Major Edible Uses of Oils and Fats

8.1   Introduction

As already indicated in the previous chapter about 153 million tonnes of 17 commodity oils and fats were produced in 2006/07. It has generally been assumed that around 80% is used for human food (122 million tonnes) but the increasing demand for biodiesel has probably reduced this to a figure close to 113 million tonnes. However, this figure is too high as a measure of fat consumption by reason of loss and waste but also too low because of other fat sources not included in statistical tables for commodity oils. This chapter describes the major food uses of oils and fats. Relevant information on the nutritional properties of these materials is given in the previous chapter.

8.2   Spreads – butter and ghee

Milk and its products must be one of the earliest foods known to man. The dairy industry is based almost entirely on cow milk but there is also a limited supply of milk from goats, camels, and sheep. Cow milk is consumed as a drink (with 2–4% of fat), as cream (30–45%), as butter (82%), and as cheese (30–50%), each of which has the fat level indicated.

Butter is a water-in-oil emulsion consisting of fat (80–82%) and an aqueous phase (18–20%) containing salt and milk-solids-not-fat. The upper legal limit for water is 16%. Butter is made from cow milk (3–4% fat) that is converted first to cream (30–45% fat) by centrifuging and then to butter by churning and kneading. During churning there is a phase inversion from an oil-in-water to a water-in-oil emulsion.

Present annual production of butter is close to seven million tonnes (Table 2.1). The biggest consumers are in the Indian sub-continent (India and Pakistan) and in Europe, particularly in France and Germany.

Butter from cow milk fat has been used as a spread and for baking and frying for many centuries but now it has to compete with good quality spreads. The disadvantages associated with butter are its high price compared to other spreads, its poor spreadability from the refrigerator, and its poor health profile resulting from its high fat content, its high levels of saturated acids and of cholesterol, and the presence of *trans* unsaturated acids. Its advantages are its wholly natural profile and its superb flavour. The name butter is jealously guarded and is legally defined in many countries. It is not permissible to take anything away or to add anything to a product called butter.

Attempts have been made to overcome the above disadvantages by modifying the diet of the cow, by fractionation of anhydrous milk fat (AMF) to give material with modified physical properties (see below), or by blending with an unsaturated vegetable oil. This last improves the healthiness of the product and makes it spreadable from the refrigerator. Products are available in many countries that are blends of butter and vegetable oil – frequently soybean oil. These cannot be called butter since they do not meet the legal specifications but are given an appropriate name that the consumer comes to think of as 'spreadable butter'. Spreadable butters developed in New Zealand are made by fractionation of butter followed by recombination of appropriate fractions.

In times of over-supply there is an interest in extending the range of applications of milk fat by fractionation (Section 3.5). However, the triacylglycerol composition of milk fat is so complex (no individual triacylglycerol exceeds 5%) that differences between crystallised fractions are not so marked as with simpler vegetable oils such as palm oil. Nevertheless, useful separations have been achieved giving fractions that are harder and softer than the original milk fat. The lower melting (softer) fractions are employed to make spreadable butter and the harder fractions find pastry applications. AMF itself is used to make cakes. Mixed with the olein fraction it is used in cookies, biscuits, and butter cream. Mixed with the stearin fraction it is used in fermented pastries and puff pastry. The olein fraction on its own is used in ice cream cones, waffles, butter sponges, and in chocolate for ice cream bars.

In Europe, 'butters' with reduced fat levels (and therefore reduced caloric values) are designated as butter only when they contain 80–90% fat, 'three quarter fat butter' has 60–62% fat, 'half fat butter' has 39–41% fat, and 'dairy fat spreads' have other fat levels. In the United States 'light butter' must contain less than half of the normal level of fat and 'reduced butter' less than one quarter of the normal level.

In India, milk fat is consumed partly as butter but also as ghee. This is a concentrate of butter fat with over 99% milk fat and less than 0.2% moisture. It has a shelf life of 6–8 months even at ambient tropical temperatures. Butter or cream is converted into ghee by controlled heating to reduce the water content to below 0.2%. In other procedures the aqueous fraction is allowed to separate and some of it is run off before residual moisture is removed by heating. The vegetable oil-based alternative to ghee is called vanaspati (Section 8.3).

8.3   Spreads – margarine, vanaspati, and flavoured spreads

Margarine has been produced for more than 100 years. During the 1860s, large sections of the European population migrated from country to town and changed from rural to urban occupations. At the same time, there was a rapid increase in population in Europe and a general recession in agriculture leading to a shortage of butter, especially for the growing urban population. As a consequence, the price rose beyond the reach of many poor people. The situation was so bad in France that the government offered a prize for the best proposal for a butter substitute that would be cheaper and would also keep better.

The prize went to the French chemist, Hippolyte Mège Mouriés, who patented his product in France and Britain in 1869. His process required the softer component from fractionated tallow, skimmed milk, and macerated cow's udder. The product was described as mixed glycerol esters of oleic and margaric acids and was therefore called oleo-margarine. Margaric acid was thought to be heptadecanoic acid (17:0), but it was actually a eutectic mixture of palmitic (16:0) and stearic (18:0) acids. Even this early process

involved fractionation and enzymes. Both 'margaric' and 'margarine' should be pronounced with a hard *g* as in Margaret. All three words come from the Greek word for 'pearl' – *margarites.*

Margarine was first considered a cheap and inferior substitute for butter. In several countries regulations were passed that prohibited the addition of colouring matter so that white margarine would compare even less favourably with the more familiar yellow butter. Now the situation is different. These impediments have largely disappeared and margarine is widely accepted as having several advantages over butter. It is a more flexible product that can be varied for different markets and modified to meet new nutritional demands, such as desirable levels of cholesterol, phytosterols, saturated or *trans* acids, and fat content, as well as the statutory levels of certain vitamins. Table margarine is made from appropriate oils and fats (soybean, rapeseed/canola, sunflower, cottonseed, palm, palm kernel, coconut), which may have been fractionated, blended, hydrogenated in varying degrees, and/or interesterified. Fish oil (hydrogenated or not) may also be included. Other ingredients include surface-active agents, proteins, salt, and water along with preservatives, flavours, and vitamins.

Margarine production involves three basic steps: emulsification of the oil and aqueous phases, crystallisation of the fat phase, and plasticification of the crystallised emulsion. Water-in-oil emulsions are cooled in scraped-wall heat exchangers during which time fat crystallisation is initiated, a process known as 'nucleation', during which the emulsion drop size is reduced. There follows a maturing stage in working units during which crystallisation approaches equilibrium, though crystallisation may continue even after the product has been packed. The lipid in margarine is part solid (fat) and part liquid (oil), and the proportion of these two varies with temperature. The solid/liquid ratio at different temperatures is of paramount importance in relation to the physical nature of the product.

Individual crystals are between 0.1 and several micrometres in size and form clusters or aggregates of 10–30 μm. One gram of fat phase may contain up to 10^{12} individual crystals. The aqueous phase is present in droplets, generally 2–4 μm in diameter, stabilised by a coating of fat crystals.

It is desirable that margarine taken from the refrigerator at 4°C should spread easily. For this to happen the proportion of solids should be 30–40% at that temperature and should not exceed the higher value. For the sample to 'stand up' at room temperature (and

not collapse to an oily liquid) it should still have 10–20% solids at 10°C. Finally, so that it melts completely in the mouth and does not have a waxy mouth feel, the solid content at 35°C should be less than 3%. These are important parameters that can be attained with many different fat blends. Formulations have to be changed slightly to make the product suitable for use in hot climates.

Fats usually crystallise in two different forms, known as β' and β. The β form is thermodynamically more stable and will therefore be formed in many fats and fat blends. But sometimes the fat remains in the slightly less stable β' form. The β' form is preferred for margarines and other spreads because the crystals are smaller, are able to trap more liquid to give firm products with good texture and mouth feel, and impart a high gloss to the product. The β crystals, on the other hand, start small but tend to agglomerate and can trap less liquid. It is therefore desirable to choose a blend of oils that crystallise in the β' form.

Margarines and shortenings made from rapeseed/canola, sunflower, and soybean oil after partial hydrogenation tend to develop β crystals. Stable β' crystals are formed through incorporation of some cottonseed oil, hydrogenated palm oil or palm olein, tallow, modified lard, or hydrogenated fish oil. The canola, sunflower, and soybean oils all have very high levels of C_{18} acids, whereas the remainder have appreciable levels of C_{16} acids (or other chain length in the case of fish oil) along with the C_{18} acids and thus contain more triacylglycerols with acids of mixed chain length.

To make spreads (and shortenings) from readily available liquid vegetable oils it is necessary to 'harden' them (*i.e.* increase the solid/liquid ratio). This requires that the proportion of solid triacylglycerols be increased and for most of the last 100 years this has been achieved by partial hydrogenation that converts linoleic acid to saturated acids and to monoene acids rich in *trans* isomers (Section 3.6). Since the latter are higher melting than their *cis* isomers this was seen as an additional route to solid compounds. However, during the later years of the 20th century researchers in Europe showed that *trans* acids have greater cholesterol-raising powers than do the saturated acids. One country in Europe (Denmark) prohibited the use of fats and fatty ingredients with *trans* content above 2% and food producers in other European countries developed recipes with lower levels of *trans* acids. This could result in the use of more saturated acids but the combined content of saturated and *trans* acids was lowered. Changes in the USA were

spurred by legislation, operative from January 2006, requiring separate labelling of *trans* acids (excluding conjugated linoleic acid, CLA). A product can be labelled as *trans*-free only if the content of *trans* acids is less than 0.5 g per serving of the food product and many food companies in the USA changed their recipes to deliver *trans* acids below this limit. They are then able to claim *trans*-free products. This has been achieved, in part, by optimising the partial hydrogenation procedure to minimise (but not eliminate) *trans* acids and also by a new approach in which unhydrogenated oil is blended with hardstock and the mixture subjected to interesterification. The hardstock may be a lauric oil, palm stearin, or a fully hydrogenated oil. Since this last contains very little unsaturated acid *trans* acids must be virtually absent. A problem may remain if it is necessary to declare the presence of hydrogenated vegetable oil because of the unwarranted perception that this is undesirable. In some quarters it is feared that one day chemical interesterification may also be perceived to be unacceptable because of the use of 'chemicals'. If that happens suppliers will have to use enzymatic interesterification. This has some advantages but is more costly than chemical interesterification (Section 3.8).

It is impossible to list all of the formulations used to make spreads, and the following list is merely indicative (in the following blends, 'hydrogenated' means 'partially hydrogenated'). These blends are now being modified along the lines indicated in the previous paragraph to give lower levels of *trans* acids.

- Blends of hydrogenated soyabean oils with unhydrogenated soybean oil.
- Blends of canola oil, hydrogenated canola oil, and either hydrogenated palm oil or palm stearin.
- Blends of various hydrogenated cottonseed oils.
- Blends of edible tallow with vegetable oils (soybean, coconut).
- Blends of palm oil with hydrogenated palm oil and a liquid oil (rapeseed, sunflower, soybean, cottonseed, olive).

For hot climates a harder formulation is required, as in the following examples from Malaysia:

- Palm oil (60%), palm kernel oil (30%), and palm stearin (10%).
- Palm stearin (45%), palm kernel oil (40%), and a liquid oil (15%).

Table 8.1 gives details of the fatty acid composition of butter and of soft tub margarine and Table 8.2 provides information on production levels of margarine in the period 2001–2006.

Spreads are expected to have a shelf life of about 12 weeks. With good ingredients and the absence of pro-oxidants (*e.g.* copper), oxidative deterioration is not likely to be a problem. However, care must be taken to avoid microbiological contamination in the aqueous phase. This is achieved by hygienic practices during manufacture, the addition of some salt (8–10% in the aqueous phase, corresponding to slightly more than 1% in the margarine), control of pH of any cultured milk that may be used, and careful attention to droplet size in the emulsion.

The levels of total *trans* acids (mainly 18:1 but also some 18:2 and 18:3) in margarines from various countries are listed in Table 8.3. Levels have declined over the last 10 years and are now noticeably

Table 8.1 Approximate fatty acid composition of spreading fats (%)

Fat	Saturated	Monoene*	Polyene
Butter	63–70	28–31	1–3
Margarine (soft, tub)	17–19	35–52	29–48

*Soft margarines traditionally contained 10–18% *trans* acids but products with lower levels of *trans* acids are now being produced.

Table 8.2 Production of margarine (million metric tonnes) expressed in terms of normal fat levels and including vanaspati in the period 2001–2006

Country	2001	2002	2003	2004	2005	2006
World	9.74	9.84	9.66	9.73	9.94	10.07
EU-27	2.66	2.66	2.55	2.50	2.48	2.51
Pakistan	1.43	1.55	1.57	1.58	1.61	1.63
CIS	0.93	0.94	1.03	1.12	1.23	1.27
India	1.40	1.43	1.21	1.22	1.10	1.13
Turkey	0.49	0.51	0.54	0.54	0.62	0.64
USA	0.82	0.77	0.73	0.72	0.64	0.66
Brazil	0.49	0.49	0.49	0.49	0.49	0.50
Other	1.52	1.49	1.54	1.56	1.77	1.73

Note: The reduction in Indian production results from increased imports from Sri Lanka and Nepal following new tariff agreements.

It has been estimated that production of vanaspati in 1998 was 4.7 MMT (mainly in Pakistan 1.4, India 1.0, Iran 0.5, and Egypt 0.4).

Table 8.3 Presence of *trans* fatty acids in margarine

Country (year of publication)		Mean (%)
Germany (1997)	0.2–5	1.5
Belgium, Hungary, and Britain (1996)	1–24	9.7
Denmark (1998), soft		0.4
Denmark (1998), hard		4.1
Canada (1998), tub	1–46*	18.8
Canada (1998), hard	16–44	34
Hawaii (2001), cup	1–19	12.1
Hawaii (2001), carton	18–27	23.4

*Mainly 15–20%.
Source: Adapted from Gunstone in Akoh and Min (2008).

lower than those cited. However, spreads are not the only source of dietary *trans* fatty acids. Such acids are also obtained from dairy produce and from baked goods made with partially hydrogenated vegetable fats. Ratnayake *et al*. reported in 1998 that with a *trans* fatty acid consumption of about 8.4 g/day in Canada, only about 0.96 g (11%) comes from the consumption of margarine. The balance comes from fast foods, bakery goods, and ruminant fats. In 2000, Wolff *et al*. drew attention to the very different profile of *trans* monoene fatty acids consumed in France and Germany compared with consumption in North America. These differences reflect the differing nature of *trans* acids from dairy produce on the one hand and industrially hydrogenated vegetable oils on the other.

Spreads are now available with added phytosterols which are claimed to reduce blood cholesterol levels. The phytosterols, added at around the 8% level, are obtained either from tall oil and added to spreads as hydrogenated sterol esters (stanols) or from soybean oil and added as unsaturated sterol esters. Spreads are suitable foods for phytosterol addition because they are used widely and regularly but are unlikely to be over-consumed. Intake of phytosterols is normally 200–400 mg/day, though higher for vegetarians, but the intake of 1.6–3.3 g/day, recommended by those offering this special margarine, is markedly higher. Normally about 50% of ingested cholesterol is absorbed but with an adequate intake of phytosterols, which are absorbed only at the 5% level, absorption of cholesterol falls to about 20%.

Spreads with reduced levels of fat (40% or less) are popular with consumers (as an alternative to discipline in the amount of normal

spread consumed). These spreads contain more water than the full-fat spreads and require emulsifiers (monoacylglycerols or poly-glycerol esters). It is also usual to add thickeners, such as gelatin, sodium alginate, pectin, and carrageenan, to the aqueous phase. Industrial margarines are used mainly for bakery products and are discussed in Section 8.4.

Chocolate spreads are increasingly popular. They consist of a soft smooth fat (generally at about a 30% level) and cocoa powder and may also contain nuts. Like other spreads there must be an appropriate mixture of solid and liquid fats. They are designed to be kept at room temperature (but are often kept in a refrigerator) and to be spread on bread, toast, or biscuits. The spread smells and tastes like chocolate but does not solidify. To prevent oiling out (separation of oil) they should be made with fats crystallising in the β' form. Traditionally partially hydrogenated fats have been used but attempts are now being made to develop formulations containing less *trans* acids.

Vanaspati can be considered as vegetable ghee and is used mainly for frying and for the preparation of sauces, sweets, and desserts. Traditionally, vanaspati was a blend of hydrogenated seed oils (cottonseed, groundnut, soybean, rapeseed/canola, and palm), but increasingly palm oil has become a significant component. The product should melt between 31°C and 41°C, though generally it is close to 37°C in India and is 36 $\pm$2°C in Pakistan. Because of the method of production involving hydrogenation, vanaspati contains high levels of acids with *trans* unsaturation (more than 50% in India and about 27% in Pakistan) but with increasing use of palm oil in vanaspati the need for hydrogenation is reduced with a consequent fall in the level of *trans* acids. Figures around 3% have been reported in Pakistan.

8.4 Baking fats and shortenings

The use of oils and fats in baking processes ranks with frying and spreads as a major food use of these materials. The products range from breads and layered doughs to cakes, biscuits (cookies) and biscuit fillings, pie-crusts, short pastry, and puff pastry. The fats used to produce this wide range of baked goods vary in their properties and particularly in their melting behaviour and plasticity.

It is possible to attain appropriate properties with different blends of oils, and preferred mixtures vary in different regions of the world. In addition to the desired physical properties, it is necessary to meet two further requirements. One is oxidative stability related to the shelf life of the baked goods. The other is the need to respond to current nutritional demands. A good baked item will be tasty, have good texture, have a reasonable shelf life in terms of rancidity and palatability and texture, and will be a healthy food. Sometimes the pressure for appropriate physical properties and nutritional requirements work in opposite directions and a compromise has to be made. As already discussed with the spreads, a plastic fat containing solid and liquid components must have some solid triacylglycerols, which implies a certain level of saturated acids or of acids with *trans* unsaturation despite the nutritional concerns associated with these compounds.

Fats used to make doughs of various kinds are almost entirely plastic fats, that is mixtures of solid and liquid components that appear solid at certain temperatures but deform when a pressure is applied. Fats exert their influence by interaction with the flour and (sometimes) sugar, which are the other major components of a baked product.

Baking fats may include butter or margarine both of which are more than 80% fat and also contain an aqueous phase, or they may be shortenings with 100% fat. These are so described as they give pastry the crispness and flakiness that is suitable for its edible purpose. Industrial margarine has the fat/water ratio required of margarine but differs from the domestic spread in that it has fat components selected specifically to produce the physical properties required by its final end use. Changes in the composition of fat in margarines and spreads designed to increase their nutritional value have not always carried through to the baking fats, which are often richer in saturated fatty acids and/or acids with *trans* unsaturation. But there seems little doubt that the appropriate changes will come. Baked goods contain what is described as 'hidden' fat, and it is easy to forget the presence of fat when delicious pastries, cakes, and biscuits are being eaten.

The prime function of fat in a cake is to assist in aeration and to modify the texture of the product. The first stage in making a cake is to produce a batter containing a fine dispersion of air bubbles largely stabilised by fat crystals. During baking the fat melts and the water-in-oil emulsion inverts with the air being trapped in

the aqueous phase. As baking continues the starch is hydrated and gelatinised, the protein starts to coagulate, and the air cells expand through the presence of steam and carbon dioxide (produced from baking powder).

In short pastry, aeration is only of secondary importance. The fat needs to be fairly firm and should be distributed throughout the dough as a thin film: lard, beef tallow olein, and hardened vegetable oils may be employed. Sometimes butter or margarine is used.

In puff pastry (pie-crusts, Danish pastries, croissants), fat acts as a barrier separating the layers of dough from one another. Liberation of gas or steam during baking produces a layer structure. This requires a fat of higher melting point fat than normal (about 42°C) with a higher solid fat content achieved through an appropriate degree of hydrogenation. Small amounts of fat (2–5%) are added to bread dough.

8.5   Frying oils and fats

The use of oils and fats as a frying medium in both shallow and deep frying mode is an important component in the whole picture of food applications. Pre-fried and fried foods are now a significant component of our dietary intake and it is reported that more than 20 million tonnes of oils and fats are used in this way. Since some of this is discarded after use, not all of it is consumed.

Frying is usually carried out at a temperature of 165–185°C and is an efficient method of heat transfer that allows quick cooking and adds flavour to fried food. Some oil is absorbed by the fried food. In shallow pan frying surplus oil is cleaned away at the end of the frying operation. In deep fat frying oil is re-used until it has to be discarded because of its poor quality. This low-grade material may be added to animal feed as an energy source or it may be converted to methyl esters and used as biodiesel.

During frying there is heat and mass transfer. When frying oil is maintained at 150–180°C within the food there is a dried food zone (103–150°C) closest to the hot oil, a vaporisation region (100–103°C), a migration region (100°C), and at the centre a liquid water region (75–100°C). There is movement of water (as steam) out of the food into the hot oil and some movement of fat into the food. With well-cooked food these changes produce a crisp outer

layer in which there have been changes to carbohydrate and protein. It is desirable to minimise oil penetration occurring both during cooking and during cooling. If the frying temperature is too low cooking is slow and more fat is incorporated into the food, if it is too high then undesirable changes in the oil are accelerated.

Frying is carried out on a domestic scale, in restaurants and fast food outlets on a batch scale using 4–20 kg of oil, and under industrial conditions in continuous mode with one tonne or more of oil to produce fried products for retail outlets. Popular fried foods include French fries, chicken, fish, meat, potato crisps, tortilla chips, extrusion snacks, doughnuts, nuts, and noodles. During frying, oil is transferred to the food so that fried foods contain additional fat at a level of 10–40%. Fat from the food is also transferred to the frying oil so that though oil quality is controlled at the beginning of the frying process the oil soon becomes contaminated, for example, with fish oil or with animal fat depending on the food being fried.

The frying process, conducted at elevated temperature and in the presence of air, results in several chemical changes in the frying oil. Oxidation is accompanied by dimerisation, polymerisation, and fatty acid cyclisation. It also produces short-chain carbonyl compounds such as decadienal from linoleate which give a distinctive flavour to the fried product (Section 6.2). Volatile products are quickly lost through steam distillation which occurs during frying and accounts for the characteristic smell of frying operations but compounds of higher molecular weight remain in the frying oil. With continued use the oil begins to smoke, to foam, and to become more viscous. Oil absorbed by the fried food has to be replaced by fresh oil and turnover and replacement of fat are important factors in a good quality frying operation. This ensures that low-quality oil is not being used. Under the best frying conditions the major health concern may not be the small amount of artefacts but rather the increased level of fat that is being consumed.

A good frying oil will have high oxidative stability, a high smoke point (corresponding to a low level of free fatty acid), and show minimum colour darkening during use. The oil may be chosen because it gives a distinctive flavour to the fried food as with corn oil, olive oil, groundnut oil, and tallow. Alternatively, a refined blend may be used (cottonseed, groundnut, soybean, palm olein) which may have been subject to partial hydrogenation.

On nutritional grounds the ideal frying oil contains low levels of saturated acid and of unsaturated acids with *trans* unsaturation.

Low levels of polyunsaturated fatty acids are also preferred since these are the precursors of undesirable oxidised and polymerised products. Consequently there should be a high level of oleic glycerol esters. In practice it may not be possible to attain all these objectives. Differing frying media are used in different parts of the world depending on local availability and on cultural preferences for particular flavours. They include lauric oils, palm oil and palm olein, groundnut oil, rice-bran oil, cottonseed oil, corn oil, sunflower oil, soybean and rapeseed oils after brush hydrogenation to reduce the level of linolenic acid, and a range of high-oleic varieties. In France and Belgium it is forbidden by law to use frying oils with more than 2% of linolenic acid. Special oils used for frying include olestra (polyacylated sucrose with virtually zero calorific value because it is not absorbed) in the USA and 'Good Fry' in Europe. The latter is a high-oleic sunflower oil with up to 6% of sesame oil and/or rice-bran oil, both of which contain powerful natural antioxidants (Section 6.2). Many high-oleic oils are being developed through conventional seed breeding or through genetic modification and all these will be considered as potential frying oils (Table 8.4).

Frying oils are monitored by measuring properties such as: acid value, peroxide value, anisidine value, conjugated diene, total polar materials (TPM), and polymeric triglycerides (PTG) (see Chapter 4). The oil should be replaced when these parameters are above specification. It has been recommended that TPM should not exceed 24% and PTG should not exceed 12%. In most European countries frying oil should be discarded when TPM and PTG together exceed 24–27%. It would be better if these standards could be made more uniform. These measurements require laboratory procedures and a number of simple instrumental methods suitable for use in a food-processing factory have also been examined. It must be remembered that oxidative deterioration starting during food processing can continue during storage even at $-5°C$ to $+10°C$ (Stier, 2004).

The discovery of low levels of acrylamide in French fries and crisps and in baked and roasted foods raised some concern and a good deal of investigation since this compound is carcinogenic and has other undesirable physiological properties at higher concentrations. The acrylamide molecule (CH_2=$CHCONH_2$) contains three carbon atoms and it is still not certain whether these come from glycerol (possibly via monoacylglycerols), from amino acids, from reducing sugars or from all these sources. Levels in French fries after frying are around 600 μg/kg (*i.e.* parts per billion) and

Table 8.4 Fatty acid composition of non-hydrogenated oils used in frying

Oil	16:0	18:0	18:1	18:2	18:3
Soybean					
Normal	10.4	4.1	22.9	52.9	7.5
High-oleic	6.4	3.3	85.6	1.6	2.2
Low-saturated	4.3	2.9	19.7	61.8	8.6
Low-linolenic	10	5	41	41	2
Rapeseed					
Normal	4.0	2.0	58.0	20.0	9.0
High-oleic	3.6	2.3	78.8	5.1	5.2
Low-linolenic	4.0	2.0	63.0	23.0	4.0
Sunflower					
Normal	7.0	4.5	18.7	67.5	Trace
High-oleic	3.6	4.3	82.2	9.9	Trace
Mid-oleic	4.6	4.2	61.3	27.2	Trace
Corn oil	10.9	2.0	25.4	59.6	1.0
Cottonseed oil	21.6	2.6	18.6	54.4	0.7
Palm oil	42.9	4.6	39.3	10.7	0.4
Palm olein	39.8	4.4	42.5	11.2	0.4

Source: Adapted from Goetz (2006) Developments in frying oils, in *Modifying Lipids for Use in Foods* (editor F.D. Gunstone), Woodhead Publishing, Cambridge, England, p. 525.
Note: Brush hydrogenation of soybean oil and rapeseed oil will give products with about half these levels of linolenic acid with more 18:1 having *trans* unsaturation. Alternative data are to be found in Table 2.5.

900–1000 µg/kg in crisps. These levels increase with temperature (another reason for frying at the lowest practicable temperature) and change with the variety of potato used.

8.6 Salad oils, mayonnaise and salad cream, French dressing

Salad oils, used to make mayonnaise and salad cream, should be oxidatively stable and free of solids even when stored in a refrigerator at about 4°C. Several vegetable oils may be used. Those containing linolenic acid (soybean oil, rapeseed/canola oil) are usually lightly hydrogenated (brush hydrogenation) to enhance oxidative stability. All oils are generally winterised (Section 3.5) to remove high-melting glycerol esters that would crystallise, as well as waxes

present in some solvent-extracted oils. The latter lead to a haze in the oil when it is cooled. Salad oils must pass a 'cold test', which requires that the oil remain clear for 5.5 h at refrigeration temperature. After appropriate treatment, soybean, rapeseed/canola, corn, and sunflower oils are used to produce mayonnaise.

Mayonnaise is an oil-in-water emulsion containing between 65% (legal minimum) and 80% of oil. The aqueous phase contains vinegar, citric acid, and egg yolk. This last contains lecithin, which serves as an emulsifying agent. Lemon and/or lime juice, salt, syrups, seasonings, spices, and antioxidants are optional constituents. These components may be mixed together at temperatures not exceeding 5°C (cold process) or at temperatures around 70°C (hot process). A typical mayonnaise contains vegetable oil (75–80% by weight), vinegar (9.4–10.8%), egg yolk (7.0–9.0%), and small amounts of sugar, salt, mustard, and pepper. 'Light' mayonnaise contains only 30–40% of oil and in low-calorie dressings the level is 3–10%.

Salad creams are similar but contain much less oil (30–40%) along with cooked starch materials, emulsifiers, and gums to provide stability and thickness. They are cheaper than mayonnaise.

French dressings are temporary emulsions of oil, vinegar or lemon juice, and seasonings. Because the emulsions are not stable the dressings should be shaken before use. A non-separating product can be made by addition of egg yolk or other emulsifying agent.

8.7   Chocolate and confectionery fats

Chocolate is an important fat-containing food based mainly, but not always entirely, on cocoa butter. Confectionery fats have similar physical/functional properties but in the EU they can only be described as chocolate if fats other than cocoa butter come from a prescribed list (Table 2.3, Section 2.3) and do not exceed 5% of the final product.

Cocoa beans contain 50–55% fat. Harvested pods are broken open and left in heaps on the ground for about a week during which time the sugars ferment. The beans are then sun-dried and are ready for transportation and storage. To recover the important components the beans are roasted (~150°C), shells are separated from the cocoa nib, and the latter is ground to produce cocoa mass. When this is pressed it yields cocoa butter and cocoa powder

still containing some fat. Typically, 100 g of beans produce 40 g of cocoa butter by pressing, expelling, or solvent extraction, 40 g of cocoa powder remaining after extraction with 10–24% fat, and 20 g of waste material (shell, moisture, dirt, etc.). Increasingly the beans are processed in the country where they grow and cocoa liquor, cocoa powder, and cocoa butter (usually in 25 kg parcels) are exported to the chocolate-producing countries.

Both cocoa butter (a solid fat melting at 32–35°C) and cocoa powder are important ingredients in chocolate. Cocoa butter is in high demand because its characteristic melting behaviour gives it properties that are significant in chocolate. At ambient temperatures it is hard and brittle, giving chocolate its characteristic snap. Also, it has a steep melting curve that permits complete melting at mouth temperature. This gives a cooling sensation and a smooth creamy texture. Typically the content of solid falls from 45% to 1% between 30°C and 35°C. The hardness of cocoa butter is related to its solid fat content at 20°C and 25°C. The melting behaviour is linked to the chemical composition of cocoa butter. The fat is rich in palmitic (24–30%), stearic (30–36%), and oleic acids (32–39%), and its major triacylglycerols are of the kind SOS where S represents saturated acyl chains in the 1- and 3-positions and O represents an oleyl chain in the 2-position. There are three major components: POP, POSt, and StOSt (P = palmitic acid and St = stearic acid). Cocoa butter has a high content of saturated acids, which raises health concerns. However, it has been argued that much of this is stearic acid that is not considered to be cholesterolemic. Cocoa butter is also a rich source of flavonoids which have powerful antioxidant activity.

Cocoa is grown mainly in West Africa, South East Asia, and South and Central America. The composition of cocoa butter from these different sources varies slightly. Typical figures for cocoa butter from Ghana are shown in Table 8.5. Small differences in fatty acid composition are reflected in the iodine value and the melting point but more significantly in the triacylglycerol composition and the melting profile. For example, the content of the important SOS triacylglycerols varies between 87.5% in Malaysian and 71.9% in Brazilian cocoa butter, with the African samples midway between these extremes. There is some evidence that the cocoa butters of different geographic origin are becoming more alike.

The crystal structure of cocoa butter has been studied intensively because of its importance in understanding the nature of chocolate. The solid fat has six crystalline forms designated I–VI

Table 8.5 Composition and properties of Ghanain cocoa butter

Iodine value	35.8
Melting point (°C)	32.2
Diacylglycerols	1.9
Free acid (%)	1.5
Component acids	
Palmitic	24.8
Stearic	37.1
Oleic	33.1
Linoleic	2.6
Arachidic	1.1
Component triacylglycerols	
Trisaturated	0.7
Monounsaturated	84.0
POP	15.3
POSt	40.1
StOSt	27.5
Diunsaturated	14.0
Polyunsaturated	1.3
Solid content (pulsed NMR) tempering for 40 h/26°C	
20°C (%)	76.0
25°C (%)	69.6
30°C (%)	45.0
35°C (%)	1.1

Source: Adapted from Shukla (1997) Chocolate – The chemistry of pleasure. *INFORM*, **8**, 152.
Note: The original paper contains more details along with information on cocoa butter from India, Nigeria, and Sri Lanka.

(Section 6.3). Transition from form V to the more stable form VI leads to the appearance of white crystals of fat on the surface of the chocolate. This phenomenon is termed 'bloom'. It is promoted by fluctuations in temperature during storage and by migration of liquid oils from nut centres. It is a harmless change but is considered undesirable because it may be mistaken for microbiological contamination. Bloom can be inhibited by addition of a little 2-oleo 1,3-dibehenin (BOB) to the cocoa butter (B = behenic acid, 22:0). A recent review of this topic is that by Lonchampt and Hartel (2004).

The simplest plain chocolate contains sugar and cocoa liquor, with cocoa butter the only fat present. A typical plain chocolate has cocoa mass (~40%, which contains some cocoa butter), sugar (~48%), added cocoa butter (~12%), and small amounts of lecithin and other materials. Other chocolates may contain higher levels of cocoa butter, generally in the range 25–35%. In EU countries it is permissible to

replace cocoa butter with up to 5% of another fat with similar fatty acid and triacylglycerol composition taken from a prescribed list of tropical fats (Section 2.3). The permitted tropical fats come from palm, illipe, shea, sal, kokum, and mango and may be used in a fractionated form (Table 2.3). Hydrogenation and interesterification procedures are not permitted in the preparation of these fats.

Milk chocolate contains less cocoa butter and between 3.5% and 9% of milk fat. White chocolate is based on sugar and cocoa liquor and cocoa butter (without cocoa mass). If the latter is not entirely refined it will retain some of the flavour normally associated with chocolate. Chocolate normally contains up to 0.4% of lecithin to aid the processing of the chocolate by reducing the viscosity of molten chocolate. Polyglycerol ricinoleate is sometimes added to optimise viscosity. Ricinoleic acid (12-hydroxyoleic) is the major acid in castor oil.

Cocoa butter alternatives (CBA) is a general name covering cocoa butter equivalents (CBE), cocoa butter improvers (CBI), cocoa butter replacers (CBR), and cocoa butter substitutes (CBS).

CBE have the same general chemical composition and hence the same physical properties as cocoa butter and include the tropical oils described above and sometimes designated as hard butters. These can be blended to give mixtures of POP, POSt, and StOSt very similar in composition to cocoa butter and fully miscible with it. The level at which cocoa butter can be replaced by a CBE is limited in some countries on a legal basis and not on a functional basis. CBE must be compatible with cocoa butter by virtue of their similar fatty acid and triacylglycerol composition. They have a melting range equivalent to that of cocoa butter, yield the β polymorph when processed and tempered in the same way as cocoa butter, and give a product that is at least as good as cocoa butter with respect to bloom.

CBR are usually based on vegetable oils such as soybean, cottonseed, or palm that have been fractionated or partially hydrogenated. They contain *trans* unsaturated acids at levels up to 60% and have a different triacylglycerol composition from cocoa butter. They do not require tempering but should be compatible with cocoa butter.

CBS are usually based on lauric fats. They share some of the physical properties of cocoa butter but have a different composition. Coatings based on CBS fats do not require to be tempered and are used in the molten state for enrobing. They give a superior gloss and have very sharp melting characteristics.

Chocolate spreads are increasing in popularity (Section 8.3).

8.8   Ice cream

The annual production of ice cream in the United States in 2002 was reported to be about 54 million hectolitres (*i.e.* 5400 million litres), suggesting that the global figure was then at least twice that level. This quantity of ice cream will contain around 0.8–1.0 million tonnes of fat. Traditionally this has been mainly milk fat along with some vegetable fat which might be sunflower, groundnut, palm, palm kernel, and coconut. Some of the newer non-dairy recipes with ~8% fat have lower levels of saturated (around 40%) and *trans* acids (zero).

Ice cream contains water (60–70%) and total solids (30–40%), with the latter including fat (5–12%), milk solids other than fat (10–12%), sucrose (12–14%), glucose solids (2–4%), emulsifier (0.2–0.5%), and stabiliser (0.1–0.3%). Legal requirements for fat vary from country to country as does the possibility of replacing some or all the dairy fat with vegetable fat.

Fat in ice cream contributes to structure. It stabilises the aerated foam, improves melting resistance, imparts creaminess, and contributes to taste. Its most important properties are melting characteristics, solid-to-liquid ratio at various temperatures, and its taste profile.

Production of ice cream occurs through nine stages: selection and weighing of ingredients, mixing of these in an appropriate sequence at 20–35°C, pasteurisation at 70–75°C or sterilisation at 95°C, homogenisation at 75°C, cooling to less than 5°C, ageing at 5°C for at least 4h, freezing at −5°C to −10°C, hardening at −25°C to −35°C, and storage at −18°C to −20°C.

8.9   Incorporation of vegetable fats into dairy products

Vegetable oils may be incorporated into dairy products as a replacement for dairy fat. This happens when local supplies of milk fat are inadequate as in some tropical countries where the climate is not suitable for large-scale dairy farming and also for consumers concerned about the saturated acids and cholesterol present in milk fat. In addition, it is possible to produce milk fat replacements

in a more convenient form as, for example, in long-life cream. The use of vegetable fat in ice cream has already been discussed in Section 8.7.

So-called filled milk is made from skim milk powder reconstituted with an appropriate vegetable oil. This latter should be free of linolenic acid, have a low content of linoleic acid, and contain antioxidant so that it is oxidatively stable. Palm oil, palm kernel oil, and coconut oil are most frequently used, and these may be partially hydrogenated to provide further stability against oxidation.

Non-dairy coffee whiteners, available in powder or liquid form, generally contain 35–45% fat, which is usually partially hydrogenated palm kernel oil.

Cheeses have been developed based on vegetable fat rather than dairy fat. Several formulations have been described incorporating soybean oil with or without hydrogenation, palm oil, rapeseed oil, lauric oils, and high-oleic sunflower oil. Attempts have been made to incorporate into these products, some of the short-chain acids that are characteristic of milk fat and give cheese some of its characteristic flavour.

Non-dairy whipping creams, made with hardened palm kernel oil and coconut oil (each about 17%), are convenient because they have a long shelf life at ambient temperature. First produced for the bakery and catering market with high overrun (increased volume when whipped) and good shape retention, they are now supplied to the retail market for domestic use. Pouring creams, containing about 9% of each of the two lauric oils, are also available. Both creams also contain buttermilk powder (7%), guar gum (0.10–0.15%), emulsifying agent (0.30–0.35%), β-carotene (0.25%), and water.

8.10   Edible coatings

Foods are sometimes coated with thin layers of edible material to extend shelf life by minimising moisture loss, to provide gloss for aesthetic reasons, and to reduce the complexity and cost of packaging. The thin layers may be carbohydrate, protein, lipid, or some combination of these. The lipids most commonly used are waxes (candelilla, carnauba, or rice bran), appropriate triacylglycerols, or acetylated monoacylglycerols. The latter are capable of producing flexible films at temperatures below those appropriate

for the waxes even though they are poorer moisture barriers. The foods most frequently coated are citrus fruits (oranges and lemons), deciduous fruits (apples), vegetables (cucumbers, tomatoes, potatoes), candies and confectioneries, nuts, raisins, cheeses, and starch-based products (cereals, doughnuts, and ice cream cones and wafers).

Vegetable oils used to coat food products must be liquid at room temperature and must have high oxidative stability. They serve as a moisture barrier, a flavour carrier, a lubricant or release agent, as an anti-dust or anti-caking agent, and as a gloss enhancer. They are used at low levels and are sprayed on to large exposed surfaces of products during roasting, frying, or handling. Traditionally they are made from commodity oils like soybean or cottonseed. These oils are cheap but require elaborate processing (partial hydrogenation and fractionation) to develop the required physical state and chemical stability. New high-oleic oils may also be used. These are more costly but they bring added value in terms of their superior nutritional properties resulting from lower levels of *trans* acids and saturated acids and in the reduced need for processing. Lauric oils, such as coconut oil, palm kernel oil, are used to spray cracker-type biscuits to provide an attractive appearance, maintain crispness by acting as a barrier to moisture, and improve eating quality.

8.11   Emulsifying agents

Fatty acids and their derivatives are amphiphilic. This means that their molecules have hydrophilic and lipophilic regions. If these are appropriately balanced, then the molecules can exist in a physically stable form between aqueous and fatty substances. They can therefore be used to stabilise both oil-in-water and water-in-oil emulsions and are important components of many of the fat-based products that have been described in the earlier sections of this chapter. Applications of emulsifiers in foods include film coatings, stabilising and destabilising emulsions, modification of fat crystallisation, dough strengthening, crumb softening, and texturisation of starch-based foods. Production of food emulsifiers was estimated to be 250,000 metric tonnes in 1994 of which about 75% is monoacylglycerols or compounds derived from these.

Monoacylglycerols are most often made by glycerolysis of natural triacylglycerol mixtures in the presence of an alkaline catalyst at 180–230°C for 1 h. Fat and glycerol (30% by weight) will give a mixture of monoacylglycerols (around 58%, mainly the 1-isomer), diacylglycerols (about 36%), and triacylglycerols (about 6%). This mixture can be used in this form or it can be subjected to high-vacuum thin-film molecular distillation to give a monoacylglycerol product (around 95% and at least 90% of the 1-monoester) with only low levels of diacylglycerols, triacylglycerols, and free acids. Attempts are being made to develop an enzyme-catalysed glycerolysis reaction that occurs under milder reaction conditions. The oils most commonly used include lard, tallow, soybean, cottonseed, sunflower, palm, and palm kernel oil – all in hydrogenated or non-hydrogenated form. Glycerol monostearate (GMS) is a commonly used product of this type.

The properties desired in a monoacylglycerol for some specific use may be improved by acylation of one of the free hydroxyl groups by reaction with acid (lactic, citric) or acid anhydride (acetic, succinic, diacetyltartaric). For the most part these have the structures shown:

$CH_3(CH_2)_nCOOCH_2CH(OH)CH_2OH$ 1-monoacylglycerol

$CH_3(CH_2)_nCOOCHCH(OH)CHOCOR$ modified monoacylglycerol
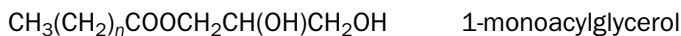
where R is CH_3 (from acetate), $CH(OH)COOH$ (from lactate), CH_2CH_2COOH (from succinate), $CHOAcCHOAcCOOH$ (from diacetyltartrate), and $CH_2C(OH,COOH)CH_2COOH$ (from citrate).

Propylene glycol ($CH_3CHOHCH_2OH$) also reacts with fatty acids to give mixtures of mono (about 55%, mainly 1-acyl) and diacyl esters (about 45%). A 90% monoacyl fraction can be obtained by molecular distillation.

Other compounds include the partial esters of polyglycerols (a polyether with 2–10 glycerol units but mainly 2–4 units), sorbitan and its polyethylene oxide derivatives, 6-monoacylate sucrose, and stearoyl lactate, usually as the sodium or calcium salt.

8.12 Functional foods

There is a growing realisation of the link between diet and health. This is important to the increasing number of older people who want to live active and healthy lives as long as possible, to

governments concerned about increasing health costs, and to the food industry oppressed by small margins on most conventional foods and looking for new products with higher profit margins. In the 30-year period 1995–2025 it is estimated that in the developed world the number of people over 80 years will increase by 50% and the number of those over 90 years will double. All this is linked with concerns that the food chain should deliver safer and healthier foods and to changed eating habits where less food is prepared in the domestic kitchen but is prepared in the factory for home consumption or is eaten out of the home. Under both these conditions there is some loss of control over the selection of food to be consumed. These trends are of interest to scientists and nutritionists seeking to improve the diet, to the food industry, to government, and to the media. This increasing interest is especially marked in Japan where for several years there has been a system in place for recognition of 'foods for specific health use' or FOSHU with its own distinctive logo. Many other developed countries such as Finland have also shown considerable interest in this topic.

Functional foods contain bio-active molecules that promote health or reduce the risk of disease and are consumed as conventional foods at levels not very different from normal. A recent book (Gunstone, 2003) devoted to this topic included chapters on anti-oxidants (carotenoids, tocopherols, flavonoids, rosemary oil, rice bran oil, and sesame oil), diacylglycerols, phytosterols, structured lipids, omega-3 acids, and CLA. Some of these have been covered in earlier sections of this chapter.

8.13   Appetite suppressants

At a time when obesity is becoming more common and is of growing concern to individuals, to the medical profession, to government health managers, and to the food industry there is increasing interest in procedures by which energy intake might be reduced (Section 7.12). There are several approaches to this issue including reducing the energy level of foods, of producing and consuming smaller portions, and through ingestion of materials that influence satiety. Satiation usually refers to the process which leads to the termination of a meal through felling 'full' and to consequent delay between meals. Several compounds are reported to enhance

satiety and some are available to be added to normal foods such as soups and yoghurt.

Among the materials claimed to promote satiety are plant glycolipids, fatty acid amides, pinolenic acid (5*c*,9*c*,12*c*-18:3) present in Korean pine nut oil, and an emulsion of a mixture of purified lipid fractions from palm and oat oils. This latter, called 'olibra' and sold under various names, prolongs the feeling of fullness resulting in energy intake reduction at subsequent meals.