

Review on Recent Trends in Rice Bran Oil Processing

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Abstract Rice bran oil (RBO) is popular in several countries such as Japan, India, Korea, China and Indonesia as a cooking oil. It has been shown that RBO is an excellent cooking and salad oil due to its high smoke point and delicate flavor. The nutritional qualities and health effects of rice bran oil are also established. RBO is rich in unsaponifiable fraction (unsap), which contains the micronutrients like vitamin E complexes, gamma oryzanol, phytosterols, polyphenols and squalene. However, the high FFA and acetone-insoluble content of RBO made it difficult for processing. Therefore, in recent years, research interest has been growing in RBO processing to obtain good quality oil with low refining loss. This review article deals with detailed reports on RBO processing including membrane-based techniques from the production and quality point of view.

Keywords Membrane based refining · Refining of rice bran oil · Rice bran oil

Introduction

Interest in rice bran oil (RBO) has been growing from the health and nutritional aspects as well as its wide application as an industrial oil. RBO in its natural state contains several constituents which would potentially provide benefits to health [1]. The oil contains 4.2% unsaponifiable matter (unsap), which includes antioxidants and

micronutrients, whereas all other oils have an unsap content of less than 1–2%. The RBO unsap fraction is rich in tocopherols and tocotrienols, γ -oryzanol, phytosterols, polyphenols and squalene. Numerous studies show that RBO reduces harmful cholesterol (LDL) without reducing the good cholesterol (HDL) [2–12]. In those studies, oryzanol is reported as the key element responsible for that function. Tocotrienol is highlighted as the most precious and powerful vitamin E source existing in nature [13] and is said to have an anti-cancer effect too [14–17]. In addition, RBO does not produce any allergenic reactions when ingested, unlike several vegetable oils [18, 19]. Moreover, RBO has a very good balance in its fatty acid composition i.e., mono-unsaturates to poly-unsaturates/saturates.

RBO has a very good shelf-life compared to other cooking oils because of antioxidants present in it. Its low viscosity allows less oil to be absorbed during cooking, reducing overall calories [20].

Crude oils of vegetable origin contain impurities of varying types. These impurity levels are affected by storage and handling as well as extraction processes. The typical composition of crude RBO is 81–84% triacylglycerols (TAG), 2–3% diacylglycerols (DAG), 1–2% monoacylglycerols (MAG), 2–6% free fatty acids (FFA), 3–4% wax, 0.8% glycolipids, 1–2% phospholipids (PL) and 4% unsap. In comparison to other vegetable oils, crude RBO tends to contain higher levels of non-TAGs, most of which are to be removed during refining processes. The FFA, MAG and DAG in RBO are associated with enzymatic hydrolysis. The phospholipids are predominantly hydratable phosphatidylcholine (PC), phosphatidyl-inositol (PI) and non-hydratable phospholipids that are calcium and magnesium salts of phosphatidic acid (PA) and phosphatidylethanolamine (PE) [21]. The wax content of RBO can be somewhat

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variable (2–8%), depending upon cultivars and processing parameters. Various sterols (β -sitosterol 0.90–1.70%, campesterol 0.50–0.66% and stigmasterol 0.27–0.25%) constitute a principal portion of the unsap fraction of nutraceutical interest.

Processing of Rice Bran Oil (Non-Membrane Based Processing)

A solvent extraction process using hexane as a solvent is usually used for the extraction of RBO. An alternative method of oil extraction from rice bran is super critical carbon dioxide extraction. Several studies have reported that supercritical carbon dioxide extraction of RBO produces oil with a lighter color, less phosphorous, wax and FFA and more essential fatty acids (EFA) and oryzanol [22]. According to the reports, there are also other methods for producing RBO enriched with micronutrients and antioxidants [23–26].

The miscella (extracted oil and solvent mixture) exits the extractor with a 70–75% (w/v) solvent content, and the solvent is usually recovered by distillation. Crude oil, so obtained, contains TAG as the major component (>80%) along with various impurities. The main object of the refining process is, therefore, to remove the impurities such as waxes, gums/phosphatides, FFA and coloring materials without altering the basic TAG composition for producing edible quality oil. Presence of impurities, besides resulting in poor color and haziness in appearance, will also cause catalyst poisoning and a slow rate of hydrogenation if the oil is used for making vanaspati. Moreover, byproducts of RBO processing are good sources of beneficial minor components.

RBO is difficult to process due to its high FFA, waxes, bran fines and pigment content. These factors lead to high refining losses when normal refining processes are employed. However, with careful attention to processing techniques, beginning with the rice mill, one can produce RBO economically with reasonable yields and quality.

Important steps involved in the processing of RBO are (a) settling or filtration of bran fines (b) degumming, (c) dewaxing, (d) deacidification, (e) bleaching and (f) deodorization.

Fines Removals

Removal of fines prior to degumming and refining gives better oil quality and yield. Zachariassen and Giasotta [27] claimed that self-opening separator has proved to be efficient in removing fines. Another author recommended preliminary filtration of crude oil at ambient temperature as the first step of refining [28].

Degumming

Solvent extracted rice bran oil contains considerable amounts of phosphatides and other mucilaginous materials which form deposits in the storage tanks. They, in combination with oryzanol, increase refining losses by emulsifying considerable amounts of neutral oil, which is lost in the soap stock. Different degumming processes namely water degumming, acid degumming (phosphoric, citric, oxalic, tartaric etc.) [29], super degumming and TOP degumming [30] for crude RBO are well described by various workers. There is a report on degumming of RBO by using surface-active compounds such as lauryl sulphate, sodium oleate etc., it was claimed to have a lower P content than that achieved by phosphoric acid and water degumming [31]. However, enzymatic degumming, simultaneous degumming/dewaxing, and membrane degumming is receiving much attention nowadays to reduce the refining loss and color of the finished oil.

Enzymatic degumming is probably the best process already available today for reducing the P content of crude RBO below 5 ppm [32]. The enzyme, phospholipase A₂, catalyzes the non-hydratable phosphatides into hydratable lysophospholipids, which are then removed by centrifugation, yielding oil that is low in P. Due to the low temperature, this process produces no color deterioration of degummed oil compared to the conventional phosphoric acid degumming. Moreover, the oil content of the gums from enzymatic degumming, is only 25–30% compared to 50–60% in the conventional one. The oryzanol present in crude RBO remains almost intact during the enzymatic process.

Processes for simultaneous dewaxing and degumming were also described in the reports. The processes used water and an aqueous solution of CaCl₂, followed by centrifugation or low temperature (20 °C) crystallization which facilitates precipitation of hydratable and non-hydratable phosphatides along with wax and the P content decreased to <5 ppm [33, 34]. The economic feasibility of these processes is quite high due to the elimination of one step from the whole process.

Degumming of RBO with mono-, di- or triethylamines to obtain low phosphorous oil have also been reported [35, 36].

Dewaxing

Rice bran oil contains up to 20% of high temperature melting saturated fatty acids, which makes it difficult to dewax this oil at lower temperature such as 8 or 10 °C. The dewaxing can be done in the oil phase as well as in the miscella phase by winterizing without or with suitable additives. One of the crude methods of separation of waxes

to some extent involves the removal of waxes settled down in a storage tank.

In the conventional dewaxing process, the oil is heated to around 90 °C to destroy any existing crystal nuclei. The oil is then cooled with stirring to around 20 °C and then allowed to mature for a minimum time of 4 h. Wax is separated by filtration in plate and frame filters [37]. Dewaxed oil is likely to become cloudy in a severe winter or in cold places, as is the case with cottonseed oil.

The use of an additive like calcium chloride is also worth trying in the separation of the waxes from RBO. Subsequent centrifugation of the oil removed about 60% of its wax content [38]. Dewaxing of RBO may be achieved, as reported by Haraldsson et al. [39], by keeping the refined oil at low temperature in the presence of soap stock before centrifugation. They also stated that dewaxing could be achieved by cooling the oil to 8 °C followed by the addition of 5% water containing a small amount of sodium lauryl sulphate. The mixture is agitated for about 4 h at that temperature to complete the crystallization. The wax crystals that become dispersed in the water phase are separated by centrifugation [40].

Dewaxing of RBO in the miscella phase by winterization has been well investigated. In Rancher's process, rice bran miscella is gradually chilled in a compartment fitted with a stirrer with speed 1–10 rpm to hasten crystal formation, and the wax crystals thus formed, are separated by centrifugation. This process removes over 90% of RBO waxes [41]. RBO dewaxing in miscella phase is well known in Japan because of the fact that they possess quite large solvent refining plants, which could reduce the initial as well as the running costs of the miscella dewaxing process. On the other hand, this process is not suitable in small refinery plants such as the refineries existing in India. Miscella dewaxing also depends on the oil content in the miscella and the winterization temperature. It is reported that the best mixture is generally 1:1 of degummed RBO with hexane. The final crystallization temperature is 5 °C and the crystallization cycle is standardized at 8–10 h per charge [42]. According to the study conducted by this author and her colleague reveals that in the usual concentration of wax in RBO miscella with TAG and gum (i.e., 30 and 1% respectively) in a hexane medium, wax crystallizes optimally in respect to size and number at 12–15 °C after 1 h of incubation [43].

Two Korean patents described the processes of dewaxing RBO using a solvent such as acetone in which oil is soluble but the wax is not [44, 45]. The first one described the process of the extraction of RBO wax from settled waste of the RBO tank and the second one described the use of a solvent in the oil phase to particulate the wax component followed by cooling at 0 °C and filtration. A recent report published by Kaimal et al. [46] describes a

two-step method for the production of food grade wax, which includes bleaching of the wax with sodium borohydride.

Refining

Refining or deacidification of RBO is rather difficult due to its high FFA, wax and unsap content. Normally RBO having FFA up to 8% is deacidified by the conventional alkali refining process after degumming or/and dewaxing, depending on the end use of the oil. However, the refining loss incurred in this process is much higher than other oils as observed in refineries in India and also according to various patents and reports [47–49].

Alkali Refining

In the conventional alkali refining process, the refineries always incur an oil loss of an average three times the FFA value. The extents of refining loss and total process loss after degumming, refining and dewaxing of RBO are also very high as reported by Sen et al. [47]. Moreover, most nutritional components present in RBO are destroyed or removed during this traditional alkali refining process. Use of a weak aqueous solution of alkali together with an indicator to monitor the pH value during the neutralization process reduces the refining loss as depicted in two other reports [48, 49].

The reason for inordinately high refining losses using a conventional sodium hydroxide solution encountered in the case of RBO in comparison to other vegetable oils with a similar FFA content has been the subject of numerous investigations [50–52]. A report by Cousins et al. [51] contains the observation that the flocs formed from crude RBO have an unusual inability to cohere and settle out of the oil clearly and it tends to emulsify the oil under the conditions of refining. In a later report, an assumption was made that the high refining losses for RBO was due to the presence of saponins [52] but without any experimental evidence to support this statement.

Miscella Refining

The refining of high FFA RBO has been accomplished by miscella refining as it provides three immediate benefits, namely, lower refining loss, lighter colored refined oil without bleaching, and elimination of the need for water washing of the refined oil or miscella [53]. The miscella refining process has been commercialized in Japan for many years. It is a simple process. It needs an explosion proof system. However, the cost of the equipment is somewhat higher than for an ordinary refining plant and control of the process is more difficult. In this process, the

extracted miscella can be directly degummed, dewaxed and refined without desolventisation [54]. This type of refining should be done at the solvent extraction plant as soon as possible and preferably within ca. 6 h after the oil is extracted from the source material. Most miscella processing is done with a 40–58% oil content (w/v). Various types of chemical conditioning and mechanical conditioning (such as stirring) or both are usually carried out for miscella refining [55].

Mixed Solvent Refining

The mixed solvent process using hexane as the main solvent and ethanol or isopropanol as the second solvent has been carried out for refining of high FFA RBO. The process has been reported to be extremely satisfactory for high FFA, dark colored RBO and the refining factor lies between 1.1–1.3 [56]. The refining of high FFA RBO by a mixed solvent alone, or by mixed solvent extraction followed by alkali neutralization had been patented by Bhattacharyya et al. [57, 58].

Steam Refining or Physical Refining

Almost 100 years ago Hefter [29] suggested the basic technique of steam distilling of fatty acids from the crude oils. Steam refining of certain high FFA fatty oils has been carried out in Europe for many years. The economics for deacidification by steam refining versus caustic refining normally favor steam refining only when high FFA oils are processed [59]. It not only reduces the refining losses, it also protects the micronutrients present in RBO specially the 'oryzanol' [60]. The problem of effluent does not exist in physical refining. In addition, the soapstocks from alkali refining process need to be acidulated by sulfuric acid and washed to recover the free fatty acids, causing extra environmental problems.

The literature has well documented that crude oils must be thoroughly pretreated to remove most undesirable constituents before being subjected to high temperature distillation [61]. In addition to degumming, prebleaching is also necessary to remove color bodies and essentially all trace metals. Small amounts of phosphatides and iron are probably the greatest cause of heat darkening during distillation. The steam refining process provides simultaneous deodorization of the oil [62]. Suitability of this steam refining process for high FFA RBO was thoroughly reported in two patents [63, 64].

Re-esterification of FFA

A novel approach to deal with high FFA RBO involves catalytic re-esterification of FFA with glycerol after de-

gumming and dewaxing. The process can be done with or without a catalyst under vacuum at various temperatures [65]. The use of a chemical catalyst and high temperature often creates color and other problems to the deacidified oil. The unique properties of some microbial lipases to synthesize triglycerides from fatty acids and glycerol was applied to deacidify high FFA RBO as an alternative refining process. Bhattacharyya et al. [66] used an enzyme from *Mucor miehei* on a 10% wt basis (on oil) to esterify the FFA in degummed, dewaxed RBO with glycerol so as to obtain the refined oil. The result obtained was very encouraging. On the basis of that study, technology developments are being continued with the financial aid of the Technology Mission of Oilseeds, Pulses and Maize (Govt. of India). In the case of very high FFA RBO (>40%), Sengupta et al. [67] suggested biorefining followed by alkali/physical refining of the crude oil to obtain a satisfactory result. The same group also studied the use of MAG instead of glycerol, and it was reported that MAG deacidified RBO more efficiently than glycerol as evidenced by the higher TAG content [68].

Bleaching

Bleaching of RBO is somewhat more difficult than most other vegetable oils primarily due to the high chlorophyll and red pigment content, and also due to the oxidized products of tocopherols and metallic salts of fatty acids. Generally, bleaching of RBO is done after degumming, dewaxing and alkali deacidification, by single or mixed solvent or miscella refining. However, in the case of steam refining, bleaching is done immediately after degumming. It is, however, always better to bleach RBO before alkali treatment because chlorophyll tends to be stabilized by alkali and heat and is then harder to remove [69]. Earth bleaching, under high vacuum, and at a temperature of around 110 °C, in addition to removing pigments, helps to reduce the amounts of oxidation products. The catalytic activity of activated earth at this temperature decomposes hydro-peroxides. The ion exchange properties of bleaching earth helps in metal removal and the activated carbon helps in reducing red pigment in the RBO.

Today, De-Smet and Alfa-Laval offer counter current bleaching and steam agitated bleaching plant for crude RBO. Industrial grade RBO is often bleached by conventional chlorate bleaching and used in soap production.

Deodorization

Deodorization of degummed, dewaxed and deacidified RBO is done in the typical way used for other vegetable oils [69]. General conditions of deodorization include a temperature between 200 and 220 °C and a pressure of

6–10 mmHg. In the case of steam refining of high FFA RBO, the deodorization is performed simultaneously with deacidification. The temperature and vacuum used in steam refining is rather high (~250 °C, under vacuum at 1–3 mmHg). The oil has to be given an adequate residence time for proper deodorization and the destruction of heat labile pigments.

The deodorized oil is counter-currently cooled first by the incoming oil and then by water to around 50 °C. The cooled, deodorized oil is then passed through a polishing press to give it a transparent look.

Special Treatment

Special treatment is sometimes performed in the case of RBO to enrich its phytosterol content. Phytosterols are minor components of all vegetable oils comprising major portions of the unsap fraction of the oil. The cholesterol lowering effect of sterols is already established. Phytosterol enriched margarines have been popularized in recent years in the US due to the increased consumer demand for such nutraceutical/functional foods. RBO is an excellent source of these nutritionally beneficial sterols. Dunford et al. [70] reported the enrichment of total phytosterol ester content of RBO by deacidification of the crude oil using a supercritical fluid fractionation (SFF) process.

Membrane Based Processing of Rice Bran Oil

Membrane based separation and purification technologies have been established as an efficient, cost effective and environmentally friendly process for solid–liquid, solute–solvent, liquid–liquid separation applications. The practical use of membrane separation began in the 1960s for the desalination of seawater [71]. Since then, this energy-efficient separation technology has been widely applied to food processing for the purpose of low cost concentration, fractionation and purification. Commercial membrane applications in food industry include wastewater treatment, fruit and vegetable juice processing, dairy processing and recovery/purification of proteins, oils and other materials [72–74]. Membrane separation is primarily a size-exclusion-based pressure-driven process. Performance of membrane separation is affected by membrane composition, temperature, pressure, velocity of flow, and interaction between components of the feedstock and with the membrane surface.

TAG (MW ~900) constitutes over 80% of crude RBO. Minor components such as PLs (MW ~700–800), β -carotene (MW ~537), chlorophyll (MW ~892), FFA (MW < 300) and tocopherols (MW ~402–472) have lower molecular weights than TAG. The membrane process

produces permeate and retentate fractions containing TAG and other oil constituents. The major advantage of membrane based oil processing is that oxidation can be avoided due to the mild operating conditions. Moreover, membrane technology can be applied to simplify processes, reduce energy consumption, and reduce wastewater production [74]. Conceptually, membranes could be used in almost all processing stages of crude RBO.

Solvent Recovery

Separating the solvent totally or partly using a membrane can save lots of evaporation energy. Wu et al. [75] investigated the ultrafiltration of a soybean oil (SBO)-hexane miscella using a ceramic membrane and Keseoglu et al. [76, 77] reported the use of reverse osmosis (RO)/nanofiltration (NF) and ultra-filtration (UF) membranes for separating cottonseed oil (25%w/w) from hexane, ethanol and isopropanol. About 1.7 kg of hexane vapor per ton of processed oilseeds is exhausted to the environment in conventional distillation processes. However, with the NF technique, this amount can be reduced, at most, to the 5% level [78]. The same process has also been tried for the separation of RBO-hexane miscellas.

Degumming

Miscella Stage Degumming

Theoretically, TAG and PL have a similar MW (~900 Da), which makes them difficult to separate by a membrane. However, PL is surface-active in nature, having both hydrophilic (polar) and hydrophobic (non-polar) ends, and form reverse micelles in a non-aqueous environment with a globular structure [79, 80]. The reverse micelles have a MW of 20 kDa or more, and molecular sizes of 20–200 nm [81, 82]. The hydrophilic core of reverse micelles holds the majority of the coloring materials, carbohydrates, peptides, metal ions, etc. Accordingly, PL can be separated from TAG in the miscella stage by using UF/NF membranes. Attempts to develop membrane-based processing for degumming of crude vegetable oils were begun in 1977 by Sengupta [81]. His pioneering work was to remove the PL present in SBO from the SBO-hexane miscella by passing the miscella through a semi permeable membrane at 50 kg/cm² pressure. Suzuki et al. [83] used an inorganic UF membrane (ZrO₂, 50 Å pore size, 0.2–10 µm thickness, 30 mm diameter, 50 cm long, 7-channel, 4 mm channel diameter) for removal of PL from vegetable oil-hexane miscella at 2–5-kg/cm² pressures and 50–90 °C temperature. Oils extracted with hexane from vegetable seeds (soybean, rapeseed, safflower, corn and sunflower) or rice bran were pre-filtered using a microfiltration (MF)

membrane made of sintered alloy, whereby solid materials in the miscella were removed. The oil-hexane miscella (TAG content 25–30%w, PL 1–2%w) was heated to 65 °C by a pre-heater and treated with first and second stage UF membranes by adjusting the linear velocity at 2.0 m/s and pressure at 3.0 kg/cm², whereby the permeate flux of 130 l/m²h, the TAG concentration of 20–25% (w/w) and PL of 20–30 ppm in the permeate were achieved.

Lin et al. [79] used two commercially available hexane resistant membranes (DS7 membrane, Desalination Systems Inc., Escodido, CA with MWCO 1.0 kDa and SEPA-AN03 membrane, Osmonics Inc., Minnetonka, MN of MWCO 15.0 kDa) for degumming cottonseed and crude rice bran oils. DS-7 exhibited a higher phospholipid rejection rate (>99%) at 21 kg/cm² pressure, 40 °C and a feed velocity of 220 l/h while its permeate flux was half that of the AN03 membrane. These differences in membrane performance were attributed to the difference in the molecular weight cut off (MWCO) of the two membranes. They reported the distribution of PL, FFAs and oil after membrane separations in permeate and retentate. About 35% of the oil remained in the retentate at a concentration factor of five and no concentration reduction of FFAs in permeate oil was achieved. However, a poly vinylidene fluoride (PVDF) membrane filtration was found to be suitable for a pretreatment step of physical refining that requires P content <10 ppm and Fe content <0.2 ppm.

Subrahmanyam et al. [84] reported degumming of an RBO-hexane miscella obtained after dewaxing of crude RBO by using ceramic membranes, which are superior to polymeric membranes due to their wide range of pH tolerance, chemical inertness and ease of cleaning. Crude RBO (phosphorous 455 ppm and unsap 7.3%) was dewaxed by mixing the oil in hexane (3:7 v/v) and maintained at 8 °C for 24 h. The clean supernatant miscella (322 ppm phosphorous) was used for membrane degumming. A tubular ceramic membrane (Orelis, France; MWCO 1.0 kDa, 19 channel monolith support, 20 mm tube diameter, 2.5 mm channel diameter, ZrO₂ selective membrane layer and 0.125 m² membrane surface area) was used. A particular trans-membrane pressure (2–5 kg/cm²) and a flow rate of 1,000–1,100 l/h were maintained. The system operated in the recirculation mode, and both permeate and concentrates were recycled to the feed tank. The membrane rejected P and other impurities. P rejection was >95%, while only a 35% reduction of chlorophyll was achieved. Water and acid degumming could not lower the P content below 85 and 60 ppm respectively as compared to much lower value of 6–12 ppm in the membrane filtration. Declination of flux (initially ~6 l/m² h) after a prolonged operation (~5 l/m² h after 4 h of operation) was attributed to secondary gel layer formation. Intermittent cleaning of membrane by using a back flush technique was suggested

as a technique to restore the original flux. The membrane degummed oil met the requirements for physical refining.

Oil Phase Degumming

Tanahashi et al. [85] and Iwama et al. [86] and described processes for purification of crude glyceride oil containing gums, waxes and FFA in the oil stage. The resultant permeate was then bleached with clay and deodorized to obtain purified glyceride oil with required specifications of refined oil.

Pioch et al. [87] reported a single dead-end or cross-flow MF to evaluate the influence of temperature, pore size, pressure etc., on the flow rate of permeate and on the FFA (as soap) and P retention ratios. After addition of aqueous solution of sodium hydroxide (5–40% of the weight of oil with 10% excess) to the crude or partly water-degummed oil, the filtration was done by dead-end MF (Whatman Cellulose, pore size 2.5 µm). The quality of oil produced met the specification of refined oil (P < 5 ppm, soap < 40 ppm, FFA < 0.1%w and water < 0.1%w) but the flow rate was very poor and rapid fouling of membranes occurred. Whereas, cross-flow filtration (tubular alumina membrane, 12.0 µm pore size) provided a better flow rate of permeate and declined slowly after operating for more than 100 h. Dead-end filtration with a 100 kPa membrane produced a permeate comparable to chemical refining. The resistance of the polarization concentration layer was decreased by elevating the longitudinal velocity of crude oil up to 3.5 m/s and was supported by the Poiseuille–Hagen law. Increasing the temperature, from 25 to 45 °C, enhanced the permeate flux from 230 to 280 L/m² h but the efficiency of P retention decreased from 88 to 24% with 70 ppm of P left in refined oil instead of 11 ppm [88, 89].

Addition of hydratable PL increased the efficiency of degumming in the membrane process by enhancing the encapsulating ability without using any electrolyte [90, 91].

Deacidification

Raman et al. [92] selected six polymeric NF membranes (flat-sheet) for deacidification of methanol-oleic acid, methanol-mixed FFAs (oleic acid and linoleic acid) and methanol-crude SBO-FFA model solutions. Methanol was selected due to its small molecular size and high selectivity for FFAs. Crude oil containing TAG and FFAs was vigorously mixed with methanol for 30 min at 25 °C. This mixture was then transferred to a separator and allowed to separate overnight into two layers, bottom oil layer and methanol extract of FFA as top layer. This methanol extract was fed into the membrane cell for FFA separation. Out of six membranes (NTR-759, Nitto Denko, Japan;

FT-30, Tec/Dow, Midland, MI; MS-10, Osmonics, MN; Desal-5, Desalination Sys. Inc., CA; NTR-759, Nitto Denko, Japan and PZ, Fluid Sys., San Diego, CA), NTR-759 and Desal-5 membranes were selected for their high methanol permeability ($27.6 \text{ L/m}^2 \text{ h}$ at 18 kg/cm^2). They had high rejections ($>90\%$) for oleic acid and $>95\%$ for a linolenic and oleic mixture. In addition, the rejection rate increased with the oleic acid concentration probably due to the formation of a fouling layer or a dynamic secondary membrane. In a similar study, Kale et al. [93] used polymeric NF membranes for deacidification of methanol-extracted FFA obtained from crude RBO containing 1.7% PL, 16.5% FFA and 4% waxes. FFA in crude RBO was reduced to 0.33% (w/w, solvent free basis) after second stage solvent extraction and it was 0.06 and 20% (w/w, solvent free basis) in a third stage membrane permeate and retentate respectively. FFA recovered from the methanol extract was increased from 93% in one stage to 99% in three stages. On the basis of cost estimates and FFA recoveries analyses, they suggested a three-stage plant as an alternative choice. A similar attempt was made to separate FFAs and TAG from the extracted phase that was obtained by alcoholic extraction of high FFA groundnut and rice bran oils [94]. Membranes employed were cellulose acetate (CA) (MWCO 0.5 kDa, Amafilter GmbH, Hanover, Germany), polysulphones (PS) (MWCO 1.0 kDa) and polyamides (PA) (MWCO 0.5–0.6 kDa from Bhabha Atomic Research Centre, Bombay, India). Model mixtures of test samples were prepared by blending mixed FFAs and refined groundnut oil in different proportions and acid-degummed RBO with an FFA content of 34%. PA membranes were more suitable for FFA separation due to its slightly less hydrophilic nature and they were less prone to compaction with pressure than the CA&PS membranes used.

Dewaxing

Dewaxing is done between bleaching and deodorization in edible oil processing. Membrane technology has been successfully applied in this step of oil processing. Wax can be removed by an MF membrane with a pore diameter 0.5–1.0 μm [95]. Prior to membrane filtration, the oil temperature is adjusted to -10 to $20 \text{ }^\circ\text{C}$ depending on the type of oil used to crystallize the wax. Major portions of the waxy substances are rejected by the membrane with a very low amount of wax in the permeate. Two patents were taken out by Mutoh et al. [96] and Asbec et al. [97] describing the processes which are useful not only for dewaxing but also for removing PL, FFA and water from vegetable oils such as rice bran, sunflower, corn, sesame, and cottonseed oils, etc., in the crude/miscella stage. They used two membranes, one membrane was made of high density polyethylene, having an inner diameter of 1.5 mm, 500 μm

thickness, 0.12 μm average pore size, 71% porosity and a critical surface tension of 31 dynes/cm, and another membrane was made of tetra-fluoro-ethylene, having an average pore size of 0.3 μm and a 26.5 dynes/cm critical surface tension. The average permeate flux was $10 \text{ l/m}^2 \text{ h}$ at 2 kg/cm^2 pressure and at $10 \text{ }^\circ\text{C}$. The membrane module was subjected to backwashing operation for 2 min using N_2 gas at $50\text{--}55 \text{ }^\circ\text{C}$ to remove the membrane fouling by the wax. Wax content of the permeate oil was 0.003% (w/w) and no cloud formed during the cold test. The quality of membrane-filtered oil was comparable with those refined by conventional process. According to the report, the oil was first conventionally neutralized and bleached and dried to a water content of less than 0.05% (w/w) and heated to a temperature high enough to ensure the absence of nucleation seeds for wax crystal formation. Then the oil was subjected to slow cooling (less than $15 \text{ }^\circ\text{C/h}$) to $2\text{--}10 \text{ }^\circ\text{C}$ and then microfiltered for wax removal using MF membranes (Asahi Chemical International Ltd, Japan, Microza TP-113) of about 100 hollow fibers having a pore diameter of 0.2 μm and a 0.2 m^2 filtration area. Dewaxed oil subjected to slow cooling passed the cold test very well ($24\text{--}28 \text{ h}$ at $0 \text{ }^\circ\text{C}$). Muraldihara et al. [98] dewaxed vegetable oil using ceramic filter (Membralox X, 0.3 m^2 surface area) of 0.5 μm pore size at 1.75 kg/cm^2 and $15 \text{ }^\circ\text{C}$. Previously refined and bleached oil was flash cooled from 65 to $15 \text{ }^\circ\text{C}$ in about 3 min and matured for 10 min at $15 \text{ }^\circ\text{C}$ to grow the wax crystals of $0.1\text{--}50 \text{ }\mu\text{m}$ size and filtered in cross-flow mode [98]. The initial flux was $42 \text{ l/m}^2 \text{ h}$ and no drop in flux was observed for hours. Back flushing was done every 3 min for 5 s at 7 kg/cm^2 . The oil produced was excellent after a 3-day chill test. The rate of cooling the oil affected the crystal size, which could have an effect on the efficiency of the MF membrane [43].

Bleaching

Color compounds in vegetable oils, e.g., chlorophyll, carotenoids, xanthophylls and their derivatives, are removed by adsorption on activated clay or carbon. The high cost of bleaching earth, the associated oil loss (equivalent to 30–70% of the weight of the activated earth) and subsequent disposal hazards have led to an interest in the application of membrane technology to replace the traditional bleaching process. An economic analysis of membrane bleaching suggests that \$730,000 could be saved each year from a 250-ton/day plant [75]. If membranes are employed for degumming in the plant, then a separate bleaching step may not be necessary since it also reduces color compounds [75, 77]. Subramanian et al. [99] demonstrated the extent of color removal by solvent-free crude vegetable oil processing using NTGS-1100 and NTGS-2100 polymeric composite membranes. Despite extensive research, there

appears to be no suitable membrane that will selectively remove color compounds from oil because of the similarity in molecular sizes [100].

Removal of Metals

Vegetable oils contain traces of heavy metals (0.1–0.7 ppm) originating from the oilseed itself and from containers and pipes. Heavy metals especially metals of variable valences in oil are detrimental because they act as a proactivator in auto oxidation and lead to color fixation at high temperatures [101]. They are generally removed by chelating with phosphoric, citric, tartaric acid (acid washing). Ceramic membranes with a pore size of 0.01–0.2 μm have proven effective in removing nickel to less than 1–10 ppm [87].

Micronutrient Enrichment

Although RBO is very important for its fatty acid profile and micronutrients, such as tocopherol, tocotrienol and oryzanol, and these valuable components of RBO are reduced drastically during the conventional refining process because of added chemicals and the high temperatures involved. However, much work has yet to be done on membrane processing of RBO [102].

Tocopherols are relatively lower molecular weight compounds (MW 402–472 Da) than TAG and do not seem to have an affinity for PL reverse micelles, but have more affinity to membranes with a silicon active layer than TAG. This characteristic of tocopherol results in less permeation of it through the membrane, or, in other words, negative rejection [89]. Therefore, membrane processes seem to be a beneficial process for refining the oil as well as preserving the natural antioxidants in oil.

Subramanian et al. [103] studied membrane permeation of TAG (>800 Da)—tocopherols (431 Da) model systems, where tocopherols did not permeate (–51 to –29% rejection) through nonporous membranes and consequently its concentration in the feed increased from 0.144 to 0.67%. However, the total permeate flux remained almost constant (0.098 and 0.104 $\text{kg}/\text{m}^2 \text{ h}$) through out the process despite a large change in tocopherol concentration in the feed.

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