20.1 Introduction

Fats and oils are water-insoluble compounds consisting of mainly triacylglycerols: three fatty acids esterified to a glycerol molecule. Products are generally called “fats” when they are solid at room temperature and “oils” when they are liquid at room temperature, although the terms are often used interchangeably. Edible fats and oils contribute to the flavor, texture, aroma, and mouthfeel of foods, while providing nutritive value. Their origin may be animal, plant, or marine.

Plant-based fats and oils are obtained from oilseeds and oil-bearing trees. While used mainly for human consumption, they also find use in animal feed, biodiesel, and industrial applications. They are integral components in a wide range of products such as margarines, shortenings, dressings, confectionery products, baked goods, snack foods, infant formulas, and non-dairy creamers.

20.2 Sources, composition, and uses of plant-based fats and oils

Oils may be obtained from hundreds of plant sources. While some are produced on a large scale and internationally traded as commodities, most are considered minor oils and find specialized use. Recent global production data for the most widely produced commodity plant oils are summarized in Table 20.1. The four predominant oils are palm, soybean, rapeseed/canola, and sunflower seed, in decreasing order of production. Within the last decade, palm has overtaken soybean as the top commodity plant oil. Total production of commodity plant oils has steadily increased over time, and further increases in production are projected (FAS, 2011).

The sources and typical fatty acid composition of selected oils are provided in Table 20.2. In general, three fatty acids dominate: palmitic (C16:0), oleic (C18:1), and linoleic (C18:2n-6). Exceptions are noted in the discussion of individual oils, below.

20.2.1 Major oils

Palm oil is produced from the fruit of the oil palm which is grown in tropical climates, mainly in Malaysia and Indonesia. It is the most widely produced plant oil and tends to be less costly than other commodity oils (Gunstone, 2008b). The crude oil is rich in antioxidants, especially carotenoids. Although most of the carotenoid content is destroyed during the refining process, a red palm oil variety is produced by reducing the distillation temperature and used as a natural colorant (O’Brien, 2004c), cooking oil, or dietary supplement. Palm oil has a high oxidative stability due to its high level of natural antioxidants and its high saturated fatty acid content. It is often fractionated to extend its range of use. Palm oil and its fractions are used in spreads, shortenings, and frying applications.

Soybean oil is produced at the highest level of the oilseeds. A high-protein meal is produced as a valuable co-product. The oil has a relatively low oxidative stability due to its high content of linolenic acid (C18:3) and is often subjected to hydrogenation after refining to improve its oxidative stability. Soybean oil is used in a wide range of products, such as margarine, shortening, salad dressing, mayonnaise, and snack foods. Soybean oil is the most commonly consumed oil in the US.

Traditional rapeseed oil is naturally high in erucic acid (C22:1). Due to health concerns, a low-erucic, low-glucosinolate variety was developed in Canada, known today as canola oil or LEAR (low erucic acid rapeseed).
In the US, canola oil received Generally Recognized As Safe (GRAS) status in 1985, although its use is not permitted in infant formulas. Canola is viewed as a “healthy” oil, as it contains the lowest level of saturated fatty acids of the commodity oils (Gunstone, 2008b), it is a good source of vitamin E due to its high \( \alpha \)-tocopherol content, and it has a favorable ratio of omega-6 to omega-3 fatty acids. Canola oil is unique in that it contains a relatively high level of brassicasterol, a phytosterol not found at a significant level in other oilseeds (Gunstone, 2006c). Canola oil is used for cooking and is often a component in salad dressing, mayonnaise, margarine, and shortening.

Traditional sunflower oil contains a high level of linoleic acid (C18:2n-6). Various modification techniques have been used to increase oxidative stability (see section 20.9 for further discussion). High-oleic and mid-oleic varieties were introduced on a commercial scale in the 1980s and 1990s, respectively (Gupta, 2002). The mid-oleic variety (NuSun\(^\text{®} \); National Sunflower Association, Mandan, ND) is lower in saturated fat content than traditional sunflower oil and has become the most highly produced variety in the US. With a high level of \( \alpha \)-tocopherol, sunflower oil is a rich source of vitamin E. Crude sunflower oil contains natural waxes, which may cloud the appearance of the oil during storage, and is typically subjected to a dewaxing procedure.

### 20.2.2 Lauric oils

Palm kernel oil and coconut oil are obtained from the oil palm and the coconut palm, respectively. Whereas palm oil is derived from the fruit of the oil palm, palm kernel oil is extracted from the kernel. Palm kernel and coconut oils are classified as lauric oils due to their high levels of lauric acid (C12:0) (see Table 20.2). This is unique, as no other commodity plant oil contains more than 1% lauric acid (Pantzaris & Basiron, 2002). Unlike other commodity oils, the lauric oils (particularly coconut oil) contain mainly saturated fatty acids, making them highly resistant to oxidation. Common food applications of the lauric oils include spreads, candies, and non-dairy creamers.

Lauric oils possess melting behavior similar to that of cocoa butter (Pantzaris & Basiron, 2002) – a sharp curve near body temperature – making them suitable for use as cocoa butter alternatives. There are three main types of cocoa butter alternatives, which impart similar snap and gloss to confectionery products and are utilized mainly for economic reasons.

- **Cocoa butter equivalents** (CBE) are typically made from non-hydrogenated fats with similar triacylglycerol composition to that of cocoa butter (e.g. fractionated palm oil). Like chocolate, tempering of CBE is required to obtain the desired crystallization behavior. CBE are often incorporated in products containing cocoa butter.
- **Cocoa butter replacers** (CBR) are typically made from hydrogenated, fractionated oils (e.g. cottonseed and soybean). No tempering is required. CBR may be incorporated in products containing cocoa butter, but in a lower proportion versus CBE.
- **Cocoa butter substitutes** (CBS) are mainly produced from hydrogenated palm kernel fractions and hydrogenated coconut oil. Like CBR, no tempering is required. CBS are not used in conjunction with cocoa butter due to their differences in triacylglycerol composition.

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut</td>
<td>3.22</td>
<td>3.53</td>
<td>3.53</td>
<td>3.62</td>
<td>3.68</td>
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<tr>
<td>Cottonseed</td>
<td>5.13</td>
<td>5.22</td>
<td>4.78</td>
<td>4.65</td>
<td>4.98</td>
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<tr>
<td>Olive</td>
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<td>2.78</td>
<td>2.78</td>
<td>3.05</td>
<td>3.01</td>
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<tr>
<td>Palm</td>
<td>37.33</td>
<td>41.08</td>
<td>43.99</td>
<td>45.86</td>
<td>47.97</td>
</tr>
<tr>
<td>Palm Kernel</td>
<td>4.44</td>
<td>4.88</td>
<td>5.17</td>
<td>5.50</td>
<td>5.65</td>
</tr>
<tr>
<td>Peanut</td>
<td>4.53</td>
<td>4.91</td>
<td>5.00</td>
<td>4.67</td>
<td>4.98</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>17.13</td>
<td>18.43</td>
<td>20.49</td>
<td>22.35</td>
<td>22.65</td>
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<tr>
<td>Soybean</td>
<td>36.45</td>
<td>37.72</td>
<td>35.74</td>
<td>38.76</td>
<td>42.13</td>
</tr>
<tr>
<td>Sunflower</td>
<td>10.70</td>
<td>10.03</td>
<td>11.99</td>
<td>11.63</td>
<td>11.33</td>
</tr>
<tr>
<td>Total</td>
<td>121.75</td>
<td>128.57</td>
<td>133.48</td>
<td>140.08</td>
<td>146.37</td>
</tr>
</tbody>
</table>

\(^*\)Preliminary data.

\(^†\)Forecast data.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Source</th>
<th>Fatty acid composition (% total fatty acids)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut</td>
<td>Cocos nucifera L.</td>
<td>&lt;C12:0 45.1-53.2 C12:0 5.0-10.0 C18:1 1.0-2.5 C18:2n-6 0.2-0.4 C20:0 ND-0.2 C20:1 ND-0.2 C22:0 ND ND</td>
</tr>
<tr>
<td>Cottonseed</td>
<td>Gossypium sp.</td>
<td>ND ND</td>
</tr>
<tr>
<td>Corn</td>
<td>Zea mays L.</td>
<td>ND-0.2 0.6-1.0 21.4-26.4 ND-1.2 2.1-3.3 14.7-21.7 46.7-58.2 ND-0.4 0.2-0.5 ND-0.1 ND-0.6 ND-0.3 ND-0.1</td>
</tr>
<tr>
<td>Olive</td>
<td>Olea europaea L.</td>
<td>ND ND 0.0-0.05 7.5-20.0 0.3-3.5 0.5-5.0 55.0-83.0 3.5-21.0 ND 0.0-0.6 0.0-0.4 0.0-0.2 ND 0.0-0.2</td>
</tr>
<tr>
<td>Palm</td>
<td>Elaeis guineensis</td>
<td>ND ND 0.5-2.0 39.3-47.5 ND-0.6 3.5-6.0 36.0-44.0 9.0-12.0 ND-0.5 ND-1.0 ND-0.4 ND-0.2 ND ND</td>
</tr>
<tr>
<td>Palm kernel</td>
<td>Elaeis guineensis</td>
<td>5.0-12.0 45.0-55.0 14.0-18.0 6.5-10.0 ND-0.2 1.0-3.0 12.0-19.0 1.0-3.5 ND-0.2 ND-0.2 ND-0.2 ND-0.2 ND ND</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>Brassica sp.</td>
<td>ND ND ND-0.2 1.5-6.0 ND-0.3 0.5-3.1 8.0-60.0 11.0-23.0 5.0-13.0 ND-3.0 30.15.0 ND-2.0 &gt;2.0-60.0 ND-2.0</td>
</tr>
<tr>
<td>Rapeseed, low</td>
<td>Brassica sp.</td>
<td>ND ND ND-0.2 2.5-7.0 ND-0.6 0.8-3.0 51.0-70.0 15.0-30.0 5.0-14.0 0.2-1.2 0.1-4.3 ND-0.6 ND-2.0 ND-0.3</td>
</tr>
<tr>
<td>Oleic acid (canola)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sesame</td>
<td>Sesamum indicum L.</td>
<td>ND ND ND-0.1 7.9-12.0 ND-0.2 4.5-6.7 34.4-45.5 36.9-47.9 0.2-1.0 0.3-0.7 ND-0.3 ND-1.1 ND ND-0.3</td>
</tr>
<tr>
<td>Soybean</td>
<td>Glycine max L.</td>
<td>ND ND ND-0.2 8.0-13.5 ND-0.2 2.0-5.4 17.30 48.0-59.0 4.5-11.0 0.1-0.6 ND-0.5 ND-0.7 ND-0.3 ND-0.5</td>
</tr>
<tr>
<td>Sunflower</td>
<td>Helianthus annuus L.</td>
<td>ND ND ND-0.2 5.0-7.6 ND-0.3 2.7-6.5 14.0-39.4 48.3-74.0 ND-0.3 0.1-0.5 ND-0.3 0.3-1.5 ND-0.3 ND-0.5</td>
</tr>
<tr>
<td>Sunflower, mid-oleic</td>
<td>Helianthus annuus L.</td>
<td>ND ND ND-0.1 4.0-5.5 ND-0.05 2.1-5.0 43.1-71.8 18.7-45.3 ND-0.5 0.2-0.4 0.2-0.3 0.6-1.1 ND 0.3-0.4</td>
</tr>
</tbody>
</table>

ND, non-detectable (≤0.05%).
Source: Codex Alimentarius (FAO, 2009a, 2009b).
20.3 Properties of plant-based fats and oils

The properties of fats and oils are highly dependent on their fatty acid and triacylglycerol make-up. In addition to the length of the carbon chain and degree of saturation in a particular fatty acid, the position of fatty acids on the glycerol molecule affects the physiochemical properties and functional characteristics of the fat or oil. While fatty acid composition varies widely between oil sources, some variability exists within species based on factors such as climate, soil quality, growing season, and plant maturity.

20.3.1 Physiochemical properties

Physical properties of fats and oils include melting point, boiling point, smoke point, density, solid fat index, viscosity, refractive index, and color. Melting point is a function of many variables: in particular, melting point increases with increasing fatty acid chain length, complexity of triacylglycerol components, degree of saturation, and content of trans fatty acids. Since they are composed of mixtures of triacylglycerols, fats possess a melting range rather than a true melting point; thus, the term “melting point” refers to the end of the melting range.

Solid fat index is a measure of the solid content of a fat at various temperatures, which is an important predictor of melting and crystallization behavior. The solid content of a fat influences its plastic range, the temperature range over which the fat is moldable. Plastic fats possess properties of both solids and liquids, as the liquid portion is trapped in the solid crystalline network (Hidalgo & Zamora, 2006). Various processing procedures are applied to fats to extend their plastic range, leading to a wider range of use in food applications.

Chemical properties include iodine value, saponification value, peroxide value, and acid value. Iodine value is a measure of the average degree of unsaturation of a fat and is a predictor of its oxidative stability. Saponification value measures the average chain length of fatty acids in a fat. Peroxide value and acid value measure peroxides and free fatty acids present in fat/oil, respectively. Standard methods for determination of physicochemical properties of fats and oils are available (Firestone, 2009; Horwitz & Lattimer, 2005).

20.3.2 Crystallization behavior

Fats are polymorphic: that is, they possess the ability to crystallize in multiple forms. The consistency of the fat is highly dependent upon the form of crystallization.
20.4 Nutritional areas of interest

Fats and oils are a fundamental component of the human diet. They have more caloric value than proteins and carbohydrates, making them a good energy source. They contain essential fatty acids, which are not synthesized by the human body and must be obtained from food sources. They serve to carry the fat-soluble vitamins A, D, E, and K as well as an array of phytonutrients.

20.4.1 Saturated and trans fatty acids

Diet high in total fat content, particularly saturated fat content, are thought to contribute to obesity (Bray & Popkin, 1998). Excess consumption of saturated and trans fatty acids has been linked to coronary heart disease (Hu et al., 2001), the leading cause of death in the US. In particular, high intake of trans fatty acids is associated with an increase in low-density lipoprotein (LDL) levels and a corresponding decrease in high-density lipoprotein (HDL) levels. Trans fatty acids originate from three sources. They are naturally present in lipids obtained from ruminants as a result of biohydrogenation in the rumen. Additionally, they are formed as a result of heating (specifically deodorization) and the industrial process of partial hydrogenation, in baked goods and fried foods. Trans fatty acids are chemically induced through hydrogenation to produce margarines and shortenings.

In response to concern over the role of trans fats in heart disease, the Food and Drug Administration (FDA) issued a final rule in 2003 that trans fat content must be declared on the nutrition facts label (FDA, 2003). Compliance with this rule became mandatory in January 2006, prompting many manufacturers to reformulate products to reduce the levels of trans fatty acids. The US Department of Agriculture (USDA) recommends minimal intake of solid and trans fats, and replacement of saturated fatty acids with mono- and polyunsaturated fats (USDA, 2010).

20.4.2 Omega-3 and omega-6 fatty acids

The essential fatty acids linoleic acid (C18:2n-6) and α-linolenic acid (C18:3n-3) are precursors of long-chain omega-6 and omega-3 polyunsaturated fatty acids, respectively. Seed oils (e.g. walnut, soybean, rapeseed/canola, and flaxseed) are rich sources of α-linolenic acid, which is linked to decreased risk of cardiovascular disease (Zhao et al., 2004). Linoleic acid is found in all plant-based oils, including soybean and rapeseed/canola. However, linoleic acid is less abundant now than in past years, as processing and seed breeding practices have been employed to reduce the level of this fatty acid in order to obtain oils with greater oxidative stability. Some processing techniques affect the level of essential fatty acids in vegetable oils; in particular, hydrogenation decreases the content of essential fatty acids by converting them to saturated and trans fatty acids.

The omega-3 long-chain polyunsaturated fatty acids DHA and EPA are found mainly in (sea) animal sources. They play a role in the secondary prevention of cardiovascular disease, brain development, and reduction of inflammation (Hu & Willett, 2002; Ruxton et al., 2004). A standard recommended daily intake of omega-3 fatty acids has not been established, but it is generally recognized that the US intake is too low (Kris-Etherton et al., 2000). The American Heart Association recommends consumption of two servings of fatty fish per week (AHA, 2011). Often, dietary restrictions (or simply preferences) preclude consumption of fish. Plant-based sources for supplementation of omega-3 fatty acids include flaxseed oil and algal oil. Additionally, products containing plant-based oils are increasingly being fortified with long-chain omega-3 fatty acids; margarines, spreads, and salad oils are good vehicles for their delivery (Muggli, 2006).
Many researchers believe that the ratio of omega-6 to omega-3 fatty acids consumed is much too high, particularly in Western diets (Lands, 1986; Simopoulos, 2008). Soybean and rapeseed/canola oils naturally have a favorable ratio of linoleic acid to α-linolenic acid. However, the balance is upset by processing techniques such as partial hydrogenation. Food manufacturers increasingly consider the omega-6/omega-3 ratio when reformulating products (Hernandez, 2005).

### 20.5 Degradation of plant-based fats and oils

Crude oils are highly susceptible to degradation via lipolysis and oxidation. Lipolysis, the hydrolysis of free fatty acids from the glycerol molecule, decreases the stability of the oil (Frega et al., 1999; Miyashita & Takagi, 1986). Lipolysis may be catalyzed by enzymes, particularly from microbial sources, or water and heat. Oxidation occurs in the presence of atmospheric oxygen and yields low molecular weight compounds responsible for development of off-flavors and odors. Care must be taken to protect oils from these reactions during refining, modification, and storage.

Plant-based fats and oils are subject to both autoxidation and photo-oxidation. Both mechanisms are selective, acting at points of unsaturation. Thus, susceptibility of fats and oils to oxidation increases as degree of saturation decreases. Oxidation may be promoted by environmental factors (e.g. temperature, light) or components naturally present in the crude oil, such as free fatty acids and trace metals. Both pathways are summarized below; a detailed review is available (Choe & Min, 2006).

#### 20.5.1 Autoxidation

The autoxidation mechanism is a three-step process (Figure 20.1). The initiation step involves formation of an alkyl radical. In the propagation step, alkyl radicals react with atmospheric oxygen to form peroxyl radicals, which in turn react with additional fatty acids to form hydroperoxides and new alkyl radicals. The process continues until the termination step ensues; all free radicals have combined to form new compounds. Oxidation proceeds slowly during the induction period but proceeds rapidly once the supply of antioxidants has been exhausted. Efforts are focused on extending the induction period, which corresponds to the shelf life of the product (Gunstone & Martini, 2010).

- **Initiation**
  \[ RH \rightarrow R^\cdot + H^\cdot \]

- **Propagation**
  \[ R^\cdot + O_2 \rightarrow ROO^\cdot \]
  \[ ROO^\cdot + RH \rightarrow ROOH + R^\cdot \]

- **Termination**
  \[ R^\cdot + R^\cdot \rightarrow RR \]
  \[ R^\cdot + ROO^\cdot \rightarrow ROOR \]
  \[ ROO^\cdot + ROO^\cdot \rightarrow ROOR + O_2 \]

**Figure 20.1** Mechanism of lipid autoxidation.

Primary oxidation products are hydroperoxides and conjugated dienes. These decompose to form secondary oxidation products, low molecular weight compounds including aldehydes, ketones, and alcohols. Secondary oxidation products reduce the sensory quality of the oil by causing off-odors and off-flavors that are collectively known as oxidative rancidity. These flavors and aromas are detectable at low levels. Repeated consumption of oxidized lipids is reported to be detrimental to human health (Kanner, 2007).

Natural antioxidants (e.g. tocopherols, tocotrienols) are present at varying levels in fats and oils and act as free radical scavengers. They are partially removed as a result of the harsh reaction conditions that occur during processing, but are often added to the finished oils. Synthetic antioxidants that are approved food additives in the US include butylated hydroxytoluene, butylated hydroxyanisole, tertiary butylhydroquinone, and propyl gallate; when two are used in combination, a synergistic relationship ensues. The use of synthetic antioxidants in US food products is regulated by the FDA and is permissible at a combined level of no more than 200 ppm of the total fat content. Citric acid, added after the refining process to chelate trace metals, acts as an antioxidant synergist.

#### 20.5.2 Photo-oxidation

Photo-oxidation occurs when light energy in the form of a photon is transferred to a sensitizer (e.g. chlorophyll), which serves to activate oxygen. The resulting singlet oxygen is highly reactive, readily forming peroxides and...
free radicals from points of unsaturation in fatty acids. Photo-oxidation occurs at a much faster rate than autoxidation. The photo-oxidation pathway is terminated by singlet oxygen quenchers (e.g. β-carotene) rather than free radical scavengers.

20.6 General handling considerations

Degradation of edible fats and oils cannot be stopped, but can be slowed by taking certain precautions during processing and storage. Where appropriate, care should be taken to avoid:

- **contamination**: equipment surfaces should be cleaned and sanitized regularly to eliminate spoilage microorganisms and other adulterants, and to avoid build-up of oxidation products
- **oxygen**: some processing steps require an inert atmosphere and may be conducted under vacuum or nitrogen blanket
- **trace metals**: trace metals (e.g. copper) act as pro-oxidants, and their levels may be minimized by the use of stainless steel equipment during processing
- **light, heat, and water**: because light and heat promote reactions that lead to oxidative rancidity (or, in the case of water, hydrolytic rancidity), oils should be stored in a cool, dry, dark location.

20.7 Recovery of oils from their source materials

20.7.1 Preparation of oilseeds for extraction

Figure 20.2 illustrates the general process for extraction of oil from oilseeds. Seeds are pretreated prior to extraction in a series of steps designed to maximize the oil obtained during the extraction process. After harvesting, seeds are cleaned to remove foreign materials, including sticks, leaves, dirt, and stones. Magnets are used to remove traces of metal. Various grades of screens are utilized, with or without aspiration, in succession from coarse to fine in order to remove materials from the oilseeds. When screens are used in conjunction with aspiration, the process is called “scraping” (Kemper, 2005). A further delinting step is necessary for cottonseeds (Anderson, 2005; O’Brien, 2004a). Material that will be stored before processing is dried to approximately 5–10% moisture content, depending on the oilseed variety. Cool, dry conditions are critical for extended storage, as excessive moisture and heat may lead to degradation (Hernandez, 2005; Wakelyn & Wan, 2006).

A dehulling or decortication step is done for many oilseeds in order to separate the meat from the hull and/or seed coat, thereby increasing the effectiveness of future processing operations. This step is eliminated for smaller seeds (e.g. safflower) because their size precludes effective separation (O’Brien, 2004a). In some cases, seeds are cracked prior to dehulling to facilitate removal of the hull. Next, seeds are subjected to one or more size reduction processes (e.g. cracking, crushing, grinding) to increase surface area and promote the release of oil from the cells.

Seeds generally undergo a conditioning step after size reduction. Seeds are heated to 90–110 °C or 110–150 °C, depending on whether they will be pre-pressed prior to solvent extraction or full pressed, respectively (Kemper, 2005). Addition of steam may be necessary to achieve the optimal moisture level for oil extraction, which varies by seed type (Fellows, 2009). Conditioning serves to denature proteins, deactivate enzymes, inhibit microbial activity, and increase oil yield by facilitating later processing steps. In the case of cottonseed, conditioning destroys gossypol, a mildly toxic pigment.

A flaking step is done for oilseeds. The seeds pass through cylindrical rollers, which rotate in opposite directions, and are flattened to approximately 0.3–0.4 mm thickness. Conditioning of the seeds prior to flaking makes them pliable and facilitates rolling. It is important to achieve flakes of uniform thickness in order to achieve maximum oil yield during solvent extraction (Kemper, 2005). Flakes (especially soybean and cottonseed) may be sent to an expander, a type of extruder that heats and shapes the flakes using steam injection under high pressure. The product is released from the expander in the form of a dense, porous pellet (also known as a collet) that expands upon contacting the air, rupturing the oil cells. Use of an expander leads to a significant increase in extraction yield compared to extraction directly from flakes (Hernandez, 2005). Dry extrusion, which utilizes friction to heat the product, is often used in small-scale facilities to enhance oil yield for seeds that are to be full pressed (Kemper, 2005).

20.7.2 Preparation of tree fruits for extraction

Due to their high moisture content, tree fruits are subject to enzymatic hydrolysis (Gunstone, 2004) and oil must be extracted within hours (e.g. palm fruits) or days (e.g. olives) of processing. Special care must be taken when
handling palm fruits so as not to damage the kernels, which are further processed for their oil. Palm fruits are sterilized immediately after harvesting by application of steam at approximately 120 °C under pressure. This process inactivates lipases and stops bacterial activity in the fruit, while preconditioning the kernels (Fils, 2000). After sterilization, the fruits are mechanically stripped from their bunches, then heated under agitation in a digester, which aids in separation of the fruit from the kernel. Olives are washed, crushed to form a paste, and mixed to allow some coalescence of the droplets. Coconuts are shelled, cracked, and dried prior to pressing.
20.7.3 Extraction

The goal of extraction is to recover the maximum amount of crude oil of highest purity, while producing a high-value co-product. The co-product consists of solids (usually protein-rich) and residual oil and may be ground into a meal or flour for use in such applications as animal feeds and industrial products. In some cases, the co-product is used as an energy source for refining operations.

There are three main types of extraction processes: mechanical pressing, pre-press solvent extraction, and direct solvent extraction. Oil-bearing fruits are pressed to extract oils. For oilseeds, the extraction procedure is selected based on variables such as oil content of the starting material, size of the extraction facility, and desired specifications for the resulting meal. Throughout the extraction process, it is critical to control moisture and temperature in order to avoid damage to the oil while achieving maximum yield.

20.7.3.1 Pressing

Pressing entails the use of mechanical force to squeeze oil from the solids. The process yields crude oil and a solid “cake” containing approximately 5–10% oil. Pressing may be either a batch or continuous process. Since pressing generates lower yields and sample throughput than solvent extraction, it is not widely used for oilseeds. However, it is still routinely used in small processing facilities and by processors of specialty and/or “natural” oils whose products are often sold at a premium price in health food markets.

Hydraulic batch presses process one group of fruit or seeds at a time, but some models have the capability to process many batches per day. For some processors, hydraulic pressing is an economical alternative to solvent extraction, as capital and operating costs are lower. Olive oil may be separated from its paste by hydraulic pressing or by a combination of centrifugation and filtration (O’Brien, 2004a). Virgin olive oil results from pressing without chemical treatment; it has a lengthy shelf life and is highly stable during frying (Boskou, 2002).

Continuous screw presses (“expellers”) are motorized pieces of equipment that consist of a barrel containing a water-jacketed horizontal screw. The pressure resulting from the rotation of the screw removes the oil from the seed. Heat generated by friction increases oil yield by decreasing its viscosity (Fellows, 2009). The water jacket serves to cool the screw so that the optimal extraction temperature may be maintained. Expeller pressing is suitable for processing both fatty fruits (e.g. palm, avocado) and seeds with high oil content that have been prefekled (e.g. cottonseed, soybean). When pressing palm fruits in this manner, care should be taken to minimize crushing the kernels, which leads to admixture of oils from the fruits and kernels (Fils, 2000).

Cold pressing refers to mechanical pressing that is done without application of heat; the oil temperature typically does not exceed 27 °C. Cold-pressed oils retain more nutrients and flavor compounds than their hot-pressed counterparts. Oils that are commonly cold pressed include olive, flaxseed, and avocado. Cold-pressed oils may simply be filtered without further refining; these products tend to be relatively expensive and appeal to consumers who value “natural” oils that are produced without the use of heat and chemicals.

20.7.3.2 Pre-press solvent extraction

Pre-press solvent extraction may be chosen when the oil content of the product is greater than 30%. The pressure of the expeller is reduced in order to leave a portion of oil in the cake (usually 15–18%) (Johnson, 2008; O’Brien, 2004a), which is then removed via solvent extraction. As a result, less solvent is needed and a smaller extractor may be used, decreasing capital costs. For some seeds with high oil content, use of an expander makes it possible to bypass the pre-press step (Johnson, 2000).

20.7.3.3 Direct solvent extraction

Direct solvent extraction is the most commonly used method of oil recovery. Additionally, it is the most efficient recovery method, removing all but approximately 1% of oil from the starting material. There are two main methods of solvent extraction: immersion of the starting material in solvent or percolation of the solvent through the material (Johnson, 2000; Wang, 2002).

Semi-continuous processes utilize multiple batch extractors connected in series. Continuous processes involve constant movement of flakes through an extractor. There are a number of extractor designs, which vary based on the depth of the bed of solids and the direction of the flow (e.g. horizontal, vertical, rotary). Many designs utilize countercurrent flow to minimize the amount of solvent needed; flakes and solvent move through the extractor in opposite directions such that flakes entering the extractor contact the oldest solvent and the freshest solvent is...
used when extraction is nearly complete. Continuous processes are most widely used, although batch processes are commonly used in production of specialty oils.

The solvent of choice is typically commercial hexane, consisting of a mixture of n-hexane and its isomers. Due to its flammability and toxicity, the use of n-hexane is a concern; its emissions from US solvent extraction facilities are regulated by the EPA Clean Air Act. Alternative extraction methods have been explored, including various solvents (e.g., isohexane, acetone, alcohols), supercritical carbon dioxide, and aqueous enzymatic processes. The latter methods offer environmental advantages but are currently cost-prohibitive on a commercial scale. In the future, enzyme-assisted extraction may become a viable option, but at present hexane is generally the most economical selection.

Solvent extraction yields two products. The miscella, a mixture of solvent and crude oil, is separated by a series of distillation steps. The marc, consisting of the solids and residual oil, is sent to a desolventizer-toaster which evaporates the solvent by heating; the solids are dried at high temperature and cooled to prepare the meal for its end use (Kemper, 2005). The solvent recovered from both the miscella and the marc is reused for further extraction.

### 20.8 Refining

Crude oil contains roughly 95% triacylglycerols, accompanied by free fatty acids, mono- and diacylglycerols, phospholipids, sterols, tocols, pigments, and other minor components such as waxes, trace metals, and pesticides. Refining of crude oil is a multistage process consisting of several operations designed to maximize the yield of oil that is free from impurities while keeping the valued components (e.g., sterols, tocols) intact. Refining is the most critical processing step, as poorly refined oils lead to problems in later processing and application steps (O’Brien, 2002; Wakelyn & Wan, 2006), increasing the cost of the end-product. In the US, the National Oil Processors Association (www.nopa.org) publishes an annual yearbook listing trading specifications for refined oils, including physical properties and maximum allowable content of various impurities.

#### 20.8.1 Physical versus chemical refining

There are two types of refining: physical and chemical (Figure 20.3). Physical and chemical refining differ in the manner in which the free fatty acids are removed from the crude oil. Physical refining uses steam distillation to remove the free fatty acids, while chemical refining uses a caustic solution. Physical refining consists of degumming, bleaching, and deodorization. Chemical (alkali) refining is more widely used and consists of an optional degumming step, followed by caustic neutralization, bleaching, and deodorization. Oils that have been through these processes are known as RBD (refined, bleached, and deodorized) oils.

Physical refining is most appropriate for oils that are low in phospholipids and high in free fatty acids. Palm, palm kernel, and coconut oils are typically refined in this manner (O’Brien, 2004a). Physical refining is less costly and involves fewer steps than chemical refining. The pretreatment prior to deodorization must be thorough or a lower-quality oil will result.

Chemical refining yields a high-quality product and is well suited for a wide variety of oils. Cottonseed oil must undergo chemical refining to remove gossypol. The chief disadvantage of chemical refining is the high cost associated with disposal of the waste water from the neutralization step, which is governed by environmental regulations. Additionally, there is greater loss of neutral oil with chemical refining than with physical refining (O’Brien, 2004a).

The general procedures for the refining process are described below. Components removed during each refining step are summarized in Table 20.3.

#### 20.8.2 Degumming

Some crude oils (e.g., soybean, canola, cottonseed) contain up to 3–4% phosphatides. Because they are emulsifiers, phosphatides interfere with refining steps, particularly bleaching (Taylor, 2005), which reduces yield. Degumming is the optional process by which phosphatides are removed from crude oil. Although phosphatides may be removed in future steps (Anderson, 2005), degumming as a first step increases the oil yield and leads to a higher-quality end-product (Farr, 2000). In addition to phosphatides, degumming removes some solid components (e.g., waxes) and trace metals, enhancing the oil’s stability. Degumming may be a batch or continuous process.

There are two primary approaches to degumming: water degumming and acid degumming. Water degumming is usually performed as a batch process in the US (O’Brien, 2004a) and involves addition of water to heated oil, followed by agitation. The hydratable phosphatides are converted into gums that are insoluble in the oil and may be removed by centrifugation or filtration. The “gum” contains phospholipids, which are recovered for their by-product value as lecithin, an emulsifier widely used in confectionery products, baked goods, and...
Figure 20.3 Flow diagram for general refining process.

Table 20.3 Components removed during the refining process

<table>
<thead>
<tr>
<th>Refining step</th>
<th>Targeted component(s) for removal</th>
<th>Other components removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degumming</td>
<td>Phosphatides</td>
<td>Filterable solids (e.g. waxes), trace metals</td>
</tr>
<tr>
<td>Neutralization</td>
<td>Free fatty acids</td>
<td>Phosphatides, soaps, trace metals, pigments</td>
</tr>
<tr>
<td>Bleaching</td>
<td>Pigments</td>
<td>Phosphatides, soaps, trace metals, waxes</td>
</tr>
<tr>
<td>Deodorization</td>
<td>Free fatty acids (physical refining)</td>
<td>Sterols, tocopherols, tocotrienols, carotenoids, pigments</td>
</tr>
<tr>
<td></td>
<td>Secondary oxidation products (chemical refining)</td>
<td></td>
</tr>
</tbody>
</table>
margarines. The quality of lecithin varies depending on the method of degumming utilized.

Treatment with acid is necessary to remove the non-hydratable phosphatides, which are associated with low-quality oils (Anderson, 2005). Acid degumming involves addition of dilute acid (most often phosphoric or citric) to warm oil, followed by rapid heating to break the emulsion. The resultant soapstock may then be removed by centrifugation.

Many modifications to the acid degumming process are available. Dry degumming, effective for oils with low phosphatide content, combines acid degumming and bleaching into one step; the gums are removed by filtration during bleaching. Enzymatic degumming uses a combination of phospholipases and acid to maximize removal of gums. In the super-degumming procedure, the acid/oil mixture is cooled to ambient temperature and agitated with water (Johnson, 2008). Acid refining involves the addition of sodium hydroxide after acid degumming to partially neutralize the acid; as a result, soaps are not formed and some remaining phosphatides are removed as sodium salts. Acid refining is often used as a conditioning step for neutralization.

Alternative methods of degumming include membrane filtration and silica adsorption. Degumming procedures have been reviewed by Cmolik and Pokorny (2000).

#### 20.8.3 Neutralization

The degummed or acid-conditioned oil is mixed with a caustic solution, most commonly sodium hydroxide, at slightly elevated temperature. Neutralization may be conducted as a high-temperature, short-mix or low-temperature, long-mix process; mixing of the oil and caustic is done for seconds or minutes, respectively. Free fatty acids in the oil combine with the caustic in a saponification reaction to form a water-soluble soap, which contains sodium salts of fatty acids. After separation of the oil and soapstock via centrifugation, the oil is washed with hot water in order to remove the remaining traces of soaps. Residual phospholipids, pigments, trace metals, and other minor impurities may also be removed in the process. The oil is dried by low-pressure heating, prior to bleaching.

Modifications to the traditional neutralization procedure are available. For example, in miscella refining, neutralization is conducted immediately after solvent extraction, prior to separation of the oil and solvent. Silica refining eliminates water washing in favor of silica adsorption to remove soaps.

Waste water from the neutralization process may contain soapstock, and is regulated in the US by the EPA Clean Water Act. Treatment and disposal of the soapstock are costly, but degumming prior to neutralization decreases disposal costs (Farr, 2000).

#### 20.8.4 Bleaching

While triacylglycerols are colorless, crude fats and oils contain pigments that impart visible color to the oil. Pigments naturally present in crude oils include carotenoids and chlorophyll which yield yellow/red and green colors, respectively. Color is viewed as an indicator of edible oil quality (Wan & Pakarinen, 1995). Consumers generally desire colorless or lightly colored oils (Taylor, 2005), and bleaching meets this need.

Bleaching is the removal of color compounds resulting from heating the oil with bleaching earth. Some residual soaps, trace metals, and waxes are eliminated in the process. For oils that have not been degummed, the bleaching step serves to remove the phospholipids, but it is difficult to achieve complete removal. Bleaching is the costliest step of the refining process due to the cost of the bleaching earth and its disposal, plus the loss of oil associated with the procedure (Gunstone, 2004).

Bleaching earth is made from mineral-based clays (e.g. calcium bentonite) and may be used in its natural form for oils with low levels of pigments or activated with sulfuric or hydrochloric acid to increase its adsorptive ability (Taylor, 2005). Acid-activated bleaching earth is typically necessary for removal of chlorophyll (Taylor, 2005) and further serves to break down peroxides into products that are subsequently removed in the deodorization process (Wang, 2002). However, the acidity may lead to isomerization of some natural cis bonds in unsaturated fatty acids to their trans configuration (Gunstone, 2008a).

Activated carbon and amorphous silica hydrogels are often used in conjunction with bleaching earth due to their affinity for polycyclic compounds and soaps, respectively (Taylor, 2005). Because they are much more costly than bleaching earth, they are typically used in small amounts. Silica gel may be added to the oil prior to addition of bleaching clay in order to first remove soaps and phospholipids, making the bleaching clay more effective for removal of color compounds (Anderson, 2005). The proportions of bleaching clay and other adsorbents are selected based on the properties of the oil to be bleached.

Bleaching may be done in an atmospheric batch process or as a batch, semi-continuous, or continuous vacuum process. Processing under vacuum is preferred, due to the reduction of oxygen that promotes degradation. Continuous processes are most widely used; some utilize
countercurrent flow for more efficient use of the bleaching earth, reducing processing costs.

The bleaching procedure involves addition of the bleaching earth to heated oil, followed by agitation. A holding period is employed to ensure complete bleaching, followed by filtration to remove the spent bleaching earth. There is some loss of oil in the spent earth, which may be treated with steam to ensure more complete removal of oil (Wakelyn & Wan, 2006). The effectiveness of the bleaching treatment is affected by variables such as temperature, time, and type of bleaching earth (Zschau, 2000). The standard for measurement of complete bleaching is a peroxide level of zero, rather than a particular color (Hernandez, 2005).

Bleaching earth is considered a hazardous material, as the spent earth is prone to self-combustion upon exposure to atmospheric oxygen, so disposal must be undertaken in a proper manner. The disposal of spent bleaching clay is regulated by the EPA Resource Conservation and Recovery Act.

### 20.8.5 Deodorization

Deodorization is the low-pressure heat treatment of oil with steam in order to remove impurities responsible for off-flavors and odors (e.g. free fatty acids, secondary oxidation products). Oxidative stability of the oil is significantly increased as a result (Pokorny, 2006).

The goal of deodorization is to produce oil with neutral flavor and odor. Deodorization is normally performed as the last step prior to packaging or transport (Wakelyn & Wan, 2006). In the case of RBD oils, the deodorization step occurs after bleaching. For oils subjected to modification procedures, deodorization follows modification.

Oil is de-aerated, heated to an intermediate temperature, then heated under low pressure to the specified deodorization temperature (generally 200–250 °C). Stripping steam is injected into the oil, removing water-soluble compounds in the course of the distillation process. In addition to the impurities mentioned above, sterols, tocopherols, and tocotrienols are partially removed. These high-value compounds may be obtained from the distillate, and recovered by condensation for addition to foods or use as nutraceuticals.

Deodorization may be done as a batch, semi-continuous, or continuous process. Semi-continuous and continuous set-ups are most widely used, while batch processes are still used in small or older facilities. Thin-film deodorization is a continuous process that yields excellent results. It involves exposure of a high surface area of oil, reducing the temperature and time needed for removal of impurities.

The harsh conditions associated with deodorization lead to additional reactions. Degradation of carotenoids causes a heat-bleaching effect. Formation of trans isomers of linolenic and linoleic acid occurs during deodorization and is dependent on reaction time and temperature (Hénon et al., 1999; O’Keefe et al., 1993). Trans isomers formed during deodorization are geometrical isomers, whereas those formed during partial hydrogenation are positional isomers (Duchateau et al., 1996) and those formed by rumen metabolism are both geometrical and positional isomers (Pariza et al., 2001). Deodorization may also cause hydrolysis or polymerization. Therefore, it is critical to weigh the benefits and costs when selecting deodorization conditions. The variables to control include temperature, time, pressure, and amount of steam. The appropriate levels may vary based on oil type, deodorizer design, and refining process (Kellens & de Greyt, 2000). Oils that are physically refined require harsher conditions than those that are chemically refined.

### 20.9 Modification of plant-based fats and oils

Modification of fats and oils is widely employed to obtain products with properties best suited to their end use. Reasons for modification include increasing oxidative stability, alteration of fatty acid composition, and improvement of textural characteristics. Gunstone (1998) classified modification techniques in two categories: technological methods include blending, fractionation, hydrogenation, and interesterification, while biological methods include plant breeding and genetic engineering.

#### 20.9.1 Blending

Blending is the simplest method of modification and involves mixing oils and fats to yield products with properties desired for specific food applications (e.g. shortenings and spreads). Blending may be used to improve the nutritional or physical properties of the product (Gunstone, 2006b). Typically, a solid base-stock is heated and blended into a liquid oil to yield a product with a wide plastic range. Agitation is required in order to ensure uniform heat (O’Brien, 2002). A wide variety of products may be used as base-stocks, including those that have been hydrogenated, interesterified, or fractionated. Blending has been utilized to produce plastic fats free of trans fatty acids (Jeyarani & Reddy, 2003).


20.9.2 Fractionation

Fractionation is the process used to separate oils and fats into two fractions of different triacylglycerol composition. Fractionation is purely a physical process; no chemical changes are involved. The resultant products have a wider range of use than the starting material. The low-melting fraction is known as “olein”, while the high-melting fraction is called “stearin.” Oleins have high oxidative stability and are well suited for use as salad oils or in frying applications. Stearins are widely used in the manufacture of margarines, shortenings, and confectionery products, often as cocoa butter substitutes, which are less costly than cocoa butter but possess similar melting characteristics. Fractions may undergo further modification, including blending and interesterification; additionally, individual fractions may be subject to refractionation (“double fractionation”).

There are three types of fractionation: dry fractionation, solvent fractionation, and aqueous detergent fractionation. Dry fractionation is the most common and least expensive process. While the procedures for solvent fractionation and aqueous detergent fractionation are more costly, the added cost is warranted for products sold at a premium price, such as cocoa butter substitutes.

20.9.2.1 Dry fractionation

Dry fractionation involves the crystallization of solids from liquid oil, followed by separation of the components via filtration or centrifugation. Crystallization occurs in three stages: cooling to supersaturation, nucleation, and crystal growth. Cooling is done gradually so as to achieve stable crystals that may be easily filtered. Because crystallization is an exothermic reaction, agitation is necessary to distribute the heat, although care must be taken to avoid disturbing the crystals (Gunstone, 2004).

Winterization is the most common form of dry fractionation and is typically used for removal of triacylglycerols with high melting points (i.e. saturated triacylglycerols), yielding oil that remains clear under refrigerated conditions. Products of winterization are known as salad oils and are widely used in preparation of dressings and mayonnaise. Cottonseed, partially hydrogenated soybean, and canola oils are commonly winterized.

The traditional winterization procedure involves placement of the oil into deep tanks in a refrigerated room (approximately 5 °C), holding for 2–3 days to allow proper crystallization, then filtration of the saturated crystals (Wakelyn & Wan, 2006). In the modern procedure, oil is cooled to refrigeration temperature by passing through heat exchangers, then held in tanks with mild agitation during the crystal growth period, which may last several days. Removal of the crystals is most often accomplished with vacuum filtration (Johnson, 2008).

Dewaxing may be viewed as a form of winterization. Some oils (e.g. corn, sunflower) have high levels of waxes, which impart a hazy appearance after settling. Dewaxing is done to improve the clarity of the oil. The oil is cooled slowly and a filter aid is added. After crystallization and settling of the waxes, they are removed using filtration.

20.9.2.2 Solvent fractionation

Solvent fractionation utilizes an organic solvent (e.g. acetone, hexane) and results in better separation of the fractions and shorter reaction times. There is some variability in the products based on the choice of solvent. Solvent fractionation is most commonly done for palm oil, but is also applied to coconut oil, palm kernel oil, partially hydrogenated soybean oil, and others. Palm oil is typically subjected to double fractionation. Palm oleins, removed in the first stage, are used as frying oils and exhibit excellent oxidative stability. Palm stearins and mid-fractions, separated in the second stage, are widely used in margarines and confectionery products.

20.9.2.3 Aqueous detergent fractionation

In aqueous detergent fractionation, a wetting agent (e.g. sodium lauryl sulfate) and an electrolyte (e.g. magnesium sulfate) are used to precipitate crystals in the aqueous phase (Kellens & Hendrix, 2000). The crystals are then removed by centrifugation and the fractions are heated and washed to remove the wetting agent and electrolyte. A drying step completes the process. Excellent separation of the fractions may be achieved, but the process is not widely used due to the high cost and potential for contamination of the oil with detergent (Kellens et al., 2007).

20.9.3 Hydrogenation

Hydrogenation results from reaction of a liquid oil with hydrogen gas in the presence of a catalyst at elevated temperature. Hydrogen atoms are added to the double bonds of unsaturated fatty acids, yielding a product with increased saturated fatty acid content. There are two predominant reasons for hydrogenation: hydrogenation improves the oxidative stability of the product via
decreasing the content of polyunsaturated fatty acids, extending shelf life; and the conversion of liquid oils to plastic fats improves their functionality for use in specific applications.

In general, hydrogenation is conducted within the temperature range of 160–200 °C. A solid catalyst (most often nickel) is added to the oil, followed by introduction of hydrogen gas with agitation. The gaseous hydrogen is dissolved in the liquid oil and diffuses to the surface of the catalyst (O’Brien, 2004a), where the reaction occurs. Because hydrogenation is an exothermic process, even distribution of the heat is required, often in the form of circulating cool water through the reactor coils (Anderson, 2005).

The reaction is typically stopped when the melting point of the product reaches the desired value (Pokorny, 2006). Because melting temperature increases with degree of saturation and level of trans fatty acids, the product is higher in solid content than the starting material. A side reaction is the isomerization of cis double bonds to their trans configuration; this particularly affects oleic acid (C18:1). Because melting temperature increases with degree of saturation and level of trans fatty acids, products of hydrogenation are higher in solid content than their starting materials and are therefore more appropriate for use in products such as shortenings and spreads.

Variables affecting the results include composition of the starting oil, amounts of hydrogen and catalyst, selectivity of the catalyst, reaction temperature, time, pressure, and level of agitation. In particular, an abundance of hydrogen, which results from increasing agitation and pressure, causes hydrogenation to be predominant and isomerization to be minor (Gunstone, 2004).

Hydrogenation is most often done as a batch process, although some semi-continuous processes are used (Gunstone, 2004). It is necessary to start with well-refined oil, as traces of gums, soaps, and metals may hinder the activity of the catalyst (Johnson, 2008). Three degrees of hydrogenation may be achieved: brush hydrogenation, partial hydrogenation, and full hydrogenation.

20.9.3.1 Brush hydrogenation

In brush hydrogenation, a minor amount of hydrogenation is done in order to improve the stability of liquid oil without conversion to its solid form (Hastert, 2000). This highly selective form of hydrogenation involves manipulation of reaction conditions to target the most unsaturated fatty acids (Wright & Marangoni, 2006). Brush hydrogenation is typically applied to oils containing high levels of linolenic acid, especially soybean and canola (Gunstone, 2008a). Isomerization from the cis to trans form may be decreased compared to the standard hydrogenation process, particularly with a lower reaction temperature and a selective catalyst (e.g. platinum) (Beers, 2007).

20.9.3.2 Partial hydrogenation

Partial hydrogenation is commonly used for soybean oil and other oils with significant levels of linoleic acid (C18:2n-6) (Gunstone, 2008a). Some partially hydrogenated oils are suitable for frying applications. As the degree of hydrogenation increases, oils become more plastic, making them suitable for use in spreads, shortenings, and confectionery applications.

20.9.3.3 Full hydrogenation

Full hydrogenation results in the virtual absence of unsaturated and trans fatty acids. Fully hydrogenated oils are typically solid at ambient temperature and are used as base-stocks for blending and interesterification.

20.9.3.4 Post bleaching

A post-bleaching step is typically conducted following hydrogenation. The purposes of post bleaching are to remove traces of catalyst remaining in the oil, colors that may have developed during hydrogenation, and primary and secondary oxidation products (O’Brien, 2002). Phosphoric or citric acid is added prior to the bleaching earth in order to chelate the metal catalyst. The bleaching procedure proceeds as previously described.

20.9.4 Interesterification

Interesterification is one of the least common methods of modifying fats and oils and is more commonly used in conjunction with other methods. It involves the rearrangement of fatty acid esters on the glycerol molecule; this redistribution may occur both within and between triacylglycerols. While the composition of triacylglycerols is altered, the individual fatty acid content is unchanged. The process yields products with different physical characteristics (e.g. melting point range, crystallization behavior, plastic behavior) than the starting product(s). Interesterification is more costly than hydrogenation, but a higher degree of specificity can be achieved, and
the products are free of trans fatty acids (Wright & Marangoni, 2006).

Interesterification may be utilized for single oils or, most commonly, blends of fats and oils, including those that have been previously modified. Usually, liquid oils are interesterified with solid fats or fractions to yield plastic fats suitable for use in applications such as shortenings and margarines. The use of starting materials with wide melting ranges yields products with an extended plastic range (Hidalgo & Zamora, 2006). Common base-stocks include partially or fully hydrogenated oils, lauric oils, and stearin fractions. Products of interesterification may exhibit less oxidative stability than their sources, possibly due to changes in the levels of pro- and antioxidants resulting from the procedure (Gunstone, 2008a).

Interesterification may be done as a batch, semi-continuous, or continuous process. The two principal types of interesterification differ based on the catalyst utilized; both chemical and enzymatic catalysts may be used.

20.9.4.1 Chemical interesterification
Chemical interesterification may be either random or directed and requires a chemical catalyst (most often a metal alkoxide), which must be soluble in the oil. The steps in random chemical interesterification are pretreatment of the oil, reaction with the catalyst, and deactivation of the catalyst. The reaction should be performed at ambient or slightly elevated temperature (Wang, 2002); temperatures above 50 °C may cause polymerization and degradation (Richards, 2006). The reaction proceeds until random equilibrium is reached; fatty acids are randomly distributed on the glycerol molecules.

Directed interesterification is used to selectively increase the level of specific triacylglycerol component(s). While the reaction proceeds, the temperature is decreased below the melting point of the desired component(s), causing crystallization of triacylglycerols with the highest melting points. The equilibrium shifts, leading to increased production of saturated triacylglycerols (Wright & Marangoni, 2006). The resulting product has an extended plastic range (Richards, 2006). Directed interesterification, most often done as a continuous process (O’Brien, 2004a), requires a longer reaction time than random chemical interesterification.

20.9.4.2 Enzymatic interesterification
Enzymatic interesterification is catalyzed by lipases, which may be obtained from bacteria, yeasts, or fungi (Richards, 2006). Lipases may either be random or specific to particular fatty acids or positions on the glycerol backbone (Wright & Marangoni, 2006). Hence, products of the reaction vary based on the lipase utilized. Drawbacks to enzymatic interesterification include higher cost, longer reaction time, and the need for more careful monitoring (Lampert, 2000). However, there is less waste, and purification of the products is simpler. Batch processes are typically used for enzymatic interesterification.

20.9.4.3 Prebleaching and post bleaching
A prebleaching step (drying under vacuum, followed by neutralization) prior to interesterification is necessary for oils with high peroxide values (Lampert, 2000). Post bleaching is done following interesterification in order to remove both chemical and enzymatic catalysts.

20.9.5 Biological methods of oil modification
There are four methods of modifying fatty acid profiles of oils: traditional plant breeding, in vitro mutagenesis, natural mutation, and genetic engineering. Traditional plant breeding methods have been used to produce canola oil and high-oleic safflower oil (McKeon, 2005) as well as a mid-oleic variety of peanut oil (Gorbet & Shokes, 2002). In vitro mutagenesis is typically used to remove an unwanted characteristic (McKeon, 2005) and has been used in conjunction with plant breeding to yield soybean oils with altered fatty acid profiles, high-oleic sunflower oils, and Linola™ oil. Natural mutation, followed by plant breeding, has led to high-oleic cottonseed, peanut, and rapeseed lines. While traditional breeding methods may transfer up to thousands of genes at a time, advances in biotechnology have led to the ability to isolate specific gene(s) for transfer (O’Brien, 2004c).

Genetic engineering of oilseeds was initially done to improve resistance to pests and herbicides. In recent years, efforts have focused on altering the fatty acid profile of oilseeds, both for nutritional purposes and to obtain desired physical properties in the resultant oils, such as increased oxidative stability. However, there is a high cost associated with commercialization of genetically modified plants, and commercial success has historically been difficult to achieve.

A growing area of interest is the development of transgenic plants that contain long-chain omega-3 and omega-6 fatty acids, especially the omega-3 fatty acids traditionally found in marine oils (Murphy, 2006). For
example, Qi et al. (2004) successfully incorporated eicosapentaenoic acid (C20:5n-3) and arachidonic acid (C20:4n-6) into Arabidopsis thaliana. This research area has been thoroughly reviewed by Venegas-Caleron et al. (2010).

20.10 Packaging and postprocessing handling

Oil and fat products intended for consumer use are packaged immediately after deodorization. According to O’Brien and Baird (2000), “the ideal container provides product protection, cost effectiveness, end use application, and appealing appearance.”

Packaging materials include paper, aluminum, and various plastics. The materials must be kept free from microbial contamination prior to filling. Liquid oils are typically packaged in clear polyethylene terephthalate (PET) containers ranging in size from 16 to 64 fluid ounces or in larger polyvinyl chloride (PVC) opaque jugs (O’Brien, 2000). Clear containers promote oxidation but are generally preferred by consumers. In the case of plastic containers, the potential exists for transfer of flavor and aroma compounds between the oil and container (O’Brien & Baird, 2000). “Scalping” refers to absorption of these compounds by the container, while “leaching” describes transfer of flavors and aromas from the packaging to the oil. Glass or metal packaging is typically used for specialty oils.

Packaging for other products is often chosen based on the shelf life necessary for the product. For example, shortening cans consist of a composite of multiple layers of paper and plastic, with the aim of extending the shelf life (Caudill, 2005). Packages may be filled by level, volume, or net weight (Caudill, 2005). After filling, nitrogen blanketing or sparging may be used to extend the product’s shelf life prior to opening of the container. Temperature control is especially important during transport and storage to maintain the quality of the product.

20.11 Margarine processing

Margarine is a solid water-in-oil emulsion that was invented in France in 1869 as a substitute for butter. Margarine is produced by blending base-stock(s) with water, milk solids, emulsifiers, and other ingredients to yield a product with similar characteristics to butter. To be classified as margarine in the US, a product must contain at least 80% fat by weight (CFR, 2010b).

The principal varieties of margarine are:
- solid (stick) margarine, usually available in 1 lb packages consisting of four sticks
- soft (tub) margarine, which has a lower melting point than solid margarine due to a higher content of polyunsaturated fatty acids
- whipped (tub) margarine, injected with nitrogen to yield a product with increased volume
- liquid margarine, available in squeezable plastic bottles. Products with reduced fat levels are widely available and are classified as “spreads.” While spreads often use the same fat blends as margarines, their water content is higher, and thus they require the use of thickeners as well as additional emulsifiers, preservatives, and coloring agents (O’Brien, 2004b). Some spreads currently marketed are fortified with nutrients such as long-chain omega-3 fatty acids, as well as esters of plant sterols and stanols (saturated derivatives of sterols).

20.11.1 Ingredients and their functionality

Standards for the production of margarine are listed in the Code of Federal Regulations (CFR 21.166.110), including ingredients and their allowable levels (CFR, 2010b).

20.11.1.1 Mandatory ingredients

Margarine must contain one or more fats or oils of plant, animal, or marine origin. Plant-based oils commonly used include soybean, cottonseed, canola, and palm oils. These oils have often been subjected to modification procedures (e.g. fractionation, hydrogenation) in order to obtain the desired functional characteristics, especially spreadability and melting behavior. Two or more base-stocks may be blended to provide properties from both. Interesterification may be utilized to produce margarines with zero trans fatty acids. The consistency of the final product is highly dependent upon the fats and oils selected.

One or more aqueous phase ingredients are required, which must be pasteurized and may be cultured. Water, milk, milk products, and edible proteins (e.g. whey, soy) are permitted. Most manufacturers use spray-dried whey, which promotes browning during pan-frying, similar to butter (Chrysan, 2005).
Vitamin A is required at a level of at least 15,000 IU/lb. β-Carotene is usually added until the desired color is reached, followed by addition of colorless esters of vitamin A until the required level is achieved (O’Brien, 2004a).

20.11.1.2 Optional ingredients

Natural and artificial flavorings are permitted, some of which simulate the flavor of butter (e.g. diacetyl). Salt and sweeteners contribute to the flavor profile of the product, and salt also possesses antimicrobial properties. Acidulants or alkalizers may be added to adjust the pH of the product, which affects flavor perception. Color additives include synthetic β-carotene as well as natural extracts that are rich sources of carotenoids (e.g. annatto, red palm oil).

Emulsifiers act at the interface of the oil and aqueous phases, stabilizing the emulsion. A combination of lecithin, mono- and diacylglycerols is typically used (Chrysan, 2005; O’Brien, 2004b). Preservatives include sorbic acid, used as an antimicrobial agent, and ethylenediamine tetra-acetate (EDTA), which chelates trace metals. Antioxidants are permitted, but the level of natural antioxidants in the fats is typically sufficient. Margarine may be fortified with vitamin D; if this is chosen, the level of fortification must be at least 1500 IU/lb.

20.11.2 Structure

Margarine consists of a continuous crystalline network; the liquid oil and solid fat crystals contribute structural support, while the aqueous phase is dispersed throughout the system (Heertje, 1993). The fat crystals provide stability for the aqueous phase. The aqueous droplets generally range in size from 1 to 20 μm (Bumbalough, 2000). The resultant product possesses plastic properties.

20.11.3 Production

The general process for margarine production is shown in Figure 20.4. The equipment used in all production steps should be stainless steel or plated nickel, which resists corrosion (O’Brien, 2004a). Since consumers desire products that are spreadable upon removal from the refrigerator, maintain their solid state at room temperature, and rapidly melt in the mouth, solid fat index values in these temperature ranges are monitored during production.

20.11.3.1 Preparation of the emulsion

Either a batch or continuous process may be used. In general, the selected base-stocks are warmed to liquid state, then blended with the fat-soluble ingredients with agitation. The aqueous phase ingredients are weighed, pasteurized, and mixed in a separate tank. Finally, the oil and aqueous phase ingredients are combined with agitation and mild heat, yielding a semi-solid emulsion.

20.11.3.2 Solidification

The emulsion is fed into a scraped surface heat exchanger (e.g. Votator®, Waukesha Cherry-Burrel, Delavan, WI), which is a jacketed chilling cylinder utilizing blades to continuously scrape the walls, promoting adequate heat transfer. For soft (tub) and whipped products, nitrogen is injected at low or high levels, respectively, to reduce the product’s density and improve its appearance. The emulsion is rapidly chilled to refrigerated temperature in less than 30 sec (O’Brien, 2004a). This super-cooling produces small nuclei for crystallization.

Super-cooling promotes the formation of α crystals, which rapidly transform to the β form. The β form is desired for margarine, as the three-dimensional network of fine crystals traps a high volume of liquid oil, resulting in a product with plastic properties. The β′ crystals may further transform to the β form if the fat blend has that crystallization tendency. Large β crystals are undesirable, as they produce a coarse texture. This transformation is irreversible in the completed product; however, melting and recrystallization may be done during production (O’Brien, 2004a).

20.11.3.3 Plasticization and tempering

The mixture is pumped from the scraped surface heat exchanger to a closed vessel. For soft (tub) and whipped margarines, a “working unit” is utilized. The working unit consists of a revolving shaft with finger-like projections that interact with corresponding projections on the wall of the tank, providing consistent mixing during the crystallization process. An aging tube is used without agitation for stick products, as hardness is desired. Crystallization is allowed to proceed slowly until equilibrium is reached. These processes serve as methods of tempering the final product, therefore extending its plastic range. Liquid margarines are tempered with a period of holding and agitation, so as to increase their stability (O’Brien, 2004a).
20.11.4 Packaging

Two methods are used to package stick margarine. The sticks may first be formed, then wrapped in paper or foil wrappers. Alternatively, the wrappers may be placed into a mold, for injection of the semi-solid product into the wrapper (Bumbalough, 2000; O’Brien, 2004a). For tub, whipped, and liquid margarines, the products are filled directly into their respective packages. Extensive labeling requirements for margarine are provided in CFR 21.166.40 (CFR, 2010c). In particular, the word

Figure 20.4 Flow diagram for margarine production.
“oleomargarine” or “margarine” must appear in prominent type on the package. Specific nutrient content claims and health claims are regulated by the FDA.

20.12 Mayonnaise processing

Mayonnaise is a creamy, semi-solid food product used as a dressing and sandwich spread. Mayonnaise is an oil-in-water emulsion and is unique in that the dispersed phase (oil) is present at approximately seven times more than the aqueous phase. Because the emulsion is thermodynamically unstable (Ghosh & Rousseau, 2010), the process for producing a stable emulsion is delicate. Specific commercial processing techniques are patented.

Recent trends in mayonnaise production include flavored products, fortification with omega-3 fatty acids and plant sterols and stanols, and the use of non-traditional oils (e.g. olive).

20.12.1 Ingredients and their functionality

Requirements for the production of mayonnaise are listed in the Code of Federal Regulations (CFR 21.169.140); in particular, ingredients and their allowable levels are provided (CFR, 2010c).

20.12.1.1 Mandatory ingredients

Mayonnaise must contain one or more vegetable oils, one or more acidifying ingredients, and one or more egg yolk-containing ingredients (CFR, 2010c). While vegetable oils must make up at least 65% by weight of the product, most commercial mayonnaise contains approximately 80% oil. Salad oils are utilized, with clarity at refrigerated temperatures, since crystallization causes breakdown of the emulsion. Oils commonly used in the production of mayonnaise include soybean, canola, and cottonseed. Soybean and canola oils may be subjected to brush hydrogenation to increase their oxidative stability.

Permissible acidifying ingredients are vinegar, lemon juice, and lime juice. Vinegar may be diluted with water so that the final acetic acid content is at least 2.5% by weight. Vinegar contributes to the flavor of the product and functions as a preservative against spoilage. Lemon and/or lime juice may be diluted with water so that the final citric acid content is at least 2.5% by weight.

Egg yolk-containing ingredients include egg yolks or whole eggs in liquid, frozen, or dried form; liquid or frozen egg whites may also be added. Egg yolk contains phospholipids, which serve as emulsifiers. The amount of egg yolk necessary to stabilize the emulsion varies based on the amount and make-up of the oil and aqueous phases, as well as the size of the oil droplets (Hill & Krishnamurthy, 2005). Egg yolk-containing ingredients affect the color, flavor, and texture of the product.

20.12.1.2 Optional ingredients

Salt and sweeteners contribute to the flavor of mayonnaise, act as preservatives against microbial spoilage, and contribute to the stability of the emulsion. Spices and natural flavorings typically include mustard flour, paprika, and white pepper; saffron, turmeric, and others that simulate the color of egg yolk are excluded. Monosodium glutamate is permissible but rarely used due to health concerns.

Citric acid and/or malic acid may be added in conjunction with vinegar at a level of no more than 25% of the weight of the acetic acid in the vinegar. Citric acid serves to chelate trace metals, which act as pro-oxidants, and malic acid contributes to the flavor of the product and increases shelf life (Moustafa, 1995). Sequestrants, including calcium disodium EDTA, bind calcium ions and are used to preserve color and flavor. Crystallization inhibitors, (e.g. oxystearin, lecithin) may be added to the oil.

20.12.2 Structure

The aqueous phase contains the acidifying ingredients, flavorings, and seasonings, while the egg yolk solids are present at the interface between the dispersed (oil) and aqueous phases. The oil droplets are closely packed (Heertje, 1993) in an arrangement resembling honeycomb, with droplet size ranging from 2 to 25 μm (Langton et al., 1999). The stability of the emulsion and texture of the final product are influenced by many factors, including the size of the oil droplets, temperature and quality of ingredients, and the equipment and techniques used for preparation (Hill & Krishnamurthy, 2005; Lluch et al., 2003).

20.12.3 Preparation

A batch, semi-continuous, or continuous process may be used. In batch and semi-continuous processes, the seasonings and egg yolks are beaten in a Dixie mixer with a portion of the vinegar. The oil is slowly added, beating constantly, followed by addition of the remainder of the
vinegar (Hill & Krishnamurthy, 2005). The coarse emulsion is then passed through a Charlotte colloid mill, which reduces the size of the oil droplets, yielding a smooth, creamy texture (Hill & Krishnamurthy, 2005; O’Brien, 2004b). Continuous operations are usually two-stage processes. First, the premixed ingredients are pumped to an in-line mixer, where a coarse emulsion is formed. Next, the mixture is fed into a colloid mill for further emulsification. Finally, the product is pumped to a filler for packaging.

20.12.4 Packaging and handling

Although mayonnaise has an extended shelf life, the emulsion is subject to breakdown. Care must be taken to avoid excessive heat, freezing, or agitation, as these may break the emulsion, leading to separation of the oil and water phases. Further, since mayonnaise has a high oil content, it is subject to oxidation. The risk of oxidation may be minimized by utilizing antioxidants and high-quality oils in production, adding carbon dioxide or nitrogen to the mixture during preparation of the emulsion, and minimizing headspace in the container while filling.

In recent years, glass jars have been abandoned in favor of plastic packaging. Mayonnaise is typically packaged in PET containers in the form of the traditional jar shape, a rectangular shape, or a squeezable bottle.

Products must be labeled “mayonnaise” and the label must include a list of all ingredients contained in the product (CFR, 2010c).

20.13 Sustainability

Sustainability has been pursued in many areas of the production of plant-based fats and oils. Energy expenditures in extraction and refining operations have been reduced by heat recovery techniques as well as the use of solid waste from starting materials to fuel downstream operations. Improvements in design and engineering, specifically solvent recovery systems and countercurrent flow techniques, have achieved reduction in hexane emissions. Physical refining is becoming increasingly popular due to the reduction in waste water versus chemical refining (Gunstone, 2008b). Efforts are directed toward the promotion of sustainable agricultural practices for oil-bearing crops, particularly the oil palm. Finally, single-cell oils and transgenic crops continue to be explored as sustainable alternative sources of long-chain omega-3 fatty acids.

References


