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New approaches in deacidification of edible oils—a review

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Abstract

In the fats and oils industry, deacidification of oils is important not only for consumer acceptance, but also because it has the maximum economic impact on production. Chemical, physical, and miscella deacidification methods have been used in the industry. There are several drawbacks associated with these conventional deacidification processes. Some new approaches that may be tried out—as alternatives to current industrial practices—are biological deacidification, reesterification, solvent extraction, supercritical fluid extraction and membrane technology. These new approaches—independently, or in combination with current technology—may be useful to overcome major drawbacks. Besides being eco-friendly, they could also lead to savings in energy and reduction in oil losses. Some of these approaches could very well replace the existing technology in the years to come.

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Keywords: Biorefining; Chemical, physical and miscella deacidification; Chemical reesterification; Membrane technology; Solvent extraction; Supercritical fluid extraction

1. Introduction

Food is mainly composed of water, carbohydrates, proteins, and fat. Fat is regarded as an important component of the diet, because it is an important source of energy, as well as of essential fatty acids, and of fat-soluble vitamins such as vitamins A, D, E and K (Hay et al., 1980). Commercial sources of edible oils and fats include oilseeds, fruit pulp, animals and fish. Oilseeds are the major source for the production of edible oils. The total world production of major oilseeds in 2002 was 326.3 million metric tons (www.soystats.com). [1]

The method chosen for oil extraction depends on the nature of the raw material, as well as on the capacity of the industrial plant. Pressing followed by solvent extraction is the method most widely employed for handling a wide variety of oilseeds (Young et al., 1994), which contribute nearly 50% of the total vegetable oil produced in the world. The crude oil that is extracted from the oilseeds is a mixture of FFA, mono-, di-, and triglycerides, phosphatides, pigments, sterols and tocopherols. Trace amounts of metals, flavonoids, tannins, and glycolipids may also be present (Cheryan, 1998). Refining usually refers to the removal of nontriglyceride fatty materials. But, in the United States, the term 'refining' is applied to the operations of pretreatment and deacidification or neutralization. In most other countries it means the complete series of treatments, including also bleaching and deodorization, to make the fat suitable for edible use (Anderson, 1953). Industrially the two most commonly used methods for refining are chemical and physical refining. A typical scheme of oil processing is presented in Fig. 1. The different impurities removed (or partially removed) at different stages of chemical and physical refining are listed elsewhere (Young et al., 1994).

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[1] www.soystats.com/2003/Default-frames.htm.

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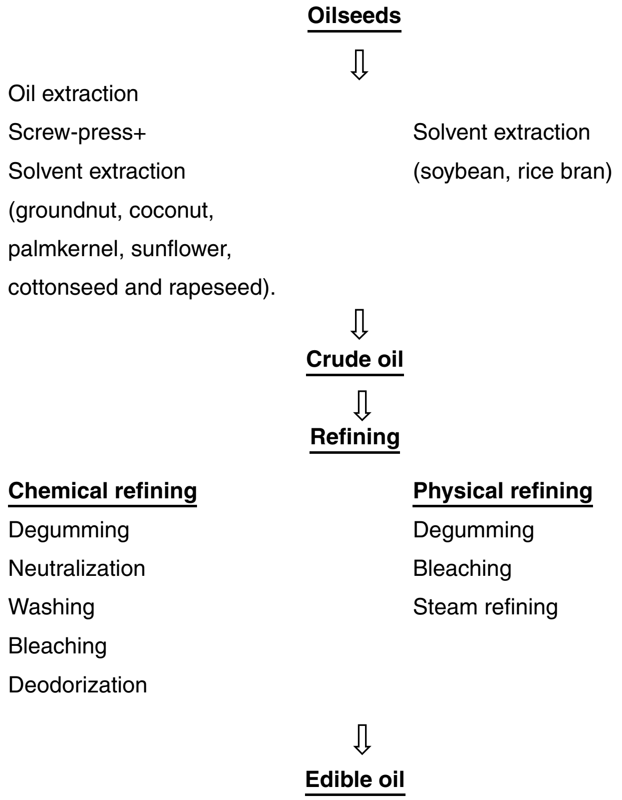

Fig. 1. Scheme of conventional oil processing.

1.1. Deacidification

Crude fats and oils consist of some quantity of FFA, along with triglycerides. FFA are virtually absent in fats/oils of living tissue. They can be formed, however, by enzyme (lipase) action, after the oilseed has been harvested, or the animal has been slaughtered. Hydrolysis of ester bonds in lipids (lipolysis) resulting in the liberation of FFA, may be caused by enzyme action or by heat and moisture (Nawar, 1996). The release of short-chain fatty acids by hydrolysis is responsible for the development of an undesirable rancid flavor (hydrolytic rancidity). Furthermore, FFA are more susceptible to oxidation than the glycerol esters of these fatty acids; and this lipid oxidation, leads to oxidative rancidity in edible oils and fat-containing foods. Therefore, any increase in the acidity of the oil must be absolutely avoided.

The deacidification process has the maximum economic impact on oil production. Any inefficiency in this process has a great bearing on the subsequent process operations. The removal of FFA from crude oil represents the most delicate and difficult stage in the refining cycle, since it determines the quality of the final product. Chemical, physical, and miscella deacidification methods have been used industrially for deacidification. These conventional methods are well documented; nevertheless, they are briefly discussed in this review, and their relative features and limitations are summarized in Table 1.

2. Conventional methods of deacidification

2.1. Chemical deacidification

Industrially the most commonly used method for deacidification is chemical deacidification. The purpose of deacidification in the conventional chemical process

Table 1
Industrial methods of deacidification

S. no.	Features	Limitations
1	*Chemical deacidification*	
	Versatile—produces acceptable quality oil from all types of crude oil	Excessive loss of neutral oil with high-FFA crude oil (occlusion) Soapstock—low commercial value
	Multiple effects—purifying, degumming, neutralizing and partially decolourizing the oils	Neutral oil loss due to hydrolysis
2	*Physical deacidification*	
	Suitable for high-FFA oil	Pretreatments are very stringent
	Low capital and operating costs—less steam and power consumption	Not suitable for heat sensitive oil—e.g., cottonseed oil Chances of thermal polymerization
	Greater oil yield	Controlled rate of removal of FFA
	Elimination of soapstock as well as reduced effluent quantity	
	Improved quality FFA	
3	*Miscella deacidification*	
	Lower strength of caustic solution	Higher investment—totally enclosed and explosion-proof equipment
	Increased efficiency of separation	Solvent loss—requires careful operation and greater maintenance
	Minimum oil occlusion in soapstock	More suitable for integrated extraction and refining plant
	Superior colour of final product	Cost intensive—homogenization necessary for effective neutralization and decolourization
	Water washing eliminated	
		For efficient operation oil conc. in miscella should be ~50% (two-stage solvent removal)

is to remove nontriglyceride impurities, consisting principally of FFA, along with substantial quantities of mucilaginous substances, phospholipids and colour pigments (Young et al., 1994). Deacidification is accomplished by the addition of an alkali to degummed oil, thereby precipitating the FFA as soap stock; the latter is then removed by mechanical separation from the neutral oil. Since the alkali most often used for neutralization is caustic soda (sodium hydroxide), the process is widely known as caustic deacidification.

In chemical deacidification, there is considerable oil loss due to the hydrolysis of neutral oil by caustic. Besides, loss of oil also occurs in the form of occlusion in soapstock. The soapstock can hold as much as 50% of its weight of neutral oil, thereby reducing the overall yield of refined product. FFA content in the crude oil has a direct bearing on the neutral oil loss and therefore the yield—in the case of a high-FFA crude oil such as rice bran oil (RBO)—is relatively low (Gingras, 2000). The FFA in their native state find many uses and therefore the soapstock is usually split with concentrated sulfuric acid, which result in heavily polluting streams. The disposal of this waste stream has become very expensive since the waste stream is to be treated to meet the statutory requirements. Another major disadvantage in the case of deacidification of RBO is the loss of valuable oryzanol (1–3%) which gets easily saponified, and is removed along with soapstock (Gingras, 2000). Alkali refining results, typically, in a decrease in total oryzanol content from 16000 to 2000 mg/kg (Orthoefer, 1996).

In spite of having several disadvantages, chemical deacidification is still commercially followed in many industries because of successful reduction of FFA up to the desired level irrespective of FFA content in raw/crude oil. Chemical neutralization reduces the FFA to an acceptable level—down to 0.03%—depending on the characteristics of the vegetable oil (Hodgson, 1996). Soaps formed during deacidification have the combined effects of purifying, degumming and partially decolouring the oils.

2.2. Physical deacidification

Physical deacidification has aroused renewed interest since the early 1970s when the process was reintroduced on a large scale to refine palm oil in Malaysia (Tandy & McPherson, 1984). Physical deacidification uses steam stripping under vacuum, a procedure that removes FFA, unsaponifiable substances, and pungent compounds, thus circumventing chemical neutralization with its environmentally objectionable soapstocks. As a consequence, oil losses are reduced, the quality of FFA is improved, and the operation is simplified. It consumes less steam, water and power, and, hence, requires less capital investment (Cvengros, 1995). Deodorization and thermal bleaching of carotenoids are also accomplished by steam stripping. Molecular distillation, if adopted instead of the conventional distillation method, would help to preserve valuable natural substances, mainly the tocopherols and phytosterols (Cvengros, 1995).

Due to the improvements in vacuum systems, as well as the competitive price of incondensable gases, nitrogen has been proposed as an alternative to live steam. The use of nitrogen instead of steam provides a higher FFA vapourization efficiency, a lower loss of the unsaponifiable fraction, a minimal entrainment of triglycerides, and a lower total amount of deodorizer distillates (Ruiz-Mendez, Marquez-Ruiz, & Dobarganes, 1996).

Physical deacidification offers many advantages over alkali neutralization such as improved product yield, elimination of soapstock as well as reduced effluent quantity. However, it has also many drawbacks; e.g., the pretreatment requirements are very stringent, and not suitable for all types of oils e.g., heat sensitive cottonseed oil (Hartman, 1978). According to Cleenerwerck and Dijkstra (1992), the phosphorus content of the oil can be $\leqslant 10$ ppm, but its iron content must be lower than 0.2 ppm because iron may cause the darkening of the oil during distillation, and reduce its oxidative stability. Further, physical refining requires high temperature and high vacuum, and often forms side reaction products, such as polymers and *trans* isomers (Sengupta & Bhattacharyya, 1992). It has been reported that physical deacidification reduces the tocopherol content and destroys all carotenes present in palm oil (Ooi et al., 1996).

Cmolik et al. (2000) compared the quality of oils produced by physical and alkali refining of crude rapeseed oil on a pilot-scale. No substantial differences in sensory acceptability and oxidative stability were observed between the refined oils, after storage over a period of 12 months at 15 °C; so they concluded that physical as well as alkali refining of crude rapeseed oil would yield oils of equivalent quality. Physical deacidification of crude vegetable oils has several advantages over traditional alkali deacidification—viz., simplicity, energy conservation, and reduced generation of environmental pollutants.

2.3. Miscella deacidification

The refining of crude oil in the solvent extraction plant, prior to solvent stripping, is termed miscella refining. In the process, miscella (typically 40–60% oil in hexane) is mixed with sodium hydroxide solution for neutralization, reaction with phosphatides, and decolourization (Hodgson, 1996). The soap stock produced is removed by centrifugation. Miscella refining has been applied to a variety of oils, including cottonseed, soybean, sunflower, palm, coconut and tallow; but commercially it is used almost exclusively for the refining of cottonseed oil (Hodgson, 1996). Most of the cottonseed oil mills in the US have converted to expander solvent extraction and miscella deacidification, which permits mills to produce a consistently light-coloured cottonseed oil at a reduced cost, and with a low refining loss (Wan, Pakarinen, & Horn, 1996).

The advantages of miscella refining over continuous chemical deacidification are: (i) dilute caustic soda solution (10–14°Be) can be used satisfactorily; (ii) the wide specific gravity differential between the lye and oil-hexane solution increases the efficiency of the centrifugal separation, and it is possible to operate the separators at 50% above their rated capacity in terms of refined oil produced; (iii) the quantity of soapstock produced is extremely low in the neutral oil—that is to say, the refining losses is at a minimum as compared to continuous alkali refining; (iv) the bleach colour of the final oil is superior to that obtained by nonmiscella refining and can be varied by increasing the percentage of refining caustic without serious losses in saponification; and finally, (v) elimination of water washing (Anderson, 1996; Hodgson, 1996).

In spite of its several advantages, miscella refining is not widely used in industry because of several disadvantages (Anderson, 1996; Hodgson, 1996). All equipment must be totally enclosed and explosion-proof, which increases investment considerably. Refining must be carried out at the solvent mills to be effective and economical. There are difficulties in obtaining efficient contact between the caustic soda solution and the miscella—full coagulation of phosphatides and satisfactory decolourization do not occur in the course of ordinary mixing. The remedies include use of homogenizer and the addition of small amounts of nonionic surfactant to the lye. Neutralization and decolourization appears to be most effective when the concentration of miscella is ~50% that of oil. Thus, removal of solvent from miscella must take place in two stages, a preliminary concentration to ~50% oil, followed by refining and washing and a final removal of solvent (Anderson, 1996; Hodgson, 1996). This preliminary concentration to desired level is done either by evaporating part of the solvent from a direct extraction operation, or combining prepressed or purchased crude oil with miscella from the extractor (Cavanagh, 1976).

3. New approaches for deacidification of vegetable oils

During the chemical deacidification process, there are always considerable losses of neutral oils, sterols, tocopherols and vitamins; furthermore, disposal and utilization of resulting soapstock may create problems of environmental pollution. On the other hand, practical experience with physical deacidification has shown that it leads to acceptable results only when good quality starting oils are used. Besides, incomplete removal of undesirable components during the pretreatment of oil has to be compensated for by an increased use of bleaching earth. The two-stage solvent removal system and the associated higher cost of installing a totally enclosed and explosion-proof equipment, for adequate safety, limit the application of miscella deacidification.

These conventional deacidification methods are not best suited for oils that contain more than 8–10% FFA (Anderson, 1962). For instance, RBO of high-FFA content could have neutral oil losses of up to 50% or more, during chemical deacidification (Gingras, 2000). Oils from corn and rice bran have high acidity due to enzymatic activity in the raw material, and need special care during refining by any process. According to Leibovitz & Ruckenstein (1983), chemical deacidification of crude corn oil with FFA content between 8.4% and 14% resulted in neutral oil loss of 15–25%, while for physical refining the loss of neutral oil varied between 11% and 20%. The basic unit operations in vegetable oil processing have remained relatively unchanged for the past 5–6 decades. There are several drawbacks to today's technology, and so alternative approaches are needed to overcome these drawbacks. Some of the approaches attempted by various researchers namely biological deacidification, solvent extraction, reesterification, supercritical fluid extraction, and membrane processing are discussed in the following sections. The features and drawbacks of these new approaches proposed for deacidification of oils and fats are presented in Table 2.

3.1. Biological deacidification

Biological deacidification/biorefining has been under study for many years and has been gaining importance over the years. Biological refining involves the use of (i) a whole-cell microorganism system, which can selectively remove and/or assimilate FFA for its own growth; and (ii) lipase systems that can esterify FFA into triglycerides.

3.1.1. Selective removal of FFA from vegetable oils by using microorganisms

Cho, Kwon, & Yoon (1990) screened a microorganism from soil that could assimilate long-chain fatty acids without secreting extracellular lipases, and identified it as a *Pseudomonas* strain (BG1). It was found to utilize lauric, myristic, palmitic, stearic, and oleic acids as carbon sources (Table 3). BG1 was shown to utilize 0.1% oleic acid in an emulsion medium almost completely within 48 h. When BG1 was grown in a mixture of triolein and oleic acid, it selectively removed the FFA without loss of triolein, and did not produce mono- and diglycerides. The limitations of this method are, that the short-chain fatty acids, having less than 12 carbon atoms, as also linoleic acid, were not utilized (Table 3);

Table 2
Alternate approaches for deacidification

S. no.	Features	Limitations
1	*Biological deacidification*	
A	Employing whole-cell microorganism that selectively assimilate FFA e.g., *Pseudomonas* strain BG1	Linoleic acid and short-chain FA (C no. <12) not utilized; besides, they inhibit microbe growth FA utilization depends on its water solubility
B	Enzyme reesterification—Lipase reesterification Increased oil yield Low-energy consumption Mild operating conditions	High cost of enzyme
2	*Reesterification (chemical modification)*	
	With or without the aid of catalyst	Random reesterification
	Suitable for high-FFA oil	Thermal polymerization
	Increased oil yield	Costly process
3	*Solvent deacidification*	
	Extraction at ambient temperature and atmospheric pressure	Higher capital cost
	Easy separation—large difference between boiling points of solvent and fatty compounds	Energy intensive operation Incomplete deacidification (TG solubility increases with FFA in feed)
4	*Supercritical fluid extraction (SCFE)*	
	High selectivity Low temp. and pollution free operation Suitable for a wide range of FFA oils Minimum oil losses	Costly process
5	*Membrane deacidification*	
	Low-energy consumption Ambient temperature operation	Molecular weight difference between TG and FFA is small for separation
	No addition of chemicals	Non-availability of suitable membrane with high selectivity
	Retention of nutrients and other desirable components	Low permeate flux

Table 3
Utilizability and biomass production by *Pseudomonas* strain BG1 depending on FFA (Cho et al., 1990)

FFA	Utilizability	Biomass (g DCW/L)
Butyric acid	N.U	0.1
Valeric acid	N.U	0.1
Caproic acid	N.U	0.1
Caprylic acid	N.U	0.1
Capric acid	N.U	0.1
Lauric acid	U	0.8
Myristic acid	U	0.6
Palmitic acid	U	0.7
Oleic acid	U	1.8
Linoleic acid	N.U	0.1
Stearic acid	U	0.6

N.U—not utilized; U—utilized; DCW, dry cell weight.

furthermore, they sometimes inhibited the growth of BG1. Long-chain saturated fatty acids with 12 or more carbon atoms, as also oleic acid were utilized (Table 3). The rate of removal of fatty acids was proportional to their solubility in water. Hence, maximum biomass was obtained from oleic acid fermentation as compared to lauric, myristic, palmitic and stearic acid fermentation. Though butyric, valeric, caproic, caprylic and capric acids all have higher solubility in water than oleic acid, they were not utilized—probably due to the toxicity of short-chain fatty acids to microorganisms.

3.1.2. Enzymatic deacidification/reesterification

In this biorefining method, the unique ability of some microbial lipases to synthesize a triglyceride from a fatty acid and glycerol has been exploited to develop an alternative process for deacidifying vegetable oils with high-FFA contents. In view of the need for low-energy processes, microbial lipase-catalyzed esterification appears to be more advantageous for deacidification than chemical esterification, which is invariably carried out at higher temperatures (180–200 °C) than the lipase-catalyzed reactions. The microbial lipase process is also promising in terms of final quality of refined oils and refining loss (Sengupta & Bhattacharyya, 1992). The potential of an enzymatic deacidification process for refining depends on several enzymatic esterification reaction variables, such as enzyme concentration, reaction temperature, reaction time, glycerol concentration, amount of moisture in the reaction mixture, pressure employed etc. (Bhattacharyya & Bhattacharyya, 1989). Enzymatic deacidification of different vegetable oils has already been achieved on a laboratory scale.

Bhattacharyya and Bhattacharyya (1989) successfully brought down the FFA content of RBO from 30 to 3.6% by esterification of the FFA with added glycerol, using a 1,3-specific lipase (*Mucor miehei*). This process produced a RBO of excellent quality by subsequent alkali deacidification, bleaching, and deodourization. The combined biorefining and alkali refining process compared well in terms of refining factor and colour with the miscella refining process; and, with regard to refining characteristics, it was even superior to the combined physical refining and alkali neutralization process. Sengupta and Bhattacharyya (1992) showed that the FFA of mohua oil (*Madhuca latifolia*) could be reduced from 24.5% to a level of 3.8%, when the degummed and bleached oil was treated continuously with 10% lipase (*M. miehei*) and the stoichiometric amount of glycerol for 20 h at a temperature of 60 °C and a pressure of 267 Pa. Makasci, Arisoy, and Telefoncu (1996) examined the potential of enzymic deacidification for degummed and dewaxed hyperacidic olive oil. The lipase used was produced by a host *Aspergillus oryzae* from a selected strain of *Candida* and immobilized on a macroporous acrylic resin. They showed that maintaining low pressure (or bubbling dry nitrogen) was important for the removal of water formed during esterification.

Sengupta and Bhattacharyya (1996a) carried out another study to find out to what extent the enzymatic deacidification was applicable to a RBO of lower FFA content. RBO having 5–17% FFA were deacidified by a lipase (*M. miehei*) esterification with glycerol. Biorefining, in combination with alkali refining or physical refining, resulted in lower oil loss and higher TG content than the alkali refining process alone. The characteristics of the refined RBO obtained by combination of biorefining process with either the conventional alkali refining process or with the physical refining process are presented in Table 4.

Sengupta & Bhattacharyya (1996b) proposed yet another method of enzymatic esterification of FFA in RBO (8.6–16.9%) with commercial monoglyceride (MG) and lipase (*M. miehei*). They reported that FFA could be brought down to 2–4%, depending on the amount of MG used. According to these researchers, MG could be used effectively instead of glycerol to reduce FFA in the oils, producing oils of better quality with respect to triglyceride (TG) content. Kurashige (1988) used diglycerides (DG) for the esterification of crude palm olein, using a lipase from *Pseudomonas fluorescens*. It was shown that the extent of esterification was high if DG were used in place of glycerol; this success was attributed to the better solubility of DG in the oil.

The main advantage of the esterification process for deacidifying vegetable oils with high-FFA contents is the increase in the content of neutral glycerides, especially TG. However, the chief barrier to enzymatic deacidification is the high cost of enzymes.

3.2. Chemical reesterification

One of the methods of deacidification of vegetable oil is converting its FFA into neutral glycerides by reesterification with the free hydroxyl groups remaining in the oil (or with added hydroxyl groups from glycerol) at a high temperature, and in an inert atmosphere, with or without a catalyst system (Anderson, 1962). Reesterification is expected to increase the yield of neutral oil. The reesterified oil will have some FFA and can be further deacidified by chemical deacidification. Reesterification could also be carried out by enzymatic esterification (discussed in the earlier section). An economical, integrated deacidification procedure would be very valuable.

The reesterification of FFA by using high temperatures has a long history. Anand and Vasishtha (1978) have chronologically reviewed these developments in a research article. Berthelot (1853, 1854) employed temperatures in the range of 200–270 °C for the reesterification of the fatty acids (in excess) with glycerol in a sealed tube; but the water formed could not escape, resulting in the establishment of an equilibrium between the reactants under the experimental conditions. Scheij (1879) succeeded in eliminating water from the reaction mixture by using an inert gas or air. Bellucci and Manzetti (1911) removed water by maintaining vacuum. Garner (1928) reesterified fatty acids at 200 °C in the presence

Table 4
Comparison of refining characteristics of RBO by enzymatic deacidification and by other refining processes[a] (Sengupta and Bhattacharyya, 1996a)

Type of oil	FFA (%)	Refining factor	Overall process loss (%)	Wax (%)	UM (%)	DG (%)	TG (%)	Lovibond colour (1 cm cell)
Crude oil	10.2	–[b]	–	3.8	4.4	–	–	8.6Y + 3.8R + 0.6B
Degummed, dewaxed and bleached oil	8.6	–	–	0.5	2.2	7.2	79.7	5.7Y + 1.1R
Biorefined oil	3.0	–	–	0.38	2.2	5.0	89.7	3.3Y + 0.3R
Biorefined, alkali-refined, bleached and deodorized oil	0.2	1.2	9.6	0.3	2.0	0.73	96.8	6.0Y + 1.1R
Biorefined, bleached and physical refined oil	0.3	1.1	10.2	0.4	3.0	2.0	93.8	8.2Y + 1.2R
Alkali refined, bleached and deodorized oil	0.2	1.8	20.4	0.2	2.0	5.6	92.2	7.6Y + 1.4R
Physical refined oil	0.4	1.3	16.2	0.4	3.9	4.7	90.7	9.0Y + 1.8R

[a] UM: Unsaponifiable matter; DG: Diglyceride; TG: Triglyceride.

[b] Not determined.

of carbon dioxide to get homotriglycerides. Bhattacharyya & Hilditch (1930) could reesterify fatty acids with glycerol; the reaction was carried out at 135–145 °C and 133 Pa for 5–6 h, using 0.5% of naphthalein-beta-sulphonic acid as catalyst. Esterification under these conditions was presumed to be essentially complete, and no mono- or diglycerides were present in the final product. Feuge, Kraemer, and Bailey (1945) investigated various factors involved in the reesterification of the mixed fatty acids obtained by saponification of peanut oil under reduced pressure. Among the many catalysts tested, zinc and tin chlorides were found to be outstanding in catalytic activity. Stannous chloride, in an amount equal to 0.0008 mol per 100 g of fatty acids, was found to be the best suited. Moreover, the catalysts could be completely removed from the esterified oils by ordinary alkali refining.

Anand and Vasishtha (1978) studied the esterification process for deacidifying high-FFA RBO with equivalent proportions of glycerol, with and without catalyst, at various temperatures, and under reduced pressure. They were successful in reducing FFA from 64.7% to 3.4% at 190 °C and to 2.8% at 200 °C, in the case of the uncatalyzed reaction. When stannous chloride was used as the catalyst, FFA were reduced to 3.5% at 180 °C, 1.2% at 190 °C and 0.9% at 200 °C. Both the uncatalyzed and the catalyzed reactions occurred in stages, the initial stage having a faster rate of reaction. Millwalla and Shitole (1987) reported that FFA content of RBO could be reduced from about 40% to below 10% by reesterifying them with glycerol using zinc as a catalyst at 200 °C under an absolute pressure of 267–533 Pa for 4 h. Bhattacharyya and Bhattacharyya (1987) studied the effect of glycerol and catalysts (stannous chloride and *p*-toluene sulphonic acid) on the deacidification of crude RBO by reesterification in a nitrogen atmosphere (Table 5). The use of glycerol in 50% excess of the theoretical amount to neutralize the FFA increased the rate of esterification reaction. The use of catalysts seemed to influence the esterification rate only during the initial stages up to 2 h. They showed that, after degumming and dewaxing, RBO with 15–30% FFA could be deacidified to low levels (1.6–4.0%) by reesterification with glycerol under vacuum in the presence of *p*-toluene sulphonic acid. They also proposed that reesterification could be combined with conventional alkali neutralization and bleaching to produce an edible oil, with a light colour.

Table 5
Effect of catalyst and glycerol on the deacidification of crude RBO by reesterification in nitrogen atmosphere[a] (Bhattacharyya and Bhattacharyya, 1987)

Time (h)	Type of catalyst	Excess glycerol on theoretical (%)	FFA in oil (%)
2	Without catalyst	0	9.6
		20	7.6
		50	6.2
	Stannous chloride	20	6.9
		50	–[b]
	p-Toluene sulphonic acid	20	6.6
		50	5.5
4	Without catalyst	0	8.0
		20	6.4
		50	5.4
	Stannous chloride	50	5.4
	p-Toluene sulphonic acid	50	5.3
6	Without catalyst	0	7.6
		20	5.6
		50	4.0
	Stannous chloride	50	5.1
	p-Toluene sulphonic acid	50	5.0

[a] FFA in crude RBO, 15.3%; amount of catalyst (on oil), 0.2%; reesterification temperature, 200 °C.
[b] Not determined.

De and Bhattacharyya (1999) investigated an autocatalytic high temperature (210 °C), low-pressure (1.3 kPa), direct esterification process using MG, for the deacidification of RBO containing high-FFA (9.5–35.0%). The study showed that MG was effective in reducing the FFA level of degummed, dewaxed and bleached RBO to an acceptable level (0.5–3.5%) depending on the FFA content of the crude oil. This approach allows RBO to be alkali refined, bleached and deodorized or simply deodorized after esterification (MG treatment) to obtain a good quality oil. From the viewpoint of cost, the autocatalytic refining process for high-FFA RBO appears to be competitive with miscella refining, biorefining or alkali refining procedures. However, taking into consideration the cost of high-acidity crude RBO, commercial pure monoglycerides, the yield of refined oil obtained, the average utility expenditure, and the price of refined oils, the process appears to be a promising one, but it is not competitive with physical refining processes (De & Bhattacharyya, 1999).

Although reesterification is a technically feasible method for dealing with high-FFA oil, the process is costly and this approach has not found commercial acceptance in the case of RBO (Gingras, 2000) that was considered as a potential candidate by many of the above researchers.

3.3. Solvent extraction

The differential solubility of fatty acids and neutral glycerides in various organic solvents has formed the basis of several processes for deacidification of crude oils and fats. Solvent (or liquid–liquid) extraction could be carried out at room temperature and atmospheric pressure, thereby reducing the energy consumption for oil refining, without any loss of natural compounds. Because of the high difference between the boiling points of the solvent and fatty compounds, solvent stripping from refined oil and solvent recovery from extract stream could be easily carried out. In fact, both separations could be accomplished by evaporation or distillation at relatively low temperatures (<80 °C), which could be further reduced (55 °C) by using a moderate vacuum (Pina & Meirelles, 2000).

Thomopoulos (1971) examined deacidification of olive oil of high acidity dissolved in the vehicle solvent (hexane); they reported that 96% ethanol could remove a large portion of the FFA from the crude oil. It was necessary to complete the neutralization by the conventional method, but the overall yield was significantly better than that obtained using chemical deacidification alone. Sreenivasan and Viswanath (1973) studied deacidification of cottonseed oil using commonly available solvents like methyl, ethyl, *n*-propyl and *n*-butyl alcohols, as also acetonitrile for the selective extraction of FFA from the oil. They represented the equilibrium data in the form of distribution and selectivity diagrams (Figs. 2 and 3). *n*-Propyl alcohol showed the most favourable distribution between the solvent phase and oil phase, however the selectivity was poor. Although methyl alcohol was found to have slightly better selectivity than ethyl alcohol, ethyl alcohol was preferred as it showed a favourable distribution of fatty acids, and also for economic reasons, including availability in abundance. Ethyl alcohol also happens to be a good solvent for removing gossypol from the oil. Bhattacharyya & Bhattacharyya (1983) deacidified the degummed and dewaxed high-FFA RBO by two-stage alcohol extraction at ambient temperature; the resulting oil with low FFA was further subjected to alkali neutralization and bleaching, to obtain an oil suitable for producing vanaspati (hydrogenated fat).

There is considerable interest in using aqueous isopropyl alcohol (IPA) for the extraction of oil from oil-bearing materials due to its low toxicity. Shah and Venkatesan (1989) employed aqueous IPA for liquid–liquid extraction of FFA from a model mixture in the ratio of 1:1. The mixtures studied contained 0–50% fatty acids in groundnut oil; the concentrations of aqueous IPA solutions lay between 75% and 99%. Phase separation depended on (1) the fatty-acid content in the model mixture; and (2) the concentration of aqueous IPA. Selective fatty acid separation and phase separation could be achieved by use of aqueous (75% and 80%) IPA over the whole range of fatty-acid content in the model mixture.

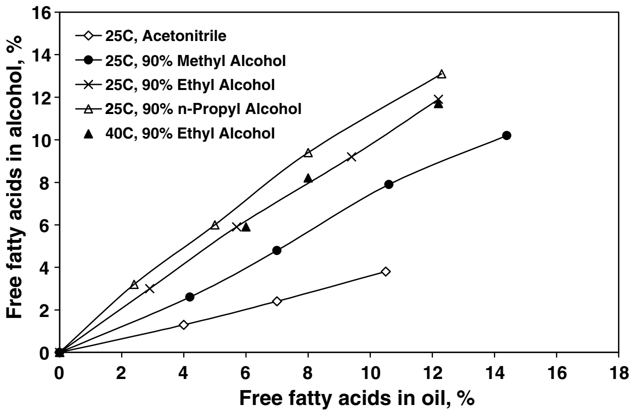

Fig. 2. Distribution diagram for cottonseed oil (mixed fatty acids) (Sreenivasan and Viswanath, 1973).

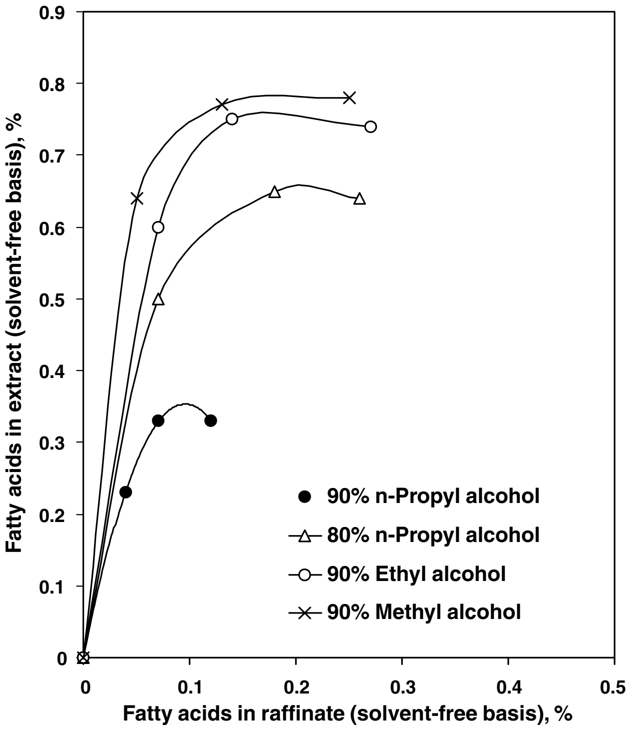

Fig. 3. Selectivity diagram for cottonseed oil (mixed fatty acids) (Sreenivasan and Viswanath, 1973).

Ethanol, methanol and acetone have been recommended as solvents for extraction of FFA for deacidification of vegetable oils (Turkay & Civelekoglu, 1991). Although the solubility of fatty acids and neutral triglycerides are individually different in these solvents, it has not been possible to obtain a complete separation, because the low solubility of triglycerides, increased in direct proportion to their FFA contents. Consequently, the deacidification with such solvents could be only partially successful, and entailed also a loss of neutral oil. Therefore, it is recommended that a final neutralization treatment with alkali be given to the extracted oil for complete deacidification. There have also been other attempts to optimize the extraction conditions for the recovery of FFA with minor loss of neutral oil (Batista, Wolf Maciel, & Meirelles, 1999; Pina & Meirelles, 2000; Turkay & Civelekoglu, 1991).

Turkay and Civelekoglu (1991) investigated liquid–liquid extraction of FFA from sulfur olive oil miscella in hexane with aqueous ethanol solutions in bench-scale single-stage extractions. They concluded that use of 30% or more dilute ethanol solutions was appropriate for extracting the miscella, in order to ensure deacidification with a low triglycerides loss. Batista et al. (1999) simulated the deacidification of vegetable oils by liquid–liquid extraction, and optimized the operating conditions for obtaining a minimal concentration of FFA in the refined oil, with minimal loss of neutral oil. Pina & Meirelles (2000) investigated the deacidification of corn oil by continuous liquid–liquid extraction in a rotating disc column, using ethanol containing ~6% water as the solvent. The results showed that it is feasible to obtain a refined oil with an oleic acid content less than 0.3% by continuous solvent extraction, provided the FFA concentration in the feed stream was not higher than 3.5%. They also indicated that the corresponding loss of neutral oil was less than 5%, which is significantly lower than the values reported for alkali or physical refining of corn oil.

In the case of vegetable oils having high FFA, solvent extraction is one of the promising alternative routes for partial deacidification. However, the use of another solvent in the process—such as methanol/ethanol/acetone, besides hexane used for extraction of oils/fats from oil-bearing material, would be associated with higher capital and energy costs, and could deter the industrial adoption of this process.

3.4. Supercritical fluid extraction

Extraction with a solvent at temperatures and pressures above its critical point is known as supercritical fluid extraction (SCFE). SCFE, with carbon dioxide as the extraction solvent, has been tested as an alternative deacidification process for high FFA containing oils. Several researchers have demonstrated the suitability of supercritical carbon dioxide (SC-CO_2) as a solvent for the extraction of seed oils (Brunetti, Daghetta, Fedeli, Kikic, & Zanderighi, 1989). Unlike the hexane extracted oils, these oils do not contain phospholipids and other complex substances; therefore, they do not require a degumming step. Deacidification and deodorization of edible oils are two potential applications for extraction with SC-CO_2.

The SCFE process has a number of advantages over conventional extraction—namely, low temperature and pollution free operation, inert solvent, selective separation and fractionation of tailor-made end-product, as well as extraction of a high-value product, or of a new product, with improved functional or nutritional characteristics (Ooi et al., 1996). Some of the solvents used in SCFE are carbon dioxide, ethylene, propane, nitrogen, nitrous oxide and monochlorofluoromethane. The most common solvent is carbon dioxide because it possesses a number of desirable properties and attractive features over the presently used organic solvents, such as nontoxicity, safety, ease of separation, low cost, and ready availability, which makes it ideal for food processing (Bartle & Clifford, 1992). Another advantage of SCFE, as opposed to hexane extraction, is that SCFE could be made highly selective by controlling temperature and pressure. Solubility data of fatty acids and triglycerides in SC-CO_2 (Table 6) showed that FFA are more soluble in CO_2 than the corresponding triglycerides at certain temperatures and pressures (Brunetti et al., 1989).

Table 6
Solubility[a] of fatty acids and triglycerides in SC-CO_2 (Brunetti et al., 1989)

Sample	Temperature (°C)	$S^0 \times 10^2$ at 20 MPa	$S^0 \times 10^2$ at 30 MPa
Myristic acid	40	9.4 ± 0.6	–[b]
	50	8.3 ± 0.6	–
Palmitic acid	40	2.2 ± 0.3	2.0 ± 0.2
	50	4.2 ± 0.4	–
Stearic acid	40	0.9 ± 0.3	0.8 ± 0.3
	50	1.9 ± 0.4	3.9 ± 0.6
	60	2.0 ± 0.1	6.0 ± 0.7
Oleic acid	40	4.0 ± 0.2	8.0 ± 0.6
	60	2.6 ± 0.5	7.4 ± 0.9
Triolein	40	0.97 ± 0.04	2.2 ± 0.1
	60	0.4 ± 0.1	1.8 ± 0.2
Tristearin	40	0.38 ± 0.04	1.0 ± 0.2
	50	0.38 ± 0.01	1.4 ± 0.2
	60	0.17 ± 0.02	1.4 ± 0.2
Stearic–palmitic acids (1:1, w/w)	40	2.9 ± 1.0	–
Triolein–tristearin (1:1, w/w)	40	0.6 ± 0.1	–

[a] Expressed in g solute/g CO_2.
[b] Not determined.

Brunetti et al. (1989) investigated the deacidification of olive oil of high acidity with SC-CO_2 at extraction pressures of 20 and 30 MPa, and extraction temperatures of 40 and 60 °C. They reported that the solvent selectivity for fatty acids was higher at 20 MPa and 60 °C, and it increased significantly as the FFA concentration of the oil decreased. Zhao, Shishikura, Fujimoto, Arai, & Saito (1987) combined the extraction and refining procedures by sequentially extracting RBO (11.9% FFA) with SC-CO_2 at 15 and 35 MPa at 40 °C. With this two-step approach, the undesirable FFA, unsaponifiable matter, and tocopherols were extracted at low pressure, and the remaining decontaminated oil could then be readily recovered with SC-CO_2 at the higher pressure. Thus, a simple process could be used for refining the oil wherein the degumming step could be omitted. Ziegler & Liaw (1993) carried out simulated deacidification and deodorization studies on pressed oil from roasted peanuts, with dense CO_2 at various temperatures, pressures and extraction factors. The studies showed that FFA solubility was directly related to the degree of unsaturation. Efficient deacidification and deodorization was accomplished with CO_2 at 47 °C and 20 MPa. They reported that deodorization was mass transfer controlled, while deacidification was thermodynamically constrained.

Turkay et al. (1996) investigated deacidification of highly acidic oils from black cumin seeds with SC-CO_2 at two temperatures (40 and 60 °C), two pressures (15 and 20 MPa), and two polarities (pure CO_2 and CO_2/10%MeOH). In the two-step process, FFA was extracted in the first step and the majority of the valuable neutral oil from the seed was recovered subsequently using a higher extraction pressure. The deacidification of a high acidity (37.7% FFA) oil to a low-acidity (7.8% FFA) oil was achieved, when pure CO_2 was used at a relatively low pressure (15 MPa) and relatively high temperature (60 °C). By reducing the extraction temperature to 40 °C, increasing the extraction pressure to 20 MPa, or increasing the polarity of the supercritical fluid via the addition of a methanol modifier, the selectivity of the extraction was significantly reduced; the amount of neutral oil that was co-extracted with the FFA increased from 23% to 94%.

Ooi et al. (1996) showed that crude palm oil could be processed by continuous SC-CO_2. The refined palm oil obtained from the process had less than 0.1% FFA, a higher carotene content, and low diglycerides. Solubility of palm oil in SC-CO_2 increased with pressure, while a co-solvent (ethanol) improved the refining performance.

A significant portion of the phytosterols naturally present in the vegetable oils is lost in the byproducts during the conventional edible oil refining process. Dunford and King (2001) proposed an approach using a two-step, semicontinuous, supercritical CO_2 fractionation process, to enrich the phytosterol ester content of vegetable oils during refining. They studied the effect of isothermal and temperature gradient operation in the fractionation column on the composition of RBO fractions, whilst minimizing losses of phytosterols and TG. The application of a temperature gradient along the column was beneficial in reducing the TG lost in the extract fraction; further, utilization of higher temperature in the stripping section improved FFA removal from crude RBO. Subsequently, these researchers also examined the potential of a continuous countercurrent supercritical CO_2 fractionation process for enrichment of phytosterols in vegetable oils (Dunford, Teel, & King, 2003). Fractionation at a low pressure (13.8 MPa) and a high temperature (80 °C) effectively removed FFA from crude RBO without any oryzanol loss in the extract fraction. Phytosterol fatty-acid ester content was also increased during the deacidification process; however, the enrichment of these moieties was not as high as that found for oryzanol.

SCFE is a costlier process. So extraction with supercritical fluid may be particularly useful for deacidifying expensive specialty oils and fats with high initial acidity, or where the quality and purity of the extracted components are of great importance.

3.5. Membrane technology

The membrane process is a remarkably simple process offering many advantages over the conventional processes: namely, low-energy consumption, ambient temperature operation, no addition of chemicals, and retention of nutrients as well as other desirable components. Owing to the vast scope for energy savings as well as potential for improvement in oil quality, edible oil processing has become one of the prime areas for membrane applications. It has been estimated that a great potential for energy savings—to the tune of 15–22 trillion kJ/year—exists in replacing or supplementing conventional degumming, refining, and bleaching processes (Koseoglu & Engelgau, 1990). Conceptually, membranes could be used in almost all stages of oil production and purification (Cheryan, 1998). Raman, Rajagopalan, and Cheryan (1994) listed some of the potential applications of membrane technology in vegetable oil processing. Many of them have been evaluated at the laboratory or pilot plant scale, nevertheless, except for gas separation for the production of nitrogen, there are few commercial membrane installations in the edible oil related industries, in spite of their vast potential and the considerable research efforts already put in. The pressure driven membrane processes are classified as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) depending on the nature of particle or on the molecular size of the solutes that are separated. Commercial membrane devices are available in four major types, namely plate and frame, tubular, spiral-wound and hollow fibre.

Several researchers have attempted the deacidification of vegetable oils with and without solvents, by using porous as well as nonporous membranes. Despite these efforts, there is no breakthrough in evolving a successful technology. The limitations of various approaches are listed in Table 7. The molecular weight of fatty acids are <300 Da and that of triglycerides are >800 Da. The ideal process would use a hydrophobic membrane with pores so precise that they could effectively separate the FFAs from the triglycerides (Raman et al., 1994). However, the differences in their molecular weights are too small to use membrane (NF) alone for the separation. There have been some attempts on the deacidification of undiluted oils using nonporous denser polymeric membranes. The process produces permeate and retentate fractions containing triglycerides and other oil constituents. The decreasing order of relative preferential permeation in the nonporous membranes is expected to be FFA, tocopherols, triglycerides, aldehydes, peroxides, colour pigments and phospholipids (Subramanian, Nakajima, & Kawakatsu, 1998; Subramanian, Nakajima, Kimura, & Maekawa, 1998). During membrane processing, FFA permeated preferentially compared to triglycerides resulting in negative rejection

Table 7
Various approaches made with membrane technology

S. no.	Description	Limitations
Direct deacidification		
1	Separation without solvent—NF	Molecular weight difference between TG and FFA is too small for separation. Suitable membranes are not available. Not attempted
2	Separation without solvent—nonporous	Selectivity and permeate flux obtained are not suitable for industrial adoption
3	Diluted with hexane—NF	Partial deacidification (40% reduction in FFA)
4	Diluted with hexane—nonporous	No selectivity
5	Diluted with acetone—NF	Good selectivity but oil flux is very low
Deacidification with pretreatment		
6	Ammonia treatment—UF	Associated handling problems
7	Sodium hydroxide treatment—MF	Needs optimization
8	Sodium hydroxide treatment followed by addition of iso-propanol—combination of membranes (hydrophobic and hydrophilic—UF/MF)	Hypothetical approach—not sufficient data to prove the hypothesis
Extraction with solvent		
9	Membrane extraction with butanediol—UF	Very high mass transfer resistance (large membrane surface required)
10	Solvent extraction and membrane separation (RO/NF)	Introduction of another solvent makes the process less attractive

of FFA. In sunflower oil, the rejection of FFA was to the extent of (−)8–(−)27% (Subramanian, Nakajima, Kimura, et al., 1998). In the triglycerides–oleic acid model system, oleic acid permeated preferentially when compared with triglycerides, due to the higher solubility as well as diffusivity of oleic acid in the membrane material (Subramanian et al., 2001). However, the selectivity obtained is not suitable for industrial adoption.

The separation of FFA from oil has been attempted in solvents such as hexane and acetone. A partial separation of the fatty acids in hexane was observed when the appropriate NF membrane was used (Raman, Cheryan, & Rajagopalan, 1996a). In this simultaneous desolventizing and deacidification process, 40% reduction in FFA concentration and greater than 50% reduction in the energy needed for hexane evaporation has been reported, while processing a model miscella (containing 20% soybean oil with 2% FFA). Bhosle (2002) observed that in the case of nonporous dense membranes, the selectivity for FFA over TG was completely lost upon dilution with hexane. Direct deacidification of model oil in acetone was observed when laboratory made, solvent stable, NF membranes, with either PEBAX [poly(amide-*b*-ether) copolymer] or cellulose-type top layer, were employed (Zwijnenberg, Krosse, Ebert, Peinemann, & Cuperus, 1999). These membranes were stable in acetone, ethanol, 2-propanol and hexane. Fatty acids were retained less than triglycerides by these membranes, indicating the possibility of deacidification. Bhosle (2002) also observed that these hydrophilic NF membranes exhibited greater selectivity. For industrial adoption, however, the oil flux needs to be significantly improved.

Sen Gupta (1985) proposed another method to modify the properties of FFA, e.g., chemically associating them into large micelles and then separating the FFA, using UF membranes. For oils having low FFA and high phospholipid concentrations (e.g., soybean and rapeseed oils), the miscella was directly neutralized with ammonia, and then ultrafiltered. But for oils containing low amounts of phosphatides (e.g., fish oil), lecithin was added to the miscella before neutralization. Almost none of the phospholipids permeated through the UF membrane, and over 90% of the FFAs were rejected. The author had used ammonia, since FFA could be obtained by mere heating of the retentate. There are some associated problems with ammonia for process applications besides environmental restrictions on its use. In a similar approach, Pioch, Largueze, Graille, Ajana, and Rouviere (1998) achieved simultaneous reduction of FFA, and phosphorus in crude vegetable oils with the addition of sodium hydroxide, but using a MF step. These experiments were performed by continuous recycling of permeate in the cross-flow filtration system, to avoid the effect of increasing concentration, that is likely to increase plugging of membranes. True optimization of this process, leading to an industrial application, needs further developmental work.

Keurentjes, Doornbusch, and van't Riet (1991), Keurentjes, Sluijs, Franssen, and van't Riet (1992) made attempts for removal of FFA with the combination of hydrophobic and hydrophilic membranes, and later by membrane extraction using 1,2-butanediol as an extractant. In the first system (Keurentjes et al., 1991), aqueous sodium hydroxide was added to the oil to form the sodium salts of the fatty acids. *Iso*-propanol was then added to form a system of two immiscible liquids, one containing water, *iso*-propanol and soaps and the other containing the oil and a trace amount of *iso*-propanol. A hydrophilic and a hydrophobic membrane in series were used to separate the two phases to obtain oil that was substantially deacidified. However, there is no data presented to prove that FFA-free oil can be produced by this approach. In the second system (Keurentjes et al., 1992), hollow-fibre UF membranes were used to extract FFA from oil using 1,2-butanediol as a selective extractant. The oil phase was circulated inside the fibres, and butanediol outside the fibres. Some of the membranes tested could be used successfully, but due to the high mass transfer resistance the required membrane surface area for a given extraction was relatively high. It has also been demonstrated that the differences in mass transfer coefficients between fatty acids of different chain lengths could be used as the basis of a fractionation of a mixture of fatty acids.

Many researchers have clubbed membrane technology with solvent extraction. There are reports on removal of FFA from model oils (Krishna Kumar & Bhowmick, 1996; Raman, Cheryan, & Rajagopalan, 1996b) and crude RBO (Kale, Katikaneni, & Cheryan, 1999) by alcohol extraction of FFA, followed by membrane separation. In this method, an appropriate solvent was used to selectively dissolve FFA. After phase separation, the extractant (FFA-solvent mixture) was processed through the appropriate RO or NF membrane to recover the solvent and the fatty acids. Raman et al. (1996b) used methanol for extraction of FFA from a model crude vegetable oil, and employed NF membrane for the separation of FFA from methanol. Of the several commercially available membranes that have been evaluated, the best result obtained was a FFA rejection of >90%, and a flux of $>25\,\mathrm{L/m^2\,h}$. A combination of high-rejection and low-rejection membranes resulted in a retentate stream of 35% FFA and a permeate stream with <0.04%, which could be recycled in the process. Krishna Kumar and Bhowmick (1996) processed the mixtures of TG and FFA with alcohol using both cellulosic and noncellulosic type membranes. Polyamide membranes (MWCO 500–600 Da) showed better selectivity towards fatty-acid separation as compared to cellulose acetate (MWCO 500 Da) and polysulphone membranes (MWCO 1000 Da). During processing of a groundnut oil/fatty acid/alcohol mixture with a polyamide membrane, the FFA concentration in the permeate was 86.8% when the feed had 61.7% FFA; a permeate flux of $67.4\,\mathrm{L/m^2\,h}$ was obtained. However, long term stability of the membrane in the process conditions has not been tested. Kale et al. (1999) studied deacidification of crude RBO by extracting with methanol followed by membrane separation. At the optimal ratio of 1.8:1 methanol/oil, the concentration of FFA in the crude RBO was reduced from 16.5% to 3.7%. A second extraction at 1:1 ratio reduced FFA in the oil to 0.33%. The FFA in the methanol extract was recovered by nanofiltration using commercial membranes. Their design estimate indicated that a two-stage membrane system could recover 97.8% of FFA, and could result in a final retentate stream with 20% or more FFA and a permeate stream with negligible FFA (0.13%) that could be recycled for FFA extraction. The estimated capital cost of the membrane plant would be about \$48 per kilogram of oil processed per hour and annual operating cost would be about \$15 per ton of FFA recovered. It appears that combination of solvent extraction and membrane separation seems to be technically feasible with the advent of solvent resistant membranes. Nevertheless, the introduction of another solvent in the process such as methanol/ethanol besides hexane used for extraction of oils/fats from oil-bearing material would not be a very attractive preposition as compared to direct membrane deacidification.

4. Concluding remarks

The chemical, physical and miscella deacidification methods used in the industry have several drawbacks. The new approaches namely, biological deacidification, reesterification, solvent extraction, supercritical fluid extraction (SCFE) and membrane technology, either independently, or in combination with current technology, may help to overcome the major drawbacks. However, further studies on these new approaches are necessary, including an assessment of the economic viability, to successfully replace the existing technology.

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