SEPARATION PROCESSES IN OIL REFINING TECHNOLOGY[#]

Vito Martinčič*
Tovarna olja GEA, d.d., Trg svobode 30, 2310 Slovenska Bistrica, Slovenia

Janvit Golob
University of Ljubljana, Faculty of Chemistry and Chemical Technology, Aškerčeva 5, SI-1000 Ljubljana, Slovenia

[#] This paper is dedicated to Professor Roman Modic at his 90th Birthday

Received 24-05-2001

Abstract

Oils are the most important source of energy in food products: more than one third, in Slovenia more than 42%, of the energetic value of an average daily food intake comes from the oils and fats present in the different food products. Besides their high energizing effect, oils also provide several essential components like vitamins, essential fatty acids and other minor components. They enlarge food energetic density and it is also generally known that prepared meals with less than 20% of fats are tasteless .

To become suitable for human consumption, most oils must be purified. The market generally requires a light colour, a bland taste and a good cold and oxidative stability. These objectives can be reached by submitting the oils to several refining and modification stages, in order to adapt their organoleptic qualities and physical properties to the required standards.

Refining

All crude oils and fats obtained after rendering, crushing or solvent extraction, inevitably contain variable amounts of non-glyceridic co-constituents like fatty acids, partial glycerides (mono- and diglycerides), phosphatides, sterols, tocopherols, hydrocarbons, pigments (gossypol, chlorophyll), vitamins (carotene), sterol glucosides, protein fragments as well as resinous and mucilaginous materials, traces of pesticides and "heavy" metals.[1]

Some of these co-constituents have a positive impact on the oil quality. Tocopherols, for example, protect the oil from oxidation, which is a vital necessity. They may thus be considered as highly useful constituents.

Now, if we take sterols, they are colourless, heat stable and for all practical purposes, inert: hence they pass unnoticed, unless present in unusually large amounts.

Phosphatides in the crude oil provide protection from oxidation, but they need to be removed because they interfere with further processing.[2]

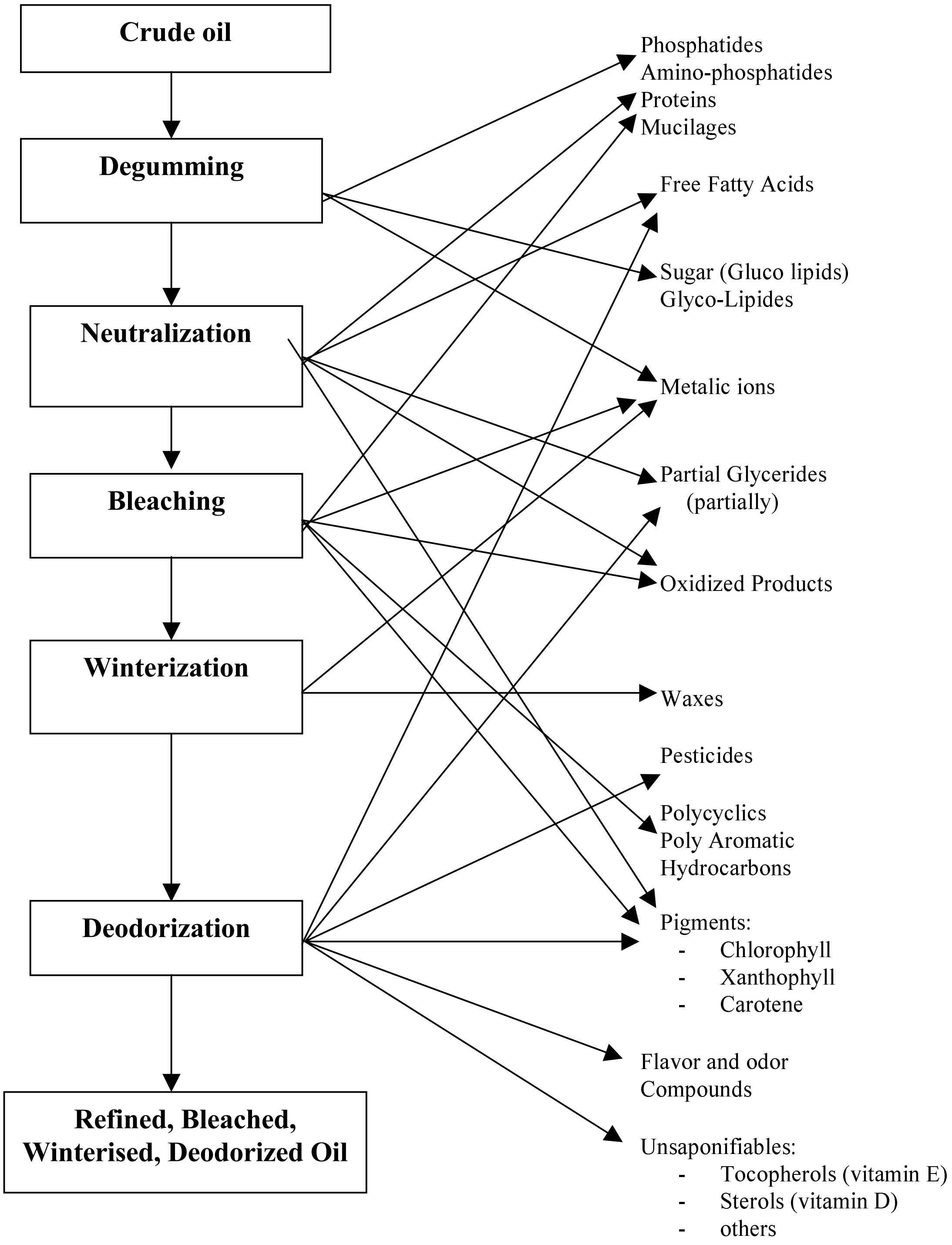

Figure 1: Stages in classical refining[2,3]

Most of other components are objectionable as they darken the oil, cause the foaming, smoking or precipitate from the oil. The objective of refining is to remove the objectionable co-constituents in the oil with the least possible damage to the glycerides and minimal loss of desirable constituents.

Figure 1 shows the different stages in a classical chemical refining line. Generally, before oil is suitable for human consumption, it must be degummmed, neutralised, bleached, deodorised and sometimes winterized. Neutralisation can also be done by distillative removal of the free fatty acids in the deodorizer. The latter sequence is better known as physical refining.

Degumming

Degumming is the first step in refining. The process is designed to remove the phosphatides and certain ill-defined slimes or mucilaginous materials from the oil. Phosphatides have the same basic structure as triglycerides with this difference that only two fatty acids are bound on a glycerol group with a phosphorus-containing group on the third position.

Degumming most generally consists in hydrating the phospholipids and mucilagenous gums in order to reduce their solubility in the oil and hence to facilitate their removal with water.

The non-chelated phospholipids (HP) are easily hydratable and therefore easy to remove by mixing with hot water in crude oil phase, followed by centrifugation. The complexated phospholipids (NHP), on the other hand, are more difficult to hydrate and undergo first an acid treatment in order to remove the cations (Ca^{++}, Mg^{++} of Fe^{++}) which are principally responsible for the non-hydratability of these phosphatides. Usually, this is done by treating the oil with phosphoric acid or with citric acid.[4]

Neutralization

In chemical refining, the complexated phospholipids (NHP) which remain behind in the oil after acid treatment, are further removed in neutralising. At this stage caustic soda converts the NHP into sodium salts which are easier to remove as they are less soluble in oil and more hydratable. A high soap content in combination with intense water washing improves the removal of the phosphatides. Values of less than 10 ppm of phosphorus, even for low quality oils, can be obtained.

Unlike most degumming processes, chemical refining is much less sensitive: a small excess of caustic soda usually produces a perfectly neutralised oil under much less severe operating conditions.

In chemical refining, the free fatty acids are transformed into soaps, usually by adding sufficient amounts of caustic soda. These soaps are no longer soluble in the oil and can therefore be removed easily by decantation or centrifugal force.

$$\textbf{Free fatty acids} + \mathbf{NaOH} \leftrightarrow \textbf{Na-soaps} + \mathbf{H_2O}$$

As it is necessary to use an excess of caustic soda to push the reaction to the right, there is a risk of an excessive saponification because certain amount of caustic soda reacts with triglycerides and causes an oil loss.

The chemical refining step also reduces the amount of metal traces as well as certain phenolic constituents (such as gossypol in cottonseed oil). Some pigments are also removed, more specifically those of oxidative origin.

It is obvious that the soaps formed during the reaction must be removed before the next refining sequence. This operation is carried out in a centrifuge, followed by one or two water washing stages.[3]

Bleaching

Bleaching is basically an adsorption process carried out before winterisation or deodorisation. The purpose of bleaching is to remove colouring pigments (carotene, chlorophyll) and minor impurities like residual phosphatides, soaps, metals and oxidation products. Although colour reduction is the most obvious effect of bleaching, the removal of these minor impurities is far more important as they have a direct effect on the organoleptic quality and oxidative stability of the deodorised product.

The removal of minor components through adsorptive bleaching is based on several adsorption mechanisms.

Most of the colouring pigments are physically adsorbed on bleaching clays, through the exercise of van der Waals' surface attraction forces. Other components are chemically bound to the bleaching clay surface via covalent or ionic bonds. Part of the impurities are removed, their molecules being trapped into the porous structure of the clays. During bleaching, some minor components are chemically altered due to the catalytic activity of the clays. A typical example is the decomposition of hydroperoxides.

Natural bleaching clays are aluminium silicates (Bentonite, Attapulgite, Montmorillonite), containing relatively high amounts of Mg, Ca or Fe. The clays are generally activated by heat treatment.

In some cases, active carbon is added in the course of bleaching to improve the removal of blue and green pigments as well as polycyclic aromatic hydrocarbons.[4]

Winterization-Dewaxing

Winterization and dewaxing are both processes, based on a thermo-mechanical separation of solidified material from the bulk liquid oil, but they have a different purpose.

The dewaxing process is used to remove the bulk wax content of an oil to a level of around 100-150 ppm. Due to the relatively high residual wax content, dewaxed oils reveal a rather poor cold stability, at the best a few hours at 0°C, which is not good enough in most cases.

Winterization serves for another purpose. It is used to remove small quantities of solids which would normally cause cloudiness of the oil when kept at refrigeration temperature. These substances are usually waxes, saturated glycerides, or even polymerised oil formed during refining. Due to the relatively small amount of solids present (usually less than 0.1%), most winterization processes are continuous. Winterization usually takes place after bleaching or after deodorisation. A properly winterized oil should have a cold stability of at least 48 hours at 0°C.[4]

During the winterisation, oil is cooled slowly in gently agitated holding tanks, following a certain temperature profile, in order to allow the high melting components to crystallise. Filter aid is added to the oil prior to crystallisation or just before filtration to improve filtration. After maturation, the oil is sent to a filter. Horizontal pressure leaf filters are commonly used. The oil temperature is often raised just before filtration to reduce viscosity and hence facilitate filtration.

Sunflower, corn or grapeseed oil winterization removes primarily waxes. In the case of cottonseed oil or slightly hydrogenated soybean oil, the solids predominantly consist of high melting triglycerides, which have a marketable value.

Deodorisation

Deodorisation is usually the last step in oil refining. Deodorisation is a steam distillation process in which the volatile odoriferous components are stripped out. The concentration of these undesirable substances, found in most oils, is generally low, between 0.2 and 0.5%. They include aldehydes, ketones, peroxides and residual free fatty acids. Processes prior to deodorisation, like neutralisation and bleaching may leave some odour in the oil, as one of earth after bleaching.

a. Principle of deodorisation

Deodorising consists in injecting dry steam into the oil, which is maintained under vacuum and at a high temperature. It is thus a process involving steam entrainment of the sapid and odoriferous substances that are more volatile than oil.

The purpose of deodorisation is a) to remove undesirable odours and flavours, in order to produce bland and odourless oils, b) to reduce the free fatty acid content to a minimum, c) to destroy the peroxides, in order to improve oil stability and d) to improve the colour by breaking down certain carotenoid pigments by a heat bleaching effect.

The efficient removal of undesirable substances depends on a) the vapour pressure of the different minor components, b) the deodorising conditions (temperature, pressure, residence time), c) the amount of stripping steam and d) the geometry of the vessel (e.g. sparge steam distribution, oil depth,...).[2]

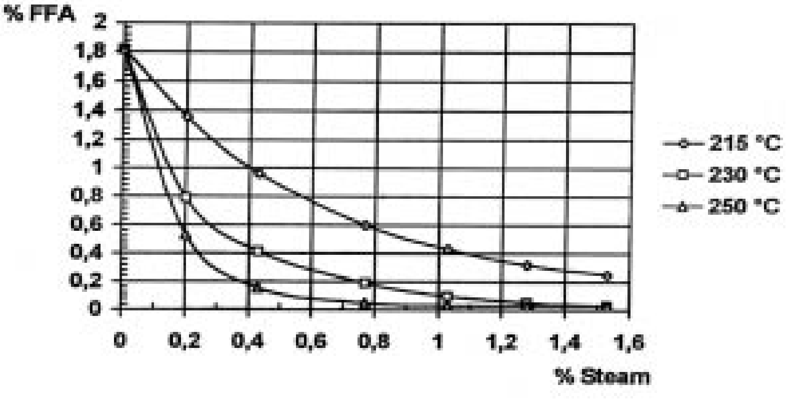

Figure 2: Example of a fatty acid distillation diagram. % Steam = (kg steam / kg oil) x 100 (deodorizer pressure 3 mbar, sparge steam 1%.)

One of the key factors in successful deodorising is to provide thin-film mass transfer of the volatiles to the vapour state.[4] The different deodoriser designs attempt to provide the best contact between the gas phase and the oil phase, by creating large contact surfaces and/or thin oil films, together with an optimal sparge steam distribution (Figure 2).

b. Determination of refined oil quality

In the determination of the quality of a refined oil, more and more emphasis is put on the real nutritional properties. Whereas in the past the stress was on the organoleptic properties (taste, odour, colour, residual free fatty acid content, oxidation degree), trans-isomerisation and tocopherol losses have now become predominant issues.

Trans-isomerisation

High poly-unsaturated oils are particularly sensitive to trans-isomerisation during deodorisation. The isomerisation rate is the highest for linolenic acid and the lowest for oleic acid:

relative isomerisation rate				
100		10		1
C18:3	>>	C18:2	>>	C18:1

The factors favoring trans-isomer production are deodorisation temperature and time. Generally, trans formation is negligible below 220°C, significant between 220 and 240°C, and nearly exponential above 240°C.

Tocopherol losses

The main components of non-saponifiables in vegetable oils are tocopherols and sterols, although the amounts vary in different oils. Tocopherols are natural anti-oxidants, present in different homologues, alpha-, beta-, gamma- and delta-tocopherol. The alpha-isomer is the most active biologically while the gamma-tocopherol is perceived as the best antioxidant.

During deodorisation, part of the tocopherols are lost as a result of distillative removal, or as a consequence of thermal degradation. The major factors affecting distillative losses are deodorising temperature, pressure and stripping steam (Figure 3).[5]

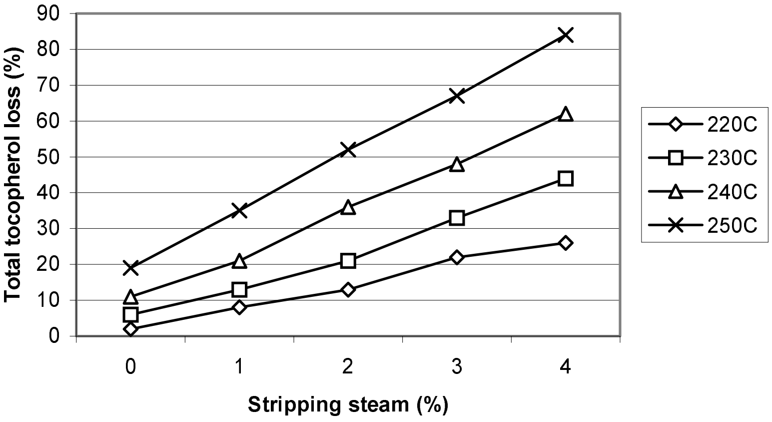

Figure 3: Effect of temperature and stripping steam on total tocopherol losses of a given corn oil with alfa – tocopherol 15%, beta/gamma – tocopherol 80% and delta – tocopherol 5%; working pressure 3 mbar absolute

c. Deodoriser distillates

Over the past few years, the deodoriser distillates from chemical refining have become an attractive feedstock for tocopherol production (vitamin E) thanks to their high sterol content (Table 1). Today, these distillates fetch a better price than conventional acid oils. The distillates from a physical refining line, on the other hand, have a much lower unsaponifiable content, which makes them less attractive.

Table 1: Typical composition of a deodoriser distillate from a physical and chemical refining plant

Composition	**Chemical refining**	**Physical refining**
Neutral oil	25 – 33 %	5 – 10 %
Fatty acids	33 – 50 %	80 – 85 %
Unsaponifiable matter	25 – 33 %	5 – 10 %

Note: unsaponifiable matter includes sterols and tocopherols

Solid and Hazardous wastes

Generation and handling of solid and hazardous waste in oil-refining industry is less problematic than waste water. However there are a number of significant sources.

Soapstock: One of the major drawbacks of chemical neutralisation is the production of a soft neutralisation mixture called “soapstock”.

In some countries, it is still possible to mix the soapstock with other ingredients for the production of soaps or animal feed.

In the other case, the soapstock is treated with sulphuric acid to transform the soaps back into free fatty acids. In this way, two phases are obtained: an acid oil with a certain commercial value and an aqueous phase which definitely requires a further treatment prior to disposal.

Spent bleaching earth: Spent bleaching clay from oil refining contains a substantial amount of adsorbed oil (20 – 40 % w/w). This product is both a problem and a potential source of recoverable oil. The problems of spent clay are well known. Fat-containing clays are prone to spontaneous combustion when in contact with air, particularly if the bleaching earth contains highly unsaturated oils. Spent clay also represents an environmental concern, both as a fire hazard and as a threat to ground waters through fat-containing runoff when discarded in landfills.

Spent filter aid: The filter cakes from winterising plants are less polluting than those from bleaching plants. The waxy cakes, which contain up to 60 % of oil, are discharged either to a landfill or are sometimes transferred to the meal stream to provide an extra source of fat for animal feed.[6]

Conclusions

In the past, scientists focused especially on a reduction of the saturated fats level in food products, as these were considered bad for health. This resulted in a sharp decrease in animal fat consumption. Today, however, more and more attention is paid to the trans-fatty acid content, natural vitamin content and sterol content in oils and fats. The polymeric triglycerides and secondary oxidation products, generated during the successive refining and modification stages, as well as the by-products like deodorization distillate, are gaining increasing interest.

The purpose of this technical paper is to give an overview of the various refining processes with special emphasis on present oil quality requirements.

References and Notes

1. Hui, Y.H. Oils and Oil Seeds, in *Baileys Industrial Oils and Fats Products; Edible Oil and Fat Products*, Vol.2, John Wiley and Sons, Inc., 1996.
2. Kellens, M. *Current Developments in Oil Refining Technology*, Lipidex 1997, Antwerp, Belgium, 1997.
3. Hui, Y.H. By – Products Utilization, in *Baileys Industrial Oils and Fats Products, Edible Oil and Fat Products,* Vol.4, John Wiley and Sons, Inc., 1996.
4. Gunstone, F.D. *The Lipid Handbook,* Chapman and Hall, 1996.
5. Kellens, M.; De Greyt, W. *New Concepts in Edible Oil Refining: Application of Dual Temperature Deodorization for the Production of High Quality Oils*, Porim International Palm Oil Congress, Kuala Lumpur, Malaysia, 1999.
6. Hui, Y.H. Processing Technology, *Baileys Industrial Oils and Fats Products; Edible Oil and Fat Products*, Vol.4, John Wiley and Sons, Inc., 1996.

Povzetek

Maščobe so najpomembnejši vir energije v prehrambenih proizvodih. V različnih prehrambenih izdelkih prisotne masti in olja zavzemajo več kot eno tretjino, v Sloveniji celo več kot 42%, povprečne energetske vrednosti dnevnih obrokov. Poleg visoke energetske vrednosti maščobe dobavljajo tudi mnoge življensko pomembne sestavine, kot so: vitamini, esencialne maščobne kisline in druge spremljajoče komponente, povečujejo energijsko gostoto hrane, in ne nazadnje je splošno znano, da je hrana, ki vsebuje manj kot 20% maščob, neokusna.

Večino rastlinskih olj je potrebno pred uporabo v prehrambene namene očistiti. Tržišče zahteva na policah olja, ki so svetla, nevtralnega okusa z visoko termično stabilnostjo in bistrino olja tudi pri nižjih temperaturah. Navedene zahteve je moč doseči z obdelavo in vodenjem olja preko več stopenj rafinacijskih procesov, da bi se prilagodile fizikalno kemijske in organoleptične lasnosti olja zahtevanim standardom.