views on the structure of the MFGM and note that complete information on the structure is still not available. Since the MFGM is a dynamic, unstable structure, it is probably not possible to describe a structure which is applicable in all situations and conditions.

3.9 Stability of the milk fat emulsion

The stability, or instability, of the milk fat emulsion is very significant with respect to many physical and chemical characteristics of milk and dairy products. The stability of the emulsion depends strongly on the integrity of the MFGM and, as discussed in section 3.8.7, this membrane is quite fragile and is more or less extensively changed during dairy processing operations.

In the following, some of the principal aspects and problems related to or arising from the stability of the milk fat emulsion are discussed. Some of these relate to the inherent instability of emulsions in general, others are specifically related to the milk system.

3.9.1 Emulsion stability in general

Lipid emulsions are inherently unstable systems due to:

1. The difference in density between the lipid and aqueous phases (*c.* 0.9 and 1.036 g cm^{-3}, respectively, for milk), which causes the fat globules to float or cream according to Stokes' equation:

$$V = \frac{2r^2(\rho_1 - \rho_2)g}{9\eta}$$

   where V is the rate of creaming; r, the radius of fat globules; ρ_1 and ρ_2, the densities of the continuous and dispersed phases, respectively; g, acceleration due to gravity; and η, viscosity of the system. If creaming is not accompanied by other changes, it is readily reversible by gentle agitation.
2. The interfacial tension between the oil and aqueous phases. Although interfacial tension is reduced by the use of an emulsifier, the interfacial film may be imperfect. When two globules collide, they may adhere (flocculate), e.g. by sharing emulsifier, or they may coalesce due to the Laplace principle which states that the pressure is greater inside small globules than inside large globules and hence there is a tendency for large fat globules (or gas bubbles) to grow at the expense of smaller ones. Taken to the extreme, this will lead to the formation of a continuous mass of fat.

Destabilization processes in emulsions are summarized schematically in Figure 3.19. The rate of destabilization is influenced by the fat content, shear rate (motion), liquid : solid fat ratio, inclusion of air and globule size.

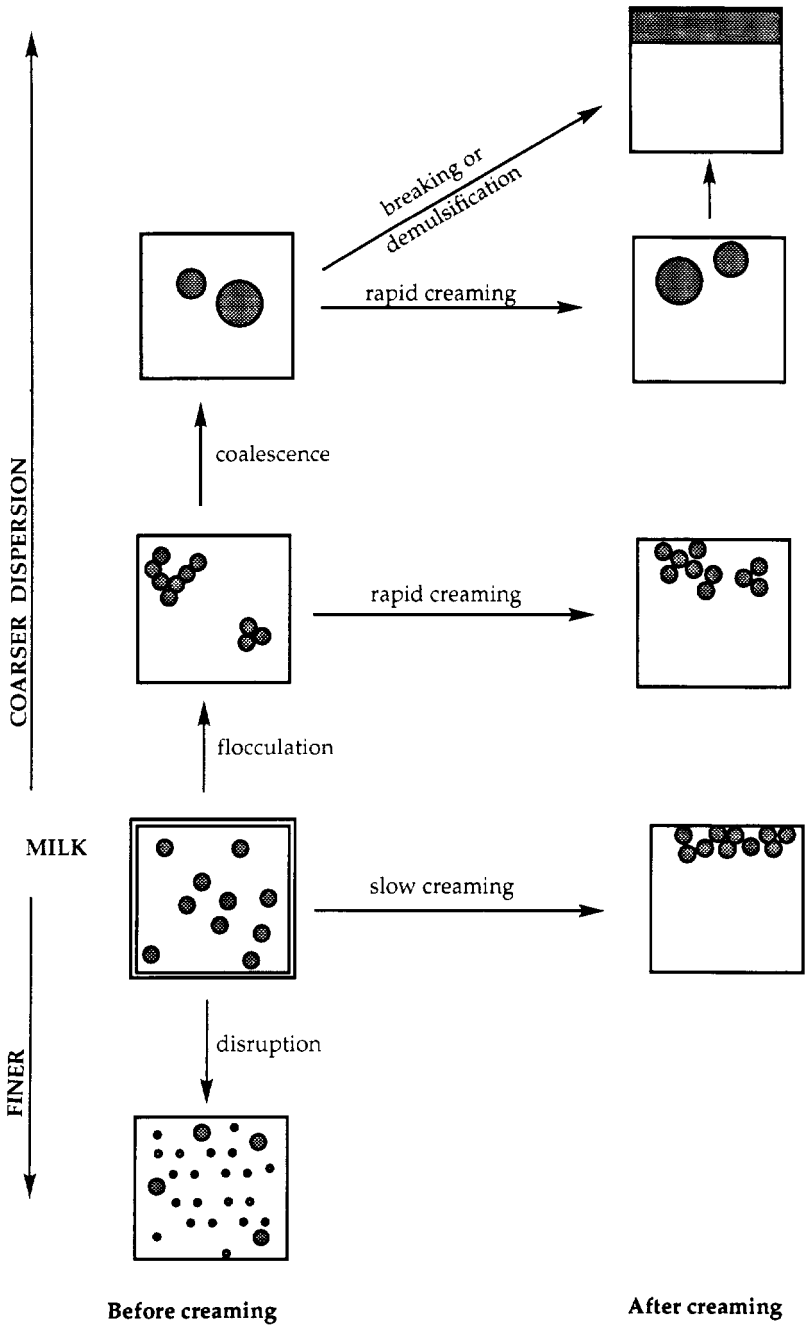


Figure 3.19 Schematic representation of different forms of emulsion destabilization (modified from Mulder and Walstra, 1974).

3.9.2 The creaming process in milk

A cream layer may be evident in milk within 20 min after milking. The appearance of a cream layer, if formed as a result of the rise of individual globules of 4 μm diameter according to Stokes' equation, would take approximately 50 h. The much more rapid rate of creaming in milk is caused by clustering of globules to form approximate spheres, ranging in diameter from 10 to 800 μm. As milk is drawn from the cow, the fat exists as individual globules and the initial rate of rise is proportional to the radius (r_2) of the individual globules.

Cluster formation is promoted by the disparity in the size of the fat globules in milk. Initially, the larger globules rise several times faster than the smaller ones and consequently overtake and collide with the slower-moving small globules, forming clusters which rise at an increased rate, pick up more globules and continue to rise at a rate commensurate with the increased radius. The creaming of clusters only approximates to Stokes' equation since they are irregular in geometry and contain considerable occluded serum and therefore $\Delta\rho$ is variable.

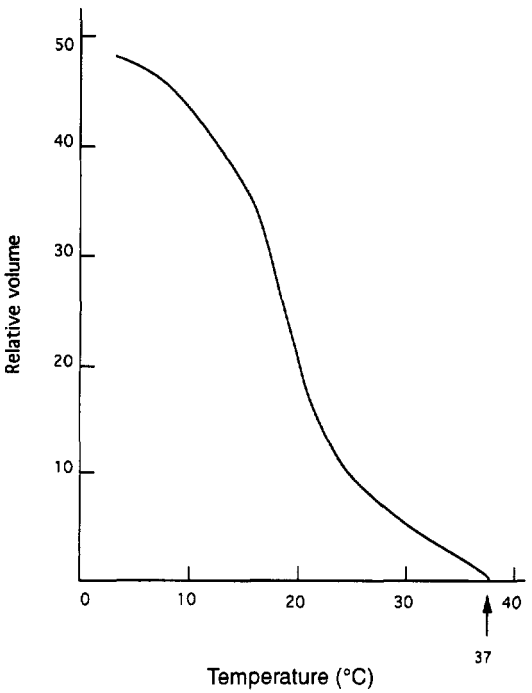


Figure 3.20 Effect of temperature on the volume of cream formed after 2 h (modified from Mulder and Walstra, 1974).

In 1889, Babcock postulated that creaming of cows' milk resulted from an agglutination-type reaction, similar to the agglutination of red blood cells; this hypothesis has been confirmed. Creaming is enhanced by adding blood serum or colostrum to milk; the responsible agents are immunoglobulins (Ig, which are present at high levels in colostrum), especially IgM. Because these Igs aggregate and precipitate at low temperature (<37°C) and redisperse on warming, they are often referred to as cryoglobulins. Aggregation is also dependent on ionic strength and pH. When aggregation of the cryoglobulins occurs in the cold they may precipitate on to the surfaces of large particles, e.g. fat globules, causing them to agglutinate, probably through a reduction in surface (electrokinetic) potential. The cryoprecipitated globulins may also form a network in which the fat globules are entrapped. The clusters can be dispersed by gentle stirring and are completely dispersed on warming to 37°C or higher. Creaming is strongly dependent on temperature and does not occur above 37°C (Figure 3.20). The milks of buffalo, sheep and goat do not exhibit flocculation and the milks of some cows exhibit little or none, apparently a genetic trait.

The rate of creaming and the depth of the cream layer show considerable variation. The concentration of cryoglobulin might be expected to influence the rate of creaming and although colostrum (rich in Ig) creams well and late lactation milk (deficient in Ig) creams poorly, there is no correlation in mid-lactation milks between Ig concentration and the rate of creaming. An uncharacterized lipoprotein appears to act synergistically with cryoglobulin in promoting clustering. The rate of creaming is increased by increasing the ionic strength and retarded by acidification. High-fat milks, which also tend to have a higher proportion of larger fat globules, cream quickly, probably because the probability of collisions between globules is greater and because large globules tend to form larger aggregates. The depth of the cream layer in high-fat milks is also greater than might be expected, possibly because of greater 'dead space' in the interstices of aggregates formed from large globules.

The rate of creaming and the depth of the cream layer are very markedly influenced by processing operations. Creaming is faster and more complete at low temperatures (<20°C; Figure 3.20), probably because of the temperature-dependent precipitation of the cryoglobulins. Gentle (but not prolonged) agitation during the initial stages of creaming promotes and enhances cluster formation and creaming, possibly because of an increased probability of collisions. It would be expected that stirring cold milk would lead to the deposition of all the cryoglobulin on to the fat globule surfaces, and rapid creaming, without a time lag, would be expected when stirring ceased. However, milk so treated does not cream at all or only slightly after a prolonged lag period. If cold, creamed milk is agitated gently, the clusters are dispersed and do not reform unless the milk is rewarmed to *c.* 40°C and then recooled, i.e. the whole cycle repeated. Violent agitation is detrimental

to creaming, possibly due to denaturation of the cryoglobulins and/or alteration to the fat globule surface. If milk is separated at 40°C or above, the cryoglobulins are present predominantly in the serum, whereas they are in the cream produced at lower temperatures. Agglutination and creaming are impaired or prevented by heating (e.g. 70°C × 30 min or 77°C × 20 s) owing to denaturation of the cryoglobulins; addition of Igs to heated milk restores creaming (except after very severe heat treatment, e.g. 2 min at 95°C or equivalent). Homogenization prevents creaming, not only due to the reduction of fat globule size but also to some other factor since a blend of raw cream and homogenized skim milk does not cream well. In fact two types of euglobulin appear to be involved in agglutination, one of which is denatured by heating, the other by homogenization. Thus, a variety of factors which involve temperature changes, agitation or homogenization influence the rate and extent of creaming.

3.10 Influence of processing operations on the fat globule membrane

As discussed in section 3.8.7, the milk fat globule membrane (MFGM) is relatively fragile and susceptible to damage during a range of processing operations; consequently, emulsion stability is reduced by dislodging interfacial material by agitation, homogenization, heat treatment, concentration, drying and freezing. Rearrangement of the membrane increases the susceptibility of the fat to hydrolytic rancidity, light-activated flavours and 'oiling-off' of the fat, but reduces susceptibility to metal-catalysed oxidation. The influence of the principal dairy processing operations on MFGM and concomitant defects are discussed below.

3.10.1 Milk supply: hydrolytic rancidity

The production of milk on the farm and transportation to the processing plant are potentially major causes of damage to the MFGM. Damage to the membrane may occur at several stages of the milking operation: foaming due to air sucked in at teat-cups, agitation due to vertical sections (risers) in milk pipelines, constrictions and/or expansion in pipelines, pumps, especially if not operating at full capacity, surface coolers, agitators in bulk tanks and freezing of milk on the walls of bulk tanks. While some oiling-off and perhaps other physical damage to the milk fat emulsion may accrue from such damage, by far the most serious consequence is the development of hydrolytic rancidity. The extent of lipolysis is commonly expressed as 'acid degree value' (ADV) of the fat as millimoles of free fatty acids per 100 g fat; ADVs greater than 1 are undesirable and are probably perceptible by taste to most people.

The principal lipase in bovine milk is a lipoprotein lipase (LPL; Chapter 8) which is associated predominantly with the casein micelles and is isolated from its substrate, milk fat, by the MFGM, i.e. the enzyme and its substrate are compartmentalized. However, even slight damage to the membrane permits contact between enzyme and substrate, resulting in hydrolytic rancidity. The enzyme is optimally active at around 37°C and pH 8.5 and is stimulated by divalent cations, e.g. Ca^{2+} (Ca^{2+} complex free fatty acids, which are strongly inhibitory). The initial turnover of milk LPL is *c.* $3000\,s^{-1}$, i.e. 3000 fatty acid molecules are liberated per second per mole of enzyme (milk usually contains 1–2 mg lipase l^{-1}, i.e. 10–20 nM) which, if fully active, is sufficient to induce rancidity in about 10 s. This never happens in milk due to a variety of factors, e.g. the pH, ionic strength and, usually, the temperature are not optimal; the lipase is bound to the casein micelles; the substrate is not readily available; milk probably contains lipase inhibitors, including caseins. The activity of lipase in milk is not correlated with its concentration due to the various inhibitory and adverse factors.

Machine milking, especially pipe-line milking systems, markedly increases the incidence of hydrolytic rancidity unless adequate precautions are taken. The effectors are the clawpiece and the tube taking the milk from the clawpiece to the pipeline; damage at the clawpiece may be minimized by proper regulation of air intake, and low-line milking installations cause less damage than high-line systems but the former are more expensive and less convenient for operators. Larger-diameter pipelines (e.g. 5 cm) reduce the incidence of rancidity but may cause cleaning problems and high milk losses. The receiving jar, pump (diaphragm or centrifugal, provided they are operated properly) and type of bulk tank, including agitator, transportation in bulk tankers or preliminary processing operations (e.g. pumping and refrigerated storage) at the factory, make little if any contribution to hydrolytic rancidity.

The frequency and severity of lipolysis increases in late lactation, possibly owing to a weak MFGM and the low level of milk produced (which may aggravate agitation); this problem is particularly acute when milk production is seasonal, e.g. as in Ireland or New Zealand.

The lipase system can also be activated by cooling freshly drawn milk to 5°C, rewarming to 30°C and recooling to 5°C. Such a temperature cycle may occur under farm conditions, e.g. addition of a large quantity of warm milk to a small volume of cold milk. It is important that bulk tanks be emptied completely at each collection (this practice is also essential for the maintenance of good hygiene). No satisfactory explanation for temperature activation is available but changes in the physical state of fat (liquid/solid ratio) have been suggested; damage/alteration of the globule surface and binding of lipoprotein co-factor may also be involved.

Some cows produce milk which is susceptible to a defect known as 'spontaneous rancidity' – no activation treatment, other than cooling of the milk, is required; the frequency of such milks may be as high as 30% of the

population. Suggested causes of spontaneous rancidity include:

- a second lipase located in the membrane rather than on the casein micelles;
- a weak membrane which does not adequately protect the fat from the normal LPL; and
- a high level of lipoprotein co-factor which facilitates attachment of the LPL to the fat surface; this appears to be the most probable cause.

Mixing of normal milk with susceptible milk in a ratio of 4 : 1 prevents spontaneous rancidity and therefore the problem is not serious except in small or abnormal herds. The incidence of spontaneous rancidity increases with advancing lactation and with dry feeding.

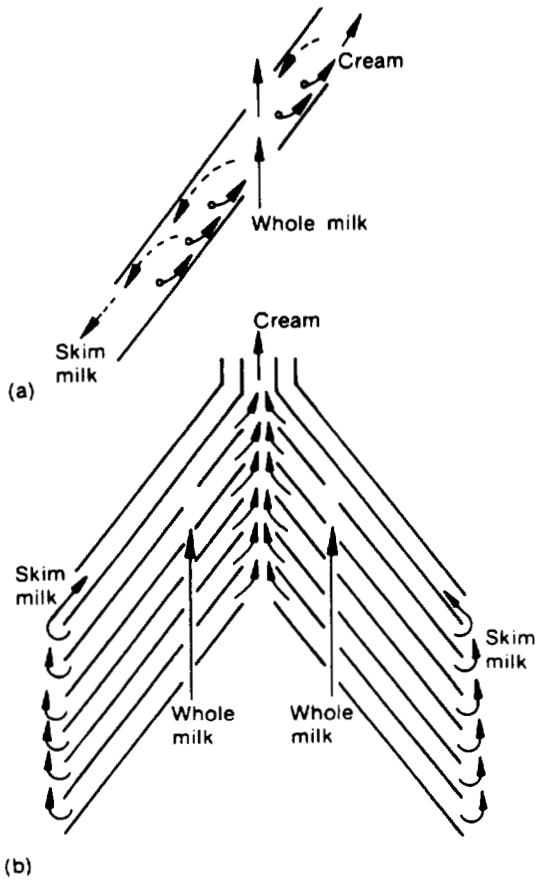
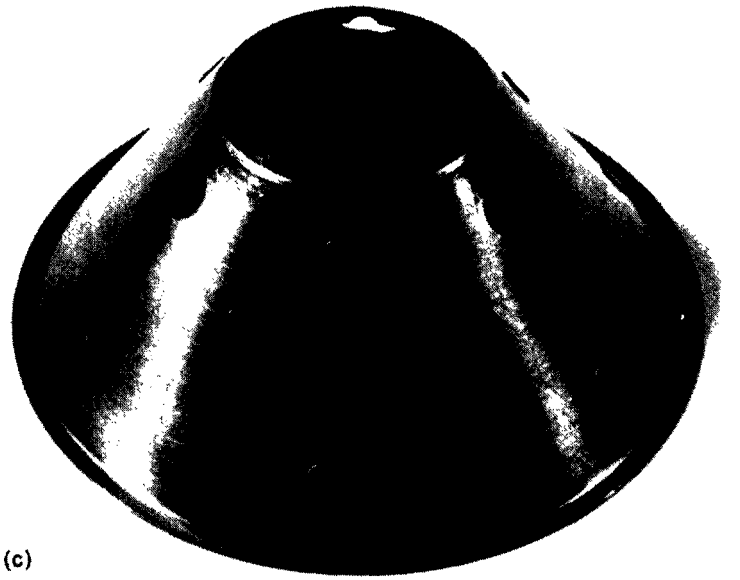


Figure 3.21 Flow of cream and skim milk in the space between a pair of discs in a centrifugal separator (a); a stack of discs (b); and a separator disc showing holes for the channelling of milk and spacers (caulks) (c). (From Towler, 1994.)



(c)

Figure 3.21 (*Continued*).

3.10.2 Mechanical separation of milk

Gravity creaming is relatively efficient, especially in the cold (a fat content of 0.1% in the skim phase may be obtained). However, it is slow and inconvenient for industrial-scale operations. Mechanical milk separators were developed independently in the 1880s by Alpha and Laval; schematic representations of a modern separator are shown in Figures 3.21 and 3.22.

In centrifugal separation, g in Stokes' equation is replaced by centrifugal force, $\omega^2 R$, where ω is the centrifugal speed in radians s^{-1} (2π radians = 360°) and R is the distance (cm) of the particle from the axis of rotation.

$$\omega^2 R = \frac{(2\pi S)^2}{(60)^2} R$$

where S is the bowl speed in r.p.m. Inserting this value for g into Stokes' equation and simplifying gives:

$$V = \frac{0.00244(\rho_1 - \rho_2) r^2 S^2 R}{\eta}.$$

Thus, the rate of separation is influenced by the radius of the fat globules, the radius and speed of the separator, the difference in density of the continuous and dispersed phases and the viscosity of the milk; temperature influences r, $(\rho_1 - \rho_2)$ and η.

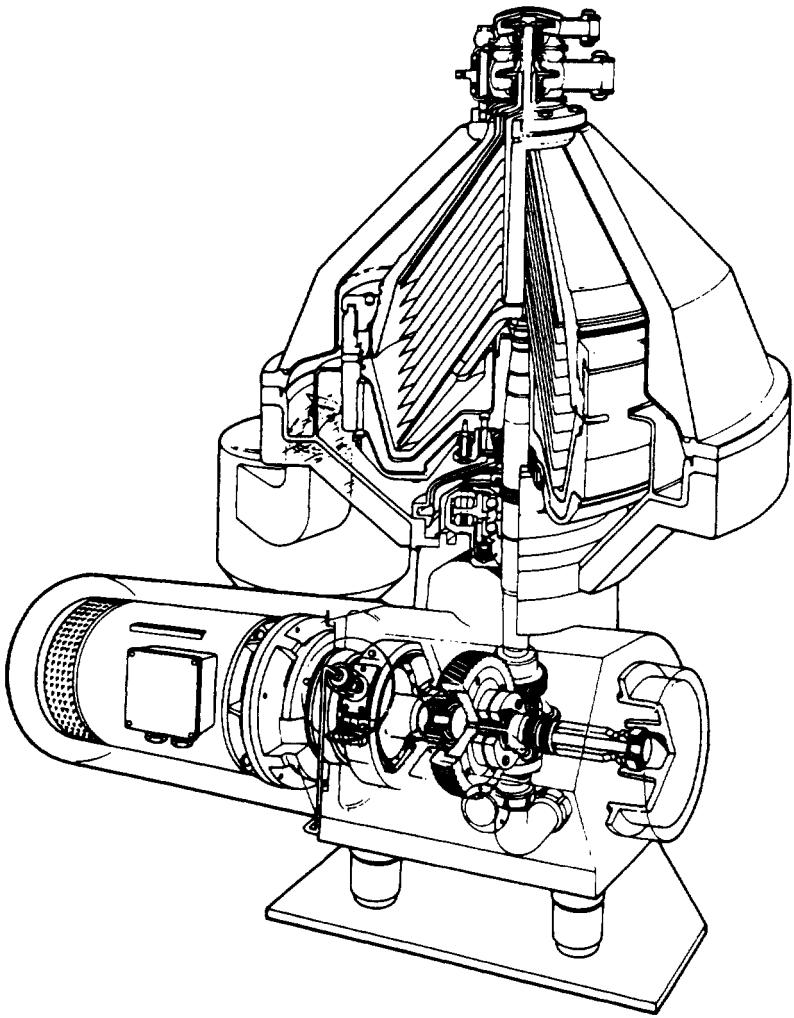


Figure 3.22 Cutaway diagram of a modern milk separator (from Towler, 1994).

Fat globules of less than 2 μm diameter are incompletely removed by cream separators and since the average size of fat globules decreases with advancing lactation (Figure 3.15), the efficiency of separation decreases concomitantly. The percentage fat in cream is regulated by manipulating the ratio of cream to skim-milk streams from the separator, which in effect regulates back-pressure. With any particular separator operating under more or less fixed conditions, temperature is the most important variable affecting the efficiency of separation via its effects on r, η and $(\rho_1 - \rho_2)$. The

efficiency of separation increases with temperature, especially in the range 20–40°C. In the past, separation was usually performed at 40°C or above but modern separators are very efficient even at low temperatures.

As discussed in section 3.9.2, cryoglobulins are entirely in the serum phase at temperatures above about 37°C, as a result of which creams prepared at these temperatures have poor natural creaming properties and the skim milk foams copiously due to the presence of cryoglobulins. Following separation at low temperatures (below 10-15°C), most of the cryoglobulins remain in the cream phase. Considerable incorporation of air and foaming may occur during separation, especially with older machines, causing damage to the MFGM. The viscosity of cream produced by low-temperature separation is much higher than that produced at higher temperatures, presumably due to the presence of cryoglobulins in the former.

Centrifugal force is also applied in the clarification and bactofugation of milk. Clarification is used principally to remove somatic cells and physical dirt, while bactofugation, in addition to removing these, also removes 95–99% of the bacterial cells present. One of the principal applications of bactofugation is the removal of clostridial spores from milk intended for Swiss and Dutch-type cheeses, in which they cause late blowing. A large proportion (around 90%) of the bacteria and somatic cells in milk are entrapped in the fat globule clusters during natural creaming and are present in the cream layer; presumably, they become agglutinated by the cryoglobulins.

3.10.3 Homogenization

Homogenization is widely practised in the manufacture of liquid milk and milk products. The process essentially involves forcing milk through a small orifice (Figure 3.23) at high pressure (13–20 $MN\,m^{-2}$), usually at about 40°C (at this temperature, the fat is liquid; homogenization is less effective at lower temperatures when the fat is partially solid). The principal effect of homogenization is to reduce the average diameter of the fat globules to below 1 μm (the vast majority of the globules in homogenized milk have diameters below 2 μm) (Figure 3.24). Reduction is achieved through the combined action of shearing, impingement, distention and cavitation. Following a single passage of milk through a homogenizer, the small fat globules occur in clumps, causing an increase in viscosity; a second-stage homogenization at a lower pressure (e.g. 3.5 $MN\,m^{-2}$) disperses the clumps and reduces the viscosity. Clumping arises from incomplete coverage of the greatly increased emulsion interfacial area during the short passage time through the homogenizer valve, resulting in the sharing of casein micelles by neighbouring globules.

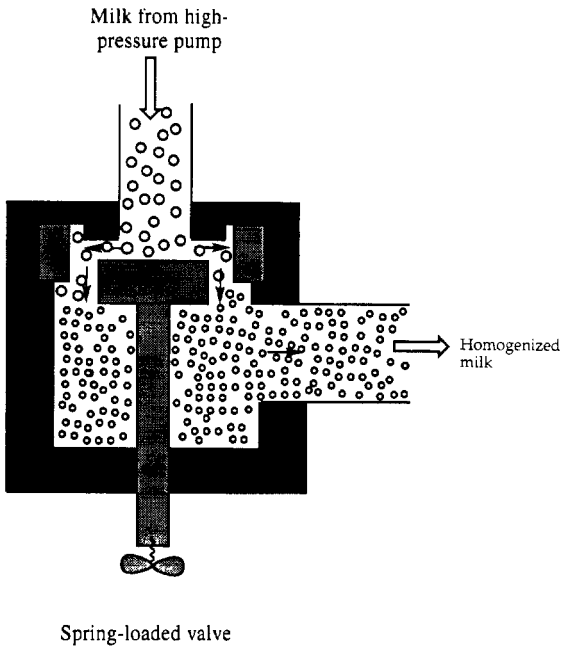


Figure 3.23 Diagram of a milk homogenizer.

Reducing the average diameter of the fat globules to 1 μm results in a four- to sixfold increase in the fat/plasma interface. There is insufficient natural membrane to completely coat the newly formed surface or insufficient time for complete coverage to occur and consequently the globules in homogenized milk are coated by a membrane which consists mostly of casein (93% of dry mass, with some whey proteins, which are adsorbed less efficiently than the caseins) (Figure 3.25). The membrane of homogenized milk contains 2.3 g protein per 100 g fat (10 mg protein m^{-2}), which is very considerably higher than the level of protein in the natural membrane (0.5–0.8 g per 100 g fat), and is estimated to be about 15 nm thick. The casein content in the serum phase of homogenized milk is reduced by about 6–8%.

Homogenization causes several major changes in the properties of milk:

1. Homogenized milk does not cream naturally and the fat is recovered only poorly by mechanical separation. This is due in part to the smaller average size of the fat globules but failure of the globules in homogenized milk to form aggregates, due mostly to the agitation-induced denaturation of some immunoglobulins, is mainly responsible for the failure to cream.

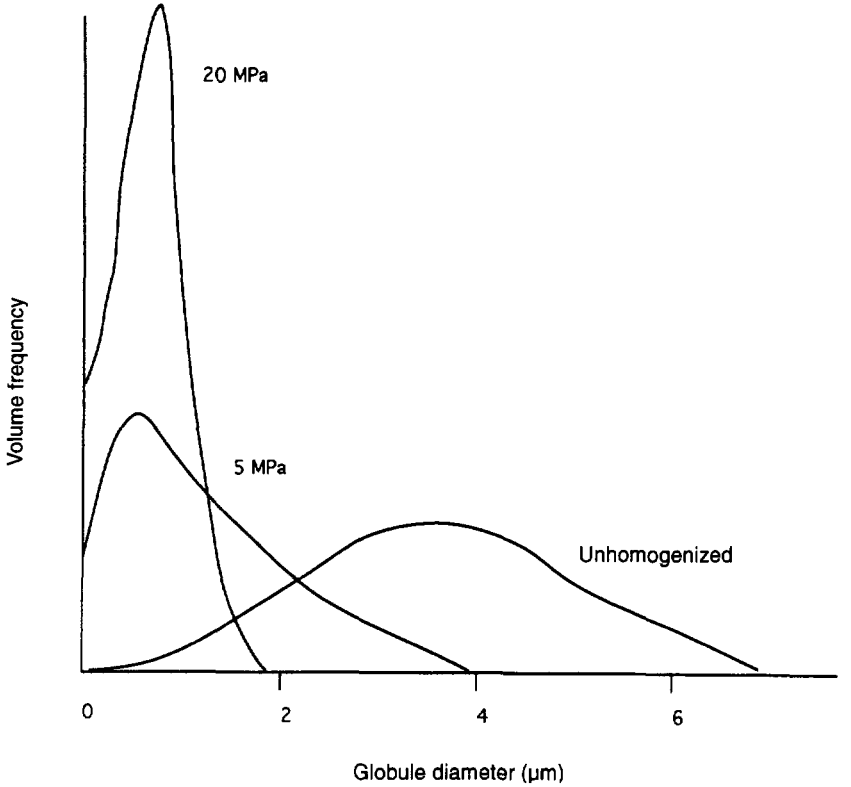


Figure 3.24 Effect of homogenization on the size (volume distribution) of fat globules in milk (modified from Mulder and Walstra, 1974).

2. As discussed in section 3.10.1, homogenized milk is very susceptible to hydrolytic rancidity because the artificial membrane does not isolate the fat from the lipase; consequently, homogenized milk must be pasteurized prior to or immediately after homogenization. Homogenized milk is also more susceptible to sunlight oxidized flavour, which is due to the production of methional from methionine, but is less susceptible to metal-catalysed lipid oxidation; the latter is presumably because the phospholipids, which are very susceptible to oxidation (highly unsaturated) and are located largely in the natural membrane (which contains pro-oxidants, e.g. xanthine oxidase and metals) are more uniformly distributed after homogenization and, therefore, are less likely to propagate lipid oxidation.
3. Homogenized milk is whiter due to finer dispersion of the fat (and thus greater light scattering) and its flavour is more bland.

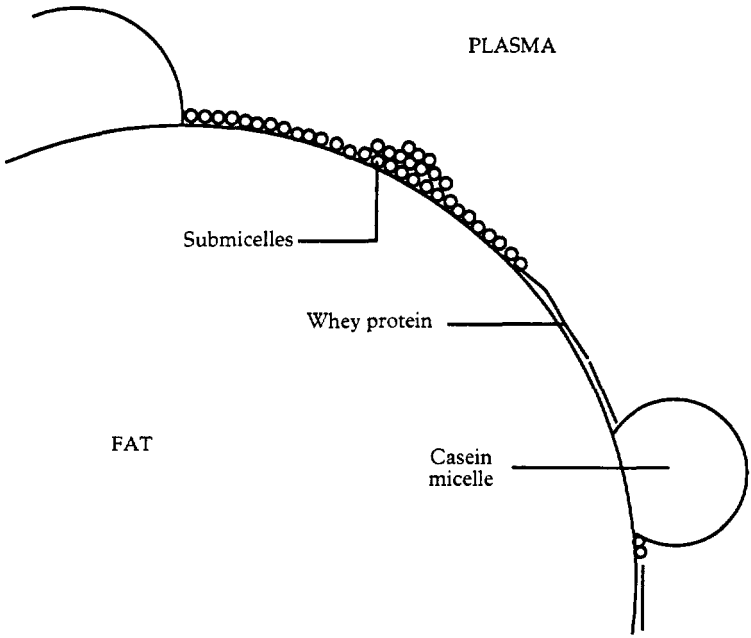


Figure 3.25 Schematic representation of the membrane of fat globules in homogenized milk (modified from Walstra, 1983).

4. The heat stability of whole milk is reduced by homogenization, as is the strength (curd tension) of rennet-induced gels; these changes will be discussed in more detail in Chapters 9 and 10. Viscosity is increased for unidentified reasons, probably independent of size changes. Homogenized milk has improved foaming characteristics, a feature which may be due to the release of foam-promoting proteins from the natural membrane or to reduction in fat globule size – small globules are less likely to damage foam lamellae. Homogenization reduces surface tension, possibly due to inclusion of very surface-active proteins in the artificial membrane and to changes in the fat globule surface. Homogenized milk drains cleanly from the sides of a glass bottle or drinking glass. Milk for homogenization should be clarified to avoid sedimentation of leucocytes.

The efficiency of homogenization may be assessed by microscopic examination or more effectively by a particle sizer, e.g. Malvern Mastersizer.

3.10.4 Heating

Normal HTST pasteurization causes very little change in the fat globule membrane or in the characteristics of milk fat dependent on the membrane.

However, excessively high pasteurization temperatures denature the cryoglobulins and aggregation of the fat globules and creaming are impaired or prevented. Severe treatments, e.g. 80°C × 15 min, remove lipid and protein material from the membrane, the fat globules are partially denuded and may coalesce, forming large clumps of fat and resulting in defects such as cream plug in milk or cream (section 3.11).

Processes such as thermal concentration also cause membrane damage, especially since many of these treatments also involve vigorous agitation in high velocity heating systems. Since milk for concentrated and dehydrated milk products is normally homogenized, damage to the natural membrane is of little significance.

3.11 Physical defects in milk and cream

In addition to the flavour defects initiated or influenced by damage to the fat globule membrane, such damage also results in a variety of physical defects in milk and especially in cream. The more important of these are 'oiling-off', 'cream plug' and 'age thickening'.

'Oiling-off', characterized by the appearance of globules of oil or fat on the surface of coffee or tea when milk, and especially cream, is added, is due to membrane damage during processing, resulting in 'free fat'; low pressure homogenization re-emulsifies the free fat and eliminates the defect.

'Cream plug' is characterized by the formation of a layer of solid fat on the surface of cream or milk in bottles; the defect is due to a high level of 'free fat' which forms interlocking crystals on cooling and is most common in high-fat creams. Cream plug is common in unhomogenized, pasteurized, late lactation milk, presumably due to a weak MFGM.

'Age thickening' is due essentially to a high level of free fat, especially in high-fat creams; the product becomes very viscous due to interlocking of crystals of free fat.

Two somewhat related instability problems are 'feathering' and 'bitty' cream. 'Feathering' is characterized by the appearance of white flecks when milk or cream is poured on hot coffee and is a form of heat-induced coagulation; the white flecks are mainly destabilized protein. The heat stability of cream and its resistance to feathering are reduced by:

- single-stage homogenization;
- high homogenization pressure at low temperature;
- high concentrations of Ca^{2+} in the cream or water;
- a high ratio of fat to serum solids, i.e. high-fat creams;
- high temperature and low pH of the coffee.

Protein–lipid interaction is enhanced by homogenization, while high temperatures, low pH and high divalent cation concentration induce aggregation of the casein-coated fat globules into large visible particles. Stability

may be improved by:

- using fresh milk;
- adding disodium phosphate or sodium citrate, which sequester Ca^{2+}, increase protein charge and dissociate casein micelles;
- standardizing the cream with buttermilk which is a good emulsifier owing to its high content of phospholipids.

'Bitty cream' is caused by the hydrolysis of phospholipids of the fat globule membrane by phospholipases secreted by bacteria, especially *Bacillus cereus*, but also by psychrotrophs; the partially denuded globules coalesce when closely packed, as in cream or in the cream layer of milk, forming aggregates rather than a solid mass of fat.

3.11.1 Free fat

'Free fat' may be defined as non-globular fat, i.e. fat globules from which the membrane has been totally or partially removed. Damage to fat globules may be determined by measuring the level of free fat present. The fat in undamaged globules is not extractable by apolar solvents because it is protected by the membrane, damage to which permits extraction, i.e. the amount of fat extractable by apolar solvents is termed 'free fat'.

Free fat may be determined by a modified Rose–Gottlieb method or by extraction with carbon tetrachloride (CCl_4). In the standard Rose–Gottlieb method, the emulsion is destabilized by the action of ammonia and ethanol and the fat is then extracted with ethyl/petroleum ether. The free fat in a sample may be determined by omitting the destabilization step, i.e. by extracting the product directly with fat solvent, and expressed as the percentage of free fat in the sample or as a percentage of total fat. Alternatively, the sample may be extracted with CCl_4. In both methods, the sample is shaken with the fat solvent; the duration and severity of shaking must be carefully standardized if reproducible results are to be obtained.

Other methods used to quantify free fat include: centrifugation in Babcock or Gerber butyrometers at 40–60°C (the free fat is read off directly on the graduated scale); release of membrane-bound enzymes, especially xanthine oxidase or alkaline phosphatase, or the susceptibility of milk fat to hydrolysis by added lipase (e.g. from *Geotrichum candidum*).

3.12 Churning

It has been known since prehistoric times that if milk, and especially cream, is agitated, the fat aggregates to form granules (grains) which are converted to butter by kneading (Figure 3.26). Buttermaking has been a traditional method for a very long time in temperate zones for conserving milk fat; in

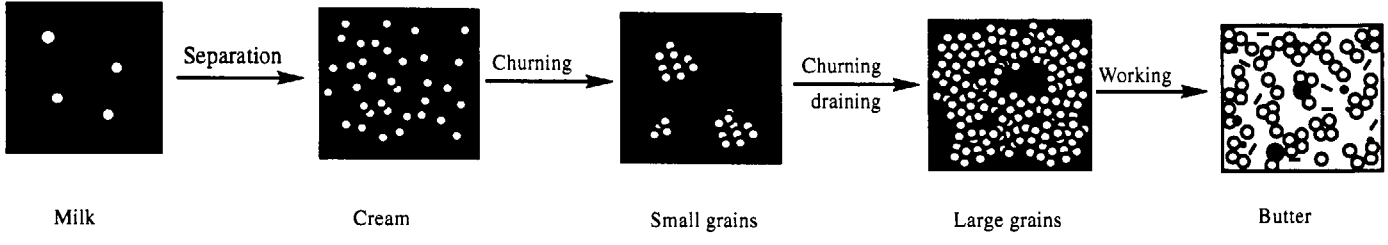


Figure 3.26 Schematic representation of the stages of butter production. ○, Indicates fat globules; ●, water droplets; and —, fat crystals. Black indicates continuous aqueous phase and white indicates continuous fat phase. (Modified from Mulder and Walstra, 1974.)

tropical regions, butter grains or cream are heated to remove all the water; the resulting product is called 'ghee', a crude form of butter oil.

The cream used for butter may be fresh (~pH 6.6) or ripened (fermented; ~pH 4.6), yielding 'sweet-cream' and 'ripened cream (lactic)' butter, respectively. Sweet-cream butter is most common in English-speaking countries but ripened cream butter is more popular elsewhere. Traditionally, the cream for ripened cream butter was fermented by the natural microflora, which was variable. Product quality and consistency were improved by the introduction in the 1880s of cultures (starters) of selected lactic acid bacteria, which produce lactic acid from lactose and diacetyl (the principal flavour component in ripened cream butter) from citric acid. A flavour concentrate, containing lactic acid and diacetyl, is now frequently used in the manufacture of ripened cream butter, to facilitate production schedules and improve consistency.

Butter manufacture or churning essentially involves phase inversion, i.e. the conversion of the oil-in-water emulsion of cream to a water-in-oil emulsion. Inversion is achieved by some form of mechanical agitation which denudes some of the globules of their stabilizing membrane; the denuded globules coalesce to form butter grains, entrapping some globular fat. The butter grains are then kneaded ('worked') which releases fat liquid at room temperature. Depending on temperature and on the method and extent of

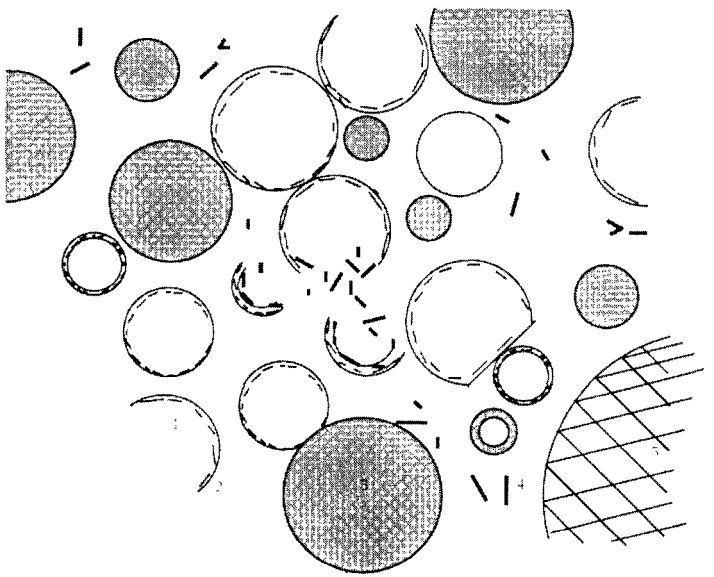


Figure 3.27 Schematic representation of the structure of butter. 1, fat globule; 2, membrane; 3, aqueous droplet; 4, fat crystals; 5, air cell. (Modified from Mulder and Walstra, 1974.)

Table 3.13 Structural elements of conventional butter

Element	Approximate number (ml^{-1})	Proportion of butter (%, v/v)	Dimensions (μm)	Remarks
Fat globules	10^{10}	10–50	2–8	Differ in composition; with complete or partial membrane
Fat crystals	10^{13}	10–40	0.01–2	Amount depends on temperature; at higher temperature occur mainly in globules; at low temperature, form solid networks
Moisture droplets	10^{10}	16	1–25	Differ in composition
Air cells	10^{7}	5	>20	

Modified from Mulder and Walstra (1974).

working, liquid fat may represent 50–95% of total fat. The liquid fat forms the continuous phase in which fat globules, fat crystals, membrane material, water droplets and small air bubbles are dispersed (Figure 3.27, Table 3.13). NaCl may be added (to *c.* 2%) to modify flavour but more importantly as a preservative; added salt dissolves in the water droplets (to give *c.* 12% salt in moisture) which also contain contaminating bacteria. Usually, ripened cream butter is not salted.

The process of phase inversion has received considerable attention (see McDowall (1953) and Wilbey (1994) for a detailed discussion). Briefly, churning methods can be divided into (1) traditional batch methods and (2) continuous methods.

1. The traditional method involves placing 30–40% fat cream in a churn (of various shapes and design, Figure 3.28) which is rotated gently. During rotation, air is incorporated and numerous small air bubbles are formed; fat globules are trapped between the lamellae of the bubbles. As the bubbles grow, the lamellae become thinner and exert a shearing effect on the fat globules. Some globules become denuded of membrane and coalesce; the aggregated globules are cemented by liquid fat expressed from the globules. A portion of the liquid fat spreads over the surface of the air bubbles, causing them to collapse, releasing butter grains and buttermilk (representing the serum phase of cream plus the fat globule membrane).

   When a certain degree of globular destabilization has occurred, the foam collapses rather abruptly and when the grains have grown to the requisite size, the buttermilk is drained off and the grains worked to a continuous mass. Proper working of the butter is essential for good

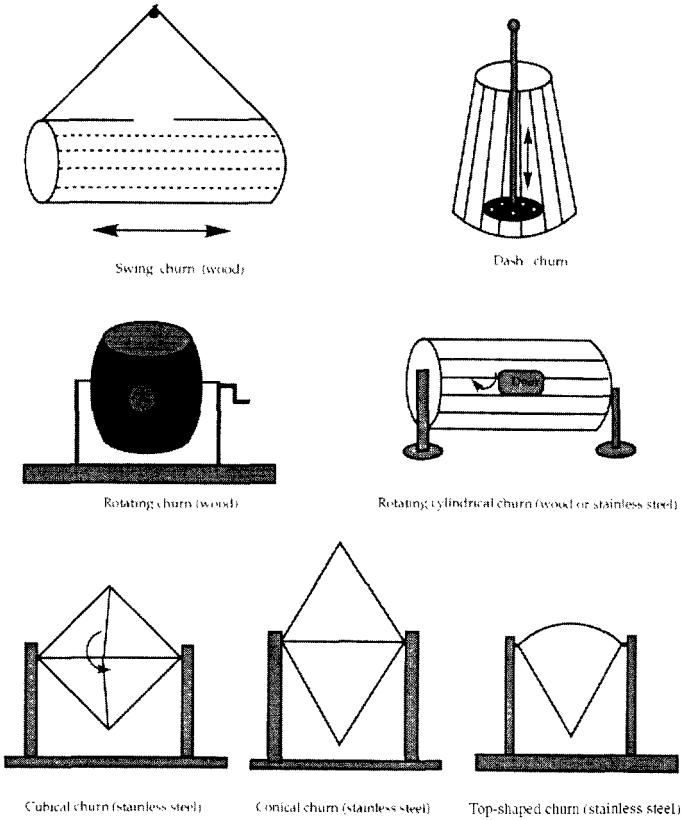


Figure 3.28 Examples of butter churns.

quality – a fine dispersion of water droplets reduces the risk of microbial growth and other spoilage reactions (most water droplets are $<5\,\mu m$). Working is also necessary to reduce the water content to the legal limit, i.e. $\leqslant 16\%$. The length of time required to churn cream, fat losses in the buttermilk and the moisture content of the butter are influenced by various factors, as summarized schematically in Figures 3.29 and 3.30.

2. Modern 'churns' operate continuously by either of two principles:
   (a) processes using about 40% fat cream (i.e. the Fritz process, e.g. Westfalia Separator AG) in which air is whipped into a thin film of cream in a Votator (Figure 3.31). The process of phase inversion in this process is essentially similar to that of traditional churning methods.
   (b) Processes using highfat cream (80% fat); although the fat in 80% fat cream is still in an oil-in-water emulsion, it is a very unstable emulsion and is destabilized easily by chilling and agitation.

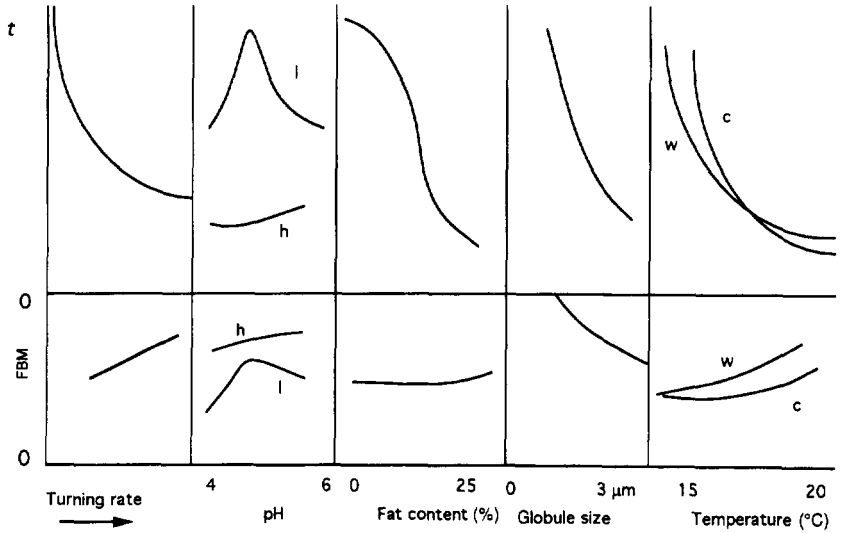


Figure 3.29 Effect of turning rate, pH, fat content, average globule size and churning temperature on churning time (t) and efficiency (% fat in buttermilk, FBM) of churning. 1, low ($\sim 11°C$) and h, high ($\sim 19°C$) temperatures; cream kept cold for several hours at 5°C (c) and subsequently warmed to 40°C (w) before bringing to churning temperature. (From Mulder and Walstra, 1974.)

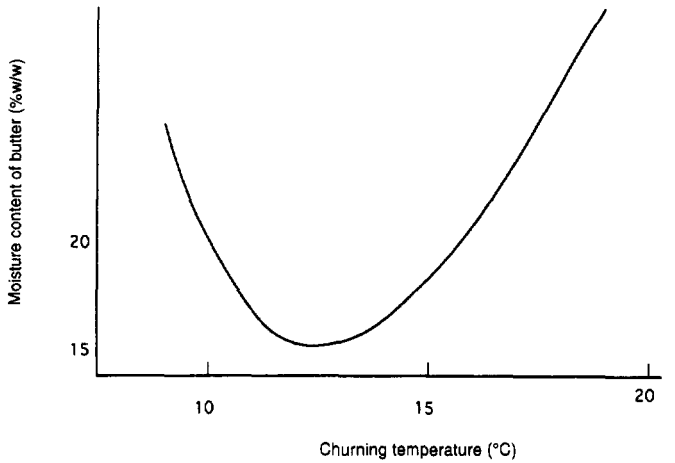


Figure 3.30 Moisture content of traditional butter as a function of churning temperature, all other conditions being equal (from Mulder and Walstra, 1974).

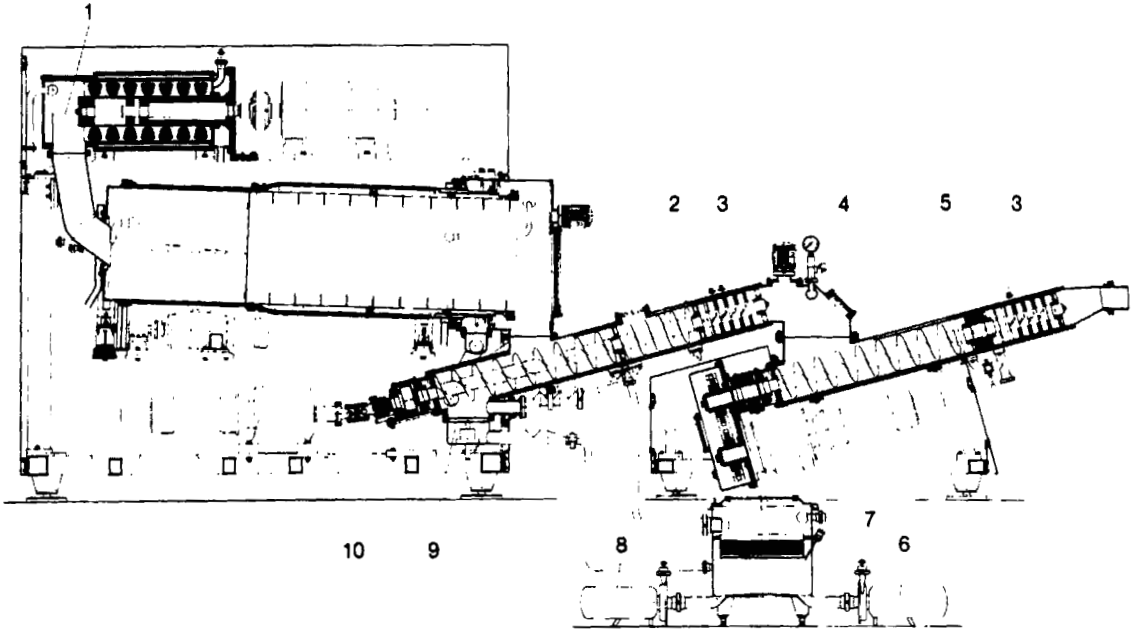


Figure 3.31 Diagram of a Westfalia continuous buttermaker. 1, Primary churning cylinder; 2, texturizer with blending section I; 3, metering connections; 4, vacuum chamber; 5, blending section II; 6, buttermilk pump II, buttermilk recycling; 7, buttermilk vat with strainer; 8, buttermilk pump I, buttermilk discharge; 9, buttermilk clarifying device; 10, secondary churning cylinder.

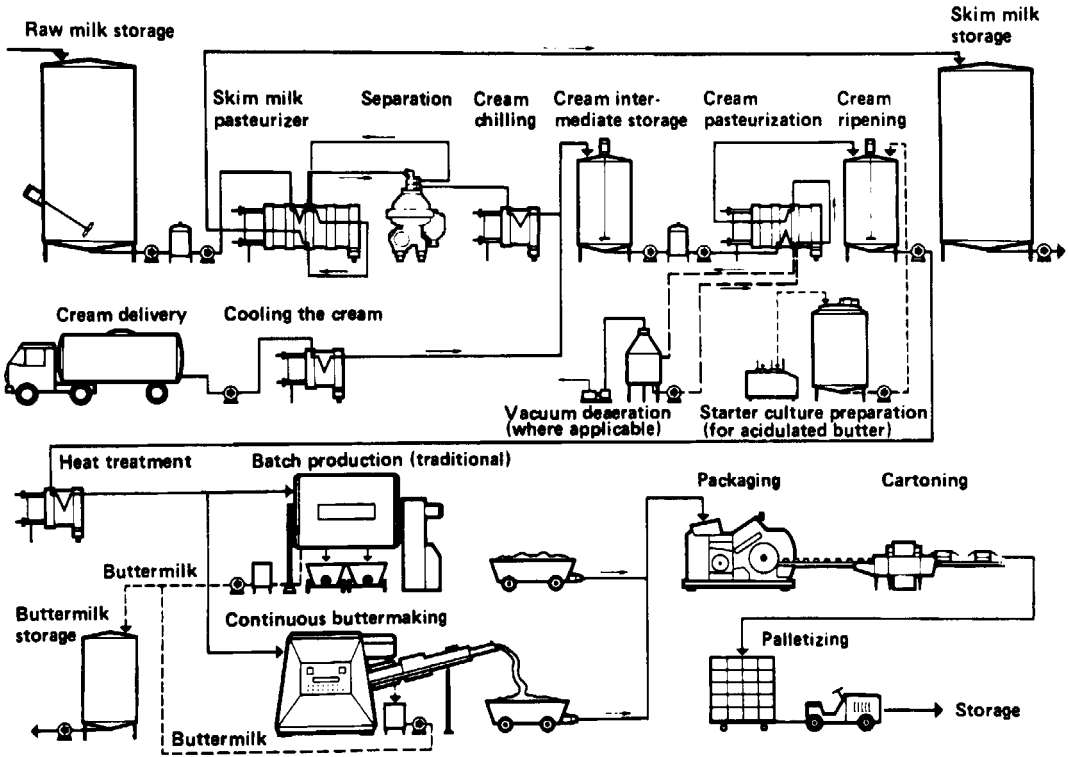


Figure 3.32 Line diagram of a modern buttermaking plant (courtesy of Alfa-Laval AB, Lund).

The line diagram for a modern buttermaking plant is shown in Figure 3.32.

All the methods of butter manufacture involve complete or partial removal of the fat globule membrane which is largely lost in the buttermilk, which is, consequently, a good source of phospholipids and other emulsifiers.

3.13 Freezing

Freezing and dehydration tend to destabilize all lipoprotein complexes, both natural and artificial. Thus, freezing of milk, and especially cream, results in damage to the membrane which causes destabilization when the product is thawed. Most of the destabilizing effect is due to physicochemical changes induced by dehydration of the lipoprotein complexes but some physical damage is also caused by ice crystals. The damage is manifest as oiling-off and free fat formation. The extent of damage is proportional to fat concentration and moderately high-fat creams (50%) are completely destabilized by freezing.

Frozen cream is produced commercially and is used mainly for the production of soups, butter-oil, butter, etc., where emulsion stability is not important. Damage may be reduced by:

- rapid freezing as thin blocks or continuously on refrigerated drums;
- homogenization and pasteurization before freezing;
- storage at very low temperature (*c.* $-30°C$) and avoiding temperature fluctuations during storage.

3.14 Dehydration

The physicochemical state of fat in milk powder particles, which markedly influences the wettability and dispersibility of the powder on reconstitution, depends on the manufacturing process. The fat occurs either in a finely emulsified or in a partly coalesced, de-emulsified state. In the latter case, the membrane has been ruptured or completely removed, causing the globules to run together to form pools of free fat. The amount of de-emulsified 'free fat' depends on the manufacturing method and storage conditions. Typical values for 'free fat' (as a percentage of total fat) in milk powders are: spray-dried powders, 3.3–20%; roller-dried powders, 91.6–95.8%; freeze-dried powders, 43–75%; foam-dried powders, less than 10%.

The high level of 'free fat' in roller-dried powder is due to the effects of the high temperature to which milk is exposed on the roller surfaces and to the mechanical effect of the scraping knives. In properly made and stored

spray-dried powder, the fat globules are distributed throughout the powder particles. The amount of free fat depends on the total fat content, and may be about 25% of total fat. Homogenization pre-drying reduces the level of free fat formed.

Further liberation of 'free fat' may occur under adverse storage conditions. If powder absorbs water it becomes 'clammy' and lactose crystallizes, resulting in the expulsion of other milk components from the lactose crystals into the spaces between the crystals. De-emulsification of the fat may occur due to the mechanical action of sharp edges of lactose crystals on the fat globule membrane. If the fat is liquid at the time of membrane rupture, or if it becomes liquid during storage, it will adsorb on to the powder particles, forming a water-repellant film around the particles.

The state of fat in powder has a major influence on wettability, i.e. the ease with which the powder particles make contact with water. Adequate wettability is a prerequisite for good dispersibility. Free fat has a water-repelling effect on the particles during dissolution, making the powder difficult to reconstitute. Clumps of fat and oily patches appear on the surface of the reconstituted powder, as well as greasy films on the walls of containers. The presence of 'free fat' on the surface of the particles tends to increase the susceptibility of fat to oxidation. A scum of fat–protein complexes may appear on the surface of reconstituted milk; the propensity to scum formation is increased by high storage temperatures.

3.15 Lipid oxidation

Lipid oxidation, leading to oxidative rancidity, is a major cause of deterioration in milk and dairy products. The subject has been reviewed by Richardson and Korycka-Dahl (1983) and O'Connor and O'Brien (1995).

Lipid oxidation is an autocatalysed free-radical chain reaction which is normally divided into three phases: initiation, propagation and termination (Figure 3.33).

The initial step involves abstracting a hydrogen atom from a fatty acid, forming a fatty acid (FA) free radical, e.g.

$$CH_3\text{----}CH_2\text{—}CH\text{=}CH\text{—}\dot{C}H\text{—}CH\text{=}CH\text{—}CH_2\text{-----}COOH$$

Although saturated fatty acids may lose a $H^{\bullet}$ and undergo oxidation, the reaction principally involves unsaturated fatty acids, especially polyunsaturated fatty acids (PUFA), the methylene, $—CH_2—$, group between double bonds being particularly sensitive:

$$C_{18:3} \gg C_{18:2} \gg C_{18:1} > C_{18:0}.$$

The polar lipids in milk fat are richer in PUFA than neutral lipids and are

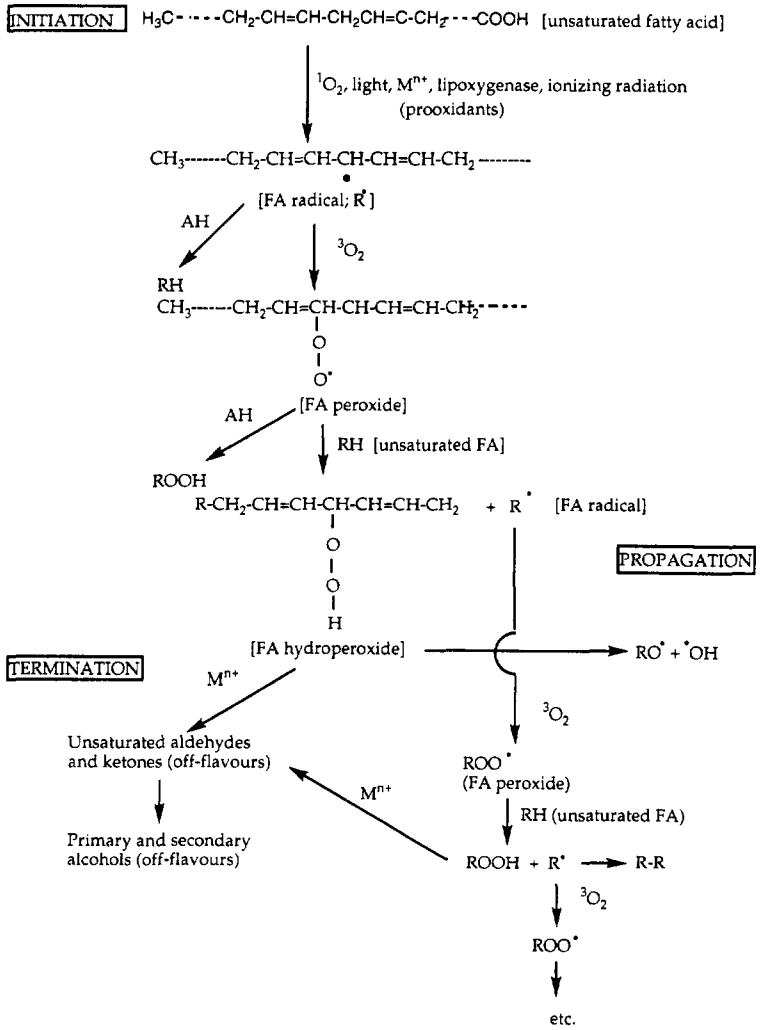


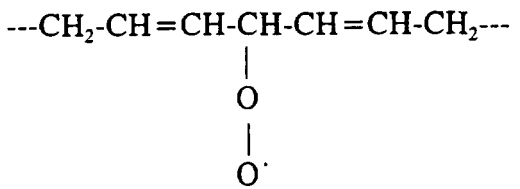
Figure 3.33 Autooxidation of fatty acids. AH, antioxidant; M^{n+}, polyvalent metal (e.g. Fe^{2+}, Cu^{2+}).

concentrated in the fat globule membrane in juxtaposition with several pro-oxidants and are, therefore, particularly sensitive to oxidation.

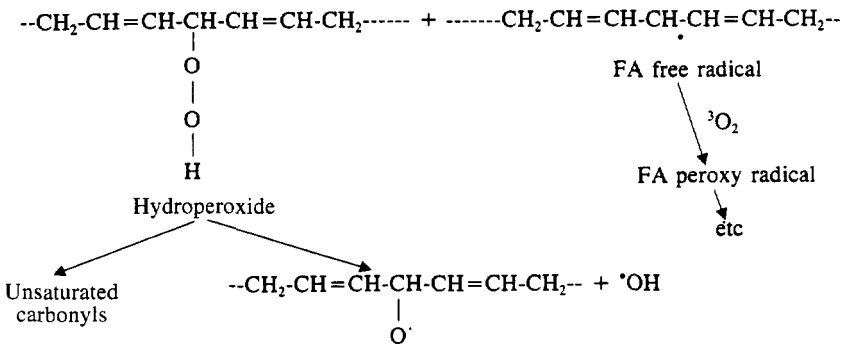
The initiation reaction is catalysed by singlet oxygen ($^1O_2$, produced by ionizing radiation and other factors), polyvalent metal ions that can undergo a monovalent oxidation/reduction reaction ($M^{n+1} \rightarrow M^n$), especially copper (the metal may be free or organically bound, for example, xanthine oxidase, peroxidase, catalase or cytochromes), or light, especially in the

presence of a photosensitizer, e.g. riboflavin (in the case of vegetable products, lipoxygenase is a major pro-oxidant but this enzyme is not present in milk or dairy products).

The FA free radical may abstract a H from a hydrogen donor, e.g. an antioxidant (AH), terminating the reaction, or may react with molecular triplet oxygen, $^3O_2$, forming an unstable peroxy radical:



In turn, the peroxy radical may obtain a H from an antioxidant, terminating the reaction, or from another fatty acid, forming a hydroperoxide and another FA free radical, which continues the reaction.



Two free radicals, each of which can initiate a new oxidation cycle

The intermediate products of lipid oxidation are themselves free radicals, and more than one may be formed during each cycle; hence the reaction is autolcatalytic, i.e. the rate of oxidation increases with time, as shown schematically in Figure 3.34. Thus, the formation of only very few (theoretically only one) free radicals by an exogenous agent is necessary to initiate the reaction. The reaction shows an induction period, the length of which depends on the presence of pro-oxidants and antioxidants.

The hydroperoxides are unstable and may break down to various products, including unsaturated carbonyls, which are mainly responsible for the off-flavours of oxidized lipids (the FA free radicals, peroxy radicals and

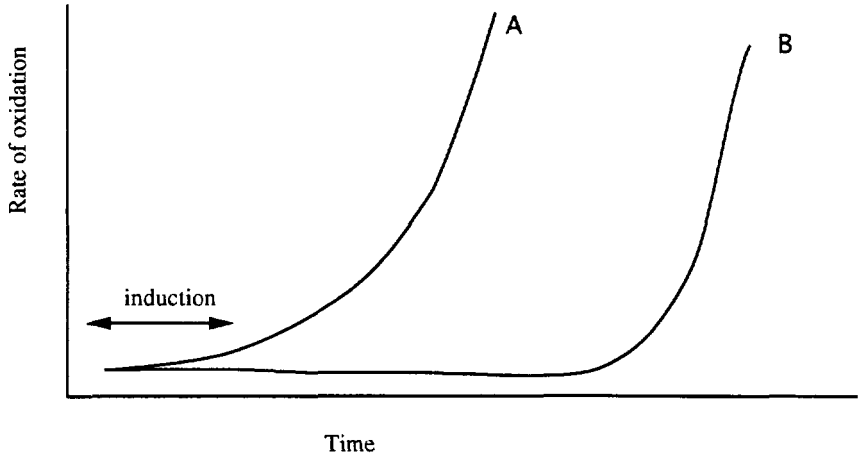


Figure 3.34 Rate of oxidation in the absence (A) or presence (B) of an antioxidant.

Table 3.14 Compounds contributing to typical oxidized flavour

Compounds	Flavours
Alkanals C_6–C_{11}	Green tallowy
2-Alkenals C_6–C_{10}	Green fatty
2,4-Alkadienals C_7–C_{10}	Oily deep-fried
3-*cis*-Hexenal	Green
4-*cis*-Heptenal	Cream/putty
2,6- and 3,6-Nonadienal	Cucumber
2,4,7-Decatrienal	Fishy, sliced beans
1-Octen-3-one	Metallic
1,5-*cis*-Octadien-3-one	Metallic
1-Octen-3-ol	Mushroom

From Richardson and Korycka-Dahl (1983).

hydroperoxides are flavourless). Different carbonyls vary with respect to flavour impact and since the carbonyls produced depend on the fatty acid being oxidized, the flavour characteristics of oxidized dairy products vary (Table 3.14).

The principal factors affecting lipid oxidation in milk and milk products are summarized in Table 3.15.

3.15.1 Pro-oxidants in milk and milk products

Probably the principal pro-oxidants in milk and dairy products are metals, Cu and to a lesser extent Fe, and light. The metals may be indigenous, e.g.

Table 3.15 Major factors affecting the oxidation of lipids in milk and dairy products[a]

A. Potential pro-oxidants
1. Oxygen and activated oxygen species
   Active oxygen system of somatic cells?
2. Riboflavin and light
3. Metals (e.g. copper and iron) associated with various ligands
   Metallo-proteins
   Salts of fatty acids
4. Metallo-enzymes (denatured?)
   Xanthine oxidase
   Lactoperoxidase, catalase (denatured)
   Cytochrome P420
   Cytochrome b_5
   Sulphydryl oxidase?
5. Ascorbate (?) and thiols (?) (via reductive activation of metals?)

B. Potential antioxidants
1. Tocopherols
2. Milk proteins
3. Carotenoids (β-carotene; bixin in anatto)
4. Certain ligands for metal pro-oxidants
5. Ascorbate and thiols
6. Maillard browning reaction products
7. Antioxidant enzymes (superoxide dismutase, sulphydryl oxidase)

C. Environmental and physical factors
1. Inert gas or vacuum packing
2. Gas permeability and opacity of packaging materials
3. Light
4. Temperature
5. pH
6. Water activity
7. Reduction potential
8. Surface area

D. Processing and storage
1. Homogenization
2. Thermal treatments
3. Fermentation
4. Proteolysis

[a]Many of these factors are interrelated and may even present paradoxical effects (e.g. ascorbate and thiols) on lipid oxidation.
Modified from Richardson and Korycka-Dahl (1983).

as part of xanthine oxidase, lactoperoxidase, catalase or cytochromes, or may arise through contamination from equipment, water, soil, etc. Contamination with such metals can be reduced through the use of stainless-steel equipment.

Metal-containing enzymes, e.g. lactoperoxidase and catalase, and cytochromes, can act as pro-oxidants owing to the metals they contain rather than enzymatically; the pro-oxidant effect of these enzymes is increased by heating (although there are conflicting reports). Xanthine oxidase, which

contains Fe and Mo, can act enzymatically and as a source of pro-oxidant metals.

Riboflavin is a potent photosensitizer and catalyses a number of oxidative reactions in milk, e.g. fatty acids, proteins (with the formation of 3-methyl thiopropanal from methionine which is responsible for light-induced off-flavour) and ascorbic acid. Milk and dairy products should be protected from light by suitable packaging and exposure to UV light should be minimized.

Ascorbic acid is a very effective anti-oxidant but combinations of ascorbate and copper can be pro-oxidant depending on their relative concentrations. Apparently, ascorbate reduces Cu^{2+} to Cu^{+}.

3.15.2 Antioxidants in milk

Antioxidants are molecules with an easily detachable H atom which they donate to fatty acid free radicals or fatty acid peroxy radicals, which would otherwise abstract a H from another fatty acid, forming another free radical. The residual antioxidant molecule (less its donatable H) is stable and antioxidants thus break the autocatalytic chain reaction.

Milk and dairy products contain several antioxidants, of which the following are probably the most important:

- Tocopherols (vitamin E), which are discussed more fully in Chapter 6. The principal function of tocopherols *in vivo* is probably to serve as antioxidants. The concentration of tocopherols in milk and meat products can be increased by supplementing the animal's diet.
- Ascorbic acid (vitamin C): at low concentrations, as in milk, ascorbic acid is an effective antioxidant, but acts as a pro-oxidant at higher concentrations.
- Superoxidase dismutase (SOD). This enzyme, which occurs in various body tissues and fluids, including milk, scavenges superoxide radicals (O_2^-) which are powerful pro-oxidants. SOD is discussed more fully in Chapter 8.
- Carotenoids can act as scavengers of free radicals but whether or not they act as antioxidants in milk is controversial.
- The thiol groups of β-lactoglobulin and proteins of the fat globule membrane are activated by heating. Most evidence indicates that thiol groups have antioxidant properties but they may also produce active oxygen species which could act as pro-oxidants under certain circumstances. The caseins are also effective antioxidants, possibly via chelation of Cu.
- Some products of the Maillard reaction are effective antioxidants.

The addition of synthetic antioxidants, e.g. β-hydroxyanisole or butylated hydroxytoluene, to dairy products is prohibited in most countries.

3.15.3 Spontaneous oxidation

Between 10 and 20% of raw individual-cow milk samples undergo oxidation rapidly while others are more stable. Milks have been classified into three categories, based on their propensity to lipid oxidation:

- Spontaneous: milks which are labile to oxidation without added Cu or Fe.
- Susceptible: milks which are susceptible to oxidation on addition of Cu or Fe but not without.
- Non-susceptible milks that do not become oxidized even in the presence of added Cu or Fe.

It has been proposed that spontaneous milks have a high content (10 times normal) of xanthine oxidase (XO). Although addition of exogenous XO to non-susceptible milk induces oxidative rancidity, no correlation has been found between the level of indigenous XO and susceptibility to oxidative rancidity. The Cu–ascorbate system appears to be the principal pro-oxidant in susceptible milk. A balance between the principal antioxidant in milk, α-tocopherol (Chapter 6), and XO may determine the oxidative stability of milk. The level of superoxide dismutase (SOD) in milk might also be a factor but there is no correlation between the level of SOD and the propensity to oxidative rancidity.

3.15.4 Other factors that affect lipid oxidation in milk and dairy products

Like many other reactions, lipid oxidation is influenced by the water activity (a_w) of the system. Minimal oxidation occurs at $a_w \sim 0.3$. Low values of a_w (< 0.3) are considered to promote oxidation because low amounts of water are unable to 'mask' pro-oxidants as happens at monolayer a_w values ($a_w \sim 0.3$). Higher values of a_w facilitate the mobility of pro-oxidants while very high values of a_w may have a diluent effect.

Oxygen is essential for lipid oxidation. At oxygen pressures below 10 kPa (≈ 0.1 atm; oxygen content $\sim 10\,mg\,kg^{-1}$ fat), lipid oxidation is proportional to O_2 content. Low concentrations of oxygen can be achieved by flushing with inert gas, e.g. N_2, the use of glucose oxidase (Chapter 8) or by fermentation.

Lipid oxidation is increased by decreasing pH (optimum ~pH 3.8), perhaps due to competition between H^+ and metal ions (M^{n+}) for ligands, causing the release of M^{n+}. The principal cause may be a shift of the Cu distribution, e.g. at pH 4.6, 30–40% of the Cu accompanies the fat globules.

Homogenization markedly reduces the propensity to oxidative rancidity, perhaps due to redistribution of the susceptible lipids and pro-oxidants of the MFGM (however, the propensity to hydrolytic rancidity and sunlight oxidized flavour (due to the production of methional from methionine in protein) is increased).

NaCl reduces the rate of auto-oxidation in sweet-cream butter but increases it in ripened cream butter (*c.* pH 5); the mechanism in unknown.

In addition to influencing the rate of lipid oxidation via activation of thiol groups and metallo-enzymes, heating milk may also affect oxidation via redistribution of Cu (which migrates to the FGM on heating) and possibly by the formation of Maillard browning products, some of which have metal chelating and antioxidant properties.

The rate of auto-oxidation increases with increasing temperature ($Q_{10} \sim 2$) but oxidation in raw and HTST-pasteurized milk is promoted by low temperatures whereas the reverse is true for UHT-sterilized products (i.e. the effect of temperature is normal). The reason(s) for this anomalous behaviour is unknown.

3.15.5 Measurement of lipid oxidation

In addition to organoleptic assessment, several chemical/physical methods have been developed to measure lipid oxidation. These include: peroxide value, thiobarbituric acid (TBA) value, ultraviolet absorption (at 233 nm), ferric thiocyanate, Kreis test, chemiluminescence, oxygen uptake and analysis of carbonyls by HPLC (see Rossell, 1986).

3.16 Rheology of milk fat

The rheological properties of many dairy products are strongly influenced by the amount and melting point of the fat present. The sensory properties of cheese are strongly influenced by fat content but the effect is even greater in butter in which hardness/spreadability is of major concern. The hardness of fats is determined by the ratio of solid to liquid fat which is influenced by: fatty acid profile, fatty acid distribution and processing treatments.

3.16.1 Fatty acid profile and distribution

The fatty acid profile of ruminant fats (milk and adipose tissue) is relatively constant due to the 'buffering' action of the rumen microflora that modify ingested lipids. However, the proportions of various fatty acids in milk lipids show seasonal/nutritional/lactational variations (Figure 3.5) which are reflected in seasonal variations in the hardness of milk fat (Figure 3.7).

The fatty acid profile can be modified substantially by feeding encapsulated (protected) polyunsaturated oils to cows. The oil is encapsulated in a film of polymerized protein or in crushed oil-rich seeds. The encapsulating protein is digested in the abomasum, resulting in the release of the unsaturated lipid, a high proportion of the fatty acids of which are then incorporated into the milk (and adipose tissue) lipids. The technical

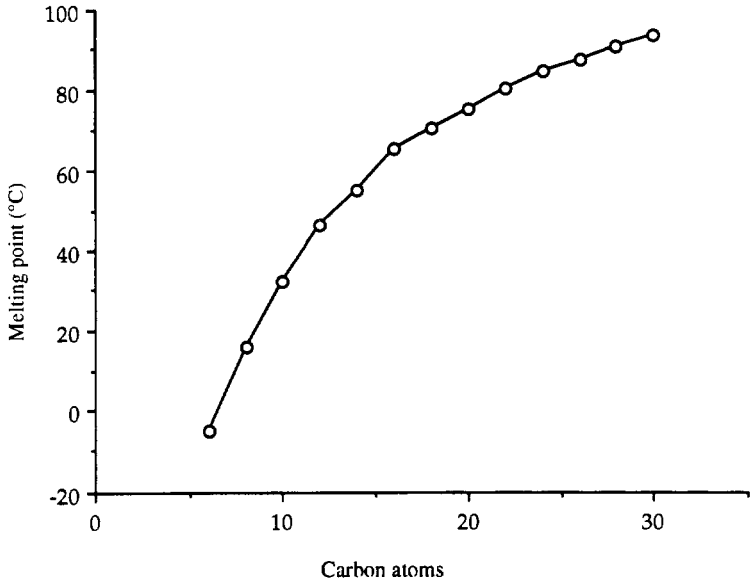


Figure 3.35 Relationship between the melting point of fatty acids and their chain length.

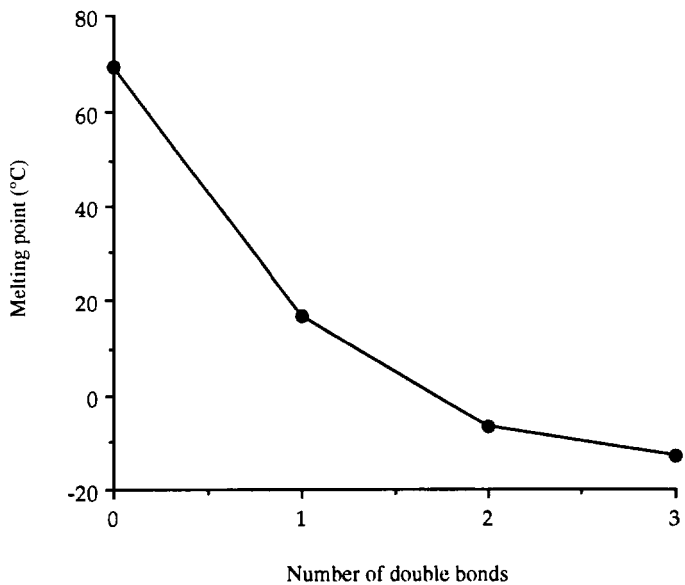


Figure 3.36 Effect of introducing one or more double bonds on the melting point of octadecanoic acid.

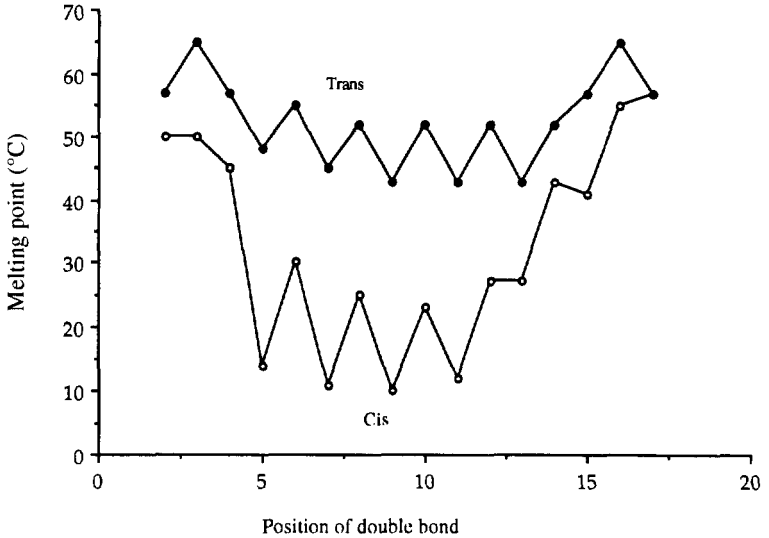


Figure 3.37 Effect of the position of the double bond on the melting point of octadecenoic acid.

feasibility of this approach has been demonstrated and it may be economic under certain circumstances.

The melting point of triglycerides is determined by the fatty acid profile and the position of the fatty acids in the triglyceride. The melting point of fatty acids increases with increasing length of the acyl chain (Figure 3.35) and the number, position and isomeric form of double bonds. The melting

Table 3.16 Effect on the melting point of shortening a single fatty acid chain of triglyceride from 18 to 0 carbon atoms and of esterification position (symmetrical or asymmetrical)

Symmetrical		Asymmetrical	
Glyceride	MP °C	Glyceride	MP °C
18-18-18	73.1	18-18-18	73.1
18-16-18	68	18-18-16	65
18-14-18	62.5	18-18-14	62
18-12-18	60.5	18-18-12	54
18-10-18	57	18-18-10	49
18-8-18	51.8	18-18-8	47.6
18-6-18	47.2	18-18-6	44
18-4-18	51	18-18-4	–
18-2-18	62	18-18-2	55.2
18-0-18	78	18-18-0	68

point decreases as the number of double bonds in the molecule increases (Figure 3.36) and *cis* isomers have lower melting points than the corresponding *trans* isomers (Figure 3.37). The melting point of both *cis* and *trans* isomers increases as the double bond moves from the carboxyl group towards the ω-carbon.

Symmetrical triglycerides have a higher melting point than asymmetrical molecules containing the same fatty acids (Table 3.16).

As discussed in section 3.6, the fatty acids in milk fat are not distributed randomly and the melting point may be modified by randomizing the fatty acid distribution by transesterification using a lipase or chemical catalysts.

3.16.2 Process parameters

Temperature treatment of cream. The melting point of lipids is strongly influenced by the crystalline form, α, β, β^1, which is influenced by the structure of the triglycerides and by the thermal history of the product. The hardness of butter can be reduced by subjecting the cream to one of a variety of temperature programmes, which may be automated. The classical example of this is the Alnarp process, a typical example of which involves cooling pasteurized cream to *c.* 8°C, holding for *c.* 2 h, warming to 20°C, holding for *c.* 2 h and then cooling to *c.* 10°C for churning. More complicated schedules may be justified in certain cases.

All these treatments exert their effect by controlled crystal growth, e.g. larger, fewer crystals adsorb less liquid fat and there is less formation of mixed (liquid–solid) crystals due to reduced supercooling.

Work softening (microfixing). The liquid fat in butter crystallizes during cold storage after manufacture, forming an interlocking crystal network and resulting in increased hardness. Firmness can be reduced by 50–55% by disrupting this network, e.g. by passing the product through a small orifice (Figure 3.38) (the hardness of margarine can be reduced by 70–75% by a similar process; the greater impact of disrupting the crystal network on the hardness of margarine makes margarine appear to be more spreadable than butter even when both contain the same proportion of solid fat). Microfixing is relatively more effective when a strong crystal network has formed, i.e. when setting is at an advanced stage (e.g. after storage at 5°C for 7 days). The effect of microfixing is reversed on storage or by warming/cooling, i.e. is essentially a reversible phenomenon (Figure 3.38).

Fractionation. The melting and spreading characteristics of butter can be altered by fractional crystallization, i.e. controlled crystallization of molten fat or crystallization from a solution of fat in an organic solvent (e.g. ethanol or acetone). Cleaner, sharper fractionation is obtained in the latter but solvents may not be acceptable for use with foods. The crystals formed may

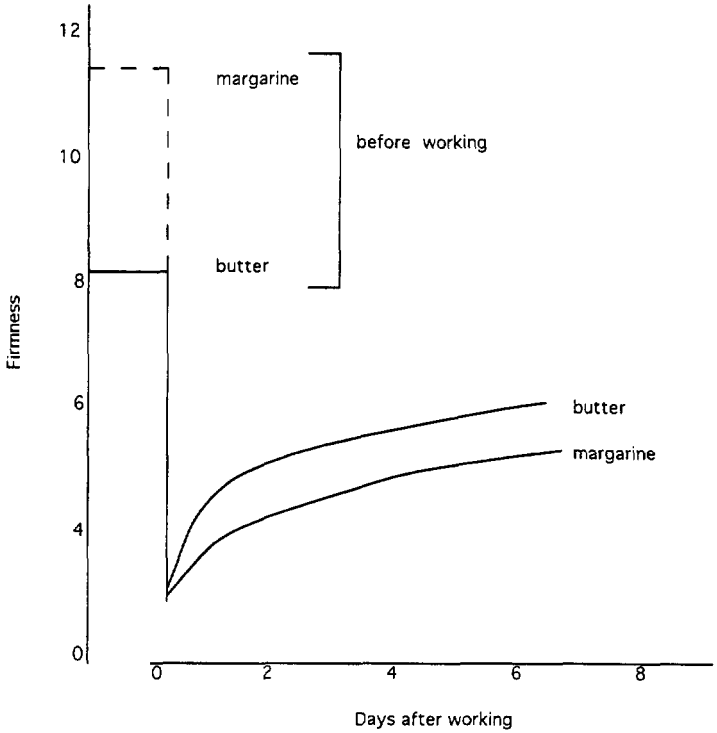


Figure 3.38 Effect of microfixing on the hardness of butter and conventional margarine (from Mulder and Walstra, 1974).

be removed by centrifugation (special centrifuges have been developed) or filtration. Early studies on fractional crystallization involved removing the high-melting point fraction for use in other applications, the mother liquor being used as a modified butter spread. This approach shifts the melting point–temperature curve to lower temperatures without significantly changing its shape (Figure 3.39). While the resulting butter has acceptable spreadability at low temperatures, its 'stand-up' properties are unsatisfactory, i.e. it becomes totally liquid at too low a temperature. A better approach is to blend low and high melting point fractions, by which an ideal melting curve can be approached. The problem of finding economic uses for the middle melting point fraction remains.

Blending. Blends of vegetable oils and milk fat offer an obvious solution to the problem of butter hardness – any desired hardness values can be obtained. Such products were introduced in the 1960's and are now used widely in many countries. These products may be produced by blending an

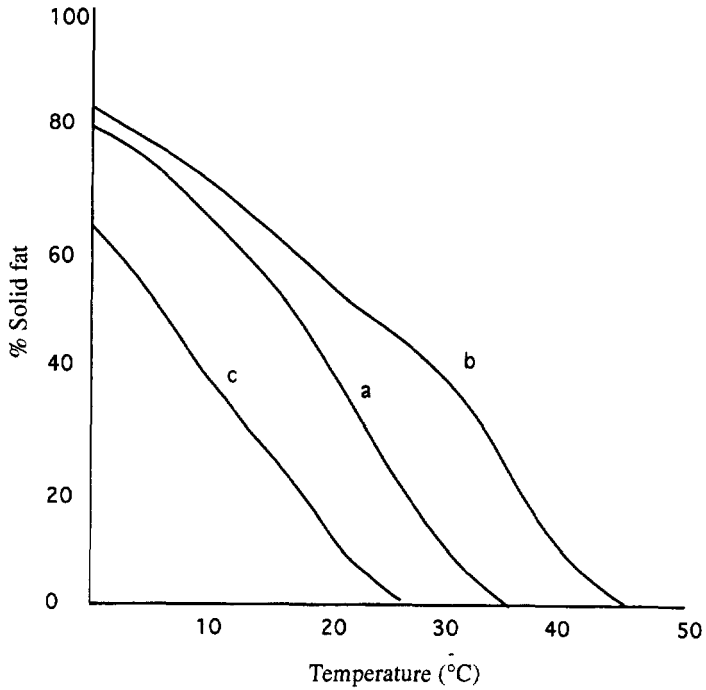


Figure 3.39 Melting point curves of unfractionated milk fat (a), fraction solid at 25°C (b), fraction liquid at 25°C (c) (from Mulder and Walstra, 1974).

emulsion of the oil with dairy cream for the manufacture of butter or by blending the oil directly with butter.

In addition to modifying the rheological properties of butter, blends of milk fat and vegetable oils can be produced at a reduced cost (depending on the price paid for milk fat) and have an increased content of polyunsaturated fatty acids, which probably has a nutritional advantage. Oils rich in ω-3 fatty acids, which are considered to have desirable nutritional properties, may be included in the blend, although these oils may be susceptible to oxidative rancidity.

Low-fat spreads. Spreads containing 40% fat (milk fat or blends of milk fat and vegetable oils), *c.* 3–5% protein and selected emulsifiers are now commonly available in many countries. These products have good spreadability and reduced caloric density (see Keogh, 1995).

High melting point products. Butter may be too soft for use as a shortening in certain applications; a more suitable product may be produced by blending butter and lard or tallow.

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Appendices

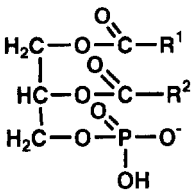
Appendix 3A Principal fatty acids in milk fat

See table overleaf.

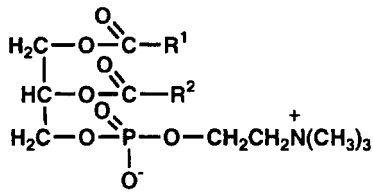
Appendix 3A. Principal fatty acids in milk fat

Abbreviated designation	Structure	Systematic name	Common name	Melting point (°C)	Odour threshold value (mg kg^{-1})
Saturated					
$C_{4:0}$	$CH_3(CH_2)_2COOH$	Butanoic acid	Butyric acid	−7.9	0.5–10
$C_{6:0}$	$CH_3(CH_2)_4COOH$	Hexanoic acid	Caproic acid	−3.9	3
$C_{8:0}$	$CH_3(CH_2)_6COOH$	Octanoic acid	Caprylic acid	16.3	3
$C_{10:0}$	$CH_3(CH_2)_8COOH$	Decanoic acid	Capric acid	31.3	10
$C_{12:0}$	$CH_3(CH_2)_{10}COOH$	Dodecanoic acid	Lauric acid	44.0	10
$C_{14:0}$	$CH_3(CH_2)_{12}COOH$	Tetradecanoic acid	Myristic acid	54.0	
$C_{16:0}$	$CH_3(CH_2)_{14}COOH$	Hexadecanoic acid	Palmitic acid	62.9	
$C_{18:0}$	$CH_3(CH_2)_{16}COOH$	Octadecanoic acid	Stearic acid	69.6	
Unsaturated					
	ω9-Family				
18:1	$CH_3(CH_2)_7CH{=}CH{-}CH_2{-}(CH_2)_6{-}COOH$	Δ9-octadeconic acid	Oleic acid	13.4	
	ω6-Family				
18:2	$CH_3(CH_2)_4{-}(CH{=}CH{-}CH_2)_2{-}(CH_2)_6{-}COOH$	Δ9,12-octadecdienoic acid	Linoleic acid	−5.0	
18:3	$CH_3(CH_2)_4{-}(CH{=}CH{-}CH_2)_3{-}(CH_2)_3{-}COOH$	Δ6,9,12-octadectrienoic acid	γ-Linolenic acid		
20:4	$CH_3(CH_2)_4{-}(CH{=}CH{-}CH_2)_4{-}(CH_2)_2{-}COOH$	Δ5,8,11,14-ecosatetraenoic acid	Arachidonic acid	−49.5	
	ω3-Family				
18:3	$CH_3CH_2{-}(CH{=}CH{-}CH_2)_3{-}(CH_2)_6{-}COOH$	Δ9,12,15-octadectrienoic acid	α-Linolenic acid	−11.0	
	Δ9-Family				
18:1	$CH_3(CH_2)_7{-}CH{=}CH{-}CH_2{-}(CH_2)_6{-}COOH$	Δ9-octadeconoic acid	Oleic acid	13.4	
16:1	$CH_3(CH_2)_5{-}CH{=}CH{-}CH_2{-}(CH_2)_6{-}COOH$	Δ9-hexadecenoic acid	Palmitoleic acid	0.5	

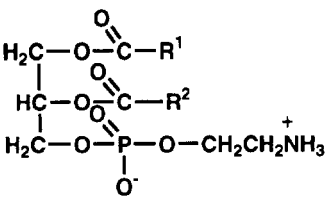
Appendix 3B Structures of the principal polar lipids



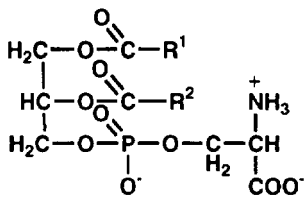
A Phosphatidic acid



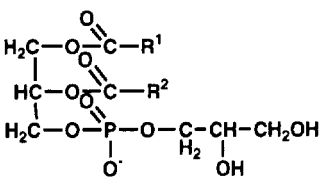
A phosphatidylcholine (lecithin)



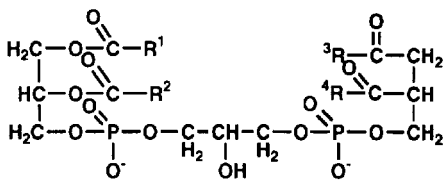
A Phosphatidylethanolamine



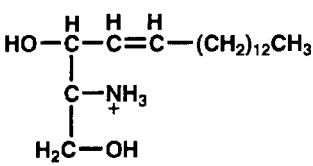
A phosphatidylserine



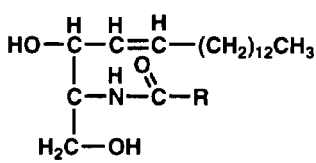
A phosphatidylglycerol



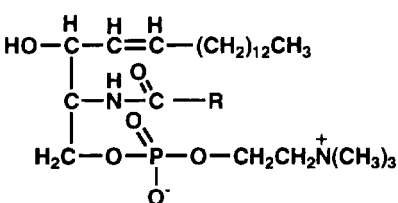
A disphosphatidylglycerol (cardiolipin)



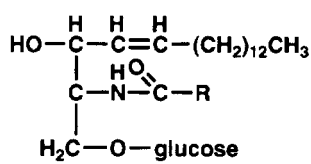
Sphingosine



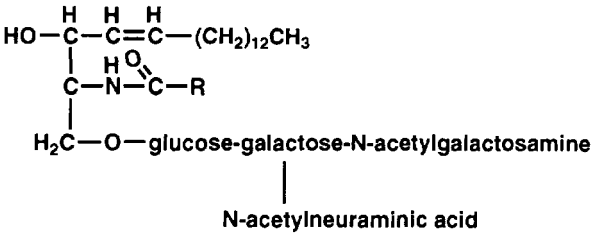
A ceramide (R = fatty acid residue)



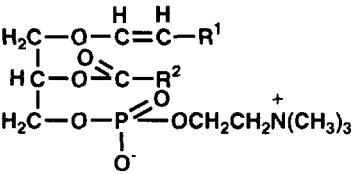
A sphingomyelin



A cerebroside



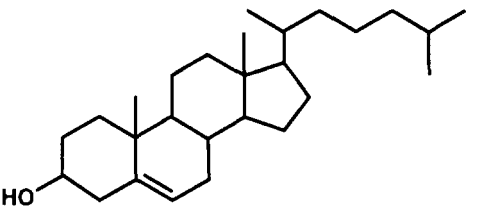
A ganglioside



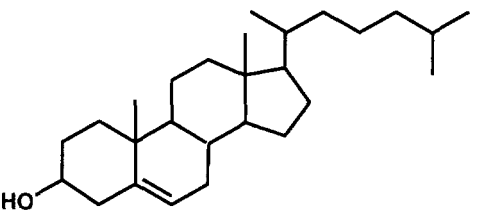
R^1 and R^2 = are long chain alkyl groups derived from a fatty alcohol or fatty acid, respectively.

A plasmalogen

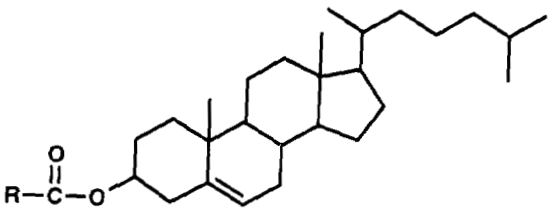
Appendix 3C Structures of cholesterol, 7-dehydrocholesterol and a cholesteryl ester



Cholesterol



7-Dehydrocholesterol



Cholesteryl ester