Extraction, Refining, and Modification Processes

3.1 Extraction

This chapter outlines the steps whereby seeds, oil-containing fruits, or animal organs or carcases are changed from their harvested or available form to fat products that the food processor can incorporate into food. These include:

- extraction to isolate crude oil or fat;
- refining of the crude product, usually through several stages;
- modification of the native oil or fat to make it more suitable for its end-use.

During all the stages of extraction, refining, and modification, and also during transport and storage the oil must be protected against deterioration. Since this is most likely to be the consequence of hydrolytic or oxidative change requiring water and oxygen (air), respectively, these materials should be excluded as far as possible. Such changes are temperature dependent and oxidation can be promoted by light and by some metals. Oils and fats must therefore always be handled under appropriate conditions.

Extraction of oily fruits (palm, olive) involves pressing while extraction of seeds (kernels, beans) is achieved by pressing and/or solvent extraction with hexane or methylpentane – commonly called isohexane. After extraction of oil from seeds the residue is generally a protein-rich meal used as animal feed or as human food. This second component is an important part of the economics of oilseeds. Oil obtained by pressing is considered by some to be more natural and superior to solvent-extracted oil but most commodity vegetable oils, other than palm and olive oil, are solvent extracted. Animal fats are usually 'rendered' by heating with dry

 Oils and Fats in the Food Industry: Food Industry Briefing Series. Frank D. Gunstone.
 ISBN: 978-1-4051-7121-2

heat or steam. This is an important step in the economic, safe, and environmentally acceptable disposal of material remaining after the removal of butcher meat.

3.2 Refining

Crude oil is mainly a mixture of triacylglycerols along with the minor components detailed in Chapter 1, undesirable pigments, oxidation products, and metals. The purpose of the refining processes is to remove unwanted impurities while maintaining as far as possible the level of desirable minor components. Where these latter are removed it is often possible to trap them in a side stream and to recover them for alternative use. If the facilities for doing this are not to hand then the minor components may be added back to the meal, incorporated into animal feed, or used as fertiliser.

In Europe the term 'refining' is applied to the whole series of processes described here but in the USA it tends to be equated with removal of free acid (neutralisation).

- Degumming involves treatment with water or dilute acid (phosphoric or citric) producing a gum containing phospholipids (and trace metals) which can be separated with a centrifuge. The phospholipids are recovered as crude lecithin. Degumming is usually linked with extraction rather than with the subsequent refining processes. Phospholipids not easily removed by these degumming procedures are said to be 'non-hydratable' (NHP) and are mainly phosphatidic acids and lysophosphatidic acids present as calcium or magnesium salts. Other degumming procedures involve the use of ethylene diamine tetra-acetic acid for removal of trace metals or the use of appropriate enzymes. In the latter, appropriate lipases promote splitting of the phospholipids into forms that are more readily separated and removed.
- Neutralisation frequently requires treatment with aqueous alkali to remove free acids. Some oil is lost along with the soaps in a (large) water stream that has to be disposed of in an environmentally appropriate manner. Free acids are also removed during deodorisation by steam distillation (physical refining). This latter method is increasingly favoured because of its reduced environmental demand.

- Bleaching requires heating the oil at 80–180°C (but mainly at 90–120°C) with acid-activated bleaching earth. As the name implies the process was designed to remove colour (carotenes, chlorophyll) but trace metals are also removed along with soaps and residual phospholipids. However, under the acidic conditions free sterols may be dehydrated to steradienes and *cis* bonds in fatty acids may change to the *trans* form. Bleaching is the most expensive refining step because of the cost of obtaining the bleaching earth, of disposing of spent earth, and through loss of some oil. Polycyclic aromatic hydrocarbons (PAH) when present in the oil are not removed by bleaching. Volatile members are removed during deodorisation but the non-volatile PAH are removed by adsorption on activated carbon added to the bleaching earth.
- Deodorisation is the final refining step and requires the oil to be sparged with steam at 170–250°C under reduced pressure to remove oxidation products responsible for off-flavour. At higher temperatures (>220°C) there is isomerisation of *cis* to *trans* bonds so highly unsaturated oils should be deodorised at the lowest possible temperature. This applies especially to fish oils with their highly unsaturated long-chain PUFA which should not be heated above 180°C and to soybean and rapeseed oils which contain linolenic acid. Polyunsaturated fatty acids only retain their important nutritional properties if they remain in the all-*cis* forms. Deodoriser distillate is itself a valuable by-product that serves as a source of sterols and tocopherols.

The sequential processes of degumming, neutralisation, bleaching, and deodorisation are called chemical refining in distinction to the alternative of physical refining which requires only bleaching and deodorisation. The latter is a useful alternative mainly for oils (like palm oil) with low levels of phospholipids. The procedure is environmentally attractive because it avoids the large volume of waste water associated with neutralisation and financially attractive because there is less loss of oil. It is applied particularly to palm oil but is being used increasingly for other oils combined with improved degumming procedures.

The products of these processes are described as RBD (refined, bleached, and deodorised) oils. Specifications are defined by the Federation of Oils, Seeds and Fats Associations Ltd (FOSFA International) in Europe, by the USA-based National Institute of Oilseed

Products (NIOP), by the Palm Oil Refiners' Association of Malaysia (PORAM), and by the American Soybean Association (ASA). These internationally recognised standards cover a range of physical and chemical characteristics including free fatty acid content, iodine value, moisture and impurities, and colour.

3.3 Modification processes

The food processor has access to only a limited number of refined commodity oils and none of these may be ideal for purpose. As a consequence, procedures have been developed to modify the oils. Before describing these processes it is useful to consider in what ways the natural oils may be inadequate.

The ideal oil or fat should have physical, chemical, and nutritional properties appropriate for its end-use. However, these requirements are not always mutually compatible and compromises must be made. For example, the desired physical and chemical properties may only be achieved with some loss of nutritional quality. Typically, physical properties related to melting behaviour and crystalline form are important in a spread and to salad oils which should be free of solid. The most important chemical property is oxidative instability leading to the lower shelf life and resulting particularly from the presence of linolenic acid in unmodified soybean and rapeseed oils. Nutritional properties relate to the levels of saturated acids, to acids with *trans* unsaturation, and to the level and nature of the polyunsaturated fatty acids. These properties are detailed in Chapter 7.

Methods of modification may be technological or biological. Technological procedures include blending, fractionation, hydrogenation, and interesterification with chemical or enzymatic catalysts. Biological procedures include the agricultural development of new (minor) crops to make them more suitable for commercial growing and harvesting, seed breeding by conventional or newer procedures to produce oils with a more desirable fatty acid composition, and production of single cell oils rich in valuable polyunsaturated fatty acids not otherwise easily available.

In the four technological procedures listed above consideration has to be given to their effectiveness in achieving the desired physical, chemical, and nutritional properties and to their relative costs. Blending is the cheapest and hydrogenation is the most costly in

terms of both equipment and consumable costs for catalyst and hydrogen. Dry fractionation does not require additional materials and there is no yield loss but there has to be an economic use for all the fractions. Interesterification can be carried out with lower capital cost than fractionation but operating costs are higher because of yield loss. Enzymatic interesterification is more expensive because the cost of enzyme is still high. The conclusion is that costs rise through the sequence: blending, dry fractionation, chemical interesterification, hydrogenation.

Only the largest food producers will carry out these processes and many working in smaller units of this industry will purchase their refined and modified oils and fats from specialist suppliers. However, the food technologist needs to know the advantages and disadvantages of these processes so that the properties of the oils that are being used are fully understood.

In the technological procedures we accept what nature provides and seek to change fatty acid and/or triacylglycerol composition thereby modifying nutritional, chemical, and physical properties to make them more appropriate for their end-use. None of these methods is very new but they have been subject to incremental improvement based either on a better scientific understanding of the process or through the development of improved equipment. By contrast, in the biological procedures we interfere at an earlier stage and either seek new sources or we take plants which already produce large quantities of oil efficiently and try to modify the composition of the oils by conventional methods of seed breeding or by exploiting newer methods based on increasing genetic understanding.

3.4 Blending

The mixing of oils and fats to produce blends with improved nutritional or physical properties has a long history. Most spreads, for example, contain blends of two or more oils to achieve desirable nutritional and essential physical properties. Interesterification is usually carried out on oil blends. Oils are also blended to obtain the desired mix at minimum cost and computer programs to give the best solution have been developed. Mixtures of vegetable oils with appropriate fatty acid composition, sometimes with added components such as a GLA-oil or a fish oil, and effective antioxidants are now offered as ‘healthy oils’. A small proportion of an oil with high

oxidative stability (such as sesame oil or rice bran oil) may be added to a less stable commodity oil to enhance its stability. Frequently lauric oils are blended with non-lauric oils.

3.5 Fractionation including winterisation and dewaxing

Fractionation is a procedure by which an oil is divided into two or more fractions differing in fatty acid and triacylglycerol composition. This can be achieved without loss of material and without need for further refining. The two fractions extend the range of usage of the original oil. The procedure most commonly employed is described as dry fractionation. This requires slow cooling of a completely liquid oil without solvent followed by efficient separation of the solid (stearin) and liquid phases (olein) by suction or by pressure. Poor separation leaves olein in the stearin and results in less olein and in more stearin with higher iodine value than is desired for a stearin. This technique is used mainly for palm oil but has other applications also (Section 2.6). It is not always easy to predict what happens to minor components and impurities during fractionation and this may have unforeseen consequences for oxidative stability.

Winterisation is the name given to a simple form of fractionation. Originally this consisted of storing an oil such as cottonseed in tanks during the winter. The more saturated triacylglycerols crystallised leaving a more unsaturated liquid fraction less likely to crystallise when stored in the domestic refrigerator.

Some solvent-extracted oils like sunflower may contain wax which makes the oil cloudy during storage, especially at sub-ambient temperatures. Such oils may be dewaxed by storage at appropriate temperatures and subsequent filtration before release for sale in order to overcome this trait.

The composition of some fractionated oils is given in Table 2.5.

3.6 Hydrogenation

Some aspects of this topic are discussed in Section 6.1 and the com-position of some partially hydrogenated oils is given in Table 2.5. Hydrogenation can be conducted at three different levels. Very light

hydrogenation (known as brush hydrogenation) is applied to oils containing linolenic acid (soybean oil and rapeseed oil) to reduce the level of this triene acid to about one half its normal value thereby extending the shelf life of foods containing these oils. At the other extreme, oils are virtually completely hydrogenated to iodine values below 2. Of greater importance is partial hydrogenation applied to soybean and other linoleic-rich oils to raise the content of solid triacylglycerols. This is achieved through formation of saturated acids and of *trans* unsaturated acids.

Partial hydrogenation of an unsaturated oil gives a product of higher melting point (more suitable for spreads and cooking fats) and of enhanced oxidative stability through having less polyunsaturated fatty acid. These benefits are only achieved at some nutritional cost. The level of essential fatty acid (PUFA) is lowered and acids with *trans* configuration are produced. These modifications follow the molecular changes resulting from partial hydrogenation including saturation of some unsaturated centres, stereomutation of unsaturated centres (conversion of *cis* to *trans* isomers), double bond migration, and conversion of linoleate mainly to *trans* 18:1 isomers.

$$18{:}3 \rightarrow 18{:}2 \rightarrow 18{:}1 \text{ (}cis\text{ and }trans\text{ isomers)} \rightarrow 18{:}0$$

3.7 Interesterification using a chemical catalyst

Interesterification is a procedure for rearranging the fatty acids in an oil or in a blend of oils so that triacylglycerol composition is changed. The fatty acid composition of the single oil or the blend remains unchanged. Usually the blend will contain two or more oils differing in chain length and/or in patterns of unsaturation. With an alkaline catalyst, such as NaOH or NaOMe, fatty acids are randomly distributed in the product in contrast to the natural vegetable oils that are produced by enzymatically catalysed biological processes and where the fatty acids are not randomly distributed. These changes in triacylglycerol composition affect thermal behaviour and may also affect bio-availability by reason of what fatty acids are in the *sn*-2 position. There is some loss of oil through conversion to acid (with NaOH) or ester (with NaOMe).

This procedure is being used to produce fats suitable for use as spreads without hydrogenation. A soft (polyunsaturated) oil is blended

with hardstock and the mixture is interesterified. The hardstock is either a suitable palm stearin or a fully hydrogenated oil. Unfortunately with the latter mixture it will probably require the term 'hydrogenated' on the label. Even though the fully hydrogenated oil will contain virtually no *trans* acids the process itself is now considered undesirable – mainly on the basis of perception rather than science.

3.8 Interesterification using an enzymatic catalyst

Interesterification can also be carried out with lipases. The enzymatic processes have advantages over the chemical process in that they occur under milder conditions, may require less costly equipment, and produce less by-product so that there is less waste and less effort is required to purify the product. However, the major benefit of using a lipase is the added control over the nature of the product as a consequence of the specificity shown by many lipases. Lipases with specificity relating to fatty acid chain length or double bond position in the acyl chain can be used to confine changes to a particular group of acids while other lipases are specific for glycerol esters (mono-, di-, or tri-acylglycerols) or distinguish between fatty acids attached to the differing the different hydroxyl groups in glycerol. Many lipases are described as being 1,3-specific implying that changes can be made at glycerol positions 1 and 3 but not at position 2 where the ester group remains unchanged. Though lipase preparations are becoming more stable and less expensive the cost of enzyme-catalysed processes is still a major disadvantage. However, the enzymatic reactions are perceived as the more natural and therefore attractive to the 'green' lobby. Compounds attracting a lot of interest are of the type MLM where M represents a short-chain acid (frequently C_8) which is easily metabolised and where L represents a long-chain acid such as eicosapentaenoic acid (EPA) or docosahexaenoic acid (DHA). These important acids attached to the 2-position are thereby made bio-available.

With either chemical or enzymatic catalysts interesterified products are generally less stable than the original oils probably through changes – not yet fully understood – in the balance of pro- and anti-oxidants. There is a perception in some quarters that the enzymatic reaction is superior because it is 'more natural' and avoids the use of 'chemicals'.

3.9 Domestication of wild crops

The oil and fat business is based almost entirely on a limited number of commodity oils differing in fatty acid composition but there are many other plant species with fatty acid composition not very different from the commodity oils. These could be used as food lipids but there would have to be a special reason for developing them through the long chain of events from agronomical improvements to retail marketing. A few of these minor oils were discussed in Chapter 2. There are also plants producing uncommon acids such as epoxy acids, acids with conjugated unsaturation, or oils with a very high level (>80%) of a single acid. Attempts to domesticate and commercialise such plants and their seed oils take a long time to develop with some niche products of this kind taking 20 and more years to bring to market. Most, but not all, of these oils are of interest to the oleochemical rather than the food industry.

3.10 Oilseeds modified by conventional seed breeding or by genetic engineering

Because of the difficulties in domesticating wild plants greater effort has been directed to the modifying of plants that are already grown and harvested on a commercial scale and where good agronomic procedures are already well developed. This has the disadvantage of minimising the range of important plant species thereby limiting biodiversity. The changes to be sought are partly agronomic such as reduced use of herbicide and pesticide but they include changes in fatty acid composition, triacylglycerol composition, and in levels of minor components. These changes must be achieved without sacrifice of yield and must be biologically stable from season to season. They have to be accompanied by procedures of identity preservation. The modified seed must be kept separate at all times from its more conventional form. This has consequences for harvesting, transporting, and extracting the seed and for the subsequent handling of the oil. Such changes may be brought about by conventional seed breeding or by newer procedures of genetic engineering. It is important to know which method has been used because of the concerns expressed by some communities about

procedures involving transgenic modification. This objection is adding to costs and is becoming harder to justify being based more on perception than on science. Oilseeds from a known source and kept distinct from seeds produced and handled in a different way are said to be 'identity preserved' (IP).

Changes of fatty acid composition which have been sought include: reduced levels of saturated acids for nutritional reasons, reduced levels of linolenic acid and/or higher levels of saturated acids to avoid hydrogenation (with consequent production of undesirable *trans* acids), and higher levels of oleic acid (see Table 2.5). One important and exciting possibility is to develop plant systems that will produce long-chain polyunsaturated fatty acids such as arachidonic acid (20:4), EPA (20:5), and DHA (22:6). There have been interesting developments in a number of research laboratories but such plants will probably be genetically modified and are 10–20 years from commercial development.

In view of the high demand for oils and fats at this time for food and non-food purposes it is important to increase supplies. This may be achieved by seed breeding to give higher yields, by developing seeds, which are more drought-resistant and will so give better yields under adverse conditions, and seeds, which will grow under harsher conditions of climate (lower temperatures or shorter growing season) or of soil (high salinity). The last could also be irrigated with poorer quality water.

3.11 Animal fats modified through nutritional changes

From a nutritional viewpoint land animal depot fats are perceived as having several disadvantages. They are generally rich in serum cholesterol-raising saturated acids such as myristic and palmitic, they often contain acids with *trans* unsaturation, and they have high levels of cholesterol. Also their level of essential fatty acids is low and they contain little if any antioxidant. Further, animal fats are not acceptable to vegetarians and to some ethnic groups. Nevertheless animal fats contain low levels of long-chain PUFA and are a valuable source of such acids in the human diet especially for those who consume little or no fish.

Some of the perceived disadvantages in ruminant animals are the consequence of biohydrogenation processes taking place within the rumen and dietary regimes have been proposed to circumvent these changes. There is also an interest in modifying the fatty acid composition of chicken eggs and meat by appropriate changes to the diet of the chicken. This has been seen as a way of enhancing the (human) dietary intake of conjugated linoleic acid (CLA) and of EPA and DHA (long-chain omega-3 acids). Care has to be taken that these changes in fatty acid composition do not reduce the shelf life of the products and that they do not lead to unexpected flavours and odours when cooked.