

medium. The cool, solvent-lean mineral oil is then recirculated to the top of the mineral oil absorber.

All water and solvent that drains from the various condensers in the solvent extraction plant enters a decanting tank. Since solvent is immiscible with water, the lighter solvent (0.65 specific gravity) floats above the water. The key to the decanting tank performance is to minimise turbulence within the tank, so as to allow sufficient time for gravity decanting to take place. The elevation of the interface between solvent and water is established by the highest elevation of the water drain pipe. Water, typically containing 0.01% solvent, exits the decanting tank to the wastewater stripper. Solvent, typically containing 0.05% water, exits the decanting tank to the solvent work tank.

The wastewater stripper is a small tank used to increase the temperature of the wastewater to approximately 95 °C, in order to evaporate residual solvent prior to discharge to the plant sump. The water exiting the wastewater stripper is typically less than 10 ppm solvent. The hot water exiting the wastewater stripper is often interchanged with the cool water entering the wastewater stripper for heat recovery.

Solvent enters the work tank from the decanting tank. The work tank is a surge tank used to hold solvent prior to the extractor, in order to ensure that there is always ample solvent available to be pumped to the extractor. If a large surge of solvent flows into the work tank, the work tank will automatically overflow to solvent storage. If the level in the work tank becomes low, additional solvent is pumped from solvent storage to the work tank. The temperature of the solvent in the work tank is typically in the range of 52–57 °C in plants equipped with a vapour contactor, and 43–49 °C in plants without a vapour contactor.

In plants with a vapour contactor, solvent is pumped from the work tank at 55 °C to a steam-heated solvent heater in order to increase its temperature to 60 °C prior to entering the extractor. In plants with a solvent preheater rather than a vapour contactor, solvent is pumped from the work tank at 45 °C to the solvent preheater, where its temperature is increased to 55 °C. The solvent is then further heated in a steam-heated solvent heater from 55 to 60 °C prior to its return to the extractor.

4.7 Heat recovery

With solvent extraction being a very established technology, many incremental improvements have occurred over the years in the optimisation of heat recovery between unit processes. Tools such as ‘pinch analysis’ are utilised today to chart and evaluate the available hot streams and cool streams in the process. Each stream can be plotted on a chart, with temperature on the y-axis and heat content on the x-axis.

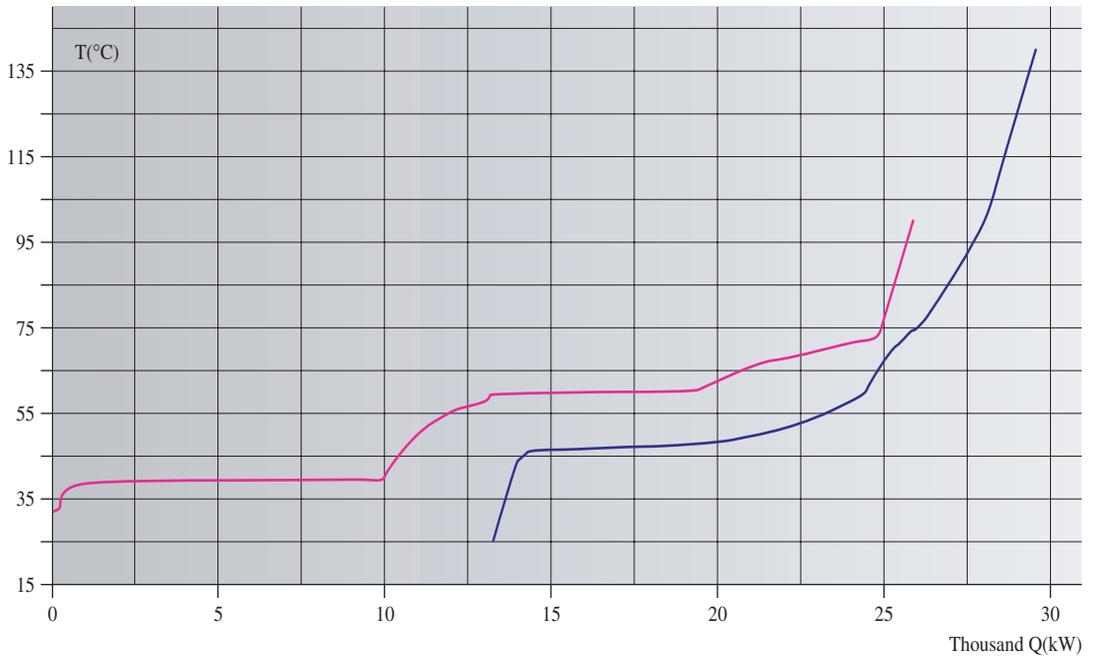


Figure 4.9 Composite pinch curves.

The vapours from the DT represent a hot stream with high heat content and moderate temperature, while the vapours from the evaporators have high heat content and very low temperature. Several hot streams exist with low heat content and high temperature, such as edible oil stripper vapours, mineral oil stripper vapours, wastewater evaporator vapours, waste water and edible oil.

The three large cool streams are miscella from the extractor, solvent to the extractor and air to the DC. A small cool stream is water from the solvent–water separator.

A composite hot stream and cool stream curve can be plotted (see Figure 4.9). The temperature range at which the two curves near each other (the ‘pinch’ range) is then determined. Ideally, heat recovery devices should be employed such that cooling water will not be used to cool any individual hot stream above the upper end of this pinch temperature range and steam will not be used to heat any individual cool stream below the lower end of this pinch temperature range. Using this tool, modern solvent extraction plants are achieving up to 96% of maximum potential heat recovery in the solvent extraction process.

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5

Edible Oil Refining: Current and Future Technologies

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5.1 Introduction

Several factors, including a growing world population, higher fat intake per capita and increasing use for technical applications, have resulted in a steep increase in the demand for oils and fats. The annual growth rate of the world demand has virtually doubled since the late nineties and is currently estimated at 6.3 million tonnes per year (Mielke, 2011). To meet this increasing demand, the total production volume of 12 vegetable oils has more than tripled, from 40.8 million tonnes in 1980 to 146.2 million tonnes in 2010 (FAOSTAT, 2012). Production of palm oil (from 5 to ~40 million tonnes) and soybean oil (from 13 to ~38 million tonnes) have particularly increased.

Since most vegetable oils need to be (at least partially) refined for edible or technical applications, increased production volumes have resulted in a serious expansion of the edible oil refining industry. The required refining capacity is currently estimated at 400 000 tonnes per day.

In edible oil refining, the continuous effort to reduce overall production costs (including capital investment and operating costs) is mainly achieved by increasing plant capacities (up to 4000 tonnes per day today, to maximise economies of scale), installation of mono feedstock plants (for palm or soybean oil) and increasing the degree of automation (to reduce required manpower). As a result, edible oil refining has turned from a locally orientated

operation with many small-scale plants into a large-scale industry dominated by a number of global companies.

Improving overall cost-efficiency has also been an important driver for new developments. Over the years, more energy-efficient processes and technologies, resulting in a higher refined oil yield, have gradually been introduced. The growing importance of the (nutritional) oil quality and the sustainability aspect of the refining process itself (minimal use of processing aids and chemicals) are new challenges for oil processors. To reach these new objectives, 'next-generation' oil refining process technologies will have to be developed and implemented.

In this chapter, an overview is given of some process improvements and new developments that have recently been introduced in the edible oil refining industry. Some potential new innovations which are currently not yet applied are also briefly discussed.

5.2 Next-generation chemical refining with nanoneutralisation

Edible oils can be refined by either a chemical or a physical refining process. Chemical refining is still the most widely applied process for soft oils with low free fatty acid (FFA) content (soybean oil, rapeseed oil, sunflower oil etc.). The main byproduct of chemical refining is the so-called soapstock, which is a mixture of fatty acid soaps, salts, phospholipids, impurities and entrained neutral oil. Soapstock is usually split with sulfuric acid, resulting in a low value, difficult-to-value 'acid oil' and a difficult-to-treat wastewater stream. The high neutral oil losses in the soapstock (especially when crude oils with higher FFA and phospholipid contents are chemically refined), the low value of the resulting acid oil and the stricter environmental legislation (making wastewater treatment more expensive) are the main reasons for oil processors to consider physical refining. On the other hand, chemical refining is quite forgiving towards crude oil quality and it usually gives a good refined oil quality. For these reasons, it is still the preferred refining process for many processors, and it is not expected that chemical refining will disappear. Hence, there will remain a serious interest in new developments that make chemical refining more attractive.

At the end of the 1990s, several new neutralisation processes, such as soluble silicate refining (Hernandez & Rathbone, 2002), dry refining with CaO (Meyers, 2000) and chemical refining with KOH, were developed. All these developments aimed at the (partial) elimination of the washing step and a better valorisation of the soapstock. Unfortunately, none of them were

finally implemented in industrial practice as the valorisation potential of Ca/K soaps was lower than expected, and soapstock-related problems thus remained unsolved.

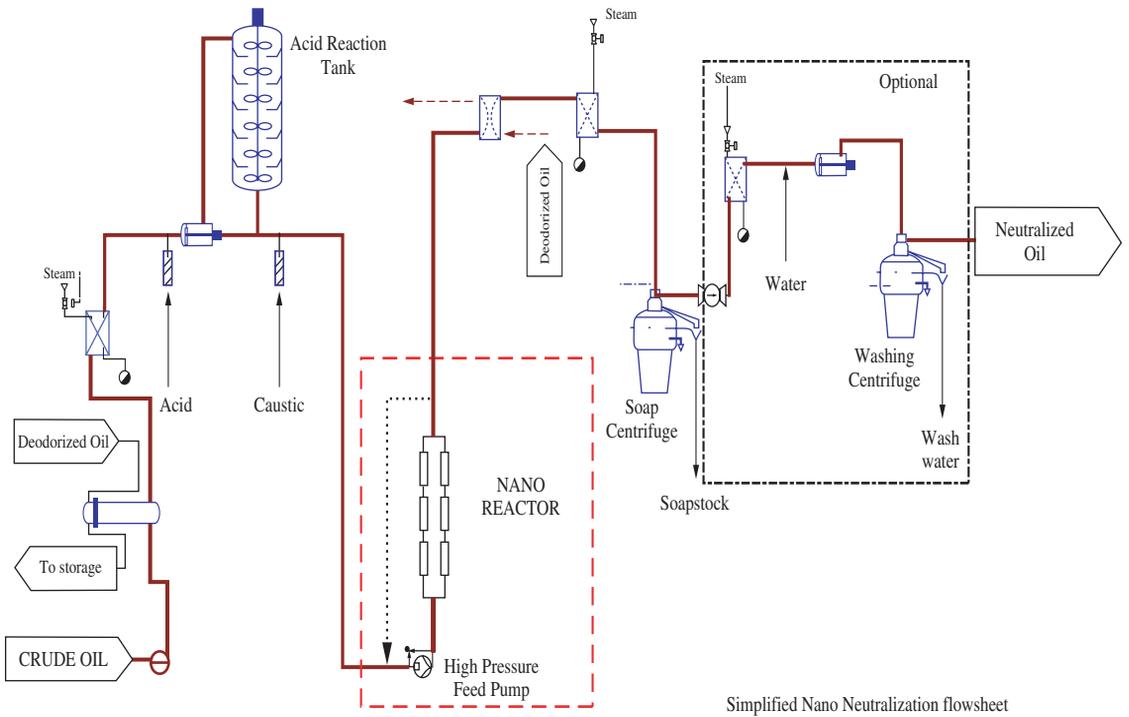
In the last decade, process improvements in chemical neutralisation focused on increasing process automation and the use of better, more powerful mixing systems. This resulted in an overall better process control and the need for less (excess) chemicals. However, these developments did not have a significant positive impact on neutralised oil yield, and the need for acid pretreatment and excess caustic still remains.

In the search for a new neutralisation process that could further reduce the use of (excess) chemicals and oil losses in soapstock, the potential of so-called Nano Reactor[®] technology was investigated. Nano Reactors[®] are hydrodynamic cavitation reactors. Their working principle and possible applications in the chemical industry (for process intensification), biotechnology (cell disruption) and drinking water treatment (microbial disinfection and degradation of contaminants) are well described in recent literature (Cogate, 2010).

The use of ultrasound cavitation (created by a cavitation effect) for edible oil degumming was studied by Moulton & Mounts (1990). Although the results were promising, this process was never industrially applied due to some inherent drawbacks: (1) no uniform cavitation effect; (2) very high energy requirement; and (3) applicability only as a batch process.

Hydrodynamic Nano Reactors[®] are inherently more suitable for use in large scale oil processing as these can be used in continuous operation and require less energy. As a first industrial application, nanoneutralisation was recently developed and successfully introduced in edible oil processing (Svenson & Willits, 2012). A typical process flow diagram is given in Figure 5.1. Crude or water degummed oil is blended with the caustic solution and then transferred by a high-pressure feed pump through the Nano Reactors[®] at a typical pressure of 40–80 bar. The combination of this high pressure and the unique internal design of the Nano Reactors[®] creates a high turbulence and strong shear forces, resulting in a very good mixing of the crude oil and the caustic solution in the Nano Reactor[®]. Discharge pressure is 3–4 bar, which allows direct feeding of the nanotreated oil to the centrifugal separator. Afterwards, the nanoneutralised oil can flow on to the water washing or silica treatment process.

The proven industrial advantages of the nanoneutralisation process are a significant reduction (up to 90%) in phosphoric/citric acid consumption and a corresponding significant reduction (over 30%) of caustic soda use. The latter is due to the lower acid consumption and the very good mixing effect in the Nano Reactors[®], which render nonhydratable phospholipids more



Simplified Nano Neutralization flowsheet

Figure 5.1 Typical nanoneutralisation process flow diagram. Courtesy of Desmet Ballestra.

easily removed and mean that almost no excess NaOH is required for complete FFA neutralisation.

The lower acid and caustic consumption results in a decreased formation of unwanted salts, with a resulting better centrifugal separation of the soapstock from the oil. As a consequence, an overall neutralised oil yield increase of at least 0.2% is observed in industrial operation. Overall oil increase can be even higher due to the lower soap content in the nanoneutralised oil. This reduces the need for silica treatment or water washing, which directly translates into lower oil losses.

The positive effects of Nano Reactors® in the neutralisation process can mainly be explained by the superior mixing effect created during the passage of the oil/caustic solution through them. However, Nano Reactors® are more than just superior mixers and a better understanding of their working principle will result in further applications in edible oil processing.

5.3 Enzymatic degumming: a missing link in the physical refining of soft oils?

Physical refining was originally developed for high(er) FFA oils (such as palm oil) for which chemical refining is not economically attractive. Physical refining results in more easily valorised side products (e.g. deodoriser distillate), but generally requires better quality crude oil. It is therefore more suitable for integrated crushing–refining plants with better control over the incoming crude oil quality.

The broader industrial application of physical refining first requires an efficient degumming process that can ensure a very good degummed oil quality ($P < 10$ ppm) even when applied to lower quality crude (soft) oils.

The traditional classification of phospholipids into so-called hydratable and nonhydratable components is well known in the literature. Hydratable phospholipids can easily be removed during water degumming, which is generally applied as first refining step in the oilseed extraction plant. The resulting gums can either be added back to the deoiled meal or valorised separately as lecithin.

Nonhydratable phospholipids are removed during so-called acid degumming. This is usually the first stage of physical refining and can be considered the equivalent process to alkali neutralisation in chemical refining. Important developments in acid degumming date from the 1980s, driven by the first real interest in physical refining. New features such as improved dosing systems, more powerful mixing systems (to get finer dispersion of the degumming acid), addition of caustic and oil cooling for gum hydration were successfully

implemented and resulted in a significant improvement in degumming efficiency. Processes such as TOP degumming (Vandemoortele) and Super- and Uni-degumming (Unilever), which are still used today in edible oil refining, were developed during that period.

First-generation enzymatic degumming (Enzymax process), soft degumming (Tirtiaux) and membrane degumming (Cargill, Desmet) were developed in the 1990s. The need for a milder but still efficient degumming process requiring less chemicals was the main driver. Unfortunately, these degumming processes were never broadly implemented on an industrial scale. Miscella membrane degumming (Lin & Koseoglu, 2004) was applied industrially for a short time but was soon abandoned due to excessive problems with irreversible membrane fouling. Industrial application of soft degumming (Deffense, 2002) was hindered by the fact that ethylenediaminetetraacetic acid (EDTA) was used as a chelating agent, which raised some acceptability issues. The main drawbacks of the Enzymax process (Clausen, 2001) were the high enzyme cost, the relatively poor stability and selectivity of the enzyme and the fact that a porcine pancreas lipase was used.

A renewed interest in enzymatic degumming has been observed in recent years. This is mostly due to the commercial availability of several new, cost-efficient and stable phospholipases with sufficiently high enzyme activity, developed and guaranteed by various suppliers (Table 5.1). In addition, there is the new market approach of the enzyme producers, who no longer present enzyme degumming as an efficient degumming process but rather as a process that results in a significantly higher refined oil yield. With the current high edible oil prices, oil refiners are very sensitive to this feature, making it the most important driver for the wider application of ‘new-generation’ enzymatic degumming.

Current commercial phospholipases are all of microbial origin. Their mode of action is illustrated in Figure 5.2. Phospholipase A1 (PL-A1, e.g. Lecitase Ultra from Novozymes) and phospholipase A2 (PL-A2, e.g. Rohalase MPL from AB Enzymes, GumZyme from DSM) both release a fatty acid from the phospholipid molecule, resulting in a lysophospholipid and an FFA.

Table 5.1 Commercially available phospholipases for enzymatic degumming.

Enzyme trade name	Producer	Activity
Lecitase Ultra	Novozymes	Phospholipase A1
Rohalase MPL	AB Enzymes	Phospholipase A2
GumZyme	DSM	Phospholipase A2
Lysomax	Danisco	Lipid Acyltransferase (type A2)
Purifine®	DSM	Phospholipase C

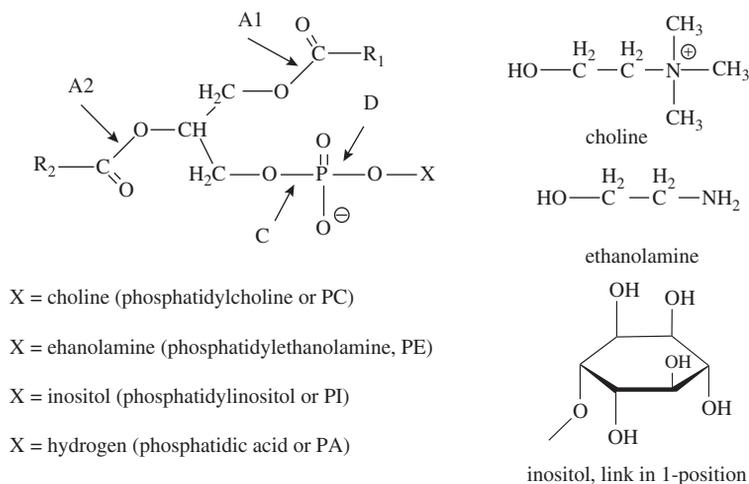


Figure 5.2 Specific activities of the various commercial phospholipases. A1, phospholipase A1; A2, phospholipase A2; C, phospholipase C; D, phospholipase D.

Theoretically, conversion of 0.1% PL (40 ppm P) leads to formation of 0.036% FFA. With sufficient reaction time (depending on enzyme dosing), phospholipases A1 and A2 are relatively unselective and will degrade nearly all phospholipids. LysoMax (Danisco) is a lipid acyltransferase (PL-A2 type) which transfers FFA released from phospholipids to free sterols, resulting in the formation of sterol esters. Unlike FFA, sterol esters are not removed during the refining process and thus represent a limited but real increase in the refined oil yield. Phospholipase C (PL-C, e.g. Purifine[®] from DSM) releases the P-containing part of the phospholipid molecule, with formation of diacylglycerols and phosphate esters as degradation products. Conversion of each 0.1% phospholipids results in the formation of 0.084% diacylglycerols. Phospholipase C will only react with phosphatidylcholine (PC) and phosphatidylethanolamine (PE) and has virtually no effect on phosphatidic acid (PA) or phosphatidylinositol (PI) (Hitchman, 2009).

A general flow sheet of an enzymatic degumming process (basically independent of the type of enzyme being used) is given in Figure 5.3. The first step is the acid conditioning/pH adjustment of the crude or water degummed oil. This step is required to make the nonhydratable phospholipids more accessible for enzyme degradation at the oil–water interface and to bring the pH closer to the optimal pH of the enzyme. Afterwards, the enzyme is added – either pure or diluted in water. High shear mixing is required to ensure optimal distribution in the oil. Enzyme dosing depends on the type of enzyme and on the phospholipids content of the oil, but usually varies between 50 and 200 ppm. The optimal reaction temperature is 50–60 °C, while the required

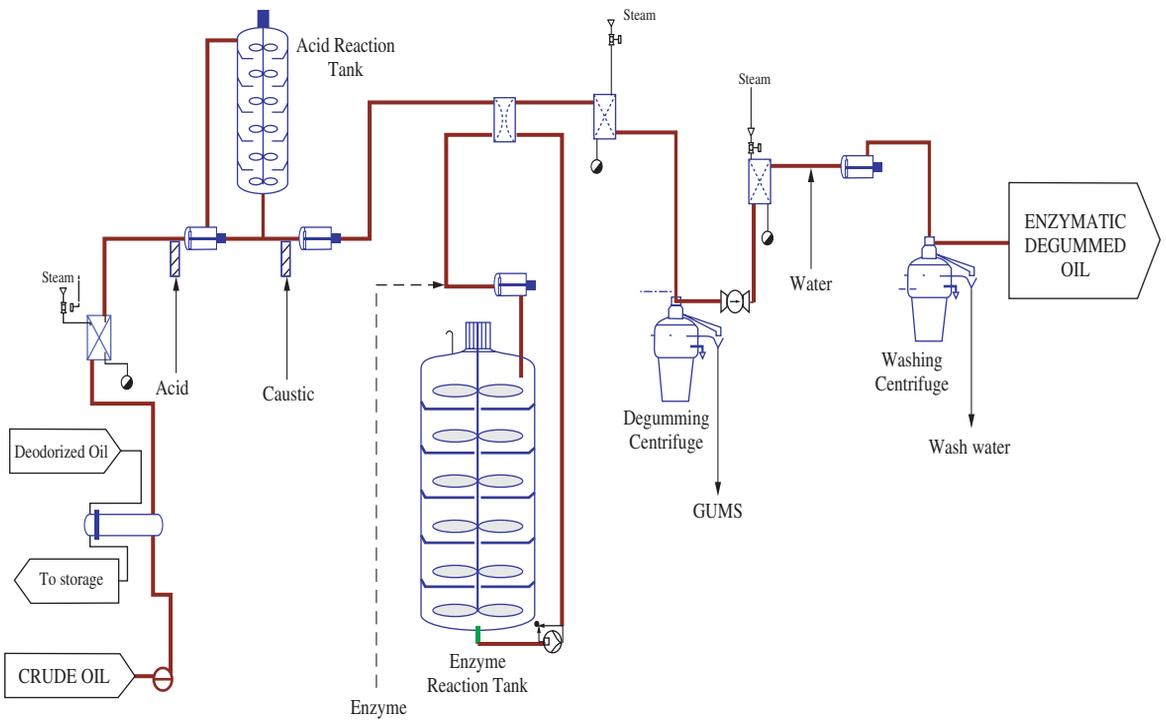


Figure 5.3 Typical process flow diagram of a deep enzymatic degumming process. Courtesy of Desmet Ballestra.

reaction time mainly depends on the enzyme dosing. While in the past it was common practice to apply a longer reaction time with a low enzyme dosage (e.g. 30 ppm enzyme for 6 hours' reaction), preference is now given to a shorter reaction time with higher enzyme dosage (e.g. 100 ppm enzyme for 2 hours' reaction). This practice is preferred because it increases the flexibility of the process while keeping the operating (enzyme) cost at an acceptable level. Finally, the heavy phase (consisting of water and lyso gums or phosphate esters) is separated by centrifugation from the degummed oil.

Two different types of enzymatic degumming can be distinguished: so-called enzymatic water degumming and deep enzymatic degumming. Enzymatic water degumming is typically applied in (soybean) crushing plants. Several large-capacity plants in South America (Argentina, Brazil etc.) are already running in this mode. Increased oil yield is the main driver for its implementation. The expected yield increase depends on the type of oil (P content) and the type of enzyme used. The highest increase (up to 1.8%) can be expected when crude soybean oil is enzymatically degummed with PL-C (Hitchmann, 2009; Kellens, 2009); in this case, the oil yield increase is the sum of the diacylglycerols formed and the lower neutral oil entrainment in a smaller heavy phase (gums fraction). A lower yield increase (1.0–1.5%) will be obtained from PL-C degumming of crude rapeseed oil or when phospholipase A1 or A2 is used on crude soybean oil (Kellens, 2009). In the latter case, the net oil yield increase is due to the lower neutral oil entrainment in the gums fraction alone.

An increase in refined oil yield is obviously a very attractive feature of enzymatic (PL-C) water degumming, but by itself it is not enough to lead to implementation in all crushing plants. In the overall cost/benefit analysis of the process, the enzyme cost and side-stream valorisation are also taken into account. Depending on the value of (lyso-) lecithin, it may be more profitable for a crusher to apply simple water degumming or enzymatic water degumming with PL-A1/PL-A2. The latter gives a lower net oil yield improvement compared to PL-C enzymatic degumming but yields a lysolecithin side stream that may have value for specific applications.

PL-C enzymatic degummed soybean oil typically still has 100–150 ppm residual P (mainly present in PA and PC). A significantly better degumming efficiency ($P < 10$ ppm) can be obtained when crude or water degummed vegetable oils are enzymatically degummed with commercial PL-A1 or PL-A2. This so-called 'deep enzymatic degumming' is already applied in several industrial plants. In addition to the increased oil yield, the very efficient phospholipid removal – making the degummed oil suitable for physical refining – is of great interest to refiners. As an alternative option, a combination of PL-C and PL-A1/PL-A2 can be used for deep enzymatic degumming (Dayton, 2011; Galhardo & Dayton, 2012). The two enzymes can be added either separately or as a cocktail, depending on the plant design. Although the potential advantages of the latter process are well described in the (patent)

literature (Dayton & Galhardo, 2008; Gramatikova *et al.*, 2011), it is still rarely applied on industrial scale.

A potential alternative to enzymatic degumming is the direct enzymatic deoiling of the lecithin fraction resulting from the water degumming of crude oils. In this patented process (De Greyt & Kellens, 2010), a phospholipase (e.g. Lecitase Ultra) is added to the wet lecithin and the phospholipids are degraded into much less hydrophobic lysophospholipids. As a result, 80–90% of the entrapped neutral oil can be recovered by simple static decantation or centrifugation (Kellens, 2009; Kellens *et al.*, 2010). The recovered neutral oil (FFA content: 25–30%) can be recycled to the crude or degummed oil or can be used as such as biodiesel feedstock, while the lysolecithin can be added back to the deoiled meal. The main advantages of the enzymatic lecithin deoiling process over enzymatic degumming are the lower enzyme consumption (~50% less) and the fact that it is applied on a small side stream, with no impact on the oil degumming/refining process. The process has been tested successfully on a pilot scale but is currently not yet applied on an industrial scale.

5.4 Bleaching: from single-stage colour removal to multistage adsorptive purification

Bleaching was introduced in edible oil refining at the end of the 19th century to improve the colour of cottonseed oil. Originally, it was a batch process at atmospheric pressure, in which natural bleaching clay was added to hot oil with the sole objective of removing colouring pigments. Today this is no longer the case, and bleaching has become a critical process in edible oil refining. It has gradually turned from a single-stage ‘bleaching’ into a multistage adsorptive purification process in which a wide range of unwanted components (soaps, phospholipids, oxidation products, trace metals, contaminants etc.) are removed prior to deodorisation.

In order to reach this point, a whole series of process improvements was gradually introduced, with the aim of reducing the overall processing cost and improving the bleached oil quality. Vacuum bleaching was implemented first, in order to avoid oxidation and related colour fixation and improve the oxidative stability. Later, as the capacity of refining plants increased, bleaching evolved from a batch to a (semi-) continuous process. This evolution further improved the bleached oil quality and made the process more energy efficient. Another process improvement was the implementation of (horizontal/vertical) pressure leaf filters. Initially, plate and frame filters were used, but these lost favour over the years due to the too high residual oil content in the spent bleaching earth (typically 35–40%) (Veldkamp, 2012).