3	<1.0
C20:0	<1.0
C20:1	<0.5
C22:0	<0.5
Characteristic:	
iodine value	104–120
saponification value	187–195
unsaponifiables (%)	2.0[a]
acid value (%)	
virgin oil	4.0[a]
nonvirgin oil	0.6[a]
Peroxide value (meq kg^{-1})	10.0[a]

Note: [a]Maximum.
Source: Based on data from Codex Standard 26-1981, Supplement 1, 1983.

The presence of sesamolin in sesame oil has meant that it has long been used in margarine and vanaspati in order to detect their use as an adulterant in butter or ghee. The sesamolin has been found to react with furfural (or sucrose) in strong hydrochloric acid to give a strong red coloration (Baudouin test).

9.7.5 Safflower oil

Safflower oil as an edible oil has one of the highest levels of polyunsaturation, which is virtually all linoleic acid. This is a strength and a weakness in that the oil is of value nutritionally; however, its stability to oxidation is low. The oil is considered to be a semi-drying oil, though the low free-fatty-acid content in the crude oil and the absence of gums make the oil easy to refine; however, exposure to air throughout the process must be avoided and nitrogen blanketing of the deodorised oil is necessary. Fresh safflower oil after refining and deodorisation is bland; however, it deteriorates very rapidly.

The oil has gained some popularity in spreads claiming to be ‘high in polyunsaturates’. Liquid safflower can be used in shallow frying applications, though ‘skinning’ of utensils is a hazard. Mayonnaise and frozen salad dressings incorporating this oil have been found to exhibit excellent appearance, flavour and odour as well as good freeze–thaw characteristics.

9.7.6 Grapeseed oil

This very pale-coloured oil is supplied for cooking purposes only in the refined and deodorised form and so has a nearly bland flavour. The oil is used in those hot and cold culinary applications where oils such as sunflower oil and groundnut oil can be used. The oil was initially popular in wine-producing countries, where the oil was produced as a by-product. The oil content of the seed is only about 15%, but as the total world production of grapes is so huge, the potential for grapeseed oil is vast. It has gained status in other countries as speciality oil, largely because of its perceived nutritional qualities. The oil is low in saturated fatty acid and high in unsaturated fatty acids, particularly linoleic acid. The oil shows good oxidative stability, possibly because of the fact the oil contains virtually no linolenic acid.

9.7.7 Walnut oil

This oil is usually supplied as a cold pressed virgin oil. The oil has a characteristic 'nutty' flavour and a golden colour. Walnut oil has the advantage of being very low in saturated fatty acids but high in unsaturated fatty acids. A major disadvantage is that the oil usually contains about 10% linolenic acid, causing it to have a very poor oxidative stability, leading to the rapid development of a flat, rather unpleasant, taste. This poor oxidative stability means that the oil is rarely used in hot applications and so is restricted to being used in salad dressing, where it provides a 'round' and 'nutty' flavour. The potential benefits in relation to cardiovascular disease means many studies are on going into the potential use of this oil, and the oil seems to being having a larger share of the supermarket shelf space.

9.7.8 Rice bran oil

Rice bran oil is a culinary oil used extensively in Japan and other rice-producing countries. Production is likely to grow in the rest of the world for the benefits of an alternative oil source with good nutritional and performance characteristics (Garcia, 2006). Rice bran makes up about 8% of the total milled rice, and the oil extracted from that is about 15–20%. The potential for rice bran oil is huge, but could be limited by the need for two-stage milling. Usually only 1 stage is used, this results in a mixture of hulls and bran, which would make oil extraction economically unfeasible. As a general-purpose frying oil, rice bran oil has been found in model trial situations to be equivalent to groundnut oil in performance (Orthoefer, 1995). Rice bran oil, when winterised, is a good salad oil and can be used in the manufacture of mayonnaise and salad dressing.

The fatty-acid composition of the rice bran oil shows it be to similar to groundnut oil in terms of the ratio of saturated to unsaturated fatty acids, except that groundnut oil contains long-chain fatty acids. Rice bran oil has an unusually high content of unsaponifiable matter, of which sterols represent the major part. Oryzanol, which is a

group of compounds containing ferulate (4-hydroxy-3-methoxycinnamic acid) esters of plant sterols and triterpene alcohols, is also found in the unsaponifiable matter.

Oryzanol intake has been associated with decreased cholesterol absorption, decrease in plasma cholesterol and decreased platelet aggregation (Nicolosi *et al*., 1992). The ferulic acid esters also have antioxidant properties, which, combined with the tocopherol content of the oil, contribute to the good stability of the oil.

One of the drawbacks in the use of rice bran oil is the very high losses of oil that can occur in neutralisation. The high losses have been assumed to be due to the presence of hydroxylated compounds (Hartman and Dos Reis, 1976). The high wax content (2–5%) is also a drawback in the production of the edible oil in that it contributes to these losses. Physical refining methods have been introduced now that not only reduce total losses but also ensure retention of up to 66% of the Oryzanol content.

9.7.9 Flaxseed oil

Also known as linseed oil, this oil was know primarily for its non-edible uses, it is a drying oil, which means it can polymerise rapidly when exposed to air, it therefore is ideal properties for use as a constituent of oil paints and printing inks. The seeds contain about 34% oil, and their fatty acid profile contains a linolenic acid content of over 50%. While this makes the oil very unstable, it is attractive in that the levels of essential fatty acids will be high. This is the key characteristic which has lead to some use in the food industry, for instance, being blended with other oils in a spread to provide omega 3 claims.

9.7.10 Avocado oil

Avocado oil is obtained from the pulp of the fruit, oil content can vary from 3–30%, with the kernel bearing only about 1% oil. The oil obtained has a beneficially high concentration of oleic acid. Avocado is gaining in popularity on the supermarket shelves, being used primarily as a salad oil, but the fully refined oil also has potential for shallow frying.

9.8 Conclusion

Despite health worries, frying is likely to continue to be a major method of food preparation, and a widening range of foods will be manufactured so that they can be prepared for the consumer by being deep fried. New and novel sources of edible oils will continue to be developed for expanding economies and consumer needs (Abdulkarim *et al*., 2005; 2007; Wang *et al*., 2012; Wassell *et al*., 2012).

Strategies will continue to be developed to improve the efficiency of deep frying systems and to extend the frying life of the oil (Kalogianni and Smith, 2013). This could manifest itself in the types of oils chosen to fry, for example, they could contain naturally high levels of components to give an antioxidant effect, or been selectively

bred to have a more robust and stable fatty acid profile. There is also the potential to use additives such as antifoaming agents and synthetic or natural antioxidant additions. This can allow the use of oils with high levels of mono-unsaturation and polyunsaturation so that the finished food product is nutritionally more acceptable. This development is exemplified by the improved frying life of high oleic sunflower oil containing sesame and rice bran oils (Kochhar, 2000; 2002). The use of solid and hydrogenated fats will continue to decline – again on nutritional grounds and the greater ease of handling pourable frying media.

Specialist frying fats produced by plant breeding, or even genetic modification, are likely to continue to be developed to provide for the specific requirements of the fryer.

The evaluation of frying media as they degrade during their use is under constant consideration. Laboratory analytical techniques have now advanced to the point where the breakdown products present can be estimated accurately. Therefore it can be monitored how these have an effect on human health and nutrition. The key components can be isolated and this will allow us to develop faster and more robust ways to determine frying stability with the result that we can continue to the safety and health of a process which has been around for many hundreds of years.

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Appendix

Nomenclature for fatty acids and triglycerides

Abbreviation	Name	Carbon number[a]
Fatty acids		
L	Lauric	12:0
M	Myristic	14:0
P	Palmitic	19:0
S	Stearic	18:0
A	Arachidic	20:0
B	Behenic	22:0
O	Oleic	18:1cis
E	Elaidic	18:1 trans
Lin	Linoleic	18:2
Triglycerides *(XYZ)*[b]		
X	Fatty acid at the 1 position of the glycerol backbone[c]	
Y	Fatty acid at the 2 position of the glycerol backbone	
Z	Fatty acid at the 3 position of the glycerol backbone[c]	

[a]The first number refers to the number of carbon atoms in the chain; the second number indicates the number of double bonds, followed by a description of the isomeric arrangement around the double bond.
[b]X,Y and $Z = L, M, P, S, \ldots$
[c]For most purposes we do not distinguish between the 1 and 3 positions.

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