

Chapter 2

Oil Technology

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Abstract The processing of oilseeds and oil-bearing fruits becomes more and more important because an increasing number of people need more and more oil for human nutrition and also for technical applications. In general, three different methods for the extraction of oil are conceivable: (1) pressing, (2) extraction by solvent, and (3) a combination of pressing and extraction by solvent. The efficiency of these methods can be improved with the assistance of enzymes or carbon dioxide.

Pressing is a very old method which nowadays is most widely displaced by the use of solvent which is more efficient, especially for oilseeds with lower oil contents such as soybeans. Seeds with higher oil contents are pre-pressed before extraction by solvent. For the production of high-quality virgin oils, only pressing by a screw press and purification by sedimentation, filtration, or centrifugation is allowed.

Because of the extensive extraction process in large facilities which results in the extraction and the formation of undesired compounds in the raw oil, making it unusable for human nutrition or technical applications, a comprehensive purification by a refining process of the raw oil is inevitable.

The chapter describes the different methods of oil processing and the different requirements necessary for the production of high-quality vegetable oils in large oil mills, and also in small and medium-sized facilities. Difficulties arising from both methods are also discussed. The chapter discusses the different aspects of oil processing from the pretreatment of the raw material via extraction by pressing or solvent extraction to the purification by filtration, sedimentation, or refining. The different steps of the refining process, degumming, chemical or physical refining, bleaching, and deodorization are described. The influence of different steps of processing on the oxidative stability of the oil is the subject of the chapter. Last but not

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least, some process-derived contaminants formed during the refining process such as *trans*-fatty acids or 3-monochloropropane-1,2-diol fatty acid esters and related compounds are discussed.

Keywords Dehulling • Flaking • Bleaching • Interesterification • Virgin oil • *Trans*-fatty acids

1 Introduction

Oil production from different sources is important to provide oil for the use as food or in several technical applications, such as fuel, lubricants, or raw material for the production of chemical products. The main point is the separation of the oil from the oil-bearing material with subsequent purification of the raw oil, but looking at the oil production as a whole not only the oil processing is important for the production of high-quality oil, but also the harvest, the pretreatment of the harvested material, and the storage conditions until processing have to be taken into consideration (Fig. 2.1).

Another important point is whether the raw material is extracted by pressing and solvent in a large facility with subsequent refining or whether the oil is processed in a small oil mill only by use of a screw press with sedimentation, filtration, or centrifugation for purification. While large facilities can compensate inferiority of raw material by the refining process, in small oil mills the quality of the raw material is decisive, because the oil quality is directly affected. On the other hand, the handling of the raw material after harvest strongly depends on the type of raw material. Under appropriate conditions, seed materials such as soy beans, rapeseed, or sunflower seeds can be stored over a longer period of time if it is possible to reduce metabolic processes and contamination by microorganisms or insects. However, fruits such as palm fruits, olives, or avocado have to be processed very fast after harvest because degradation processes start directly, impairing the oil quality with regard to sensory quality and storage stability.

The aim of the extraction method is to optimize the oil yield with simultaneous maintenance of the oil quality. In this connection, not only the removal of contaminants or substances affecting the sensory quality or storage stability of the oil are important, but also compounds formed during the processing such as *trans*-fatty acids or 3-monochloropropane-1,2-diol fatty acid esters (3-MCPD-esters), and related compounds should be taken into consideration.

While mechanical extraction of seeds or fruits, a very old method for the processing of oil is nowadays used only for fruit oils or specialty oils, in the extensive extraction process in large facilities, mechanical and chemical means are applied. This results in raw oil that has to run through different steps of a refining process to make the oil usable. A further method for the extraction of oil is the use of



Fig. 2.1 Influence of agriculture, pretreatment of the raw material before processing, and oil production on the quality of vegetable oils

high-pressure carbon dioxide, which has, under supercritical conditions, similar extraction properties as hexane. This method is relatively new, but only in use for very susceptible and expensive oils or constituents, since it is very expensive. Nowadays, also the use of more environment-friendly methods for the oil processing has been considered, either to increase the oil yield without using solvent extraction by the use of enzymes or to improve the refining process.

In addition to the oil, the meal or press cake is an important economical factor in oil processing. These products can be used as a source of protein in animal feeding; however, today more and more research is being done to extract proteins from residues of oil production for use in human nutrition. In that case, the oil processing has to be adapted to the necessary quality of the meal or press cake. Normally, meal or press cake is the by-product of oil processing, but this relation can change depending on the price of oil and meal.

This chapter describes the different methods of oil processing and explains the differences between the oil qualities obtained by the different methods. While describing oil processing the fact that different types of raw materials and oils need different types of processing has to be taken into consideration. Although steps such as dehulling, flaking, or cooking are not used for oils extracted from fruits, these steps are necessary for oils extracted from oilseeds both to improve the oil yield and to make the process more economical. On the other hand, the use of solvent is not allowed for the production of extra virgin olive oil or other virgin oils and it is also not useful for the production of oil from fruits.

2 Pretreatment

For the production of high-quality oil, it is important to use high-quality raw material. Therefore, it is necessary not to start oil processing only with the oil extraction from the raw material, but the process has to start on the field. This is important for large-scale facilities, although they have the possibility to improve oil quality by the refining process, however, it is essential for small and medium-sized plants, which use screw presses for oil processing and sedimentation or filtration for oil cleaning only (Fig. 2.2). The producer of this type of oil has no chance to improve the oil quality after the pressing process. Purification by sedimentation or filtration removes only turbid

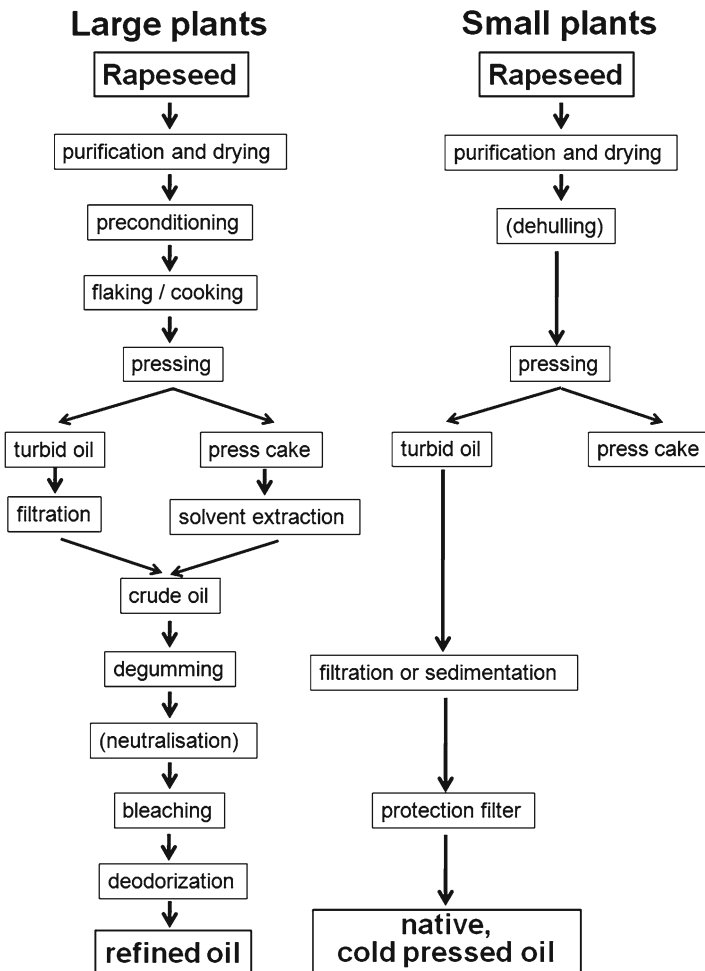


Fig. 2.2 Oil processing in large and small plants

matter, but not the components that impair the quality of oil, such as free fatty acids or products of oxidative degradation. Therefore, small- and medium-sized plants depend for better or worse on the quality of the raw material. While large-scale facilities with an extensive oil extraction can remove free fatty acids or chlorophyll with some losses from oil, obtaining a high-quality product with a constant quality, the quality of small- and medium-sized plants strongly depends on the quality of the raw material. The quality of the raw material the producer fills into his screw press influences the quality of oil he gets.

One reason why the handling of oil-bearing fruits or oilseeds and the production of high-quality oil is so difficult is the high oil content of the fruits or seeds, which constitute up to 40% or more of the dried matter and the low content of carbohydrates, for example, in comparison to cereals. Oil is very susceptible to oxidation, and degradation products of the oxidative process are already noticeable in very low concentrations. In addition, this effect is enhanced because oil is an excellent carrier for aroma components, which retains and concentrates volatile compounds. Therefore, the oil fraction of the raw material acts as a sensory memory that remembers everything that has been done during pretreatment and storage until the processing.

Another important point is the low content of carbohydrates in most oil-bearing materials, which results in a remarkable lower tolerance against moisture. Carbohydrates are able to bind certain amounts of moisture resulting in lower amounts of free available water, which otherwise could act in processes in the seeds as reaction partner directly or as reaction medium indirectly. Higher amounts of free available water are responsible for increasing metabolic processes and the increase of the population of microorganisms (Niewiadomski 1990; Schumann and Graf 2005).

From this high susceptibility of the oil-bearing raw material, it can be derived that it is absolutely necessary to maintain the good quality of the seeds or fruits after harvest until processing, which means for oil-bearing fruits such as palm fruits or olives the processing of the matured fruits has to be done in a very short time. For example, palm fruits are harvested manually, whereas pickers control the ripeness of the fruits before they cut them from the tree (Fig. 2.3). The cycle of the control decides about the conditions how the fruits are harvested. If the trees are controlled every week, there is a good chance to harvest the fruits in optimal ripeness, but if the cycle is longer, the probability of quality getting worse increases. Important is also how fast the fruits come to the process, because the fruits contain higher amounts of free water improving the condition for metabolic processes if the involucre is destroyed.

The situation is a little different for oilseeds. They have a relatively solid hull and should have low moisture content after harvest. Therefore, it is necessary to store the seeds after harvest under appropriate conditions and then they can be processed continuously over at least 1 year. The aim of an optimal storage is to maintain the good quality of the seeds until further processing without losses in quality during storage. However, the problem is that the seeds are living organisms. On the one hand, they have the natural desire to develop new plants, which results in the

Fig. 2.3 Harvest of palm fruits



degradation of storage compounds such as lipids, carbohydrates, or proteins; on the other hand, only the viable and germinable seeds can be optimally stored. Additionally, the ingredients of the seeds are livelihood for microorganisms or insects, which also leads to a degradation of storage compounds.

Improper pretreatment of the raw material after harvest can result in remarkable financial losses for the owner of the raw material; however, on the other hand, the owner is also responsible for the quality of the product and could be made liable for possible occurring damages.

After harvest, cleaning and, if necessary, drying of seeds are the most important steps. Both the amount of foreign matter and the content of moisture are basis for the settlement of the oil mills with the farmers when seeds are delivered. In Canada, for canola seeds, the so-called Canola standard was established by the Canadian Grain Commission defining the maximum amount of foreign matter in the seeds as 2%, while the amount of moisture should be between 6 and 9%. In Germany, oil mills have similar conditions, but the content of moisture has to be below 9%;

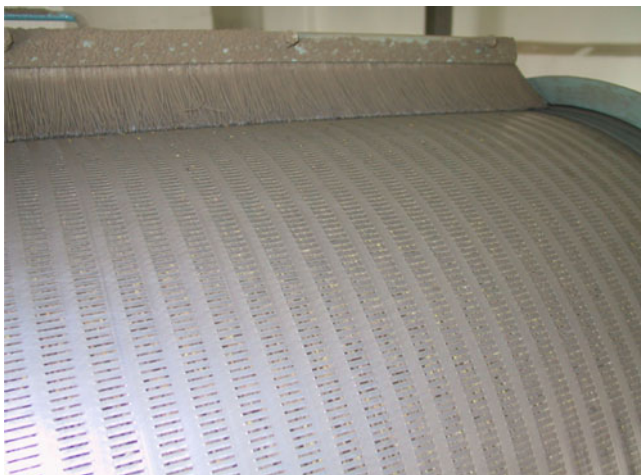


Fig. 2.4 Trieur for the separation of foreign matter from oilseeds

otherwise the farmer has to accept deductions. In contrast, soybeans with a lower oil content and a higher content of protein and fiber are allowed to come from the field with about 13% moisture, which is considered as useful for a long-term storage.

Since foreign matter, such as stems, broken seeds, and foreign seeds, often contains higher amounts of moisture, chlorophyll, or free fatty acids or a higher population of microorganisms, the limitation has some advantages to ensure that high-quality oil and meal are obtained, because both of them negatively influence the quality of the seeds during storage.

In addition, the moisture content of the raw material and the content of foreign matter are important, because depending on the form of the seed material, up to 40% of the volume of stored seeds consists of hollows, in which an appropriate relative humidity is adjusted, depending on the amount of seed moisture. This humidity sets the speed of metabolism in the seeds and favors the growth of mold, yeast, and bacteria on the seeds during the storage period.

Since foreign matter in the raw material deeply influences the quality of the seeds during storage, it is advisable to do seed cleaning directly after harvest and before storage to keep a high seed quality for a longer time. Foreign matter should be removed as much as possible with justifiable efforts. In general, it is useful to clean the material to less than 1% foreign material if a longer storage period is necessary. For the separation of foreign material, aspirators, graders (Fig. 2.4), and sieves (Fig. 2.5) for the removal of over- and undersized particles are used either individually or in combination to improve the purification. Metal fragments are separated in an additional step by magnets. This is necessary to spare the screw press, which can be damaged by these fragments, resulting in a decrease of the average useful life of the press.



Fig. 2.5 Sieve for the separation of foreign matter from oilseeds

In addition to the purification of the seed material from foreign matter, the use of sieves, graders, and aspirators results in a significant drying of the seed surface and a decrease of the seed temperature. These positive effects result in worse conditions for fungus spores and a delay of metabolic processes.

3 Dehulling

Since some seed materials consist of significant amounts of hulls, which contain major parts of fiber, sometimes waxes and a group of pigments impairing the oil quality in some cases, the removal of the hulls is recommended. The resulting oil will have a lighter color resulting in less effort during bleaching. Additionally, dehulling may have some advantages if the meal or press cake from the processing should be used for the extraction of protein, because it results in a better quality of the plant protein due to the removal of major parts of the fiber and pigments. From an economical point of view, dehulling reduces the amount of material that has to be processed resulting in a higher efficiency of the plant and reduced energy costs per ton extracted oil.

Examples for oilseeds which could be dehulled before pressing are rapeseed with a content of hulls between 16 and 19% (Matthäus 1998) and sunflower seeds which consist of about 30% hulls (Roth and Kormann 2000) coated with a thin layer of wax which protect the seeds against evaporation or soybeans, from which most of the material is dehulled today because of demands of the feed industry.

During sunflower oil processing of whole seeds, waxes from the hulls come into the oil resulting at lower temperatures is harmless, but undesired, turbidity. Most consumers are not familiar with this phenomenon and reject such products. Therefore, producers take care to avoid waxes either by removal of the seed hulls or by removal of waxes by suitable filtration or separation steps after pressing.

Advantages of dehulling of the seeds before processing are higher quality of the oil with regard to the sensory characteristics, clearly lower amounts of waxes in the oil, and a lower temperature development during pressing.

Usually, the seed material is not completely dehulled because it results in poor oil yields. Due to the high oil and low fiber content of the kernels, only less elastic retractive forces are formed. This leads to a blockage of the drainage ways in the material during pressing, resulting in high oil contents in the press cake. A second pressing of the press cake together with the hulls from the dehulling process improves the elastic retractive forces during the process and results in better oil yields. However, the quality of this oil is remarkably worse in comparison to the quality of the first pressing. Therefore, using partially dehulled seed material is a compromise between oil yield and oil quality.

Dehulling starts with the purification of the raw material to remove different impurities such as foreign seeds, broken seeds, and dirt. Undesirable constituents should not negatively affect the quality of the product during the following process. A certain content of seed moisture is necessary both to ensure an appropriate elasticity of the material and to avoid broken seeds. At high-moisture contents, the elasticity of the seeds is too high for the dehulling process necessitates drying of the raw material as a conditioning step before dehulling. At lower moisture contents, the part of broken seeds increases which results in losses of material during the following separation between dehulled seeds and hulls.

3.1 *Sunflower Seeds*

Dehulling of sunflower seeds cannot be done on rolling mills as for rapeseeds, because the form of seeds is too asymmetrical. Instead of rolling mills, impact dehullers are in use. During this process, the seeds are accelerated to a hard surface and the resulting impulse during the impact leads to a break of the hull which exposes the kernel of the sunflower seed.

The resulting mixture of seed hulls, kernels, and intact seeds is separated in a two-step separation. Within the first step, hulls are removed by airflow; within the second step, the dehulled kernels are separated from intact seeds by gravity. The intact seeds are added again to the dehulling process.

In comparison to whole sunflower seeds, the processing of dehulled sunflower seeds is problematic, because of the plastic consistence of the kernels. From this, the needful elastic retractive forces during the pressing process are absent. With the geometry of screw presses usually used for the production of virgin oils, this job is barely manageable. Screw presses have to be adapted to pressing of dehulled sunflower seeds. Then the press can work with clearly lower frictional heat and press temperature in comparison to the processing of whole sunflower seeds. Dehulling of seeds and modification of the screw geometry of the press enable the production of virgin sunflower oil with an outlet temperature below 40°C resulting in mild fruity sunflower kernel oil.

Another advantage of the dehulling process is the reduction of waxes in the resulting oil, which mainly come into the oil from the hulls. A further winterization after filtration of the oil is not necessary. It is sufficient to polish the oil by a cold filtration.

3.2 *Rapeseed*

Contrary to sunflower seeds, dehulling of rapeseed is not a commonly used process, since it is expensive due to the small size of the seeds. For the production of refined oils, this type of pretreatment is not economical, although the resulting meal has some advantages with regard to the use in animal feeding and also for the extraction of protein for human consumption. Phenolic compounds, and also fiber are reduced in the resulting meal, which is favorable for the animals from a nutritional point of view. The use of dehulled seeds also has some advantages concerning the reduction of processing costs, because the energy effort during further processing is lower. But dehulling has the disadvantages that the amount of antinutritive compounds such as sinapine, glucosinolates, and inositol phosphates is enriched in the resulting dehulled material (Matthäus 1998) and percolation of solvent is impaired, since hulls increase the porosity of the material being extracted.

From this, is only interesting for some small- and medium-sized plants that produce cold-pressed rapeseed oil by screw pressing with an added value. An advantage of dehulling before screw pressing is in these types of plants the possibility to keep the press temperature below 40°C which limits the activity of seed's own enzymes and reduces the transfer from undesired components of the seeds into the oil (Schneider 1979a, b; Schneider and Khoo 1986; Piva et al. 1985). As a result of dehulling, the taste and smell of this type of oil should be milder than those of conventional virgin, cold-pressed rapeseed oils, with a less intensity of its typical sensory attribute *seed like*.

Different techniques are conceivable for the process of dehulling: pneumatic impact on a rebound plate, splitting in a gap between rollers, and a designed deformation of the seed material. As a result of the designed deformation, the hulls flake from the meat and the meat consisting of germ as well as internal and external part of cotyledons fall to pieces. It is important that the seed material is not completely pulverized and a certain amount of hulls is necessary to enable a successful pressing process. The separation of the hulls from the dehulled material takes place by air floating and sieving.

3.3 *Soybeans*

For dehulling of soybeans, the material is tempered for 24 h before the process to allow uniform distribution of moisture in the seeds. Even today hot dehulling systems are in use where the cleaned seeds are heated to 60°C for half an hour, resulting

in the migration of moisture to the surface with following quick heating to about 85°C which removes the moisture from the material to a content of 1–3%. By this treatment, hulls break loose from the beans and the beans become crisp and can be divided into two halves. In the conventional dehulling, the beans are cracked into six to eight pieces by roller mills. Afterward, hulls are separated by shaker screens, aspirators, or gravity tables, which also can be used in combination.

To maintain the oil quality from dehulled seed material, it is necessary to work continuously without any delay and carefully to disrupt as few cotyledons as possible, because dehulled material is remarkably more susceptible to settlement by microorganisms and degradation by enzymes such as myrosinase or lipases. The enzymes being separated in compartments prior dehulling come together with the substrates, forming isothiocyanates and nitriles from glucosinolates and free fatty acids from triacylglycerides. This results in a fast degradation of the dehulled seed material and the formation of degradation products strongly influencing the oil quality. As a good carrier for aroma components, the oil takes up and keeps the formed volatile and nonvolatile compounds.

The following steps, preconditioning, flaking, and cooking, are not necessary and not allowed for the production of virgin, cold-pressed oils. This type of oil is limited to some special oil-bearing materials which are available only to a small extent and for which a solvent extraction is not economical, such as olives, argan seeds, macadamia nuts. On the other hand, more and more consumers are interested in less processed food and thus the interest in edible oils only extracted by a screw press and purified by sedimentation or filtration without the use of solvent or refining becomes more and more popular resulting in an increasing production of virgin oils from commonly used oilseeds such as rapeseed or sunflower.

4 Preconditioning

Before the extraction process starts seeds are often heated to about 30–40°C to prevent shattering during the flaking process. Another important point is that this preconditioning helps to improve the screw-pressing capacity, cake formation, extractability, and hexane recovery from the extracted oilseed flakes (Unger 1990). This step is also important for plants in colder climates. Preheating of the whole seeds is performed either by direct contact of the seed material with hot air or by indirect heating.

5 Flaking

The next step in large-scale facilities is the flaking operation. The aim of this step is to rupture as many cell walls as possible to improve the release of oil from the seeds by destruction of the seed coat and the oil cells. In these cells, lipid particles are

surrounded by cell membranes or cell walls, which avoid that oil is delivered from the intact seeds. After the flaking process, about 80% of these membranes or walls are destroyed resulting in the unimpeded drain of oil. Another important point is that the surface of seeds is drastically enlarged by flaking, which results in an easier contact of the lipid particles among each other by which they more easily migrate from the seed material. Additionally, solvent can more easily dissolve the lipid fraction from the seeds, which leads to a more comprehensive extraction of the material. The result is that extraction of the seeds needs less thermal energy input during cooking and less mechanical energy during extraction by screw presses.

In general, flaking is carried out by using two cast-iron rolls with a smooth surface, which are set at an appropriate gap to control the thickness of the flakes. During running, one roll revolves at 2–5% higher rpm with the result that the roll surfaces wipe each other. Distribution of seeds on the whole width of the rolls is achieved by using vibrating feeders which result in an even spreading. While preheated seeds pass through the rolls, the seed coat and cell walls are destroyed as a result of the pressure that occurs during this process. Often, flaking is carried out in a two-step process, in order to ensure a high grade of flaked seeds. In the first step, the seeds are cracked to about 0.4–0.7 mm thickness. The result of this step is that the hull or seed coat of the seeds is broken. In a second step, the thickness of the flakes is reduced to about 0.2–0.4 mm, whereas the optimum is between 0.30 and 0.38 mm. Flakes thinner than 0.2 mm are very fragile, while flakes thicker than 0.4 result in lower oil yield (Carr 1995). The problem of thin flakes is that they contain a large part of small particles that can get into the oil resulting in problems during filtration of the oil.

After flaking, the oil processing has to be carried out without any delay, because vergleichbar mit comparable with dehulled seeds the protective seed coat is destroyed resulting in the beginning of the work of the appropriate enzymes and attendant microorganisms. The result is a drastic impairment of the flakes and subsequently of the oil. Therefore, storage of the flakes before further processing is not advisable.

6 Cooking or Conditioning

Cooking or conditioning of the flaked seeds has different advantages for the following process, and also for the product quality itself. First of all, intact cells that overcame the flaking process are disrupted during the thermal treatment with temperatures between 75 and 85°C. This results in an easier extractability of oil from the solid residue.

Then, as a result of higher temperature during cooking, viscosity of the oil droplets is reduced facilitating the mergence of small lipid particles coming from the oil-bearing cells to form larger oil droplets. This relieves the drainage of the oil from the solid during the extraction. A successful cooking process can be seen by the oily appearance of the flakes as a result of the larger oil droplets, whereas the appearance of uncooked flakes is dry and the oil is not noticeable.

Another important point is that the moisture content of the material can be adjusted by the cooking process before starting the extraction. Most screw presses need moisture contents between 3 and 6% for an optimum result, because within this range the seeds have the correct elasticity necessary for the use of screw presses.

Most enzymes have a temperature optimum between 50 and 60°C. Within this range, the conversion rates of the enzymes with its substrates are highest. Therefore, it is important to pass through this range as fast as possible. At higher temperature, the process of cooking results in deactivation of the enzymes. This deactivation is important since breakdown products of glucosinolates in rapeseed, such as isothiocyanates or nitriles, partially remain in the solid residue after the extraction process. They are suspected to be harmful to animal when using the residue as fodder. Another point is that glucosinolates consist of sulfur, which can be found in the oil as a result of degradation. Sulfur poisons catalysts and therefore influences their activity during a possible hydrogenation process.

The inactivation of lipases by heat treatment is important since these enzymes lead to the degradation of triacylglycerides and phospholipids resulting in higher amounts of free fatty acid responsible for a reduction of the shelf life of the oil.

In general, conditioning of flakes takes place by using drum- or stack-type cookers. The stack-type cooker is a vertical vessel consisting of several steam-heated floors. The flaked material is given on the first floor on the top of the cooker and a stirrer mixes the material for the desired time on the floor to ensure that a uniform uptake of temperature takes place by the flakes. The temperature run of the plate is adjusted so that the desired temperature is achieved as quickly as possible, to avoid enzymatic degradation reactions in the material. The resting time of the flakes on each plate depends on the properties of the flakes before cooking; however, in most cases, a time between 20 and 40 min is used. After this time, the material falls down on the next floor and so on. By this procedure, the flakes run progressively through each plate of the cooker. As a result of temperature and time control, as well as mixing of the material on each plate, a uniform heating is possible. During the process, all enzymes are deactivated, and by the use of hot steam or hot air it is possible to adjust the final water content of the seeds to optimal conditions for the pressing process.

Drum cookers consist of a number of individual horizontal tubes which can be heated. Each tube is equipped with a stirrer to enable the equal motion of the seeds in the cooker. The material is filled into the first tube by screw conveyers, and depending on the properties of the seeds a certain number of tubes are used for cooking.

The temperature used for cooking should be higher than 80°C to deactivate enzymes, but at temperatures higher than 100°C changes in aroma and taste of the resulting oil arise. In addition, higher cooking temperatures result in an increase of the amount of phosphorus and free fatty acids in the oil. For example, a rise in temperature from 80 to 100°C results in an increase of phosphorus from 125 mg/kg to more than 300 mg/kg and at the same time the amount of free fatty acids increases from 0.5 to about 0.6% (Unger 1990). A further aspect of the use of high temperatures during cooking over a longer period of time is the damage of protein components, which can impair the protein quality of the residue.

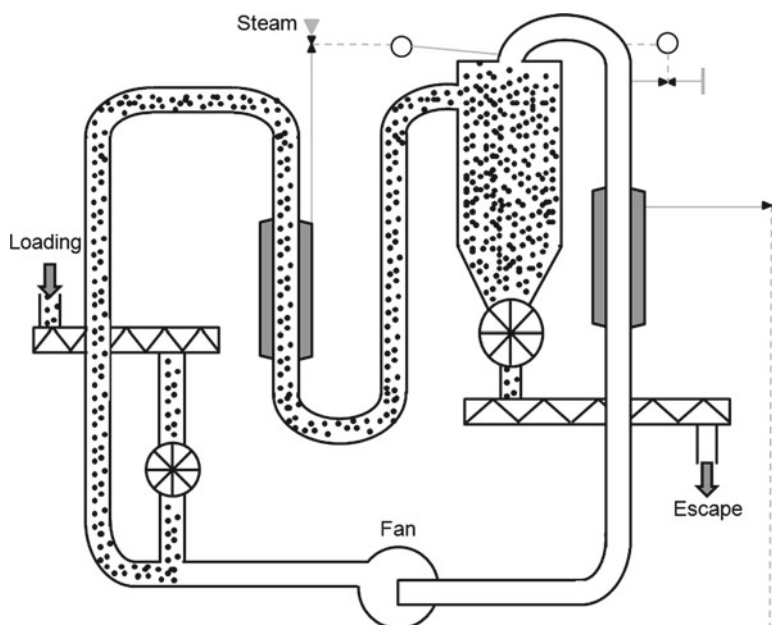


Fig. 2.6 High-temperature–short-time (HTST) conditioning of seeds

A relatively new method for conditioning the raw material before extraction is the high-temperature–short-time (HTST) conditioning of the seeds (Fig. 2.6). The material is treated less than 20 s with heated steam as heat carrier at temperatures between 120 and 145°C, which results in the seeds at temperatures higher than 100°C and an immediate deactivation of the enzymes. Another effect is a better extractability of valuable minor components such as polyphenols, while the content of tocopherols remains unchanged (Eggers 2008).

7 Extraction of Oilseeds

7.1 Pressing

Pressing of oil-bearing materials for the production of oil has been known for several hundred years and only after World War II this process was replaced by solvent extraction. Today, more than 98% of the oil production worldwide is carried out by solvent extraction, but for specialty oils, such as extra virgin olive oil or virgin rapeseed oil, oils produced in rural areas, or for pre-pressing before solvent extraction this old technique is still in use.

The aim of the pressing process is to separate the oily phase from the solid phase of the seed material. In large-scale facilities, two different pressing techniques are

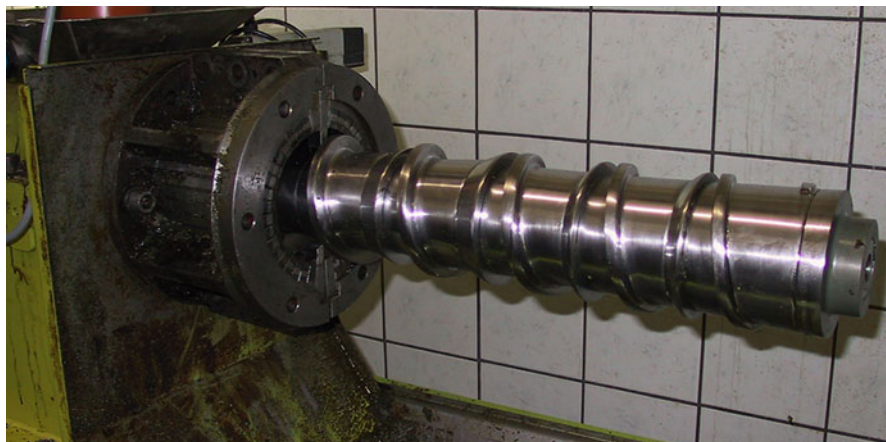


Fig. 2.7 Screw press without barrel cage to show worm sections

used for the separation of oil from the seed. The first one is pre-pressing of the flaked seeds which leave about 15–20% oil in the press cake. Today, this is the commonly used technique, which is followed by the extraction of the press cake by solvent. The advantage of pre-pressing is that a press cake is formed from the small flakes which allow a good solvent contact and percolation in the extractor. The result is an optimized removal of oil from the seeds (Unger 1990). Extraction by combining screw press and solvent extraction has the economical advantages – low costs using a screw press and higher oil yield using solvent extraction.

The other technique is a more extensive pressing of the oilseed without further extraction by solvent. This straight pressing is interesting for oilseeds with high oil content, where it is no problem to get over the release of some percent of oil in the residue. Nowadays, this method is used only barely in large-scale facilities since it is not possible to reduce the oil content to less than 5% oil in the press cake by this technique. From an economical point of view, this is not sufficient for this type of oil mill. Nevertheless, this technique has the advantages of lower investment and maintenance costs and of achieving higher oil quality (Niewiadomski 1990).

Different manufacturers for oil presses are on the market and the design and functionality vary from one manufacturer to another, but, in general, the principle is nearly the same for all presses. Most of them consist of a rotating screw shaft (Fig. 2.7) within a horizontal barrel. This screw shaft transports the seeds through the screw flight, in order to increase the pressure onto the material during the passage, the volume of the screw increases or the diameter of the screw flight decreases in the direction of the seed flow resulting in less space for the material and increasing pressure onto the material. Depending on the needs of the seed material, it is possible to vary the slope of the screw which results in a variation of the pressure increase within the screw press. The barrel is surrounded by flat bars, made of hardened steel, which form a cage around the screw (Fig. 2.8). Between the bars is some space, just as much that the oil can flow out of the barrel while most of the solid



Fig. 2.8 Barrel of a screw press surrounded by flat bars during pressing of oilseeds

material leaves the screw press at the end. By changing the space between the bars, it is possible to change and to adjust the pressure within the barrel. Another possibility to influence the pressure within the barrel is the size of the press cake exit at the end of the barrel and the slope of the screw. Because of high pressures up to 1,600 bar in screw presses used in large plants, temperatures up to 170°C can occur, since kinetic energy of the rotating screw shaft is changed into heat.

For a successful following solvent extraction, the resulting press cake should be spongy, permeable, and resistant to disintegration on its way to the solvent extractor. The optimum moisture content is between 4 and 5%, because otherwise the press cake does not have the correct consistency for solvent extraction, which impeded the contact between solvent and press cake. Additionally, a certain thickness of the cake is important; otherwise, the percolation of the solvent through the cake is influenced.

The result of the pressing process is the reduction of the oil content from 42% in rapeseed to about 16% in the press cake which is used for further solvent extraction.

7.2 Oil Extraction in Small- and Medium-Sized Facilities

For the production of the so-called virgin oils, only the use of a press without further treatment of the raw material or the resulting oil except filtration or sedimentation is allowed. The extraction is remarkably less efficient than for the production of



Fig. 2.9 Screw press of a small plant for the production of virgin, cold-pressed vegetable oils

commodity, but the consumer associates with virgin oils a healthier and better product, which allows selling it for a higher price. So, it is possible to get an added value for the product which is necessary from an economical point of view. In contrast to large plants, small- and medium-sized facilities often work and economize in regional material cycles which lead to an increased acceptance of the products by the consumers. In the case of other virgin oils than virgin extra olive oil, which is distributed worldwide, the distribution channel for this type of oil is characterized by short routes of transport and therefore reduced costs for transportation. Thus, these plants are able to supply a manageable and quantitatively limited market with high-quality virgin oils.

In general, the extraction method by screw presses (Fig. 2.9) is comparable to pre-pressing in large facilities, but it is necessary to carry out the process more gently, because the small plants have no chance to improve the quality of the oil by a refining process after the extraction. Nevertheless, the oil yield after pressing in small- and medium-sized facilities is higher than during pre-pressing in large plants. Depending on the type of press and the settings, about 10–15% oil remains in the press cake, whereas after pre-pressing the press cake contains 15–20% oil.

A gentle pressing process is recommended because the content of chlorophyll and phosphorus and the amount of free fatty acids are strongly influenced by the pressing conditions. Especially an increase in the temperature within the compressed material leads to an increase of these components in the oil. The amount of free fatty acids, chlorophyll, and phosphorous is of special interest because they negatively influence the stability of the oil and, additionally, phosphorous is an

important parameter if the oil is used as fuel. In the case of rapeseed oil, the amount should be below 3 mg/kg (Anonymous 2010). Therefore, it is necessary to avoid the formation of these components during production to improve the quality and to prolong the shelf life of the oil. However, if high-quality seed material is used for the pressing process, the settings of the screw press can be varied in a wide range without running the risk of changing the quality of the resulting oil.

The most important parameter for the evaluation of the quality of virgin oils is the sensory impression, because more than any other parameter the appearance and the taste of a product deeply influence the buying decision of the consumer. Typical attributes are *seed like* and *nutty* for virgin rapeseed oils; *fruity*, *bitter*, and *pungent* for extra virgin olive oil; and *sunflower-seed like*, *nutty*, and sometimes *fruity* for virgin sunflower oil or *vinous* and *fruity*, which also reminds of *raisins* for virgin grape seed oil. On the other hand, attributes such as *rancid*, *straw like*, *wood like*, *fried*, *burnt*, *fusty*, *musty*, *bitter*, and *astringent* belong to the typical off-flavors resulting from the formation of volatile degradation products or the development of aroma-active compounds during faulty processing (Attenberger et al. 2005). In virgin grape seed oil, aroma-active compounds such as ethanol, ethyl acetate, or acetic acid can appear if the raw material was not dried immediately after mashing, because of degradation processes due to microorganisms.

7.3 Extraction by Solvent

Extraction by solvent is recommended if it is necessary to reduce the oil content in the raw material to lower than 2%. This means the aim of extraction by solvent is to remove as much oil as possible from the oilseed. From an economical point of view, pre-extraction by screw presses is advisable, because equipment and maintenance for solvent extraction is very costly. In most cases, hexane is used as solvent, because it is cheap, has good oil solubility at relatively low temperature, has an appropriate boiling temperature, is noncorrosive to metal, does not react chemically with the oil, is stable under the process conditions, is not mixable with water, which eases the separation of water from the seeds, and it is easily and completely removed from the residue with low energy input and without impairment of the raw oil. Nevertheless, this solvent also has some disadvantages with regard to its potential danger from which results high requirements concerning the equipment. Hexane is highly flammable and mixtures of air and hexane are explosive, which entail the risk of fire and explosion if the plant does not consider appropriate cautionary measures. From this, it is urgently recommended to use explosion-proofed electrical equipments, to avoid the possibility that hexane being accumulated at deeper locations, since hexane is heavier than air and to avoid hexane coming into contact with hot components of the extraction apparatus. Despite such measures every year some solvent-extraction plant explodes somewhere in the world. Often, plants purge all vessels with an inert gas to reduce the risk of fire or explosion.

Because of this disadvantage, also some other solvents such as hydrogen sulfide or trichloroethylene are in the discussion, but finally the advantages of hexane overbalance the disadvantages in comparison to the other solvents. Hydrogen sulfide has a high toxicity, a low boiling point, and an extremely high vapor pressure. The heat of evaporation of trichloroethylene is higher than that of hexane, considering the density.

During solvent extraction of the oilseed, an intensive contact between solvent and press cake is necessary to achieve an exhaustive removal of oil. For this, the solvent is heated to 50–60°C, but it is important to avoid boiling when hot press cake comes into contact with the solvent. Since press cake comes hot from the pressing process, a further temperature supply is only necessary when the extractor starts working. Temperature is important for the extraction since viscosity of the solvent is reduced and the solubility of the extract increases with higher temperatures. The result is a higher rate of extraction. Additionally, the composition of the extract is influenced by the extraction temperature. While most oils mainly consist of triacylglycerides, minor components such as phospholipids, chlorophyll, free fatty acids, color pigments, and degradation products of oxidative reactions are co-extracted by the solvent. This amount of minor components increases drastically with the temperature. For example, an increase in temperature from 40 to 58°C raises the content of phospholipids in rapeseed oil from 0.2 to 0.8% (Kock 1981). This should be taken into consideration, because removal of minor components during refining is costly.

Another important factor influencing the result of solvent extraction is moisture, which can come from the surface of the press cake or from poor water/hexane separation after distillation. This moisture can avoid an optimal penetration of the press cake by the solvent, resulting in low extraction rates and high residual solvent in the meal. In some cases, “blinding off” of the perforated cell floors occurs resulting in the necessity of a complete shutdown of the plant and cleaning of the floors.

The extraction rate not only depends on temperature and moisture but also on the adjustment of equilibrium between diffusion of solvent into cake particles to dissolve oil and diffusion of oil from within the particles out into the solvent for which a certain time is necessary. This time is needed for an extensive extraction of the press cake. Therefore, each plant has to find a balance between time necessary for the extraction and the oil yield necessary for an economical work. The highest amount of oil is extracted within the first few minutes of the process: 75% in the first 25 min, whereas the total oil yield depends on the further number of extraction steps and the total extraction time. The extraction of the remaining 25% oil from the press cake takes disproportionately more time.

The structure and the behavior of the cake particles are significant for the result of the extraction process. Excessively fine press cake resulting from excessive handling of the cake before processing, from poor settings of the screw press during pressing or from improper moisture content of the raw seed material negatively influences the percolation rate of the solvent through the cake. While soybean flakes, for example, are stable enough to survive the mechanical and hydraulic strain during the extraction process, rapeseed flakes are more fragile and susceptible.

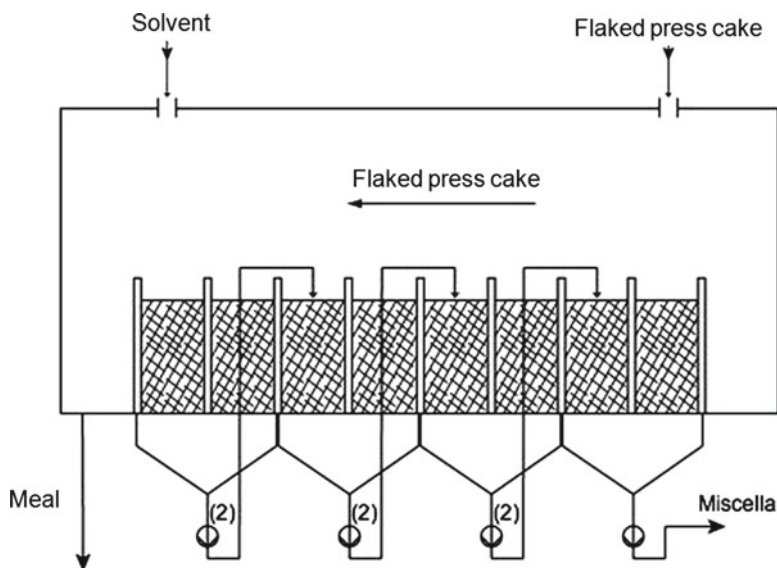


Fig. 2.10 Extractor

The result is small particles with a worse surface/volume ratio, which lead to a remarkable worse percolation of the solvent through the cake bed. This again results in poor extraction efficiency, higher residual oil content in the press cake (Unger 1990), and also high levels of solvent in the meal. Thus, more extraction steps and a higher solvent requirement are necessary to achieve a sufficient oil yield.

In most cases, solvent extraction of the press cake is carried out by using a continuous counter-current extraction process moving the press cake and the solvent in opposite directions (Fig. 2.10). This method is most efficient in reducing the oil content of the press cake to a minimum, while the need of solvent remains comparably low. During the process, the cake is brought into contact with solvent several times and after a certain time of adjustment of equilibrium the solvent/oil mixture, called as miscella, is allowed to drain away from the cake. With each step, the amount of oil in the cake is reduced, but since it is not possible to remove all of the solvent from the cake a certain amount remains together with oil in the cake. Therefore, theoretically, the extraction process is an infinite process and the processor has to balance between economical aspects and an extraction as extensively as possible.

The number of extraction steps depends on the performance of the extractor. Often, seven to ten successive wash stages have been used. However, an extensive extraction with fewer steps is possible if the cake is saturated by solvent allowing it to soak over a sufficient time followed by flushing the enriched miscella from the surface of the particles and replacing it with a leaner miscella. In that case, only two or three extraction steps are necessary with a reduced number of pumps, thereby reducing costs of energy, capital, and maintenance (Beach 1983).

For the extraction of the press cake, a mixture of n-hexane and oil is used and the concentration of oil in hexane decreases with each extraction step. In the last step, before the meal leaves the extractor it will be washed with pure solvent.

Several different types of extractors are in use, including rotary, shallow bed or deep bed, horizontal belt, and continuous loop extractors. The use of the one or the other method is a question of belief and the main difference between the different extractors is the how they transport the solid through the extractor. The principle of all these extractors is comparable, but there are some differences in the technical equipment and performance. Some extractors immerse the solids in the solvent, comparable to a Soxhlet extractor in laboratory use, while some percolate the solvent through the solids, and some others use a combination of both immersion and percolation. Disadvantages of percolation extractors are higher requirement of solvent and problems during transport of material. Therefore, today, percolation extractors are the method of choice in industry.

Another important difference is the depth of the cake bed. It is about 20–50 cm in the case of shallow-bed extractors, which allow a fast percolation by the solvent while the throughput is less. Using deep-bed extractors, the depth of the cake bed is much higher and the percolation takes much more time, but the extractor is more compact and provides much more capacity per unit of building volume (Beach 1983). Good extractors offer the possibility to modify the height of the cake bed, in order to consider different percolation parameters of different materials.

In most cases, the percolation extractors consist of compartments or cells in which solids are washed with successively less concentrated miscella and finally with fresh solvent. The final miscella contains 20–30% oil. The flakes, given a final wash with raw solvent, have had about 95% of their oil extracted. Another type of extractor is the horizontal belt extractor which conveys solids through a series of solvent sprays. After percolating through the bed, the miscella is collected in a hopper below the conveyor. Continuous-loop extractors are shallow-bed extractors that carry the solid material through an enclosed vertical loop. The miscella, low in oil and high in n-hexane, at the beginning is circulated counter-current to the flow of the cake until the cake leaves the extractor. In a last step, pure solvent extracts the cake just before it leaves the extractor. The solids go through both percolation and immersion, and are completely turned over, allowing the solvent to contact flakes from both sides.

In addition to the equipment, the size of the extractors varies as well. Stationary extractors are available, but it is also possible to use transportable equipments to work more variable.

7.4 Palm Kernel Oil

From the fiber-nut mixture obtained after extraction of palm oil, the nuts are separated for the production of palm kernel oil. Often, palm kernel oil is produced in separate facilities. In the so-called depericarpers consisting of pneumatic separation

columns with a strong suction the nuts are separated from the fiber at a different specific gravity. The air removes the fibers and transports them to a cyclone from which it is used as fuel for the generation of steam. Due to the higher weight, nuts are collected at the bottom of the depericarper, cleaned in a rotary drum, and transported to a silo for further drying to about 10% moisture before storage.

For the release of the kernels, the nuts are cracked in centrifugal or barrel crackers, whereas depending on the speed of the cracker the kernels break into more or less pieces. Therefore, this step is crucial for the quality of the resulting palm kernel oil, because break of the kernels during the process results in an increase of free fatty acids and losses of kernels during the separation of shell and kernels at a different specific gravity of kernels and other materials in a combination of winnowing and hydrocyclones. The moisture content of the kernels is reduced to about 7% to minimize enzymatic activity from lipases and to maintain the quality of the kernels during storage. The extraction of the kernels takes place either by a screw press or by solvent extraction.

7.5 *Enzymatic Pretreatment*

An interesting method to enhance the oil recovery from the seeds or fruits is the treatment of the raw material by enzymes. The aim of this procedure is to modify the seed coat and cell walls to increase the oil yield. By this, the need of disruption of cell walls by mechanical treatment during flaking is reduced. Additionally, the extraction time decreases, which increases the efficiency of the pressing process for 92%. Further on, this procedure has a lower energy requirement and results in less losses of hexane during solvent extraction. Normally, rapeseed meal tends to retain twice the level of residual hexane found in soybean meal. This hexane has to be removed from the meal by more heat, resulting in an increase of the overall energy requirements of the process. During the removal of hexane, the meal becomes a darker color and worse availability of nutrients.

For enzyme pretreatment, different enzymes of the type carbohydrase are in use: β -glucanase, pectinase, hemicellulase, cellulose, or mixed enzyme preparations. The enzymes degraded the cell walls of the seeds which mainly consist of carbohydrates. In this process, the different enzymes show the following relative order of efficiency in enhancement of oil extraction: mixed enzymes > β -glucanase > pectinase > hemicellulase > cellulose (Sosulski et al. 1988). Investigations showed that treatment with enzymes improved throughput of the screw press and increased oil flow rate and oil recovery. Material throughput was increased by 30–50%, depending on rapeseed variety, and recovery of the oil was increased from 72% of the seed oil extracted after conventional treatment to 90–93% for enzyme-treated samples (Sosulski and Sosulski 1993).

The enzymatical treatment of oil-bearing fruits or oilseeds strongly depends on the processing temperature and the pH conditions for the hydrolysis. In general, the values of these parameters should be in the optimum range of the maximum activity

of the enzyme and additionally the quality of the product should not be affected. Often, a stepwise increase of the temperature is used to get the optimal conditions for the enzymes. Fullbrook (1983) started a temperature program for the enzymatical treatment of rapeseed and soybeans at 50°C for 60 min, went to 63°C for 120 min, and then deactivated the enzymes by a short heat treatment at 80°C. Another sequence of increasing temperatures (40, 50, and 65°C) over a period of 3 h was used by Lanzani et al. (1975) for the treatment of sunflower, rapeseed, and peanut. The optimal pH value ranges between 4.5 and 5.5, whereas the maximum is between 3 and 8. The particle size of the seeds also has a strong influence on the efficiency of the enzymatic treatment, whereas for a fixed particle size moisture contents of 60 and 40% for soybean and sunflower seeds, respectively, are recommended to efficiently increase the extractability of the seeds (Dominquez et al. 1993).

It has to be taken into consideration that the effectiveness of the treatment depends upon the material which is treated and the extractive process. While water-extracted sunflower seeds give higher yields after enzymatic treatment, the effect of this treatment was only small for peanuts.

7.6 *Extraction by Carbon Dioxide*

One alternative to the commonly used extraction methods is the extraction by carbon dioxide under supercritical conditions. Under these conditions, if temperature (>31.1°C) and pressure (>73 atm) both increase, carbon dioxide adopts properties midway between a gas and a liquid, with comparable dissolving power as n-hexane. Carbon dioxide has the following advantages: it is not toxic, is easy to remove from the oil and the meal, and it is nonflammable. Additionally, depending on the conditions, the temperature of the process is relatively low. Thus, the method is very gentle to minimize deteriorations of the product during extraction and the amount of minor compounds co-extracted with the oil from the seeds is reduced since carbon dioxide is highly selective for triacylglycerides. The disadvantage of carbon dioxide is that the application is very expensive, which makes the use only interesting for specialty oils produced in low amounts and sold at a high price. Another drawback is the difficulty to use supercritical carbon dioxide in a continuous extraction procedure, which would be preferred for large-scale processing (Booth 2004).

Recently, a gas-assisted oilseed pressing has been developed that extracts the oilseed by a mechanical solid–fluid separation aided by the application of a dense gas. The gas is contacted with the oilseed before or during pressing in order to achieve lower residual oil contents. Especially the use of carbon dioxide showed good results regarding oil yield. For rapeseed, a considerable increase in oil yield from 27 to 71% was found (Voges et al. 2007). In this system, the gas is injected into the press resulting in a lowering of the viscosity and an easier drainage of the oil from the material. The system works hexane-free, allows the extraction of oil under more gentle and low-temperature conditions, and may result in higher quality of the resulting oil. A higher oil yield than under normal pressing conditions can be expected.

8 Extraction of Oil-Bearing Fruits

Different from oilseeds, oil-bearing fruits consist of fruit flesh (mesocarp) which contains oil and a seed kernel providing a solid fat. Additionally, the must of a fast processing after harvest is completely different from the processing of oilseeds. In an optimal case, the oil-bearing fruits have to be processed within hours after harvest, because they are very susceptible to damage resulting in the degradation of the oil. In the case of palm oil, lipolytic enzymes such as lipases have to be inactivated almost directly after harvest, because with progressing maturity of the fruits enzyme and substrate come together, leading to the degradation of triacylglycerides. To avoid this degradation, fruits have to be sterilized or cooked before further processing. Also, microorganisms cause oil degradation through attack on overripened and bruised fruits, thereby causing an increase in the free fatty acid (Ademosun 1982).

8.1 Palm Oil

The most widely processed oil fruits are fruits from the palm tree (*Elaeis guineensis*). The palm fruits are located in fruit bunches which contain between 600 and 3,000 fruits with total weights between 10 and 80 kg. The fruits are about 2–5 cm long and 3–30 g in weight.

As for oilseeds, processing of oil-bearing fruits starts with the harvest, because for the production of high-quality palm oil a careful collection of bunches is absolutely necessary. While the content of free fatty acids at the time of cutting is about 1% or lower, it rises up very fast if the cell structure of the fruit has been adversely affected by improper handling.

The very active lipase, which is responsible for the formation of free fatty acids from the intact triacylglycerides, has to be inactivated in autoclaves directly after arrival of bunches in the oil mill. This treatment not only inactivates enzymes but also enables an easier separation of the fruits from bunches, weakens the pulp structures, and solidifies proteins in which oil-bearing cells are microscopically dispersed (Poku 2002). The use of high-pressure steam also causes an easier separation of the kernels from the hulls. Sterilization takes place by the use of steam at temperatures between 100 and 130°C at pressure between 2.5 and 3 bar for about 1 h. Often, a three-step process with different pressures and residence times is used for sterilization which is more efficient than sterilization for a longer time under the same conditions. The specific conditions mainly depend on the size of bunches.

After separation of fruits from bunch stalks by use of shakers or so-called strippers in the form of beater arm strippers or rotary drum strippers, the fruits are treated in a digester in order to open the cell walls of the mesocarp, which improves

the extractability of the oils during pressing and strongly influences the oil yield. The use of a higher temperature during the procedure reduces the viscosity of the oil, destroys the exocarp, and opens cell walls which withstand the sterilization. In a vertical cylindrical vessel, fruits are mixed by a central agitator consisting of a rotating shaft carrying a number of beater arms at about 100°C for 10–30 min. Heat is produced either by a double steam jacket or by direct steam injection. A risk of the digestion procedure is the contamination of the raw material with iron, because the process shows the highest rate of meal wear during the milling.

The separation of the oil from the solid material takes place similar to the extraction of oilseeds using continuous screw presses. The aim of this procedure is to extract the oil from the mesocarp without affecting the kernels, which are used for the production of palm kernel oil. This procedure is also called as “dry” method, while in a “wet” method hot water is used for the extraction of the oil. Similar to the extraction of oilseeds, the digested material is continuously filled into the cage of the screw press and then transported to the outlet by a conical running up screw resulting in the formation of pressure that is sufficient for the extraction of oil from the material. At the end of the process, a mixture of about 65% oil, 25% water, and 10% solid material consisting of cell debris, fibrous material, sand, shells, and other “nonoily solids” is obtained. In comparison to batch systems using hydraulic presses, the extraction by continuously working screw presses has the advantage that this procedure is suitable to disrupt unopened cell walls which have passed the digester unscathed.

For the removal of impurities from the resulting oil/water mixture, a clarification of the product is necessary. In a first step, parts of the “nonoily solids” are removed by using single- or double-deck vibratory screens, before the crude oil is transferred into continuous settling tanks. In these tanks, the specific gravity differences between oil, water, and solid material are used for the separation and in order to improve the conditions for the separation hot water is added in a ratio of 3:1 at a temperature of about 85°C. The use of heat is necessary to break emulsions encouraged by mono- and diacylglycerides after addition of water. The mixture is allowed to stand for 2 h resulting in the separation of the mixture into oil, water, and slurry. The clarified oil is decanted into another tank. It still contains traces of water and dirt, which can adversely affect the oil quality regarding the content of free fatty acids by autocatalytic hydrolysis. Therefore, the moisture content has to be further reduced to contents between 0.15 and 0.25%. Other impurities are removed by centrifugation or three-phase decanters.

A final drying of the crude oil is necessary because palm oil contains small amounts of phosphatides which can slowly dehydrate resulting in an insoluble precipitation. The removal of residual moisture is done either by atmospheric pressure dryer or by vacuum dryer, whereas the use of a vacuum dryer is recommended, because a more careful handling is possible due to a lower temperature. After drying, the purified oil is transferred into a storage tank and in large facilities temperature is kept at 50°C using hot water or low-pressure steam-heating coils to prevent solidification and fractionation (Poku 2002).

8.2 Olive Oil

The production of olive oil is a very old technique and the basic steps have not really changed over the last thousands of years. In a first step before extraction, it is necessary to clean the olives and to remove stems, leaves, twigs, and other residues that can affect the quality of the resulting olive oil regarding sensory quality and storage stability. It is also necessary to wash the olives to remove pesticides and other contaminants as well as dirt and rocks that can damage the mill. The life span of centrifugal decanters or oil separators can be reduced drastically.

After a careful cleaning, grinding of the olives by metal tooth grinders, hammer mills, or stone mills into a paste is the next step resulting in the damage of the cells for a better release of the oil. The used method for grinding influences the flavor of the resulting oil. Especially the use of metal tooth grinders or metallic disks increases the presence of polyphenols which are responsible for a bitter and pungent taste. Normally, the olives are not destoned, because on the one hand the oil yield decreases and on the other hand the presence of stones seems to have no adverse effect on the flavor of the oil. Nevertheless, destoning also has some advantages such as the pomace can be more easily used for animal feeding, the polyphenol content may be higher resulting in a better oxidative stability and acidity, and peroxide values are slightly lower. Disadvantages are the implementation of a further processing step, the need for special equipment for destoning, and longer mixing time with the formation of undesired oxidation products.

After grinding, the resulting paste is mixed for 20–60 min at 25–35°C in horizontal troughs which allows the small oil droplets from the cells to agglomerate to bigger ones that are better extractable from the paste. Additionally, unbroken cells are destroyed. It is possible to heat the paste or to add water to the paste, thus increasing the oil yield but lowering the oil quality. Heating results in lowering of the viscosity of the oil droplets, but accelerates oxidation processes and enzymatic breakdown of the paste. During this process, also called as malaxing, enzymatic processes take place resulting in the formation of the typical flavor of olive oil. The longer the mixing time, the higher the chance of the oil taking up minor components that can improve the flavor. On the other hand, it has to be taken into consideration that oxidation processes occur which impair the oxidative stability of the oil and decrease the shelf life. With increasing mixing temperature and constant mixing time, the content of polyphenols increases while longer mixing time with constant mixing temperature results in a decrease of the total polyphenol content in the oil.

For the separation of the oil from the solid material, different techniques are in use. The oldest ones are the separation by means of gravity (Fig. 2.11) or pressing with either lever or screw presses. In that case, the paste was put on mats or in bags that were squeezed by pressing (Fig. 2.12). Disadvantages are low oil yields resulting from low pressure and time-consuming labor due to the discontinuous process. The oil quality was bad because it was not possible to clean the mats or bags sufficiently. Later, hydraulic presses were used with a higher efficiency.

Today, the use of centrifuges is the method of choice, whereas two-phase and three-phase centrifuges are known. The proportion of these methods is more than 90% in Spain, more than 50% in Italy, and these methods are also used in other

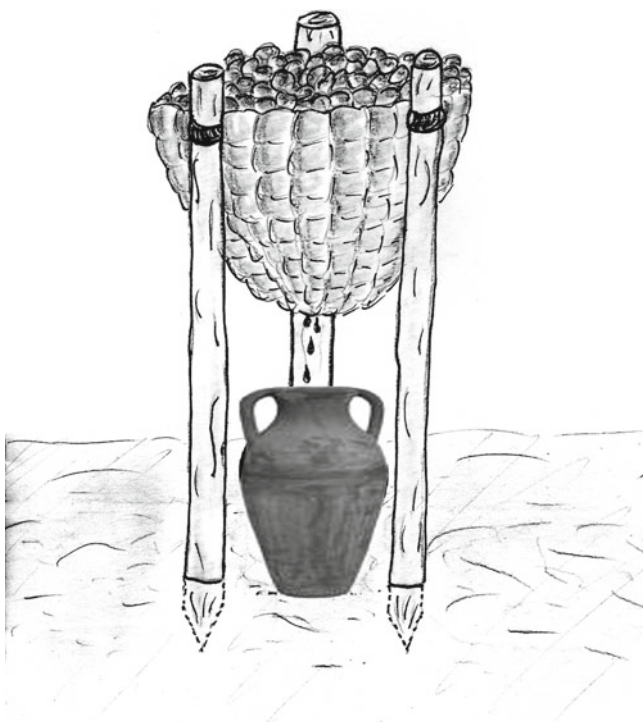


Fig. 2.11 Extraction of olive oil by gravity (by courtesy of M. Matthäus, Münster, Germany)



Fig. 2.12 Old wooden screw press (by courtesy of the museum for folklore, Spittal an der Drau, Austria)

Table 2.1 Different quality parameters of virgin olive oils processed by different methods (di Giovacchino et al. 1994)

| Parameter | Pressing | Three-phase-centrifugation | Percolation |
|--|----------|----------------------------|-------------|
| Free fatty acids (%) | 0.23 | 0.22 | 0.23 |
| Peroxide value (meq O ₂ /kg) | 4.0 | 4.9 | 4.6 |
| Total content of polyphenols (mg/L as gallic acid) | 158 | 121 | 157 |
| <i>O</i> -Diphenols (mg/L as caffeic acid) | 100 | 61 | 99 |
| Induction period (h) | 11.7 | 8.9 | 11.2 |
| Chlorophyll pigments (mg/kg) | 5.0 | 9.1 | 8.9 |
| K ₂₃₂ | 1.93 | 2.01 | 2.03 |
| K ₂₇₀ | 0.120 | 0.127 | 0.124 |
| Organoleptic assessment | 6.9 | 7.0 | 7.0 |

Mediterranean countries such as Greece, Turkey, or Tunisia. Three-phase centrifuges separate oil, water, and solids individually, whereas the two-phase centrifuge separates the oil from the wet paste. Both methods have low operating costs and the pomace only contains low amounts of residual olive oil; however, the investment is high, the pomace is wetter than for the production by pressing, and a high volume of wastewater is produced. The use of centrifuges results in lower amounts of polyphenols in the oil because of the use of water. This results in not only less bitterness of the oil but also a lower oxidative stability. The paste is pumped together with lukewarm water through the decanter which increases the fluidity of the mixture and improves the separation of oil and solid material, but produces high amounts of wastewater.

Another extraction system is called as cold percolation, where the oil is extracted from the paste by using the Sinolea (1991) equipment. Due to the different surface tension of oil and water, the olive oil is separated from the paste by steel blades which deliver the oil. The plates are coated with the oil and when withdrawn from the paste olive oil drips off in a continuous process. Advantages of the process are higher polyphenol contents of the oil because of no use of water, low temperature load of oil during processing, no use of additional water, and the possibility to automate the process resulting in less labor and lower operating costs. It is unfavorable that the oil yield is lower (only 70–75% of the oil contained in olives is extracted) so that the process has to be combined with one of the other processes and the use of plates results in a large surface with a risk to accelerate oxidation. Nevertheless, Sciancalepore et al. (2000) showed that oil obtained by a cold percolation system had lower free acidity, peroxide value, and ultraviolet (UV) absorption (K₂₃₂ and K₂₇₀) and higher polyphenol contents in comparison to oils from a two-phase centrifugation. They also confirmed these results by the autoxidation stability of the oils. Di Giovacchino et al. (1994) showed that virgin olive oils from percolation or pressing contained remarkably higher contents of polyphenols than oils from three-phase centrifugation, because during centrifugation water-soluble polyphenols are removed together with the used water. Also, concerning the induction period, oils from percolation and pressing showed better results while the oil quality of the oils processed by different methods regarding other parameters such as free fatty acids, peroxide value, or organoleptic assessment was comparable (Table 2.1).

As a final step, the residual water and solids have to be removed by a second centrifugation with faster centrifuges and then the oil is stored in tanks, where a further purification takes place by sedimentation due to differences between oil and solids in gravity. If necessary, the oil can be filtered before bottling.

9 Separation of Solvent and Oil

After the solvent-extraction process, the resulting miscella contains 20–30% oil in hexane. For an economical procedure, the recovery and re-utilization of the solvent are necessary. Since recovery of solvent needs energy and equipment, the aim must be to obtain as much oil as possible from the miscella with an economically justifiable need of energy.

After leaving the solvent extractor, finest particles of the seed material resulting from the treatment during solvent extraction, but also from the treatment during screw pressing, have to be separated from the miscella, because they can influence the heat transfer during distillation. The amount of particles depends on the equipment used for the extraction. While direct solvent extraction without pre-pressing results in comparably higher amounts of particles, the amount is much lower if pre-pressing is used before solvent extraction.

The separation of solvent and oil is achieved by conventional distilling methods by combining a series of sills, stripping columns, and condensers. In general, a two- or three-stage process is carried out. In a first step, hexane and steam vapors from the desolventizer toaster used for the removal of hexane from the meal are applied as heat source. In this step, the mixture reaches temperatures of about 50°C. Afterward, the resulting oil enriched liquid is treated in a steam-heated exchanger where the concentration of hexane decreases to about 5% of the miscella mass at a temperature of about 80°C. The hexane is recycled to the extractor for further use.

Finally, the concentration of hexane in oil has to be reduced to less than 800 ppm to reach a flash point of the oil higher than 250°C. Residues of hexane in the oil are finally removed during deodorization. To reach the mentioned amount of hexane in the oil, the miscella is passed through an oil stripper tower under pressure of 13.3 kPa and temperature of about 100°C. As temperature higher than 105°C adversely affects the quality of the crude oil, steam distillation is used. For this purpose, the oil is heated to 90–100°C in a preheater and then steam is injected from the bottom to increase the effectiveness of the process. For a well-operated extraction plant, it is possible to maintain hexane losses during the process lower than 3.0 L/metric ton (Unger 1990).

10 Toasting of the Meal

For the further commercialization of the resulting meal, it is necessary to remove all hexane from the solvent-extracted cake in order to observe the limits of the feeding stuff regulations and to avoid the danger of explosions. After the extraction process,

about 25–35% solvent remains in the cake which has to be removed by evaporation in a desolventizer toaster. Another effect of this procedure is drying and crisping of the meal and the recovery of the solvent for further use. A further purpose of steam treatment is the degradation of antinutritive compounds, such as glucosinolates in rapeseed meal or protease inhibitors in soybean meal (trypsin and chymotrypsin inhibitors) and the inactivation of enzymes such as myrosinase (rapeseed) or urease (soybeans) is achieved. Additionally, the digestibility of proteins is improved, but, in the case of soybean meal, the protein is denaturated and loses some water solubility.

During the toasting process in large oil mills about 1/3–2/3 of the glucosinolates in rapeseed meal are removed depending on the settings of the process (Schumann 2005). To avoid the degradation of amino acids resulting in lowering the feeding value of the meal, a strict control of temperature, moisture, and retention time in the desolventizer toaster is important.

Older equipments consisted of several superimposed horizontal tubes with a jacket. The meal was filled into the first tube and a screw conveyer transported the product to the end of the tube where it fell into the next tube. Each tube was heated by steam to ensure a temperature of the meal of about 100°C.

Today, most of the desolventizer toasters consist of an enclosed vertical vessel equipped with several steam-heated horizontal floors. The solvent-extracted cake enters the first floor by a screw conveyer and a rotating sweep arm ensures a uniform heat transfer by mixing the cake on the floor. In addition, the rotating sweep arm transports the cake down onto the next floor. The cake enters the apparatus at about 60°C and is heated during the process to 105°C (Fig. 2.13). To improve the recovery of solvent, the addition of direct steam is used which ensures the recovery of hexane absorbed by the protein and “trapped” within the cell walls. Steam also acts as a carrier to transport the solvent through the bed of extracted cake.

At the end of the process, the meal moisture is about 15–18%. For storage and delivery to feed manufacturers, it is necessary to dry the meal to a moisture content of 8–10%. Afterward, the meal is cooled down and milled.

10.1 Batch Fluidized-Bed Desolventizer System for Production of High-Quality Protein

The most crucial step in conventional processing is meal desolventizing after solvent extraction. These conditions negatively influence protein extractability, the proteins will be damaged, and the protein dispersibility index (PDI) will be reduced resulting in a loss of the techno-functional properties. After processing, such products are only usable for animal feeding. Especially rapeseed meal with high protein content and an interesting amino acid composition is almost only used for animal feeding which means a relatively low added value. Besides their valuable nutritional properties, rapeseed storage proteins possess a high potential of functionality offering a wide range of human nutrition and technical–chemical applications. They are able to stabilize emulsions and films and to form gel-like or other structured systems with high water binding capacity.

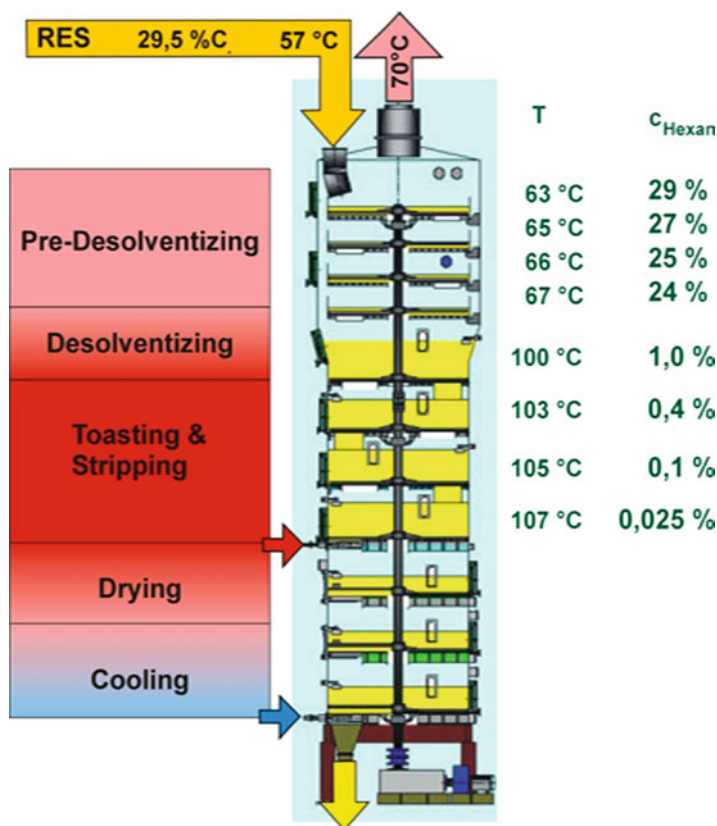


Fig. 2.13 Conventional desolventizer-toaster system

To avoid PDI decrease during desolventizing in soybean processing, the so-called flash desolventizers (FDSs) are used to produce white flakes (Fig. 2.14). Flaked meal is given in a pipe, in which superheated hexane at about 85°C is circulating with high velocity, evaporating most of the solvent from the flakes. This treatment is finished after few seconds. Subsequently, residual solvent is removed from the meal by stripping with superheated steam in a flake stripper. In this way, PDI up to 85% can be reached depending on the used raw material. To fulfill other requirements on PDI of the flakes it can be adjusted by a final flake cooking system. Cooking with the addition of water, desuperheated or saturated steam leads to PDI values between 15 and 85% (Milligan and Suriano 1974).

Flash desolventizing is possible due to a very high heat and mass transfer surface of the flakes. Vavlitis and Milligan (1993) described that in the case of 0.23-mm-thick flakes there is an active surface in the tube of about 6.700 m² available. But, if flakes are only a little bit thicker, this active surface will be drastically lower. Finally, spherical particles lead to a very low active surface of about 1.500 m². Hexane wetted rapeseed

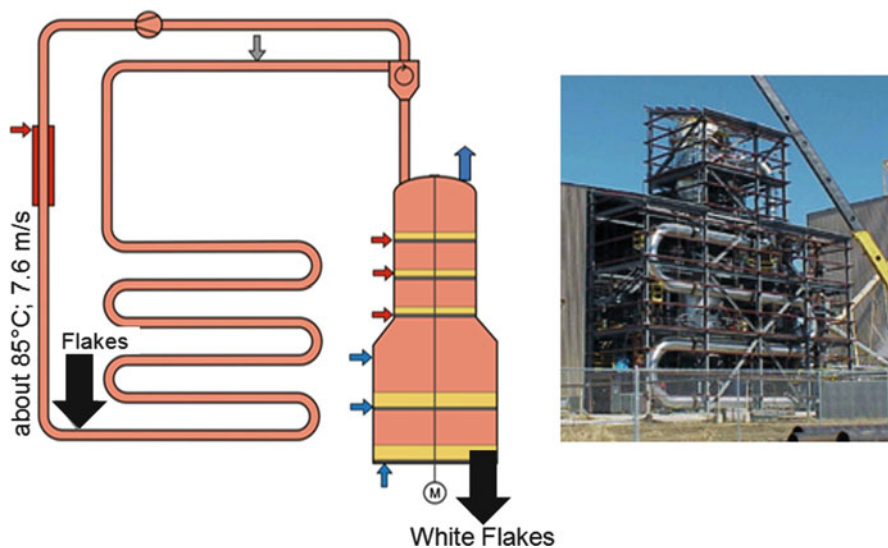


Fig. 2.14 (a) Scheme of a flash desolventizer system (FDS); (b) Industrial flash desolventizer system (by courtesy of Dr. F. Pudel, PPM, Magdeburg, Germany)

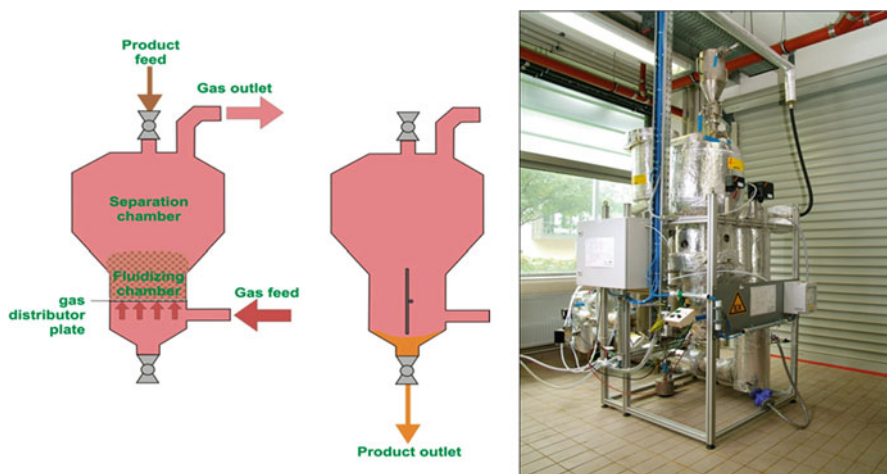


Fig. 2.15 (a) Scheme of fluidized-bed desolventizer system and (b) small pilot scale fluidized-bed desolventizer (by courtesy of Dr. F. Pudel, PPM, Magdeburg, Germany)

meal has rather a spherical shape than that of flat blanks. Therefore, a flash desolventizer system does not seem to be suitable for gentle desolventizing of rapeseed meal.

An alternative process to realize very high heat and mass transfer is the application of a batch fluidized-bed desolventizer system developed in a joint project from PPM Pilot Pflanzenöltechnologie Magdeburg e.V., Dr. Weigel Anlagenbau Magdeburg and Otto-von-Guericke-University of Magdeburg (Fig. 2.15). A fluidized

bed consists of solid particles which are placed by a fluid under such conditions that the solid/fluid mixture behaves as a fluid. The fluid (superheated hexane) is fed up from the bottom and distributed by a perforated plate. It leaves the separation chamber on top. The meal is fed in from top and fluidized by the fluid. After treatment, the distributor plate is turned and the desolventized meal can be removed from the equipment. After filtration, the fluid is partially condensed; hexane and water are separated and led back into the system.

The velocity of the fluid must be higher than the minimum fluidized-bed velocity; below that point a fixed bed occurs. At the upper end, the velocity has to be lower than the fluctuation velocity; above that pneumatic transport begins. Minimum fluidized-bed velocity and fluctuation velocity depend on particle size. Therefore, the operating range of a stable fluidized bed is defined by the minimum fluidized-bed velocity of the largest particles and the fluctuation velocity of the smallest particles. Particles with a size less than 0.4 mm would begin to leave the apparatus if the fluid velocity is just high enough that particles of about 5 mm can be fluidized.

11 Purification of the Crude Oil

Additionally to about 98% triacylglycerides, crude oil contains phospholipids, free fatty acids, colored pigments, sterols, waxes, oxidation products, moisture, and aroma components, as well as plant parts and dirt in varying amounts depending on the conditions of the extraction process. The more extensive the extraction conditions, the higher the amount of minor compounds, which strongly impair the quality and the shelf life of the oil. From this, it is necessary to connect a purification of the crude oil after the extraction process. In the case of crude oil from solvent extraction, this process, called as refining, involves different steps because otherwise the oil is not consumable. Virgin, cold-pressed oils are only freed by filtration, sedimentation, or centrifugation of particles from the disrupted seed material which come into the oil during screw pressing. A separation of undesired minor compounds does not take place. Some cold-pressed oils are also washed by hot-water steam with the aim to improve the taste and the smell of the oil as well as the oxidative stability.

11.1 Cold-Pressed Oils

Purification of virgin, cold-pressed oils only contains the separation of solid impurities, mainly particles of the seed material. This is an important step to ensure the quality of the oil for a longer time of storage. Disrupted particles of the seeds contain enzymes, and also adherently microorganisms which can metabolize the oil to form degradation and metabolism products impairing especially the sensory quality of the oil. Depending on the settings of the screw press, speed of the rotating screw shaft, size of the press cake exit, temperature during pressing, and moisture of the

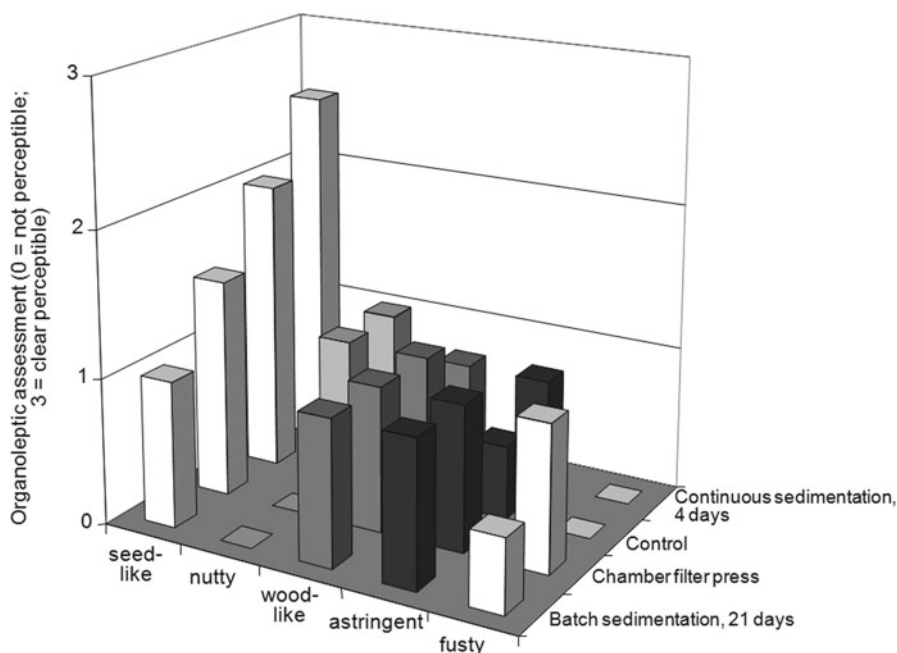


Fig. 2.16 Influence of purification facility on the quality of the resulting oil

seed, the amount of solid components in the oil ranges between 1 and 13%. The aim of this type of purification is the separation of the two-phase system consisting of oil (liquid phase) and seed particles (solid phase). In general, two different methods, sedimentation and filtration, are in use, depending on the performance of the plant. A third method, centrifugation of the crude oil, is not widespread, but seems to be very gentle.

Sedimentation uses the different specific density of the liquid and solid phase which leads to a slow settling of the solid particles as a result of gravity. There are two possibilities to use this method. The first one can be used as a batch system, at which a container is filled with crude oil and seed particles are allowed to sediment within 15–30 days. Since the throughput of oil of this method is strongly limited, the method is only suitable for small plants with a low production of oil up to 50 kg/h. A drawback of this type of purification is the long contact of oil with the disrupted seed material. During this long time, enzymes and also microorganisms from disrupted seed material start to degrade the oil. Investigations have shown that sedimentation in the batch system over a period of 21 days impairs the oil quality significantly in comparison to other types of purification (Fig. 2.16) (Attenberger et al. 2005).

From this point of view, a second method seems to be more practical. This method is working continuously using a multilevel sedimentation tank, at which addition of crude oil, removal of purified oil, and elimination of enriched solid particles



Fig. 2.17 Multilevel sedimentation system for the purification of rapeseed oil (by courtesy of Technologie und Förderzentrum, Straubing, Germany)

take place simultaneously (Fig. 2.17). By this, a greater throughput of oil is possible, only limited by the number and size of the sedimentation tanks and economical aspects. Additionally, the contact time between oil and disrupted seed material is noticeably shorter, resulting in a much better quality of the purified oil (Fig. 2.16).

Filtration is the mechanical separation of solid and liquid phase which allows removing insoluble solids or suspended material from a liquid by passing it through a porous medium that is only permeable for the liquid phase. In small- and medium-sized plants, this is mostly achieved by means of the formation of a filter cake from the seed particles between porous filter materials within a pressure gradient. The filter cake improves the result of the filtration. Sometimes filter aids can be used to increase the effect of the filter materials. These are inert cellulose materials which improve the formation of a filter cake for the filtration process. Filtration in small- and medium-sized plants is carried out by the use of chamber filter presses or vertical pressure plate filters (Fig. 2.18), which enable a much higher throughput in comparison to sedimentation.

The last step of the purification process in small- and medium-sized plants is passing the oil through a fine-pored protection filter to ensure a defined clarity of the oil. This is necessary especially when pure rapeseed oil should be used as fuel for cars since according to DIN V 51605 (Anonymous 2010) the amount of total impurities should be below 25 mg/kg.

Sometimes virgin, cold-pressed oils as edible oils are also on the market as natural turbid oils, which are not or insufficiently purified. For example, the intensity of

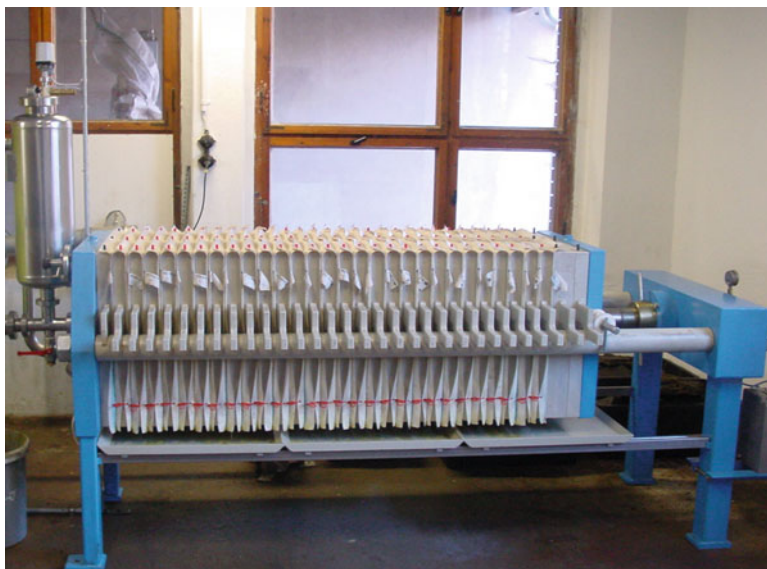


Fig. 2.18 Chamber filter press for the purification of native, cold-pressed rapeseed oil in small and medium-sized plants

the sensory attribute *seed like*, typical for virgin rapeseed oil is stronger than in purified virgin oil. Also, grape seed oil as turbid oil presents a stronger intensity of the typical sensory attributes. However, this type of oil has some problems with the formation of free fatty acids as a result of the formation of metabolism and degradation products from enzymes and microorganisms located on the seed particles (Attenberger et al. 2005; Matthäus 2008). Therefore, a longer storage of these oils is not advisable.

Some producers of cold-pressed edible oils use a treatment of oil with hot-water steam after the removal of seed particles. The aim of this treatment is the removal of undesired volatile compounds, which negatively influence the sensory quality of the oil. Additionally, the storage stability of the oils should be improved. In that case, purified oil is treated with hot-water steam at about 120–180°C over a period of 1–4 h in a batch system. Under these conditions, no changes in the fatty acid composition or in the composition and the amount of tocopherols are noticeable. Nevertheless, the appearance of oligomer triacylglycerides or stigmasta-3,5-dien, as degradation product of β -sitosterol, a phytosterol, often may be good indicators for a hot-water steam treatment.

As a result of this treatment, volatile compounds with a steam pressure below the used temperature are removed from the oil. The resulting oil should be milder in taste and interfering aroma compounds that negatively influence the sensory evaluation of the oil should be removed. If the temperature is too high or the treatment time too long, the result of the steam treatment is an odorless and tasteless product.

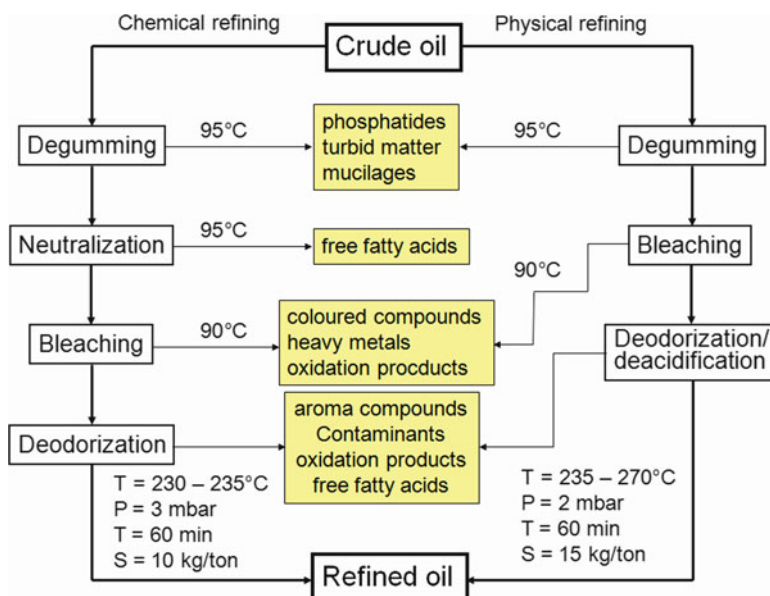


Fig. 2.19 Different steps of the refining process

Another problem is that aroma compounds which are responsible for the positive sensory attribute like *seed like* in cold-pressed rapeseed oil are removed first, while aroma components which account for negative sensations remain in the oil. Thus, often, the result of a hot-water steam treatment is that the oils get a nasty taste and smell, which make them inedible.

11.2 Refining Process

The aim of the refining process after solvent extraction is a comprehensive purification of the crude oil from compounds which negatively influence the quality and the shelf life. Thus, in comparison to virgin, cold-pressed oils this procedure has the advantage to ensure a product on a constant high-quality level. In contrast, processing of virgin, cold-pressed oil results in partly great differences of quality concerning sensory evaluation and shelf life, because it is not possible to correct faults during choice or storage of the raw material and the production process. Additionally, refining is necessary before carrying out hydrogenation, because catalyst poisoning is another problem.

The refining process takes place in a refinery, often directly connected to the oil mill, but sometimes also located at separate places. In general, refining is a multistage process which is carried out as either physical or chemical refining (Fig. 2.19).

Table 2.2 Content of phospholipids and phosphorous in different vegetable oils

| Oil | Phospholipids (%) | Phosphorous (mg/kg) |
|----------------|-------------------|---------------------|
| Cottonseed oil | 1.0–2.5 | 400–800 |
| Peanut oil | 0.3–0.7 | 100–250 |
| Corn oil | 0.7–2.5 | 250–700 |
| Palm oil | 0.04–0.1 | 15–30 |
| Rapeseed oil | 0.6–3.0 | 200–1,000 |
| Soybean oil | 2.0–5.0 | 600–1,500 |
| Sunflower oil | 0.5–1.0 | 200–400 |

Both methods differ in the type and performance of the neutralization process. Using physical refining, free fatty acids are removed by hot-water steam, while chemical refining uses alkaline solutions to neutralize free fatty acids.

Oil refining involves the steps of degumming, neutralization, bleaching, and deodorization in different variations and performances, whereas in most cases the oil mills carry out degumming.

11.3 Degumming

The first step of the refining process is degumming which reduces the content of phospholipids (Table 2.2). The aim is to achieve a phosphorous content <200 mg/kg for soybean oil and <300 mg/kg for rapeseed oil and other seed oils. The phospholipids can act as emulsifying agents, lead to loss of neutral oil, and result in a low-grade finished product (Young et al. 1994); they are responsible for deterioration during storage. They result in white precipitation as emulsifier between oil and residues of water, which is separated from the oil during storage and cause difficulties during hydrogenation. In addition, autoxidation reactions lead to the formation of dark-colored substances from phospholipids during storage and processing. These substances are called melanophosphatides and they are the result of condensation reactions of the amino groups from phospholipids with aldehydes from autoxidation of the oil. Depending on the extraction conditions and the type of raw material, oils can contain high amounts of phospholipids, which should be eliminated from the oil.

Two forms of phospholipids exist, hydratable and nonhydratable phospholipids, which often can be found together with different cations such as magnesium, calcium, or iron. The ratio of both forms depends on the processing conditions and nonhydratable phospholipids usually amount between 20 and 45% of the total phospholipids found in rapeseed oil. The removal of hydratable phospholipids is relatively easy by using water to form hydrated gums, which can be easily removed by centrifugation.

The hydrated gums obtained from crude rapeseed oil, mainly consisting of lecithin (phosphatidylcholin) and cephalin (phosphatidylethanolamine), are too dark for use in the production of food or pharmaceuticals. Therefore, the gums are often

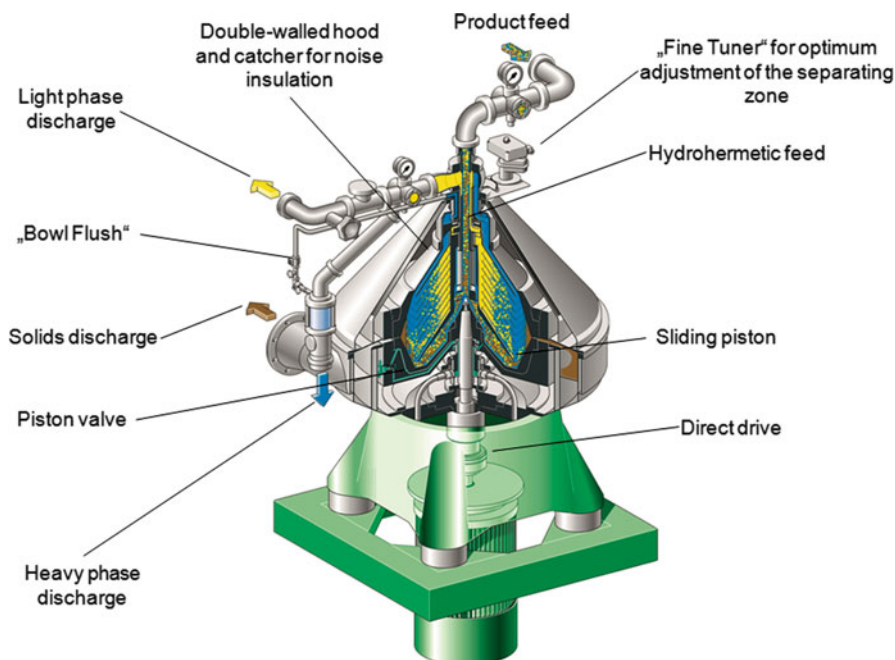


Fig. 2.20 Centrifuge for the separation of oil/water mixtures (by courtesy *Source: GEA Westfalia Separator Group GmbH*)

added back to the meal to improve the feeding value and to reduce dustiness during the usage of the meal. In the case of soybean oil, the obtained soy lecithin is further purified and separated from practically all oil by a series of solvent extraction and precipitation processes. It is widely used as a natural emulsifier and stabilizer in various food applications. Soy lecithin consists of phosphatidylcholine, phosphatidylethanolamine, and phosphatidylinositol.

Much more difficult is the elimination of nonhydratable phospholipids which requires the use of mild organic acids, such as citric and malic acid or phosphoric acid. These acids act as chelating agents to the nonhydratable phospholipids resulting in oil-insoluble metals, salts, and hydratable phospholipids, which can be easily removed.

Water degumming is carried out by using water at about 80°C in an amount of about 2% and intensive mixing with the oil. Within 5–45 min, hydratable phospholipids become insoluble in the oil and form a precipitate, which is kept in suspension by gentle agitation of the reaction vessel. Another result of gentle agitation is that precipitate agglomerates to larger particles, which are easier to separate. After this time, the mixture consisting of oil and hydrated phospholipids can be separated by using a centrifuge; however, about 35–40% of the separated material is oil (Fig. 2.20). The result is a reduction of the amount of phosphorous to 100 and 200 mg/kg. It is also possible to use hot steam instead of hot water which improves the contact between oil and water resulting in a better separation of the phospholipids.

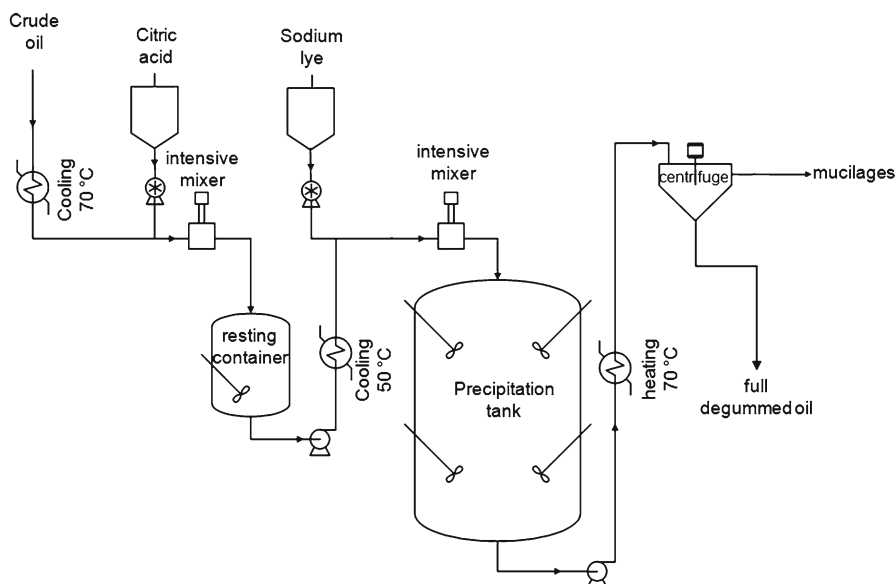


Fig. 2.21 Degumming (by courtesy of MUEZ-HEST Process Technologies Pvt. Ltd., Mumbai, India)

During water degumming, it is not possible to remove nonhydratable phospholipids. For this, the oil is mixed with small amounts of acid, e.g., 0.1–0.5% of a 50% solution of citric or malic acid or 0.1% of 75% phosphoric acid at temperatures between 60 and 70°C (Fig. 2.21). An intensive mixing of the solution is necessary to ensure an appropriate contact between oil and acidic solution which influences the reaction time from few seconds to 20 min. During this time, nonhydratable phospholipids are changed to hydratable ones which can be removed from the oil by further addition of about 2% of water. After mixing the mixture for 30 min to 3 h for the formation of large-enough agglomerates, the oil is separated from the phospholipids by centrifugation. The resulting oil should contain less than 25 mg/kg phospholipids, measured as phosphorous (Mag 2001), in the range between 5 and 25 mg/kg.

Since the following processing steps sometimes need very low contents of phospholipids, which cannot be achieved by conventional degumming without high costs for equipment and energy, the use of enzymatic degumming seems to be an interesting alternative. This process has been developed in the 1990s by Lurgi and is known as “EnzyMax® process” (Aalrust et al. 1992). The aim of the process is to transfer the nonhydratable phospholipids into a hydratable form, with the advantages that less wastewater arises, the oil yield increases, and the operation costs can be reduced (Klaus 1998). In general, the process is divided into three steps: (1) adjusting the pH value of the oil by buffer, (2) enzyme reaction in a tank, and (3) removal of gum and sludge from the oil. Although in small-scale processes several phospholipases from different sources have been used successfully, for industrial applications only three enzymes are in use: phospholipase A₂ from porcine pancreas,

phospholipase A_1 from *Fusarium oxysporum*, and *Thermomyces lanuginosus*/*Fusarium oxysporum* (Clausen 2001). When the pH was kept in an optimal range, less than 10 mg/kg of phosphorous content of the oil was obtained. Gum and oil were easily separated after centrifugation and the oil loss was minimal under the process conditions.

In the process, the raw oil is heated to 70–75°C and 0.5–0.6 kg acid per metric pound raw oil is added. After intensive mixing, the mixture stays in a residence container for 15–20 min. Then the temperature is adjusted to about 55°C. Afterward, 1.5–2 mol equivalents of soda lye in comparison to the acid, 10 kg demineralized water as well as 30–50 g enzyme per metric pound raw oil are added. After intensive mixing, the mixture stays for 4–6 h in a residence container resulting in the separation of mucilages. Finally, the mixture is heated to 80°C for a better separation, centrifugated, and then dried.

11.4 Alkali and Physical Refining

Before further processes such as bleaching, deodorization, or hydrogenation can be carried out efficiently, free fatty acids and phospholipids have to be removed to a very low level. This is achieved either as alkali or as physical refining, depending on the realized degumming process. Both methods differ basically in the way how free fatty acids are removed. If the oil is water degummed or the quality of seeds processed in the oil mill is variable, alkali refining is the procedure of choice, since heat-sensitive compounds in the oil strongly influence the result of physical refining. Such compounds are phospholipids, which result in difficult removable degradation products, proteins, and carbohydrates, which also form degradation products and heavy metals catalyzing oxidation reactions. Therefore, a uniform and known product quality is important for physical refining. On the other hand, if the oil is well degummed physical refining has some advantages from an economical point of view: losses of neutral oil are reduced, less number of processing steps are necessary, no problems with the use of environmentally harmful alkaline solution, and lower capital and operation costs. Particularly environmental problems arise from huge amounts of acid water resulting from the neutralization process. This water is highly acidic (pH 2–3) and contains additionally to fatty matters from the oil other organic and inorganic materials which are considered as harmful to environment. Thus, before the water can be disposed to municipal sewers the pH value has to be neutralized to pH 6–9 and the main part of the oil phase must be separated.

11.5 Alkali Refining

The first step of alkali refining is adding of about 0.05–0.1% of concentrated phosphoric acid to the oil in a high-intensity mixer to precipitate phospholipids and especially chlorophyll and related compounds. Further on, traces of prooxidant metals

are removed. The results are lower losses of neutral oil, less need of bleaching earth during the further process, and better flavor and flavor stability of the oil after deodorization. Other organic acids such as citric acid are not as effective as phosphoric acid (Ohlsen and Svensson 1976).

Then free fatty acids are neutralized with a 2–3N sodium hydroxide solution under continuous mixing to ensure contact between oil and alkaline solution and heating. The amount of sodium hydroxide solution depends on the content of free fatty acids and should be in excess to neutralize phosphoric acid as well. The need for sodium hydroxide solution can be determined by using a specific gravity hydrometer calibrated in degrees Baumé (Be).

The soapstock resulting from this procedure is removed together with precipitate phospholipids and other compounds either by continuously centrifuging or, in smaller plants, by gravity settling in a tank. Small amounts of soaps are removed by washing the oil with water, sometimes hot, which results in soap concentrations less than 50 mg/kg. In a last step, water is removed by drying the oil in a vacuum dryer. In large plants with high throughput, this process is carried out continuously, which has high capital costs because of the use of centrifuges. Small plants also can use batch alkali refining which is much cheaper, because the separation of the soaps is achieved by gravity only, but the method has disadvantages with regard to the oil yield because of higher losses during the process. By alkali refining the amount of free fatty acids is reduced to <0.05%, phosphorous <5 mg/kg, chlorophyll <30 mg/kg, and sulfur <10 mg/kg.

11.6 Physical Refining

Using physical refining free fatty acids are removed from the oil by steam distillation. Therefore, this step is combined with the removal of volatile compounds during deodorization to obtain bland and odorless oil. Another effect is the degradation of color compounds such as carotenoids. Advantages of the physical refining are environmental and economical benefits, because less wastewater and discharges are produced. Requirements for a successful physical refining are a low phosphorous concentration of the oil with less than 15 mg/kg, preferably less than 10 mg/kg and in some cases less than 5 mg/kg after degumming (Narayana et al. 2002), and bleaching of the oil in order to remove compounds susceptible to heat treatment. The efficiency of the physical refining is directly correlated to a proper degumming and influences the quality of the resulting oils.

During the process, the oil is treated with 0.05–0.1% of 85% phosphoric acid and then contacted with 1.0% acid-activated bleaching clay at 95–105°C. After about 15 min, the oil is separated from the clay and other impurities, such as precipitated phospholipids, chlorophyll, and carotenoids, absorbed onto the clay, and transferred into the deodorizer. Depending on the performance and equipment, the deodorizer is used at temperatures between 220 and 260°C under 1–3 mbar vacuum for 1–3 h. Another important factor affecting the result of physical refining is the amount of stripping steam used for the process. For physical refining, at least 15 kg steam/ton

oil is recommended, while the steam consumption during chemical refining is about 10 kg/ton. For a successful process, the interplay between temperature, pressure, and amount of stripping steam is important for the result. The lower the pressure and the higher the temperature, the higher is the volume of steam resulting from one kilogram of water. Since the amount of volatile compounds removed from the oil during the process depends on the volume of stripping steam produced, the process is the more effective if more steam is produced.

During this process, most of free fatty acids and volatile compounds responsible for the odor and taste of the oil are removed. The result is almost tasteless and odorless oil usable universally in kitchen.

11.7 Bleaching

Bleaching of oil by the use of adsorbents is necessary not only for physical refining or hydrogenation but also for the processing of bottled edible oils. The objective of this step is to remove colored compounds such as chlorophylls and carotenoids, and also soaps, oxidation products, and other minor compounds which are retained on the absorptive material. Especially the removal of chlorophyll is necessary since it acts as a photo-sensitizer catalyzing the oxidation of oil in light. Bottled edible oils often are presented in clear glass bottles in the stores, which give no protection against light. Thus, a low concentration of chlorophyll is important to enlarge the shelf life of the oil. Additionally, higher amounts of chlorophyll result in an undesired dark green color of the oil. Since rapeseed oil contains significant high levels of chlorophylls, the removal of these compounds from the oil is more difficult than for other oils. Carotenoids and other colored compounds are removed from the oil only in small amounts during bleaching. More effective is deodorization through high-temperature thermal destruction of the compounds by heat treatment and the oils become brighter and less reddish-yellow colored.

The bleaching process is especially important if physical refining is carried out, because it is the last chance to remove residual phosphatides, soaps, metals, or oxidation products prior to deodorization. These compounds have a direct effect on the organoleptic evaluation and the oxidative stability of the resulting oil.

For a successful and economically useful bleaching process, it is necessary that the oils fulfill some requirements regarding the content of free fatty acids, soaps, phosphorous, and water. In the case of alkali refining, the following limits should be kept: free fatty acids <0.05%, soaps <50 mg/kg, phosphorous <5 mg/kg, and water <0.1%, while soaps and phosphorous should be below 50 and 20 mg/kg, respectively, for oil provided for physical refining (Zschau 1999). Notably, the amount of soaps and phosphorous is critical, since these compounds inactivate the active centers of the clays, which results in worse quality of oil or higher needs of clay. A higher content of water influences the speed of bleaching concerning drying and adsorption. An excessive amount of water supports hydrolysis of oil during processing (Bockisch 1993).

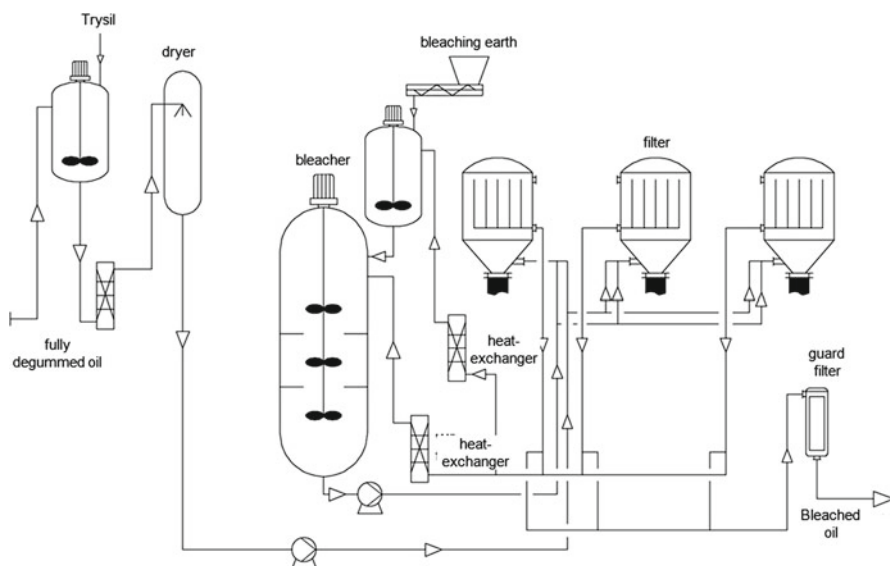


Fig. 2.22 Bleaching (by courtesy of MUEZ-HEST Process Technologies Pvt. Ltd., Mumbai, India)

Different types of bleaching processes and sorts of clays are in use. The main types are batch bleaching, suitable for small plants with small throughput of oil, and continuous bleaching, which is commonly used in most plants. As absorptive materials, in most cases, acid-activated clays are used, which are obtained from inactive aluminum silicates (bentonite, montmorillonite, and attapulgite), activated by mineral acids such as sulfuric or hydrochloric acid, washed and dried to a moisture content of 10–15%. The activation process results in the enlargement of the available surface and in the reduction of the metal content of the clay which improves the absorptive activity of the material.

In recent years, some efforts were made by adsorbent manufacturers to improve the efficiency of the clays in order to reduce the consumption and the resulting waste. One result of these efforts is the development of synthetic silicas, from an aqueous solution of alkali-silicates, acidified with diluted sulfuric acid. Unfortunately, these clays are not suitable for absorption of chlorophylloids, but they have a high activity and selectivity for the absorption of soaps and phospholipids.

The process of bleaching is based on the interaction between the absorptive material (clay) and the solute, which has to be removed from the oil by the formation of van der Waals bindings. In the case of soaps and phosphatides, the removal takes place by adsorption of the compounds in pores of the clays.

Usually, bleaching is carried out under vacuum to reduce oxidative reactions because of high temperature and large surface of the bleaching material. Important for the result of bleaching are the temperature, the period of contact between oil and clay, the amount of clay, and the degree of drying of the oil/clay slurry (Fig. 2.22).

The oil is heated in the bleacher to about 70–80°C before the acid-activated clay is added directly or as a slurry (premix of oil and clay). Then heating continues to about 95–105°C, while the oil–clay slurry is continuously dried to about 0.1% moisture. For the bleaching of palm oil, the temperature inside the bleacher must be around 100–130°C to get the optimum bleaching process for 30 min of bleaching period. The amount of clay depends on the oil quality (e.g., chlorophyll content) and the product specification expected as a result of the process. Usually, the amount of clay is between 0.5 and 2.5% in the oil. One important point is the contact time between oil and clay which should be between 5 and 30 min, depending on the quality of oil and the amount of clay used for the processing. Within this time, an equilibrium between coloring compounds adsorbed by the clay and coloring compounds remaining in the oil should be reached, whereas the ratio should be moved in the direction of coloring compounds adsorbed by the clay. By intensive mixing of the slurry, which improves the contact between oil and clay, this equilibrium can be reached within a relatively short time. After reaching this point, no more coloring compounds are absorbed from the oil by the clay. Therefore, a multistep counter-current process seems to be more effective with regard to clay consumption. In two or more consecutive steps, clay is added to the oil which improves the result of bleaching with a lower consumption of clay. It is recommended to carry out the bleaching process under vacuum.

The separation of oil and clay takes place by filtration. In most cases, horizontal or vertical leaf filters are in use and the mixture pumped through the filter returns to the bleaching vessel in order to build up a filter cake. At the end of filtration, the cake is dried by steam blowing or nitrogen to lower the amount of remaining oil in the bleaching earth. Nevertheless, 20–40% of the cake consists of oil.

11.8 Deodorization

The last step in purification of crude oil in large-scale plants is deodorization. The main objective of this step is to remove all compounds which negatively influence the taste and odor of the oil. This is the typical taste and smell of the seed material from which the oil is derived, e.g., in the case of rapeseed oil *seed-like* and sometimes pungent *mustard-like* attributes or in the case of sunflower oil *sunflower-seed like* or *fruity*. Additionally, products formed during the processing, e.g., bleaching and hydrogenation, are also removed. The result is oil, neutral in taste and smell, only light yellow colored, and low in free fatty acids with a good stability. Therefore, deodorization often is carried out after hydrogenation if the fatty acid composition of the oil should be changed. Another effect of deodorization is heat bleaching of colored carotenoid compounds or other pigments at higher temperatures as mentioned above. Last but not least, deodorization is an important step in physical refining to remove free fatty acids.

The principle of deodorization is steam distillation at high temperature (220–250°C and 270°C for physical refining) and low pressure (0.3–0.6 kPa). By the use of low pressure, the volatility of compounds to be removed increases and the compounds are kept away from the oil. Under these conditions, the volatility of compounds to be removed is high enough to leave the deodorizing vessel with steam as carrier, while triacylglycerides remain. The most important point during the process is that sufficient contact between oil and steam has to be achieved to ensure the removal of all undesired compounds.

Deodorization can be carried out either as batch process or in a semi-continuous or continuous process mode. In modern plants, the latter types are preferred, because they have some advantages regarding the efficiency of the process and the consequential better quality of the resulting oil. The batch process needs up to 10% more steam, because the oil bed, which has to be penetrated by the steam, is much higher than in continuously working processes. Additionally, a relatively long processing time (>4 h) makes batch deodorization less interesting to large plants. Advantages of the batch type are lower capital investment and simplicity of operation. Batch deodorization is suitable for small plants with capacities up to 50 tons/day or plants with a wide range of different oils. In principle, the process is divided into four steps: deaeration, heating, deodorization, and cooling of the oil.

The deodorizer vessel in the batch process is a cylindrical tank. Amounts of 10–20 tons of oil are pumped into the vessel and after deaeration it is heated up by heating coils. Deaeration is necessary to ensure a low concentration of oxygen in the vessel to reduce the risk of oxidation and polymerization during the heat treatment. Hot steam, necessary for the process, is supplied near the bottom of the vessel and a vacuum system provides for low pressure. The process takes about 3–5 h and 3–5% of steam is used. During this time, the temperature is between 180 and 240°C, whereas the effect of deodorization starts at about 160°C. Afterward, the vessel is cooled down to 60–80°C under vacuum and the oil is sparged with nitrogen before storing in tanks or bottles.

For continuous working processes, different types of deodorizers are available. One commonly used type consists of a vertical stainless-steel vessel in which four to seven trays are stacked. At the beginning of the process, the oil is pumped under vacuum into the top tray of the deodorizer, which is heated. Here, the oil is deaerated and heated to about 160°C within 15–20 min. Then, the oil moves down step-wise from one tray to the next counter-current to a superheated, stripping steam flow. In this way, the oil is further heated to 220–270°C, depending on the conditions, and agitated with sparging steam at about 0.5% per hour. In the deodorizing section of the vessel, about 1.5% of sparging steam is used, before the oil reaches the final cooling to about 50–60°C. The advantage of this process is that the oil bed is much smaller resulting in shorter processing time (50–80 min), reduced labor, and less heat treatment of the oil, resulting in less formation of degradation products. Then, the oil is transferred to a storage tank by passing through a polishing filter (Figs. 2.23 and 2.24).

Another type is based on a series of horizontal, single-shell, cylindrical vessels. In this apparatus, hot steam is injected by several pipe distributors running the length

Fig. 2.23 Continuous deodorizer (1 – bleached oil; 2 – vacuum degaser; 3 – heat exchanger; 4 – cups in the deodorizer; 5 – heating by indirect steam; 6 – direct steam; 7 – pump; 8 – cooler; 9 – exit of the exhaust vapor to the vacuum system)

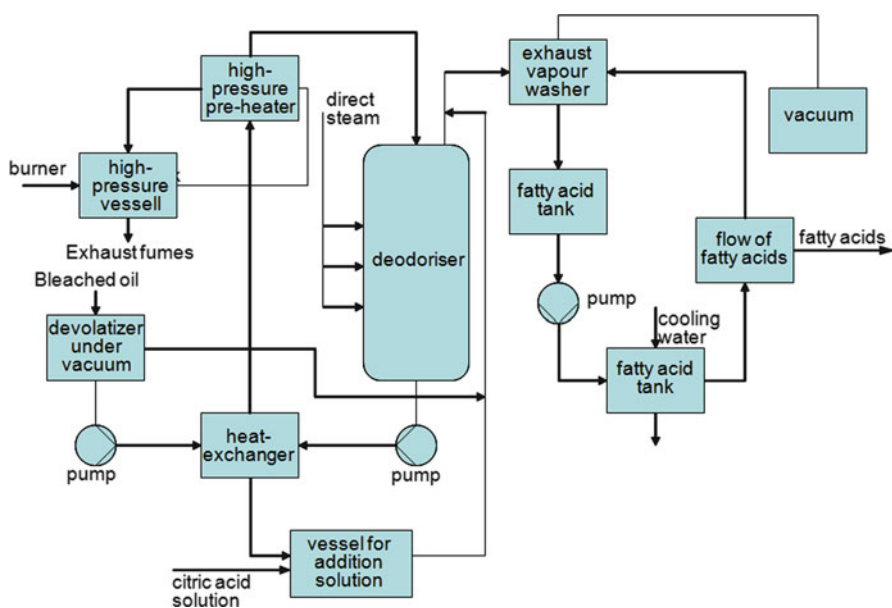
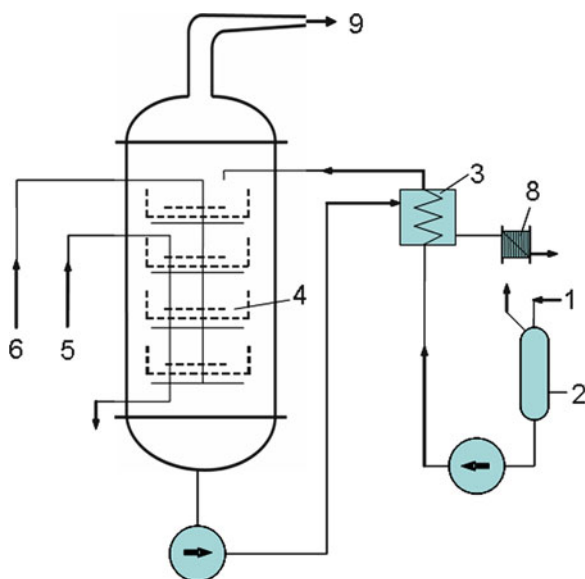


Fig. 2.24 Deodorization

of the vessel. The advantage of this type is that this arrangement enables the maximal surface for the contact between oil and hot steam. The cylindrical vessels are combined to a plant, whereas each vessel is about 1 m in diameter and 4.5–12.5 m in length.

The material removed from the edible oil is usually recovered in a scrub cooler where it is separated from the steam. Depending on the composition, a further use of the deodorizer distillate, the material collected from the steam distillation, is meaningful. The value of this distillate depends on the procedure applied for refining and the conditions used during deodorization. Distillates from physical refining mainly consist of free fatty acids and a lower amount of unsaponifiable matter. It can be used for feed industry if the amounts of pesticides are low enough. Distillates from chemical refining are more valuable because they often contain higher amounts of tocopherols which can be recovered for the production of vitamin E. On the other hand, higher amounts of tocopherols and sterols make the use of the distillates from rapeseed oil unsuitable for the production of fatty acids for technical purposes, although they are excellent sources for C18 fatty acids.

12 Modification

Worldwide, the consumption of oil for either human nutrition or technical applications increases year by year. In human nutrition, vegetable oils are widely used as salad oils, in food formulations as prepared salad dressings or mayonnaise, and in food preparation. The oils are also the basis for the production of margarine, frying oils, and shortenings. Often, the composition and especially the physical properties of the oils do not match the demands for the preparation of an appropriate product or do not achieve a desired quality of a product. The modification of vegetable oils is a practicable way to change the properties of the oils as desired and required. Often, a cheap oil is used as the basis for further modifications and here the use of rapeseed oil volunteers, because the oil is cheap and available in huge amounts. By modification, it is possible to change the properties of the oils within wide bounds, which enables the production of perfect-fitting fats and oils for nearly every purpose.

In general, four different processes are in use for the modification of vegetable oils: winterization, fractionation, interesterification, and hydrogenation (Fig. 2.25). Fractionation and winterization are physical processes which do not change the triacylglyceride molecule, but separate different fractions on the basis of different melting points or solubilities. Interesterification uses the fact that fatty acids can change their position within the triacylglyceride molecule under certain conditions. By this, it is possible to build new triacylglycerides without changing the components of the oil. Only the process of hydrogenation directly interferes into the fatty acid molecule by adding hydrogen onto the double bonds. The results are saturated or mono-unsaturated fatty acids with a higher stability against oxidation reactions and higher melting points.

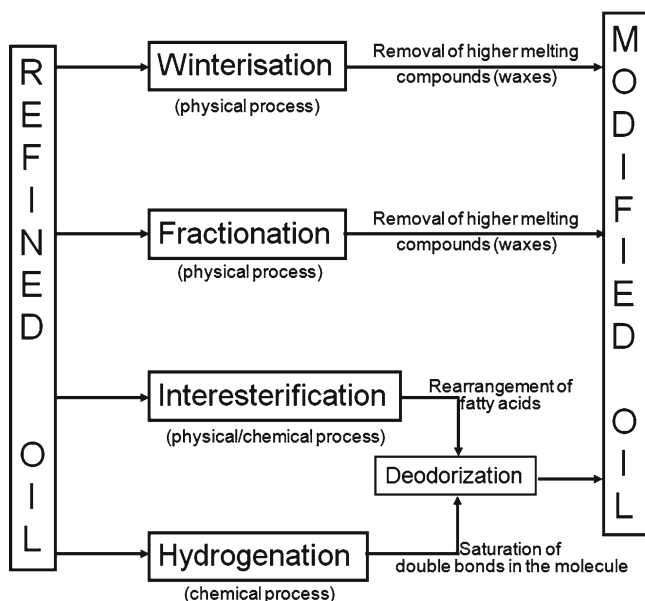


Fig. 2.25 Different possibilities to modify rapeseed oil to oil with well-defined properties

12.1 Winterization

Winterization is a sort of fractionation, which is used to remove traces of higher melting parts such as waxes from the oil. These esters of fatty acids and long-chain alcohols are responsible for cloudiness in the oil during storage at lower temperatures. Waxes come into vegetable oils from the seed coat. Low amounts can be found in rapeseed oil, but in comparison to sunflower oil the amount is only very low. Other high-melting triacylglycerides also lead to hazy appearance in the oil. The name winterization is a leftover from earlier times when oil was stored outside in the winter in barrels to allow higher-melting components to solidify.

Oils with a hazy appearance are often disliked by the consumer, although these components have no negative health effect. Nevertheless, industry endeavors to produce clear oils with a good cold stability, which remain clear also during storage in the refrigerator. In that case, the level of higher-melting compounds should be below 10 mg/kg. Another point is that vegetable oils are used in the production of salad dressing and mayonnaise. Especially in the case of sunflower oil from undehulled seeds, and also small amounts of waxes in rapeseed oil can result in fat crystals that destroy the emulsion or the desirable properties since these products are normally stored in the refrigerator.

The principle of the procedure is to cool down the oil to temperatures between 0 and 19°C for at least 6 h. During this time, the crystallization of high-melting compounds becomes complete and after addition of a filter aid these compounds

can be removed by filtration at about 15°C. In most cases, rotary drum filters and horizontal and vertical tank filters are used for the filtration process. Another possibility is the centrifugation of the cooled oil. In this process, the oil is introduced into a crystallizer, where waxes have time to agglomerate. Afterward, the oil is gently heated and pumped into the centrifugal separator. This procedure results in excellent oil qualities, but high oil losses have to be taken into consideration and the residual wax content of the product is too high for a good cold stability (50 mg/kg).

12.2 *Interesterification*

Interesterification is a method that does not change the composition of vegetable oil, but changes the distribution of the fatty acids within the triacylglyceride molecules. This means that the fatty acid composition remains and the triacylglyceride composition is changed with the change of the melting behavior and physical properties of the oil. The advantages of this procedure in comparison to modification of the oil by hydrogenation are that the equipment is readily available and no explosive gases are necessary. Another important advantage from a nutritional point of view is that the products are very low in *trans*-fatty acids.

The principle of the method is that the oil is separated for a short time into the different components, fatty acids, and glycerin, and then these components are rearranged. The result is a new product with new physical specifications.

Different types of interesterification are known: (1) interchange between a fat and free fatty acids (acidolysis), (2) interchange between a fat and an alcohol (alcoholysis), and (3) rearrangement of fatty acids within triacylglycerides (ester interchange) (Fig. 2.26) (Going 1967).

For the process, an alkaline catalyst is necessary to skip the energy barrier for the rearrangement of the fatty acids. Such a catalyst is sodium methoxide; metallic sodium or sodium hydroxide is used as well. In addition to the chemical interesterification process, the use of enzymes is possible. One advantage is that it is possible to obtain positional specificity of the resulting interesterified product, but enzyme catalysts are expensive and the reaction time is much longer.

The reaction of the chemical interesterification can take place in a randomized or a directed form. In the random interesterification the fat or oil is heated in a closed vessel under vacuum or nitrogen to 70–100°C, 0.05–2% catalyst is added, depending on the sort of catalyst and then the mixture is mixed for 1–120 min. Normally the reaction takes place with an amount of catalyst between 0.05 and 0.15% for about 30 min. For the reaction, it is necessary that the oil and the catalyst are completely dry, because otherwise the catalyst is inactivated or soaps are formed. Other critical points are free fatty acids or peroxides which also will poison the catalyst. The reaction takes place spontaneously and the appearance of a brown coloration, resulting from oxidation products shows the beginning of the reaction. This brown color has to be removed during the following bleaching process. At the end of the process, the catalyst must be neutralized by the addition of diluted mineral acids.

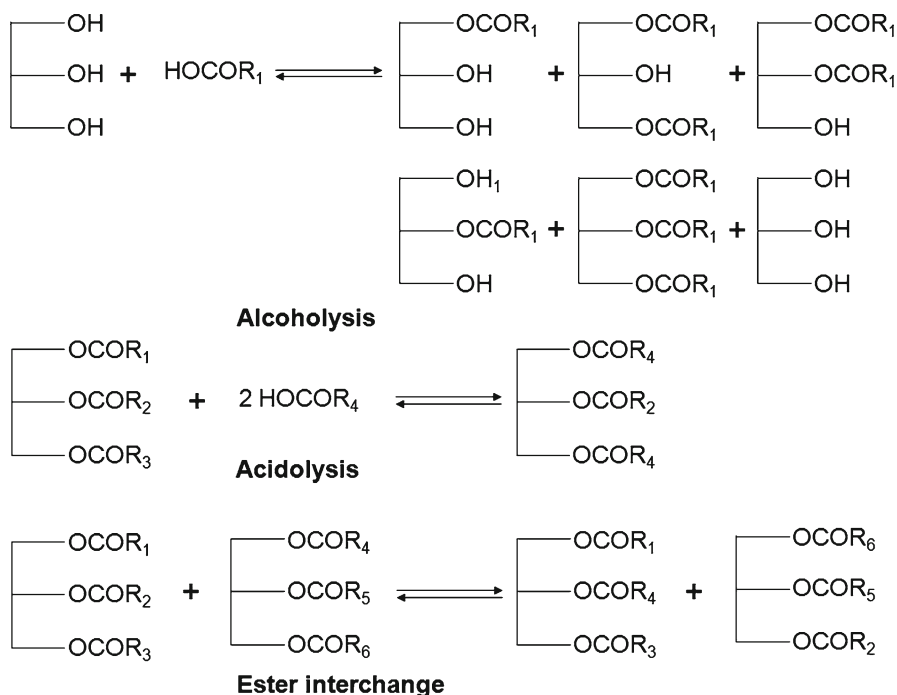


Fig. 2.26 Different types of interesterification

Is a certain temperature used during the interesterification higher melting components are removed from the oil. This results in the attempt of the reaction mixture to rebuild these components in order to get back the balance of the reaction partners. Thus, it is possible to lead the reaction in a desired direction with the formation of a certain fraction. The temperature used in this process has to be below the melting point of the separated fraction. Therefore, very effective catalysts are necessary to obtain the desired reaction.

12.3 Hydrogenation

For many purposes, the use of vegetable oils is not suitable, because the oils are liquid and the stability is not sufficient; e.g., rapeseed oil contains about 30% of polyunsaturated fatty acids which are 10–100 times more susceptible to oxidative deterioration than monounsaturated or even saturated fatty acids and the part of polyunsaturated fatty acids in soybean oil amounts to nearly 60%. Additionally, the melting point of both oils is characterized by this high degree of unsaturation. Linolenic acid melts at -13°C , linoleic acid at -7°C , oleic acid at 16°C , and stearic acid at 70°C . Thus, for the production of margarines and shortenings or for

the use as frying oil the properties of these oils have to be changed. Hydrogenation is one method to improve the oxidative stability and to increase the melting point of the oil.

The principle of the procedure is to saturate double bonds within the fatty acid molecule by addition of hydrogen, which eliminates the possibility of reaction with oxygen. By this, the iodine value of rapeseed oil decreases from 110–125 to 75–95 in hydrogenated oil. First, in 1903, W. Normann obtained a patent for the industrial hydrogenation of animal and vegetable oils. At high temperatures, increased pressure, and in the presence of a catalyst, hydrogen was introduced into the oil.

A slight hydrogenation results in higher oxidative stability of the oil since polyunsaturated fatty acids are changed into monounsaturated oleic acid, which is more stable. The aggregate state is not significantly changed by this procedure. If a more solid state is needed, further hydrogenation converts the liquid oil into a solid fat.

Although some continuous processes have been developed, hydrogenation is usually carried out in the batch mode. This procedure is easier to handle especially when changing from one degree of hydrogenation to another. The main components of the hydrogenation process are a vessel or converter in which the reaction takes place, equipped with components for heating, cooling, and agitation and means for the supply with hydrogen. Two different methods for the production of hydrogen are in use, either the electrolytic process or the steam hydrocarbon process. For processing, oil is loaded into the vessel and then the oil is heated under agitation and vacuum to remove air and moisture from the oil. After adding the catalyst and reaching the desired hydrogenation temperature, the evacuated vessel is pressurized with hydrogen gas. When reaching the desired degree of hydrogenation, the vessel is evacuated, the oil cooled down, and then filtered to remove the catalyst.

The most important parameters responsible for the degree of hydrogenation are temperature, pressure, concentration of catalyst, properties of catalyst, and agitation. For the process, temperature between 120 and 180°C and hydrogen pressures in the range from 10 to 30 bar are used.

One disadvantage of hydrogenation, which comes more and more into discussion from a nutritional point of view, is the formation of *trans*-fatty acids during partial hydrogenation. Because of the process conditions, isomerization occurs at the double-bond linkage in the fatty acid molecule comparable to the deodorization process. Another effect which has to be taken into account for the further use of partially hydrogenated vegetable oils is that the melting point of elaidic acid (44°C), the *trans* form of oleic acid, is much higher than that of the *cis* form (16°C). This is important for the preparation of products such as margarine, shortenings, and confectionery fats, where the melting point is one of the critical parameters.

There are two possibilities to avoid *trans*-fatty acids in vegetable oils during hydrogenation. The first one is to adjust the operating conditions (temperature and pressure) in a way that the amounts of *trans*-fatty acids remain low. Another way is to harden the oil to very low iodine values with following interesterification with unhydrogenated oil (List et al. 1995).

13 Process-Derived Contaminants

The main objective of the refining process is the removal of components affecting the quality of the resulting oil regarding sensory quality and storage stability. Additionally, the elimination of contaminants such as mycotoxins, phthalates, polycyclic aromatic carbohydrates, dioxins, etc., which can come into the oil via contamination of the raw material, is an important task of refining. Besides these positive effects, refining also results in some undesired impacts such as removal of valuable compounds such as tocopherols, phytosterols, or phenolic compounds and the formation of undesired components such as *trans*-fatty acids or 3-MCPD-esters. The removal and formation of compounds, respectively, during processing strongly depend on the processing conditions and the type of oil.

13.1 *Trans*-fatty Acids

Normally, double bonds in fatty acid molecules from crude vegetable oils are arranged in a *cis* configuration, which is energetically more inconvenient than the *trans* configuration. The hydrogen atoms are located on the same side of the double bond which results in a bending of the molecule. The more the double bonds in the molecule, the more the molecule is bent. In *trans*-fatty acids, the hydrogen atoms are on opposite sides of the double bond resulting in a more convenient state without bending of the molecule. Thus, the molecule is straight, comparable to saturated fatty acids such as stearic acid. Similar to saturated fatty acids, *trans*-fatty acids are reputed to be responsible for adverse effects on serum lipoproteins and apolipoproteins, which cause cardiovascular diseases (Precht and Molkenin 1995; Stender et al. 1995). Since the energy barrier to form *trans*-fatty acids from *cis* ones is low (125 kJ/mole), conditions occurring during deodorization are sufficient to increase the amount of *trans*-fatty acid in refined oil to amounts up to 2% depending on the conditions during processing (Fig. 2.27). In comparison, virgin, cold-pressed oils such as rapeseed oil or olive oil do not contain more than 0.2% *trans*-fatty acids; otherwise, a higher amount is a strong indication for a heat treatment of the oil during production. Sometimes pressed oils are treated by steam at temperatures between 120 and 180°C in order to remove unpleasant aroma compounds or to improve oxidative stability. Also in these oils, notable higher amounts of *trans*-fatty acids can be found in comparison to virgin oils as a result of a treatment with hot steam.

13.2 *Stigmasta-3,5-Dien*

In addition to *trans*-fatty acids, stigmasta-3,5-dien is formed from β -sitosterol, a naturally occurring phytosterol. This reaction takes place in the presence of heat as acid-catalyzed reaction with the elimination of water (Fig. 2.28), and also during treatment with strong bleaching earths. The resulting compound, stigmasta-3,5-dien, can be used

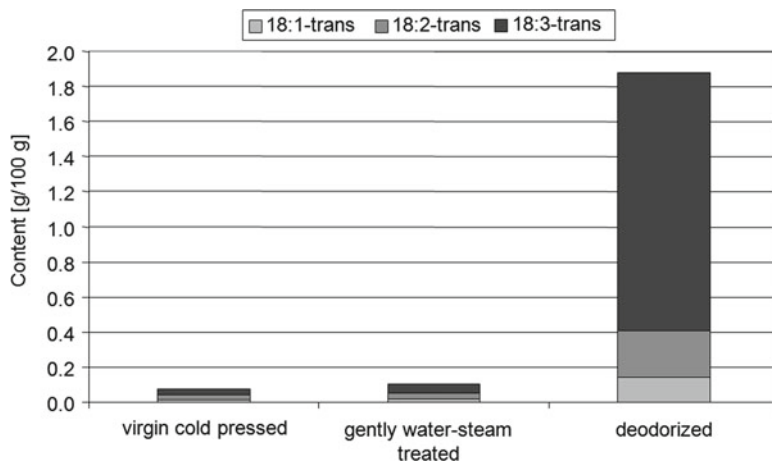


Fig. 2.27 Formation of *trans*-fatty acids during processing (by courtesy of Dr. L. Brühl, MRI, Münster, Germany)

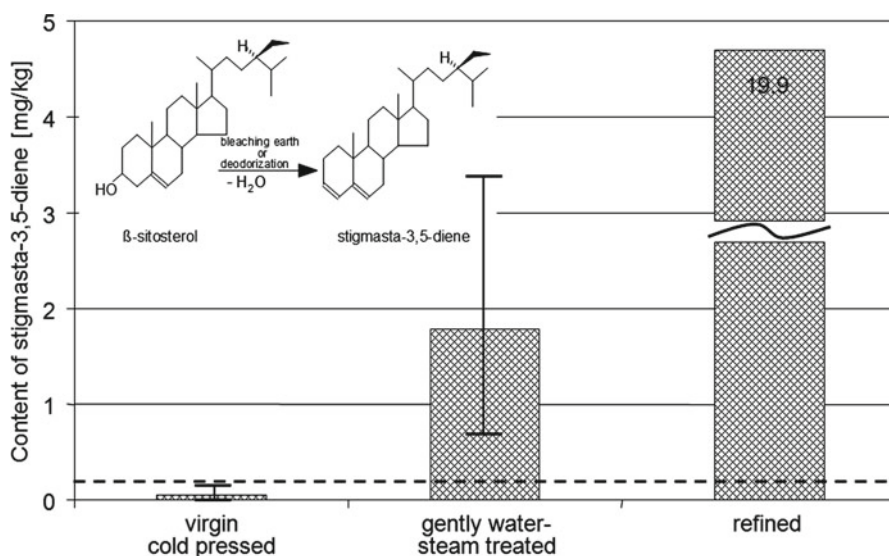


Fig. 2.28 Formation of stigmasta-3,5-diene during processing

as an indicator for such treatment of oil. While the amount of stigmasta-3,5-dien in crude oils should be below 0.15 mg/kg, comparable to the specification in EEC No 2568/91 for native olive oil, in fully refined oils remarkably higher amounts can be found indicating a deodorization or bleaching process. Already during gentle steaming of the oil to remove undesired aroma compounds the content of stigmasta-3,5-dien in the oil increases.

13.3 Oligomer Triacylglycerides

Owing to the high temperature during deodorization and also during bleaching refined vegetable oils contain considerable amounts of oligomer triacylglycerides (Gomes and Catalano 1988; Dobarganes et al. 1989; de Greyt et al. 1999; Gomes et al. 2003). Additionally, oxidized triacylglycerides can be found in refined oils. De Greyt et al. (1999) found 0.32–2.01% (mean = 1.07%) oligomer triacylglycerides in 19 samples of refined corn, sunflower, soybean, peanut, rapeseed, palm, and olive oil and 1.53–4.83% (mean = 3.11%) oxidized triacylglycerides. Similar contents of oligomer triacylglycerides were found by Gomes and Catalano (1988). De Greyt et al. (1999) described the major increase of oligomer triacylglycerides during the neutralization and deodorization, respectively, while oxidized triacylglycerides increased mainly during bleaching. Gomes et al. (2003) described an increase of oligomer triacylglycerides accompanied by a decrease of oxidized triacylglycerides for 42.2% on average in different industrial refined seed oils. The authors suggested that the decrease of oxidized triacylglycerides was due in part to the occurrence of polymerization reactions. Both parameters could be used for the assessment of the oxidative quality of refined oils since the level of oxidative degradation in the crude oil corresponds to the percent amount of oligomer triacylglycerides found in the refined oil.

The content of oligomer triacylglycerides can also be used to distinct virgin oils from heat-treated oils. In virgin oils, the content of oligomer triacylglycerides should be below 0.1%, while during steam washing or refining the content increases remarkably. However, it has to be taken into consideration that the content of oligomer triacylglycerides also can increase during storage. Therefore, this parameter alone is not sufficient for the assessment of virgin oils as heat-treated.

13.4 3-Monochloropropane-1,2-Diol Fatty Acid Esters and Glycidyl Esters

In 2006, a detailed report was launched on bound 3-MCPD in edible oils and fats (Zelinkova et al. 2006). Mono- and di-fatty acid esters of 3-MCPD were found in different products. Very soon after the first finding of 3-MCPD esters in edible oils and fats it was clear that the main problem was closely related to the refining process, because no 3-MCPD esters were found in virgin or unrefined oils and fats, sometimes only in traces, probably as a result of steam treatment of the oil (Weisshaar 2008). The most crucial factor for the formation of 3-MCPD esters and related compounds is the deodorization step. While during the other steps of the refining process no 3-MCPD esters and related compounds are formed, the amount can drastically increase during deodorization (Fig. 2.29).

For free 3-MCPD in food such as soy sauce and acid-hydrolyzed vegetable proteins (HVP), the European Union (EU) has provided a threshold value of 20 µg/kg.

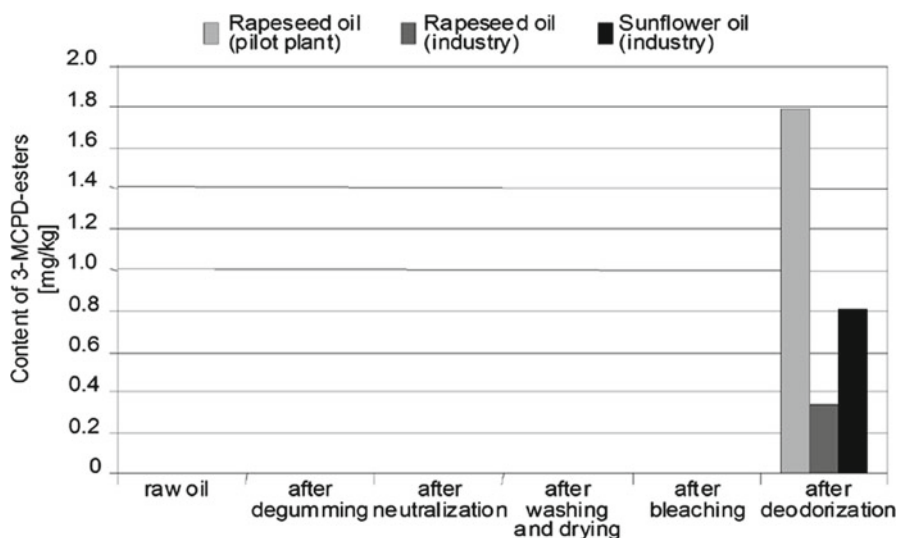


Fig. 2.29 Formation of 3-MCPD-esters during the refining process

In 2001, the Scientific Committee on Food (SCF) of the EU in collaboration with the WHO has decided a Tolerable Daily Intake (TDI) value of 2 μg 3-MCPD/kg BW/day (Anonymous 2001). In 2003, the German Federal Institute for Risk Assessment (BfR) has published the results of a study concerning the values of 3-MCPD in food and a toxicological assessment. High concentrations of free 3-MCPD have proven to cause kidney tumors but not genotoxic activity in animal experiments with rats (Anonymous 2001, 2003; Robjohns et al. 2003). Since there is no information available so far on the toxicology of the 3-MCPD-esters, BfR and the European Food Safety Authority (EFSA) decided to expand the threshold value of free 3-MCPD to the esters, i.e., TDI 2 μg /kg BW/day with the assumption that 100% of the esters are metabolized to free 3-MCPD (Anonymous 2007, 2008). In addition to 3-MCPD esters, other related and toxicologically relevant substances such as fatty acid esters of 2-monochloro-1,3-propanediol (2-MCPD esters), 1,3-dichloro-2-propanol (1,3-DCP-esters), 1,2-dichloro-3-propanol (1,2-DCP-esters), and glycidyl esters (GE) (Seefelder and Schilter 2009; Weisshaar and Perz 2010) can be found in refined edible oils. Especially GE may have some toxicological relevance because of the epoxy ring structure. The glycidol structure is known to be a genotoxic and carcinogen, so that glycidol is classified as probably carcinogenic to human (Group 2A) by an evaluation of the International Agency for Research on Cancer (IARC) (Anonymous 2000).

The mechanism for the formation of 3-MCPD esters and related compounds is only little understood, but it is assumed that glycerin, mono- and diacylglycerides, and phospholipids (Hamlet et al. 2004a; Hamlet et al. 2004b) are precursors on the way to the esters. Velisek et al. (2003) and Calta et al. (2004) showed that the formation

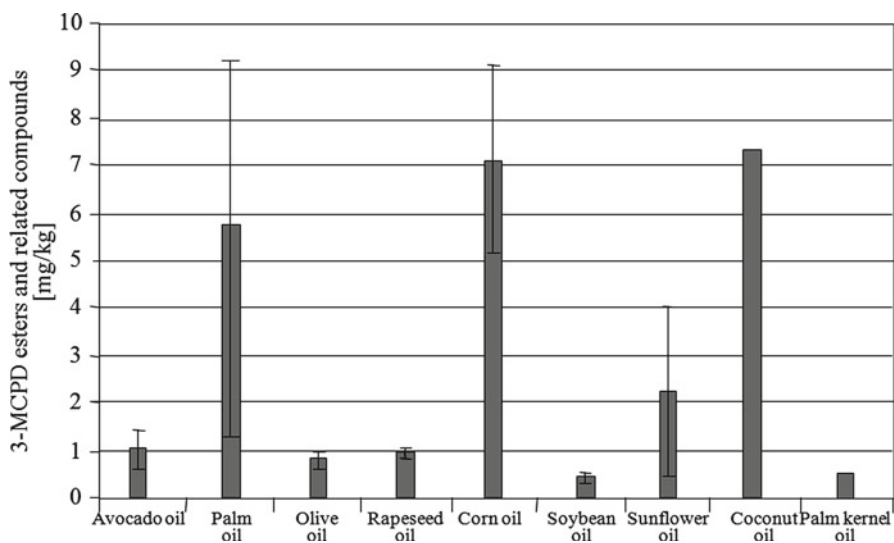


Fig. 2.30 Capability of raw oils to form 3-MCPD esters and related compounds during heating (240°C, 2 h)

of free 3-MCPD strongly depends on temperature and the content of lipids, glycerin, salt, and water.

The capability of oils to form 3-MCPD ester and related compounds can be assessed by heating the oils under standardized conditions at 240°C for 2 h to simulate the refining process. While some oils such as rapeseed or soybean oil show a low capability to form the esters with contents below 1 mg/kg after treatment under standardized conditions, in palm oil, corn oil, and coconut oil much higher amounts of the esters are found showing that different types of oil have different capabilities for the formation (Fig. 2.30). Although olive oil and avocado oil are also fruit oils such as palm oil, the capability of these oils for the formation of 3-MCPD esters and related compounds was much lower. One explanation could be the lower content of diacylglycerides in these oils. It is also interesting to note that palm oils from different locations show strong differences in the capability of the raw material to form 3-MCPD esters and related compounds (1.5–9 mg/kg). Conceivable reasons could be different soil and climate conditions, the use of different fertilizers, or different types of handling after maturity until processing.

During deodorization, the formation of 3-MCPD esters and related compounds strongly depends on the temperature. Up to a temperature of 240°C the formation of 3-MCPD esters and GE is relatively low, also at longer deodorization time. At higher temperature, the formation of contaminants increases strongly with time, whereas the formation of the GE seems to be favored (Fig. 2.31). While between 2 and 4 mg/kg 3-MCPD esters were found in the oil independently of the deodorization temperature, for the formation of GE a strong increase was found the higher the temperature.

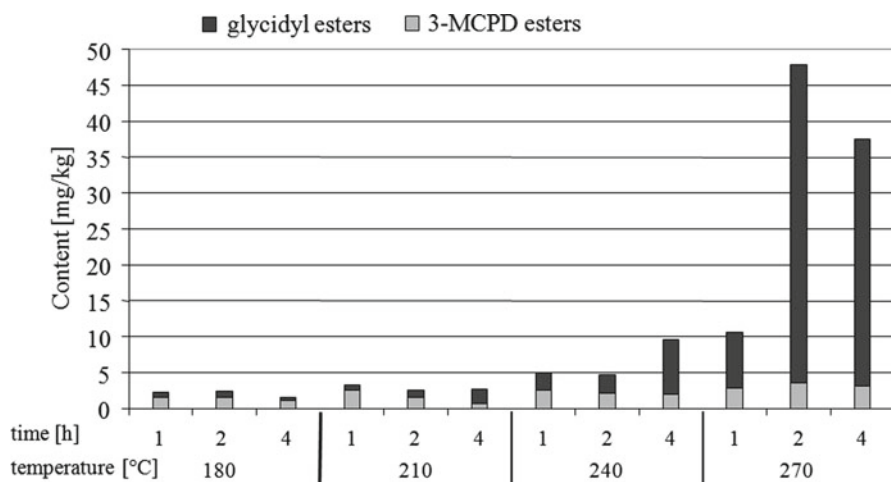


Fig. 2.31 Influence of temperature and time on the potential palm oil to 3-MCPD-E and related compounds formation during deodorization

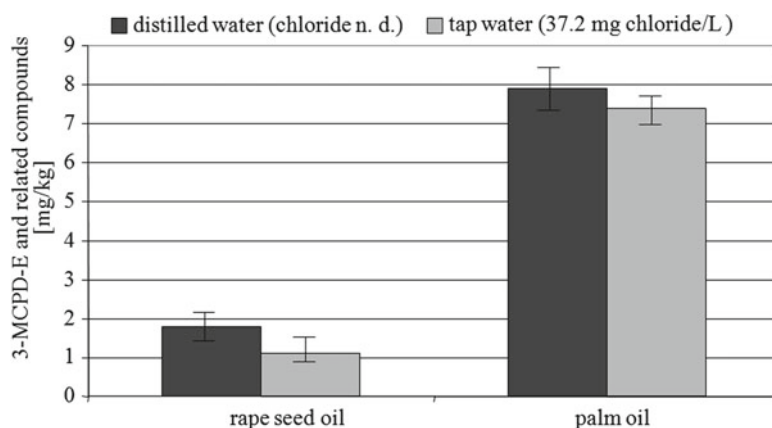


Fig. 2.32 Influence of the chloride content of water for the generation of the strip steam during deodorization

Just at 290°C, the concentration of contaminants decreases with time, probably caused by thermal degradation reactions. However, from a practical point of view this temperature has no importance and is only for a worst-case comparison.

At the beginning of the discussion about the 3-MCPD ester formation in edible oils the question arose, whether the chloride content of water used for the generation of strip steam during deodorization has an effect as source for chloride. Figure 2.32 shows that the chloride content of the strip steam used for the deodorization of crude palm oil or rapeseed oil has no significant influence on the formation of

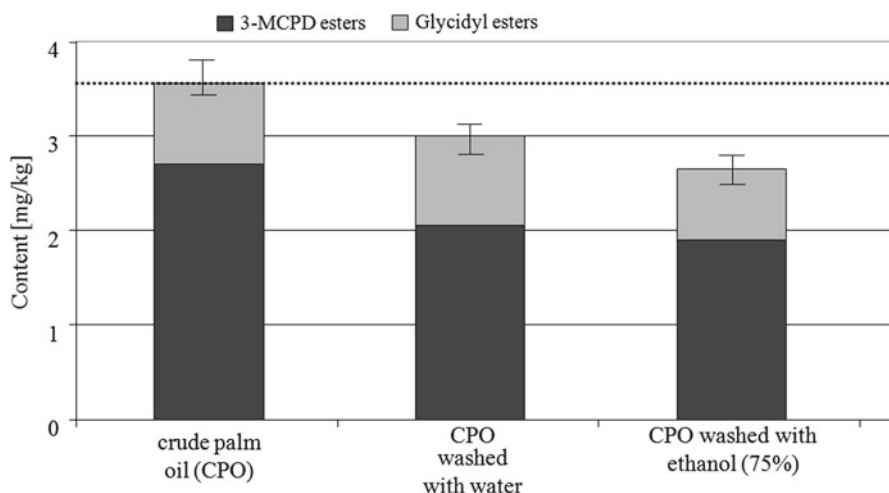


Fig. 2.33 Influence of washing on the capability to form 3-MCPD esters and related compounds

3-MCPD esters and related compounds. Either the chloride in the tap water is not available in a form which can be involved in the reaction or there is no chloride in the strip steam.

Although there are different setscrews to reduce the formation of 3-MCPD esters and related compounds during deodorization, like reaction partners, temperature, and time, it seems to be very difficult to optimize the refining process regarding 3-MCPD ester formation without impairing product properties, such as sensory quality, stability, and appearance of other contaminants. The optimization of the refining process is a balancing act between the necessary purification of the oil and the formation of process derived and the remaining of other undesired contaminants. Therefore, the most promising way to gain control on the formation of 3-MCPD esters and related compounds seems to be the removal of reactants from the raw material before refining.

Figure 2.33 shows one example for a pretreatment of the raw material. Crude palm oil was washed by water and ethanol (75%), respectively, before deodorization and the capability of the raw material to form 3-MCPD esters and related compounds was compared. The result is a significant lower amount of 3-MCPD esters and related compounds after the washing steps in comparison to not washed palm oil. This reduction was due to a decrease in the amount of 3-MCPD esters while the amount of glycidyl esters was nearly unchanged. One interpretation of this result could be that the amount of chloride was reduced by the washing step resulting in the decrease of the content of 3-MCPD esters.

The other steps of the refining process, degumming, neutralization/washing, and bleaching, have a positive effect on the formation of 3-MCPD esters and related compounds and lead to a reduction of the capability of the raw material to form 3-MCPD esters and GE.

14 Effect of Processing on the Oxidative Stability of Edible Oils

The processing of edible oils is important for the oxidative stability and shelf life of the product which is correlated to the appearance and interaction of the pro- and antioxidant compounds. The extraction process and the further treatment of the oil strongly influence the content and composition of minor components in the oil. While extensive extraction conditions together with heat-treatment result in higher extractability of phenolic and other antioxidative active compounds, such a treatment also conduce higher concentrations of oxidation products possibly impairing the product quality. Refining reduces both types of components. Extraction by a screw-press only is much milder with regard to the formation of oxidation products, on the other hand more antioxidant active compounds remain in the press cake. Thus, the processing of edible oils is a balancing act between avoiding oxidation and removal of antioxidant active compounds from the raw material. The better the producer achieve this, the higher is the oxidative stability and the shelf life of the oil. From the differences in the processing of refined and virgin edible oils some differences in the oxidative stability of both types of oil can arise, but some general aspects have to be taken into consideration during processing to avoid reduced shelf life and bad quality.

The influence on product quality and shelf life starts directly with the harvest and each step from the harvest to the selling may have a certain impact on the quality of the oil. Gupta (2000) summarized the requirements for the formation of free radicals in oilseeds and – fruits which can start the oxidative deterioration of the oils during storage as: (1) poor-quality oilseeds, (2) improper handling and storage of oilseeds, (3) improper conditions during crushing, (4) poor handling and storage of the crude oil, (5) overheating the oil during processing, (6) undue exposure of the oil to oxygen during processing, (7) atmospheric bleaching, (8) deodorization under poor vacuum, and (9) storage and handling of the finished oils under oxygen.

14.1 *Refined Oils*

The effect of the different refining steps is very specific for the removal of minor components from the oil. Degumming removes phospholipids, proteins, and also mucilaginous gums. Alkali refining takes off free fatty acids, phospholipids, metal ions, and chlorophyll, while bleaching reduces the amount of colored compounds like chlorophyll and carotenoids, metal ions and oxidation products. In the final deodorization step volatile aroma compounds and free fatty acids, but also tocopherols, phytosterols, phenolic compounds and carotenoids are removed from the oil. Additionally, due to the high temperature used for the deodorization hydroperoxides partially decompose to short-chain degradation products which are removed

during steam treatment. On the other hand, secondary oxidation products, which can propagate autoxidation, remain in the oil and can result in a fast deterioration of the product during storage. Thus, although the peroxide value is reduced to zero during deodorization, the anisidine value in the oils increases showing that low peroxide value of refined oil is not necessarily an indication for high quality. A crude soybean oil heavily oxidized before deodorization may show a good flavor, but during storage it develops an oxidized flavor and becomes rancid very rapidly (Gupta 1994).

At the end of refining, the content of minor compounds in the oil has been reduced. While phospholipids, iron, chlorophyll, and free fatty acids are removed almost completely from the oil, the amount of tocopherols is reduced for 10–60% and phytosterols are eliminated for 20–50%, depending on the type of oil and the refining conditions (Jung et al. 1989; Ferrari et al. 1996; Ramamurthi et al. 1998; Shahidi et al. 2005).

Several papers have been published on the comparison of the oxidative stability of vegetable oils from different stages of the refining process (Going 1968; Kwon and Brown 1984; Jung et al. 1989; Gordon and Rahman 1991; Pekkarinen et al. 1998). In general, the refining process causes a decrease of the stability from the crude to the refined oil and Rutkowski (1961) described the decrease for desolventizing, neutralization, and bleaching as 18.6, 34.6, and 52.7%, respectively.

Going (1968) showed that clean-dry crude soybean oil was less susceptible to oxidation than refined and bleached oil and he stated that oil should be stored as crude oil to minimize deterioration of the oil by oxidation. Additionally, Going concluded that already relatively low levels of oxidation prior to deodorization are necessary to impair the oxidative stability of the finished oil. Similar results were found by Kwon and Brown (1984) who compared the oxidative stability of soybean oil at seven different stages of commercial refining by measuring the weight increase during storage. In this experiment, the oxidative stability of the processed oils decreased in the order crude > degummed >> bleached > deodorized. The lowest oxidative stability was found for soybean oil triacylglycerides, purified from minor compounds by column treatment. The authors assumed, as a most likely reason for this finding, the loss of antioxidant active components such as phospholipids and tocopherols during column treatment and refining. In addition, Kwon and Brown (1984) showed that phospholipids have a synergism on the antioxidant effect of tocopherols. While tocopherols and phospholipids alone improve the oxidative stability of soybean oil triacylglycerides to a certain extent with only a small effect by the respective concentration, the combination of tocopherols and phospholipids strongly improved the oxidative stability. The higher the concentration of phospholipids, the better was the oxidative stability of the oil.

The importance of phospholipids for the oxidative stability of vegetable oils was also described by Linow and Mieth (1976) who found that the addition of selected phospholipid fractions improved the effect of tocopherol on the oxygen absorption of methyl linolate. Especially nitrogen-containing phospholipids such

as phosphatidylcholine were able to have a synergism with tocopherols. They also found that the positive effect of phospholipids did not base on the regeneration of tocopherols in the redox-system tocopherol/tocopherylcholine, but that phospholipids inhibited the degradation of tocopherols. For concentrations between 0 and 1%, Bratkowska and Niewiadomski (1975) described a prolonging effect of phospholipids isolated from rapeseed oil on the induction period of refined rapeseed oil. Hildebrand et al. (1984) found that the addition of tocopherol and phospholipids except phosphatidic acid alone or in combination increased the stability of soybean oil and they explained this effect by synergism of phospholipids with tocopherols rather than by a special ability of the phospholipids to bind traces of metal ions.

Phospholipids isolated from coconut oil by column chromatography and added to degummed, bleached, and deodorized coconut oil increased the induction period of the oil in the Rancimat test at 120°C from 5.1 to 32.3 h, a value close to the induction period of crude coconut oil (Gordon and Rahman 1991). On the other hand, phospholipids can act as natural surfactants, similar to mono- and diacylglycerides, which reduces the interfacial tension between the contrary materials water and oil, and also air and oil. Thus, higher amounts of phospholipids in the oil during storage in the presence of water can result in hydrolysis of triacylglycerides and the formation of free fatty acids. Gupta (2000) described that a phosphorus content in vegetable oils ≥ 3 ppm results in the formation of free fatty acids during storage. Additionally, the solubility of oxygen from the air in the oil is improved by higher amounts of phospholipids.

Jung et al. (1989) found in crude soybean oil a peroxide value of 2.4 meq/kg which increased to 10.5 meq/kg during degumming and 16.5 meq/kg after bleaching. Resulting from the high temperature during deodorization, the hydroperoxides were completely decomposed and the peroxide value fell to 0 meq/kg. The increase of the peroxide value after degumming was explained by the moisture content (1–3%) and the temperature (70–80°C) during the processing. The formation of hydroperoxides during bleaching strongly depends on the type and amount of clay used (King and Wharton 1949). The use of lower concentrations of clay resulted in higher peroxide values. Morrison (1975) mentioned that bleaching with 1% activated clay decreased the storage stability, while 3% clay had no effect on the storage stability of sunflower oil.

The effect of the processing steps on the oxidative stability of soybean oil was found in the order crude > deodorized > degummed > refined > bleached (Jung et al. 1989), which was explained by the effect of the presence and absence of pro- and antioxidants. While crude oil is relatively low in prooxidants such as hydroperoxides, the oil contains high values of antioxidants such as tocopherols and phospholipids. On the other hand, bleached oil has a high peroxide value and only low amounts of antioxidants.

Farhoosh et al. (2009) investigated the development of the peroxide value and carbonyl value of soybean and canola oil during the different refining steps. While PV decreased from 1.89 meq O₂/kg (crude) to 0.64 meq O₂/kg (deodorized) for

soybean oil and from 1.94 meq O₂/kg (crude) to 1.78 meq O₂/kg (deodorized) for canola oil, the carbonyl value increased from 2.77 to 6.36 μmol/g for soybean oil and 19.9 to 26.9 μmol/g for canola oil. The main increase was observed during the bleaching step, probably due to the decomposition of hydroperoxides and the formation of secondary oxidation products.

High temperature during deodorization is responsible for the degradation of tocopherols which are important for the shelf life of edible oils (Jawad et al. 1983). During refining of soybean oil, the induction period at 100°C decreased significantly with increasing temperature during deodorization (240–300°C) and the authors assumed that this effect was probably due to the reduction of tocopherols.

Rice bran oil (RBO) is a very rich source of bioactive phyto-chemicals, which include tocopherols and γ-oryzanol, an ester of *trans*-ferulic acid with sterols and triterpenic alcohols, with high antioxidant and radical scavenging properties. During chemical refining, γ-oryzanol is removed from the oil to 1.1, 5.9, and 93.0–94.6%, respectively, with a resulting content of 1.1–1.74%, while physically refined RBO contains 1.63–2.72% γ-oryzanol (Gopala Krishna et al. 2001). As a result of alkali-refining the content of tocopherols and γ-oryzanol is reduced to 34 and 51%, respectively, and the order of oxidation stability is crude >> degummed > bleached = deodorized > alkali-refined (Yoon and Kim 1994). Also, Mezouari and Eichner (2007) found that crude RBO had better storage stability than full refined oil. The authors explained the good OSI value after 240 days of storage by the remaining large quantity of sterols, γ-oryzanol, and tocopherols in the crude oil. They recommended that the conditions of the refining process should be improved to retain a maximum of desirable compounds.

In the Rancimat test at 120°C, the induction period of soybean and canola oil decreased during refining from 6.86 (crude) to 4.33 h (deodorized) for canola oil and from 5.02 (crude) to 3.63 h (deodorized) for soybean oil (Farhoosh et al. 2009). The main decrease was found after neutralization and showed no considerable changes during the further refining steps. Similar results were found by Zacchi and Eggers (2008), who showed that the induction period of rapeseed oil decreased remarkably after the degumming and neutralization steps, but only a little decrease was found for the other refining steps. One explanation was that during neutralization antioxidant active phenolic compounds were almost completely removed.

14.2 Virgin Oils

Owing to the easy processing in virgin oils, compounds responsible for oxidation processes during storage, normally being removed during the refining process, are present in virgin oils to a higher extent resulting generally in a lower oxidative stability of virgin oils. On the other hand, no tocopherols or other antioxidant active compounds are removed, which improves the oxidative stability of virgin oils. Therefore, in virgin oils two reversed aspects have to be taken into consideration when discussing the oxidative stability in contrast to refined oils. The oxidative

stability of high-quality virgin oils produced from sound raw material with utmost care under optimal conditions should be higher or comparable to refined oils, because as a result of the careful processing the amount of oxidation promoting compounds is low, but the concentration of antioxidants such as tocopherols is higher. Only when failures were made during production the oxidative stability of virgin oils is remarkably lower.

An important factor which strongly influences the storage stability and shelf life of virgin vegetable oils is the initial content of hydroperoxides after processing. Depending on the processing conditions and the quality of the raw material oxidation processes together with the formation of hydroperoxides as primary oxidation products can start already in the raw material. This results in higher initial peroxide values in the virgin oil and the producer has, in contrast to the processing of refined oils, no possibility to reduce the content of hydroperoxides after oil extraction. Satue et al. (1995) showed that the oxidative stability of virgin olive oil was significantly lower in comparison to refined, bleached, and deodorized olive oil, although virgin olive oils contained higher levels of phenolic compounds. They assumed that the higher initial peroxide value of the virgin oils could be the reason for this finding.

Also, Pekkarinen et al. (1998) assumed that the high initial level of hydroperoxides in virgin rapeseed oil was responsible for the low oxidative stability in comparison to crude or processed oils. The oils reached a peroxide value of 10 meq/kg during storage in the dark in the order virgin > superdegummed > steam stripped \approx crude > refined. During storage under light conditions, the formation of hydroperoxides in virgin oil was much slower over a storage period of 13 days, due to the lower content of chlorophyll in this type of oil which acts as a photo-sensitizer and enhances photo-oxidation.

As important as the initial content of hydroperoxides is the content of antioxidant active compounds, which should be higher in virgin oils than in the corresponding refined ones, since during refining these compounds are removed to some extent. On the other hand, the extensive extraction by heat treatment and the use of a screw press and solvent result in a better extraction and higher amounts of minor compounds with some antioxidant activity such as phenolic compounds in solvent-extracted crude oils. In a market survey with 21 samples of virgin olive oils, Gutfinger (1981) showed that solvent-extracted olive oils were richer in polyphenols than the virgin oils. He also found a linear relationship between the content of polyphenols and the oxidative stability of the oils during storage at 60°C. After removal of the polyphenols, the oxidative stability of the oils decreased remarkably.

A similar phenomenon and the strong influence of the temperature on the content of phenolic compounds in the resulting oil were found for coconut oil. The extraction of coconut oil from coconut milk under hot conditions results in higher contents of phenolic compounds than extraction under cold conditions, because hot extraction improves the extractability of the compounds from the raw material (Seneviratne et al. 2009). Temperatures above 100°C result in a better transfer of the phenolic compounds from the water phase of the coconut milk emulsion into the oil.

The phenolic extracts of hot-extracted coconut oil showed a remarkably higher DPPH radical scavenging activity and inhibition of deoxyribose degradation compared to phenolic extracts of cold-extracted coconut oil. The authors did not investigate the influence of the extraction procedure on the initial content of hydroperoxides or free radicals in the resulting oils.

In a storage experiment with olive oils obtained with different extraction technologies (pressure extraction (traditional system), centrifugation without mill wastewater recycling (continuous system), and centrifugation with mill waste water recycling), Cercaci et al. (2007) found no significant effect of the total sterols obtained from extra virgin olive oil on the oxidative stability of a vegetable model system.

Arranz et al. (2008) found a good correlation between the antioxidant activity measured by the DPPH method and oxidative stability determined by the Rancimat method in different nut oils. They ascribed this finding to the tocopherols in the oils, and also a contribution of phospholipids was found. The ranking of antioxidant capacity of nut oils, by both assays, was pistachio > hazelnut > walnut > almond > peanut.

For the evaluation of the antioxidant activity and for the assessment of the oxidative stability of edible oils, it is important to take into consideration that different parameters respond differently on oxidation resulting in different results for the trend of oxidation during storage. One example was given by Satue et al. (1995) who showed that α -tocopherol behaves as a prooxidant at concentrations >250 ppm in refined olive oil when following the oxidation by the peroxide value, but was most effective in inhibiting the formation of hexanal. With the peroxide value as parameter, phenolic extracts from olive oil showed the best effect at 50 ppm, but at 100 and 200 ppm the inhibition of hexanal formation was predominant.

Another point is that it is more difficult to detect oxidative deterioration of virgin oils than of refined oils, because of the very strong and dominant odor of its own, which covers rancid sensations. This is the reason for the phenomenon that a producer sometimes indicates very long dates of expiry and consumers use the oils from a bottle for a long time without noticing the oxidative deterioration.

Virgin oils usually contain only low amounts of oligomer triacylglycerides, because no heat was used for the extraction. Thus, the values should be below 0.1% and higher values give some indication for the application of heat during the production. However, it has to be taken into consideration that depending on the type of oil the amount of oligomer triacylglycerides also can increase during storage. This makes the decision whether the oil was treated by heat or whether it was stored under improper conditions difficult.

14.3 Oils from Heat-Treated Raw Materials

A special phenomenon can be observed for cold-pressed edible oils from roasted seeds such as nut oils or pumpkin seed oil, which show a higher oxidative stability than corresponding virgin oils from unroasted seeds (Wijesundera et al. 2008).

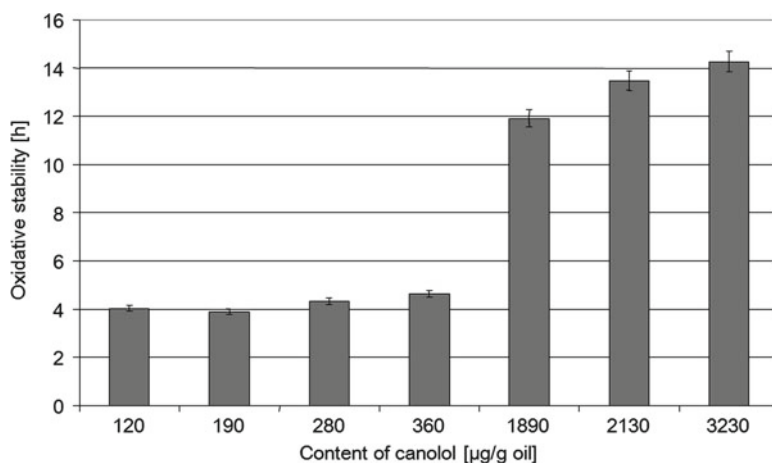


Fig. 2.34 Effect of canolol on the oxidative stability of rapeseed oil (Rancimat test at 120°C)

Also, Prior et al. (1991) found a higher oxidative stability of canola press oil after heat treatment of the seeds, which decreased with subsequent refining. They explained this by the appearance of nontriacylglyceride material in crude oil and stated that the greater the initial quality of the oils, i.e., the lower the content of nontriacylglyceride material, the lower their oxidative stability. A good correlation with the phosphorus content was found in the range from 0.025 and 0.22% phospholipids. Higher amounts of phospholipids did not further improve the oil stability.

During the roasting process, the intact or crushed seed material is treated by heat between 140 and 160°C resulting in a better availability and extractability of bioactive compounds as well as the formation of new antioxidants such as Maillard reaction products, canolol from the decarboxylation of sinapic acid in rapeseed (Wijesundera et al. 2008), or generation of sesamol from the degradation of sesamol during roasting of sesame seeds (Lee et al. 2009) which improve the stability of the resulting oil. For example, heat treatment of rapeseed leads to a better oxidative stability of the oil in the Rancimat test likely resulting from the better extractability of antioxidant active substances during the pressing and the formation of canolol during roasting (Fig. 2.34).

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