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ARTICLE

Membrane Assisted Edible Oil Deacidification

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1. Abstract

Although humans started using edible vegetable oils as a part of food, ages ago, there have been considerably lesser improvements in the way they are refined. Chemical and Physical Refining processes are surely the best in terms of the quality of the oil obtained, but they lead to neutral oil loss and higher energy consumption respectively, necessitating the urge to find processes with lower oil losses or energy required, yet giving similar quality oil. These drawbacks are majorly due to the deacidification step, which is a part of the whole refining process. To address this, many researchers and scientists have been working for decades and have found some good alternatives, which carry out decidification in a sustainable and greenway. This article focuses on one such solution i.e., Membrane Assisted Edible Oil Deacidification, which has the potential to be introduced as an alternative for the conventional refining methods.

Keywords: Edible Oil, Free fatty acid, Membrane Processes, Green Processes.

2. Introduction:

Since the inception of human life, food has been the basic necessity for survival and growth. There are many kinds of foods that are consumed daily which contain some nutritional components responsible for the effect that the foodstuff is expected to do. These foods are derived from plant or animal sources and therefore contain nutrients in different proportions. There are three main classes of foods namely carbohydrates, fats/oils, and proteins. The edible oils majorly consist of vegetable oils and need to be obtained from plant sources. The oil is naturally formed in the parts of the plants and exists in cellular structures, which need to be ruptured by various treatments to obtain the oil. The extraction of edible oils has been practiced for a long time and requires different techniques for different sources. This extracted oil was initially used as is, without any further treatment. But in the 20th century, methods were developed for the refining of these crude vegetable oils. The refining process includes a series of steps that are carried depending on the composition of the crude oils.

The steps include degumming, dewaxing, deacidification, bleaching, and deodorization. The process of chemical refining was the first process to be adopted for edible oil refining and yielded pure edible oil with very few impurities. But this process yields large amounts of neutral oil losses due to saponification during alkali refining, residual oil during dewaxing, and filtration processes to remove bleaching earth. The major neutral oil loss occurs in the alkali refining step, and a substitute was needed for the same. In the 1960s, a better process for the refining of the oils was introduced which physically refined the oil by stripping the free fatty acids. Though this process was effective in reducing the free fatty acid content with lower loss of neutral oil, it was very energy-intensive requiring loads of energy to vaporize the fatty acids, let alone the deodorization process, which is similar in fashion, requiring lower temperatures. After the development of the physical refining process, there has not been any new invention or modification in the process since the 1960s. This raises a need to formulate a process that is less energy-intensive, causes lower neutral oil losses and reduces the free fatty acid content to acceptable standards.

A variety of different processes have been tried including biological, physical and chemical methods to reduce or convert the free fatty acids present in the oils, leading to acceptable oil quality. One of the very logically simple methods is the re-esterification of the free fatty acids back to the TAGs. One scientist enzymatically carried out the re-esterification of the FFA (34), using the Novozyme 435 enzyme. The reaction was carried out at 60oC and a stoichiometric or less amount of glycerol was added for the re-esterification since some MAGs and DAGs were also re-esterified. Chemical re-esterification with or without catalyst was carried out requiring temperatures as high as 270oC and inter atmosphere, resulting in higher energy usage and costs. Another method that is superior to chemical and physical refining is solvent extraction using short-chain hydrocarbons as solvents (39, 40). These solvents selectively dissolve the fatty acids and can be separated from the remaining oil phase. After extraction, the solvent and FFA mixture can be stripped to get the solvent back. The stripping can be performed at about 80oC. A recent study (46) suggested the conversion of the FFA to valuable products, which fetch a higher price, thus making up for the expenses. The researchers conducted the deacidification of high-acid Rice Bran Oil using ethanolamine and CaO as the catalyst for amidation, yielding fatty acid ethanolamines. The process resulted in the residual FFA content of 1.1% in the RBO.

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Membranes were also used for the deacidification of edible oils, since the 1980s. Looking at the big picture, there are majorly three schemes in which the membrane deacidification can be carried out; Direct Deacidification, Deacidification with pre-treatment followed by membrane separation, and Deacidification by solvent extraction, followed by membrane separation. The direct deacidification process is not a feasible option as the size difference between the FFA and TAG is not substantial to give acceptable oil quality. The Pretreatment in the second scheme yields soaps which are to be separated by membranes, making the process not very different from alkali reefing. The third scheme of solvent extraction followed by membrane separation is a feasible and superior option resulting in edible oils of acceptable quality. This method of deacidification is less energy-intensive, causes lower oil loss, and yield good quality oil, which is fits for processing and consumption.

3. Composition of Edible Fats and Oils

Fats and Oils are composed of triglycerides (>95%), and the remaining 5% are termed as minor constituents. The main difference between fats and oils is the physical state in which they are present, and both of these are a part of the term “Lipids”. The fats are semi-solid to solid at room temperature while the oils attain the liquid state at the same conditions. The edible oils can be obtained from sources like seeds, pulp, leaves, nuts of different plants and trees, and also from animal sources like chicken, beef, mutton, whale, shark, and so on. These oils, apart from their edible uses, are also used for cosmetics, personal care, laundry, and other applications. The minor constituents forming the 5% weight of the oils obtained include lipid moieties like phospholipids, monoglycerides, diglycerides, glycolipids, antioxidants like tocopherols, tocotrienols, which are also a part of Vitamin E, pigments like chlorophyll, beta-carotene, xanthophyll, free fatty acids, short-chain odoriferous compounds like aldehydes, ketones, esters, and some trace metals too 1. All these minor components are termed as the unsaponifiable fraction of the oils, as these will not lead to soaps on reaction with alkalis.

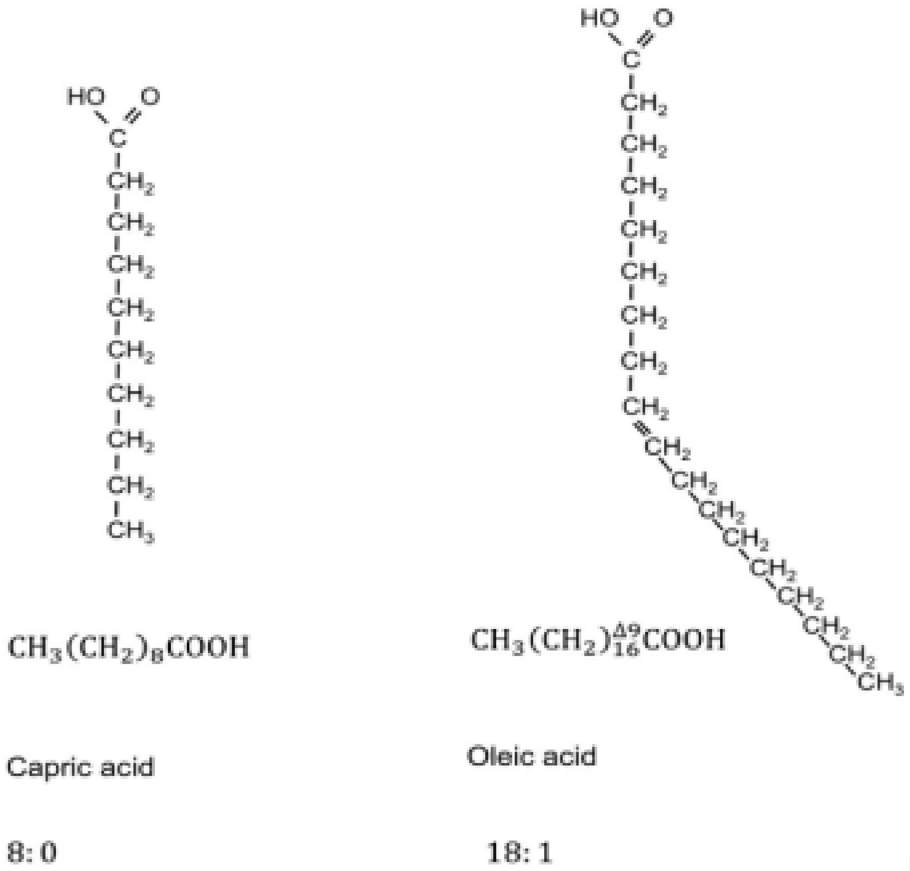

Fig 1

The structure of edible oils is generally referred to as the structure of triglycerides as they form the major components of the oils and fats. The triglyceride structure has a glycerol backbone which is substituted by three fatty acid chains as esters. This is the reason why some papers mention Triglycerides as Triacylglycerols (TAGs). The oils are mainly defined based on the fatty acid compositions and not the triglyceride compositions. The fatty acids in oils exist in the esterified form or are present as free acids. The fatty acids are long-chain carboxylic acids that chain lengths from C8 to C18, but fatty acids with C20, C22 and C24 are also found. These fatty acids are both unsaturated and saturated, with the fractions from C18 to C16 being completely saturated, while the fatty acids with carbon numbers from C18 to C22 may be mono-unsaturated, or poly-unsaturated referred to as MUFA and PUFA, respectively2. The cis geometrical isomer of the unsaturation is the one that is commonly found in nature, despite its lower thermodynamic stability. This cis geometry is prone to the formation of trans isomers when exposed to prolonged heating. The composition of the oils, i.e., the triglyceride and the unsaponifiable matter may vary in content and composition based on the source. This is the reason why there is no typical type of triglyceride that can be termed as oil. These variations arise due to the presence of different species and environmental conditions which leads to the growth of the plants or animals 3.

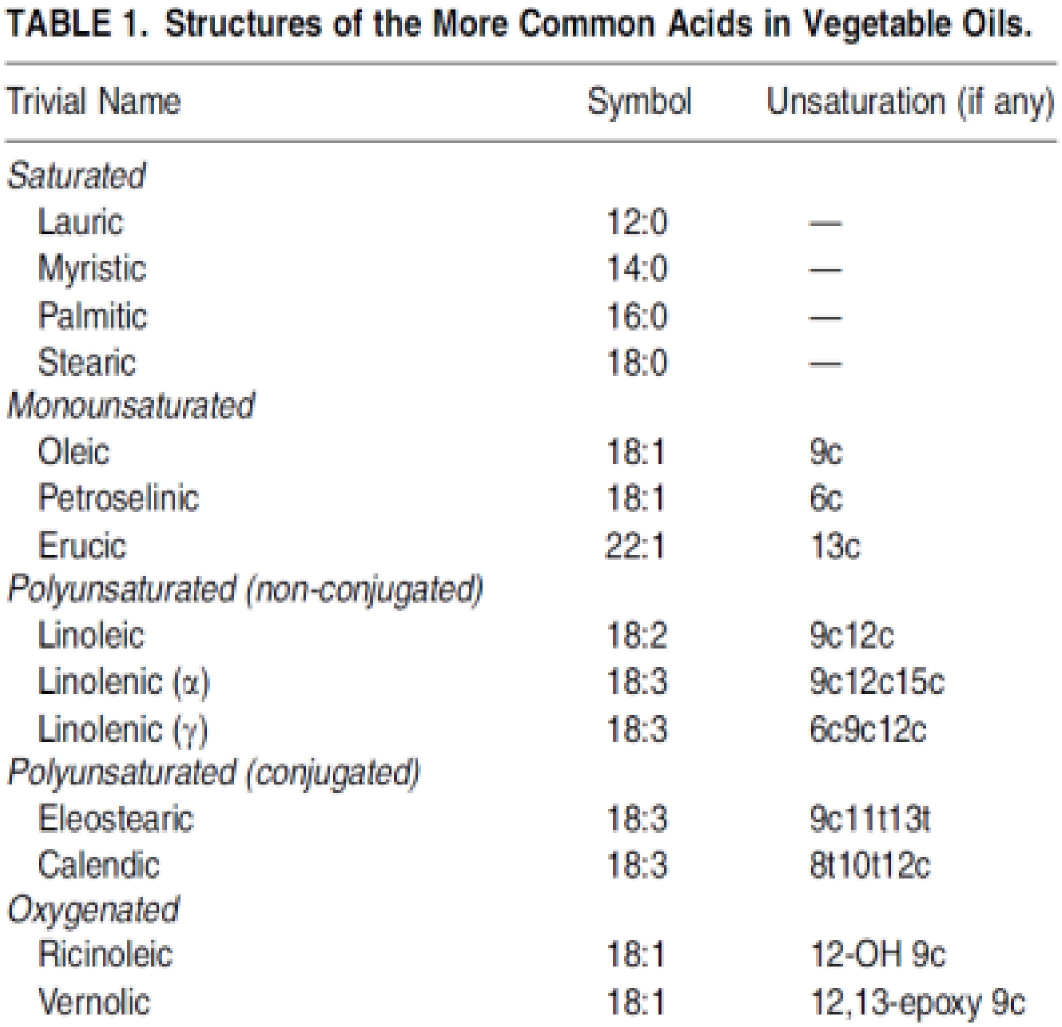

TABLE 1. Structures of the More Common Acids in Vegetable Oils.

Trivial Name	Symbol	Unsaturation (if any)
Saturated		
Lauric	12:0	—
Myristic	14:0	—
Palmitic	16:0	—
Stearic	18:0	—
Monounsaturated		
Oleic	18:1	9c
Petroselinic	18:1	6c
Erucic	22:1	13c
Polyunsaturated (non-conjugated)		
Linoleic	18:2	9c12c
Linolenic (α)	18:3	9c12c15c
Linolenic (γ)	18:3	6c9c12c
Polyunsaturated (conjugated)		
Eleostearic	18:3	9c11t13t
Calendic	18:3	8t10t12c
Oxygenated		
Ricinoleic	18:1	12-OH 9c
Vernolic	18:1	12,13-epoxy 9c

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4. Extraction and Processing of Edible Oils

Man, since his early days of life, started to find techniques and methods to extract oil from plant and animal sources. The production or extraction techniques to be used depending on the raw materials, like oilseeds, pulp, fruits, nuts etc. Of these, the oilseeds and nuts are the most durable and can be stored under certain conditions for future use, but the fruits or pulp has to be processed right away as the deterioration can start immediately after the oil is in contact with the external environment. This is also true for animal fats 5. The methods for extraction of oil from the oilseeds requires seed preparation procedures like dehulling, cleaning, drying, size reduction, crushing, heating/drying, flaking and extruding. These seeds are then further sent for extraction which can be done by various methods like mechanical extraction processes like filter press, full press extraction, and solvent extraction as shown in Fig.2. The type of techniques used depends on the oil content present in the oilseeds1.

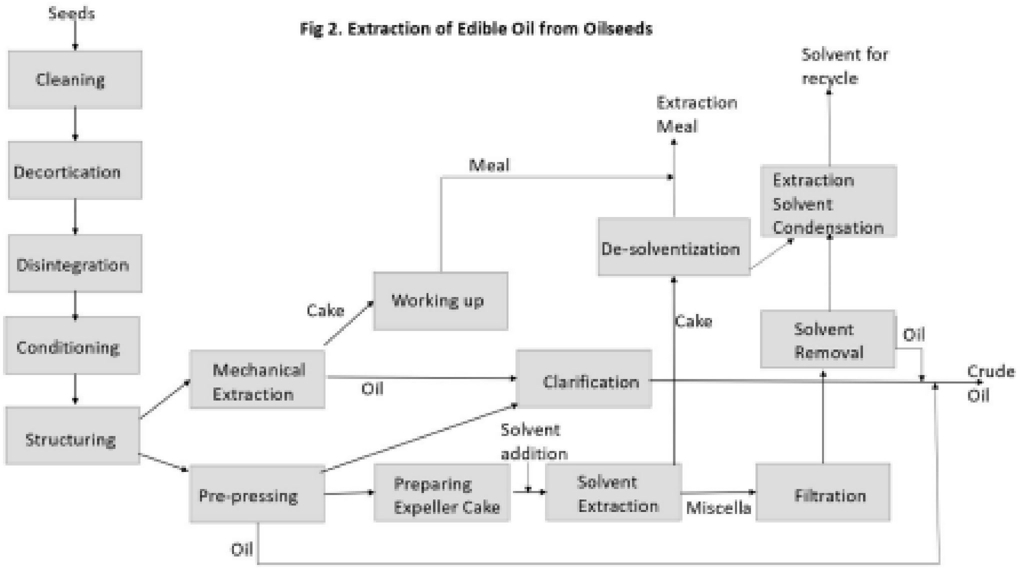


Fig 2. Extraction of Edible Oil from Oilseeds

After extraction of the oils from the raw materials, the next step is to carry out the refining process. The sequence of the steps carried out during refining is as depicted in Fig 3. The oils contain more than 95% triacylglycerols, while the remaining 5% are the free fatty acids, waxes, phospholipids, pigments, and hydrocarbons. The presence of these unsaponifiable materials makes the oils look darker in colour, leading to odours, high viscosity, presence of residue and precipitation. This makes the oil unappealing to the consumer and he/she refrains from buying the oil as it is. Another reason for refining the oils is that the presence of free fatty acids will lead to storage problems as they are highly corrosive and damage the storage vessel or container, in the plant or at the store. These free fatty acids also lead to the formation of oxidation products, especially if they are unsaturated, and this leads to the deterioration of the neutral oils also. While cooking, the oil will smoke at a lower temperature, as the fatty acids have a lower smoke point.6 The fatty acids are removed by chemical or physical refining at increased temperatures of 55-80oC, also leading to some oil loss 7. The presence of waxes and phospholipids in the oil will not cause any harm if consumed but it makes the oil look dirty and their sedimentation is evident at low temperatures. The main reason the phospholipids are removed from the oils is because of their emulsifying properties which will lead to oil loss due to soap formation in the chemical refining step for the removal of free fatty acids and also due to the vulnerability to microbial infestation. The waxes are generally cooled and centrifuged or precipitated, facilitating their removal. There are two types of phospholipids, namely hydratable and non-hydratable phospholipids. The hydratable ones are removed by water washing leading to precipitation. The removal of non-hydratable phospholipids is not possible by this method directly and requires an additional step of acid treatment at high temperatures with phosphoric acid or citric acid. The temperature of the degumming vessel is raised slowly. This acid treatment makes the non-hydratable phospholipids hydratable, and they can be subsequently removed by water washing 8. The pigments give colour to the oil and are naturally present in it. These include carotenes, xanthophylls, chlorophyll, etc which are also not harmful but due to their colour, the consumer feels resistant to consumption. The cottonseed and rice bran oils contain gossypol and Maillard Browning compounds respectively which lead to the presence of dark colour in the oils and needs to be removed for sure. Another reason for the removal of the pigment chlorophyll is the fact that it leads to the initiation of oxidation in the oils and can cause rancidity in the presence of light. This removal of colouring compounds from the oils is termed the bleaching process. This process uses acid-activated earth at 2-3% concentration and is based on the process of adsorption. The temperature is 120-130oC and vacuum pressure is maintained. After the completion of this process, spent bleaching earth is generated which is a waste and also leads to oil losses by retaining the oil during adsorption 9. The hydrocarbons like aldehydes, ketones, ester which are short-chain hydrocarbons formed during the oxidation lead to unpleasant odours due to their low volatility, and therefore need to be removed. These short-chain hydrocarbons are removed by steam stripping at an almost complete vacuum of 1-4 mmHg pressure and a high temperature of 120-200oC 10. After the completion of each of these refining steps, the oil is suitable and fit for storage, consumption, and other oleochemical applications. Due to this multistep process extremely high amount of energy consumption is seen in terms of heating and cooling of the feeds, pumping costs, treatment of aqueous effluents, maintenance of vacuum or high pressure, etc. Apart from this, a high amount of waste is generated in the form of bleaching earth, and oil losses occur throughout the steps 1.

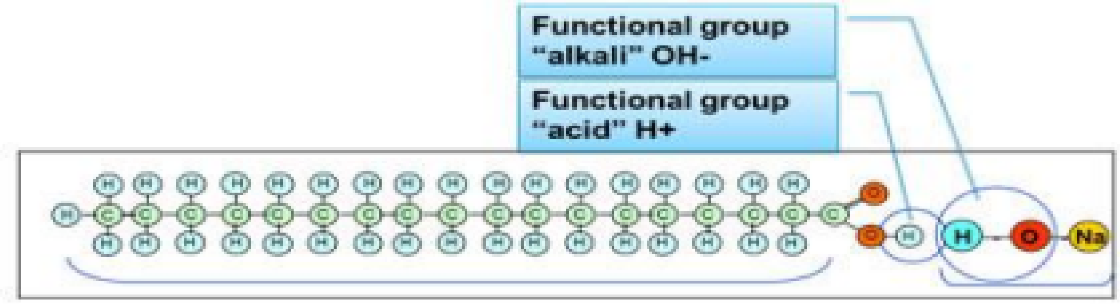
5. Conventional Methods of FFA removal and their drawbacks

After the oil has been extracted from its source, it immediately starts to deteriorate in its quality, though at an extremely slow rate and produces free fatty acids. These fatty acids need to be removed since they decrease the pH of the oil, which is meant to be neutral. The presence of fatty acids leads to corrosion of the vessel in which they are stored are used, and can cause frequent replacement of such equipment. Smoking of the oils at lower temperatures is also a major cause of the removal of FFA 7. This problem was identified much earlier and processes for the removal of these fatty acids were developed. Since then, these processes have not been through any major developments and are in use for the last 8 decades or more. Apart from this these conventional processes lead to high energy consumption and oil losses 1, which in turn have to be compensated in the edible oil prices, leading to an increased burden on the pockets of the manufacturers and consumers. The aim of this paper is to suggest possible alternatives to the conventional process by reviewing the literature and the feasibility and limitations of those process technologies. The oils can be refined by a series of processes under the terms Chemical Refining and Physical Refining. Physical refining is a cost-effective method with low waste and oil loss, but cannot be applied for all the oils, due to their varied compositions 11. The terms Physical and Chemical Refining arise from the kind of processes that are used to get rid of the FFAs from the crude oils 12.

5.1. Chemical Refining

The removal of free fatty acids is essential as oils containing high amounts of FFA are cannot be stored for an extended period, especially in presence of moisture and high temperature as these conditions make the oils prone to oxidation and rancidity. This step follows the degumming operation in the whole refining process (6).

The fatty acids are detached from the triglyceride molecule, which contains three fatty acid molecules esterified with the glycerol backbone, leaving behind a mono- or diglyceride. This leads to an increase in the FFA content and hence acidity of the neutral oil. The FFA content of oils are measured by determining the Acid Value of the oil. The Acid Value is measured as the milligrams of alkali (KOH) required per gram of oil. The desired FFA content and Acid Value in the edible oils are 1% and <0.5 mg KOH/ gram of oil, respectively [13]. Apart from this standard method by IUPAC, some other methods of determining the FFA content in oils have also been devised, which use fewer chemicals and produce lower amounts of waste [14].



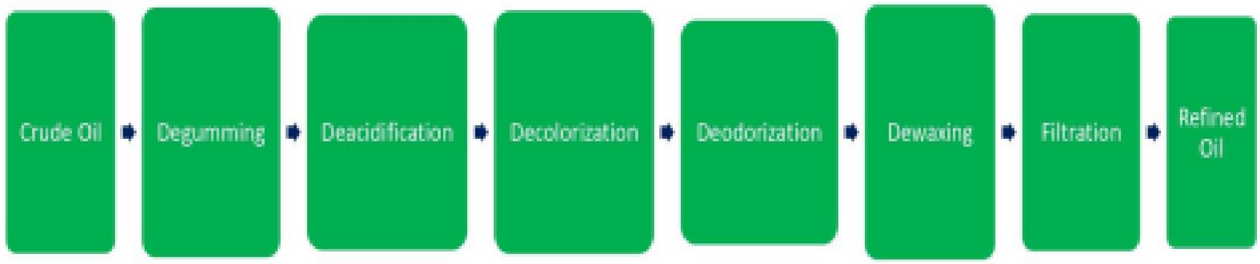


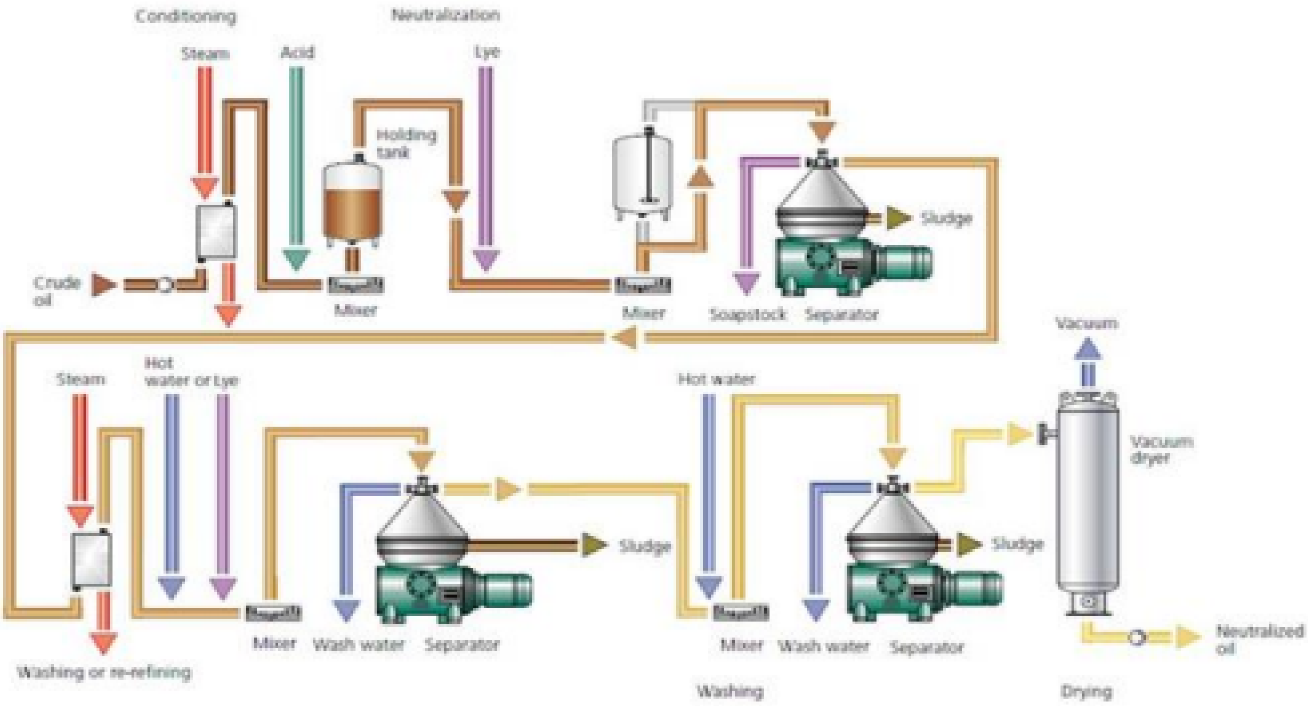
Fig3. Steps in Edible Oil Refining (Chemical Refining)

(12)

The most widely used process which applies to almost all the oils and provides very efficient removal of free fatty acids is Chemical Refining, Alkali Refining or Neutralization Process. The main aim of this process is to convert the FFAs to soap by use of alkalis, and by subsequent dilution of the soap and removal by phase separation or centrifugation. The commonly used alkali in the industry is NaOH, while potassium hydroxide can also be used [7]. This process is extremely essential for the crude oils containing high acidity and is therefore mandatory to carry out for high Acid Value Oils. The FFA content of the oil is important for the determination of the required amount of caustic soda.

The process of chemical refining demands a clean and dry oil, devoid of any impurities like particulate matter which may damage the equipment. The most commonly adopted operation is a two-stage separation process, while three-stage and single-stage processes also exist. The three-stage process (Fig. 4) is used for special oils like cottonseed oil, which contain high FFA and to obtain a superior oil quality and reduce process losses [12]. The careful removal of FFA is very important to ensure a good yield of the further refining steps [7].

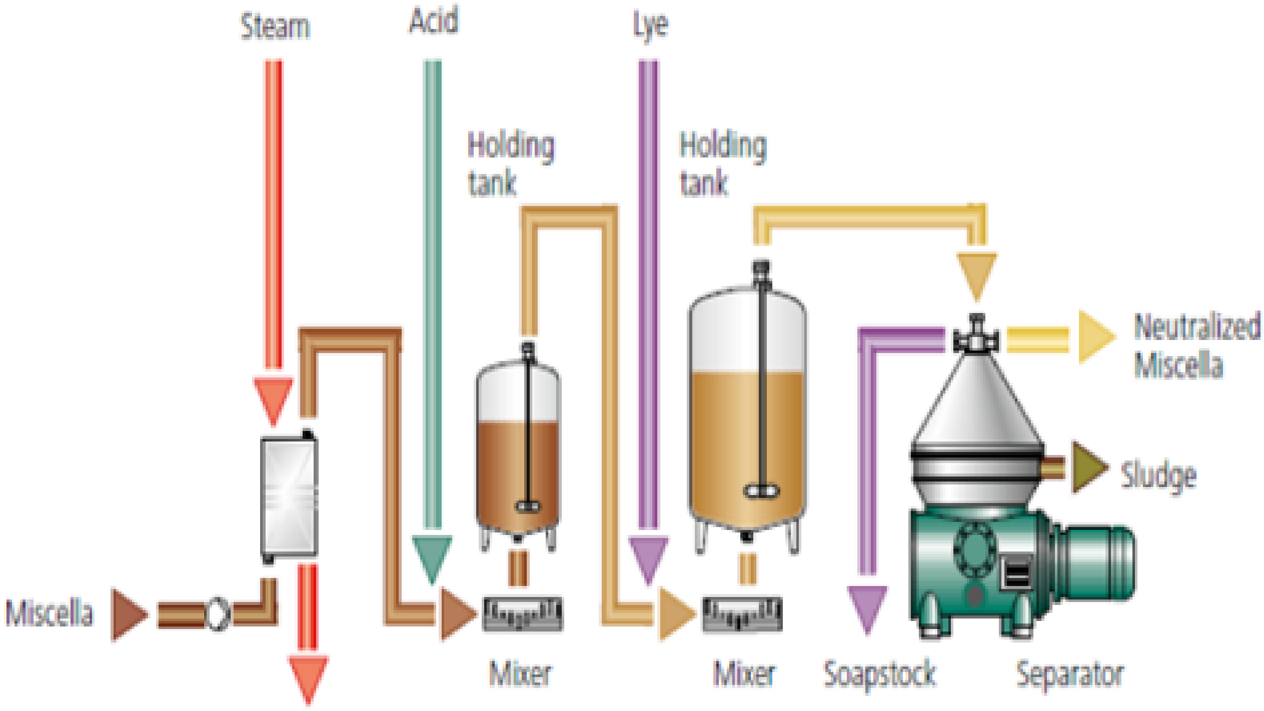
The first stage includes the crude oil



(12)

Fig. 4 Three-stage Neutralization

heating, conditioning, and neutralisation steps. The heating of the oil is performed with the help of steam using a plate heat exchanger. The oil is fed to the heat exchanger by a positive displacement pump before which, filter/strainer is installed to trap and particulate impurities. Low-pressure steam at 3 bar abs, and 133°C is fed in the heat exchanger and the oil is heated to 80-85°C. After this step, the hot oil is passed to a mixer, before which a sufficient quantity of 75% H_3PO_4 is used to condition the non-hydratable phospholipids (NHP) if present. This oil and phosphoric acid mixture is pumped to a holding tank to allow for the desired contact between the NHP and H_3PO_4. These phospholipids are now converted to hydratable phospholipids and can be removed during the water washing step. In the neutralization step, the caustic soda is added right before a dynamic mixer then leading to a hydration tank. The amount of the caustic soda is such that the FFA present in the oil, and the H3PO4 added in the conditioning step get completely neutralized. Apart from the required stoichiometric amount required for the neutralization, certain excess of NaOH is added, depending on the quality and type of oil. Generally, NaOH in an excess of 5-20% is added. The NaOH stored in the caustic tank is of 32% or 50%



concentration. The NaOH must be diluted to the desired concentration before mixing, and the dilution is determined by quality and type of oil. This mixture of oil and alkali is transferred from the mixer to a hydration tank and agitated at a slow stirring speed. The is done to improve the hydration of the phospholipids and to coagulate the soaps. The total time required for neutralization is 30 minutes. This coagulated mixture is passed on to the centrifugal separator which separates the mixture into the oil phase and an aqueous phase containing soaps and phospholipids.

The second stage, also called re-refining, is only employed in certain cases like poor-quality oil or especially Cottonseed oil which contains the colour compound called gossypol which needs to be eliminated. For all other types of oils, this re-refining is skipped. Another plate heat exchanger is used to heat the oil again to the optimum temperature using steam. The procedure is similar to the neutralization step followed by the centrifugal separation generating soap stock and neutral oil. This oil is passed through a step called First Washing, where the residual soap from the first and the second stage is removed using a hot water stream. The hot wash water stream is added to the oil at the optimum temperature and mixed intensively in the dynamic mixer and this mix is passed on to the centrifugal separator to separate the oil phase and the water phase enriched with soap.

The third stage consists of water washing and will be the second stage in case re-refining is skipped. The washing is performed in the same way and leads to low residual soap contents in the neutral oil. If extremely low residual soap contents are desired, as in the case of pharmaceutical applications, an additional step of wash water acidification is performed. In this step, water acidified with either citric or phosphoric acid is used and the neutral oil is washed with it and subsequently separated using a centrifugal separator.

The last step of vacuum drying, which is carried out at a low pressure of about 50-100 mbar absolute with the help of a multi-stage steam jet vacuum pump with mixing or surface condensers. The high surface area created in the dryer ensures efficient evaporation of residual water from the oil phase.

A special method developed originally for the refining of crude cottonseed oil consists of a few steps leading to some effect on the economics. This process is called Miscella Refining and is used for solvent-extracted edible oils (Fig 5). The hexane oil miscella obtained after seed extraction has to be concentrated by the addition of cold pressed oil or by evaporating some of the hexane. This concentrated miscella is then brought to a temperature just below the boiling point of hexane and phosphoric acid or citric acid is added to hydrate the NHP and mixed intensively. Subsequently, caustic soda solution is added to neutralize the FFA and the acids added. The mix is then transferred to centrifugal separators which give an efficient separation of the polar and the non-polar phase due to large differences in their densities, rendering the elimination of the vacuum drying step.

(12)**Fig. 5 Miscella Refining**

5.2. Limitations of Chemical Refining and some modifications:

Although chemical refining is the most efficient method for FFA neutralization, there are some disadvantages which are a reason why some alternatives to this process must be looked out for [15]. The presence of NaOH in the chemical refining process also leads to hydrolysis of TAGs leading to increased FFA content in the oils. The alkaline environment can lead to undesirable oxidative processes causing stability issues [16]. Along with the deacidified edible oil obtained using caustic soda, a large amount of soap stock is obtained [17]. The presence of soap, water and neutral oil leads to appropriate conditions for the emulsification of oil in the aqueous phase, and due to the excellent emulsifying properties of the sodium soaps, a considerable amount of neutral oil is lost in the separation step. This loss is higher in crude oils containing higher FFA and also in Rice Bran Oil, due to the presence of oryzanol, waxes, and long-chain fatty alcohols than the oils with similar FFA contents [15]. The emulsion of oil in the aqueous phase can be broken to some extent by the centrifugal separation process or a little higher breaking can be obtained by using electrolytes like NaCl, Na_2SO_4, KCl, etc according to the research conducted on model crude oils by Chumsantea et.al. [18], but the loss of neutral oil will still occur as when this method is applied to crude oils. Apart from this, a huge amount of wastewater is generated containing soap, unreacted alkali, and other compounds formed by the reaction of NaOH with impurities. This wastewater generated must be treated before discarding it and therefore leads to higher energy consumption demanding more capital. Another problem is that the soap stock that is generated due to the neutralization reaction needs to be either acidulated with sulphuric acid, to produce fatty acids again or needs to be purified to be used in soap making, this again leads to pollution and more energy consumption.

To tackle some of these issues, an approach to re-esterify the high amount of FFA in rice bran oil was used. This required the addition of glycerol at a high temperature in the presence of 0.2% $SnCl_2$ as a catalyst. The maximum efficiency was attained at 200^{o}C and 70% excess glycerol than the FFA content and the maximum reduction in AV obtained was from 24.3 to 4 in 4 hours. Since there is no way to form only triacylglycerols from this process, this oil cannot be used for edible purposes and has to be used in oleochemical applications [19]. There are some modifications to the conventional refining process that can be potential alternatives, but need to be investigated thoroughly [20]. One approach to reducing the oil losses was used by Tang et.al., employing perforated distribution plates for better contact of FFA with the alkali [21]. De and Patel demonstrated a modified approach to alkali refining using $Ca(OH)_2$, high temperature and low pressure, and obtained an FFA content of 0.8% in 2 hours [22]. An efficient way for alkali refining was suggested by De Greyt providing reduced use of alkali by over 30%. This process was based on hydrodynamic cavitation carried out in nano-reactors at pressures of 40-80 bar. This method was not approved by the industry despite its high efficiency, due to high energy requirements [23].

A completely different approach to eliminate the FFA from crude palm oil with lower energy consumption and thus lower cost, and lower amount of waste and pollution, the process of Physical Refining, was thought of due to the compulsion by the Malaysian government to reduce pollution and wastage in the 1970s [17] and is used even today for a variety of oils.

5.3. Physical Refining

An alternate method to the very first method of edible oil refining was developed in the 20th century, during World War II, when developments in the continuous deodorization process were in force. The process was initially only used for the deodorization of saturated fats too low unsaturated fats. The Physical Refining of oils and fats to remove FFA, odoriferous compounds, and some flavour compounds uses steam as the main component required for stripping off the volatile components 24. Initially, only batch industrial deodorizers were operated, under vacuum to facilitate in stripping of the volatile compounds while avoiding the oxidation of oil 25. The steam used was super-heated so that hydrolysis of the oils could be avoided. At the beginning of its development, it was only used for the deodorization of the alkali-refined oil. As the years passed, the deodorization step evolved into a complete process that involved the removal of not only the volatile compounds from lipid oxidation but also free fatty acids and unwanted pigments by heat degradation 26. The saturated and low unsaturated oils like palm oil, palm kernel oil, coconut, oil, lard, cocoa butter were the source of fats in the 19th and 20th centuries, and this led to the development of deodorization only for these oils. Due to the stability of the fats, the temperatures employed for deodorization were very high. The deodorization temperature for lard was 205-265oC when the acid value was desired to be reduced and about 193oC with a considerable amount of phospholipids, the deodorization temperatures needed to be decreased to inhibit oxidation of FFA and some pre-treatment methods like heat treatment of seeds before extraction to reduce the NHP content in oils need to be employed as the presence of NHP led to difficulties in the deodorization process 24.

when FFA removal was not desired. The process also lasted for 3-4 hours 24. The refining of palm oil requires temperatures of about 230-260oC which removes the FFA and volatile components and also destroys some of the carotene content due to extreme heat, leading to a relatively light coloured oil. For the application of the deodorization process to oils containing MUFA and PUFA in higher proportions, Physical refining, in its broader sense, includes the processes of degumming and bleaching too, before the deodorization/deacidification process. The ideal deodorization or physical refining in its narrower sense will include the removal of volatile compounds, naturally present in the oil and also the removal of off-flavours formed as a result of thermal degradation of larger flavour molecules. This removal of these unnatural compounds requires a longer time. If the duration of the process is very short, these flavour compounds would be partially removed and may lead to the development of odours again on storage and usage. This is also known as “flavour reversion” of the oil 26.

The main parameters for the process of deodorization are temperature, time, pressure, and the amount of stripping steam used. These process conditions affect the sensory and nutritional quality of the final product 27. Due to high temperatures, the FFA and other volatile compounds can get polymerized which also make the oil undesirable. The significance of the process conditions on the removal of unwanted components is listed with the ranges of the parameters for the desired results.

The physical refining of the edible oils can be performed in batch semi-continuous, or continuous processes, with the type of process to be used generally depending on the capacity of the plant and the type of feedstock used.

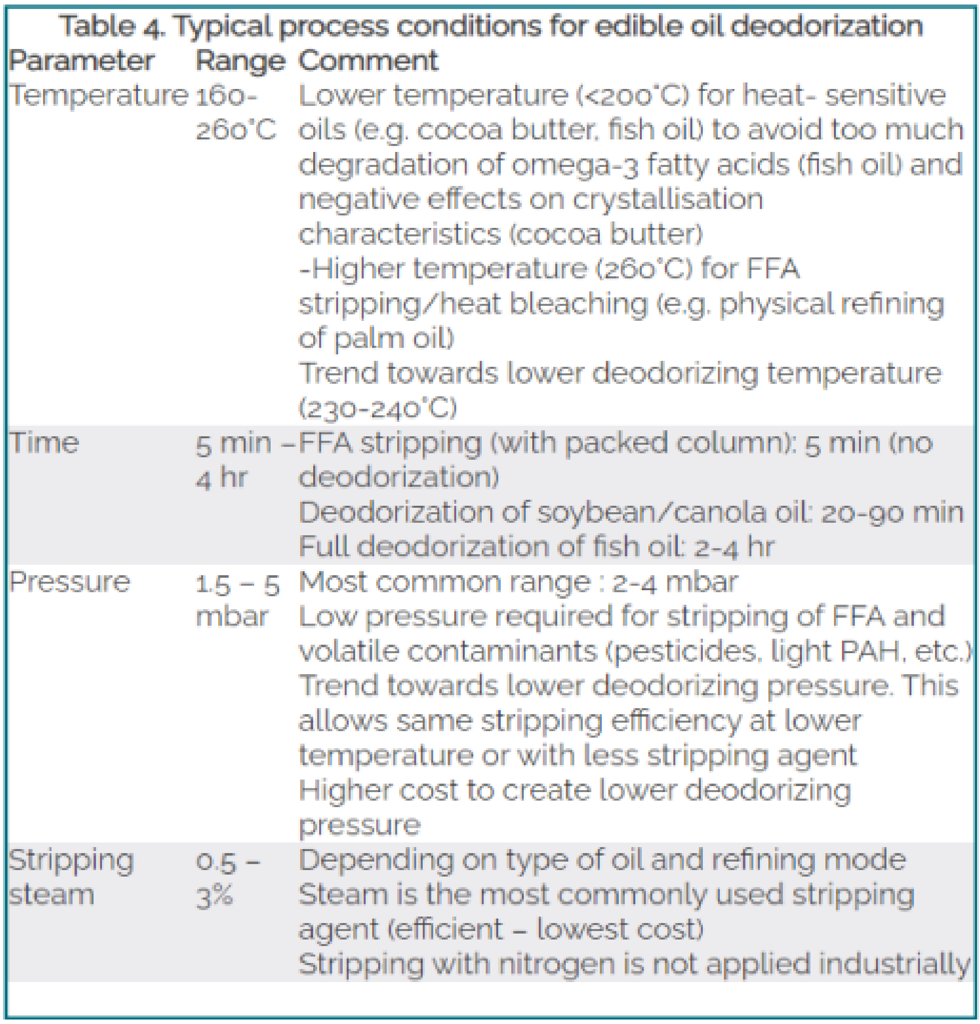


Table 4. Typical process conditions for edible oil deodorization

Parameter	Range	Comment
Temperature	160-260°C	Lower temperature (<200°C) for heat- sensitive oils (e.g. cocoa butter, fish oil) to avoid too much degradation of omega-3 fatty acids (fish oil) and negative effects on crystallisation characteristics (cocoa butter) -Higher temperature (260°C) for FFA stripping/heat bleaching (e.g. physical refining of palm oil) Trend towards lower deodorizing temperature (230-240°C)
Time	5 min – 4 hr	FFA stripping (with packed column): 5 min (no deodorization) Deodorization of soybean/canola oil: 20-90 min Full deodorization of fish oil: 2-4 hr
Pressure	1.5 – 5 mbar	Most common range : 2-4 mbar Low pressure required for stripping of FFA and volatile contaminants (pesticides, light PAH, etc.) Trend towards lower deodorizing pressure. This allows same stripping efficiency at lower temperature or with less stripping agent Higher cost to create lower deodorizing pressure
Stripping steam	0.5 – 3%	Depending on type of oil and refining mode Steam is the most commonly used stripping agent (efficient – lowest cost) Stripping with nitrogen is not applied industrially

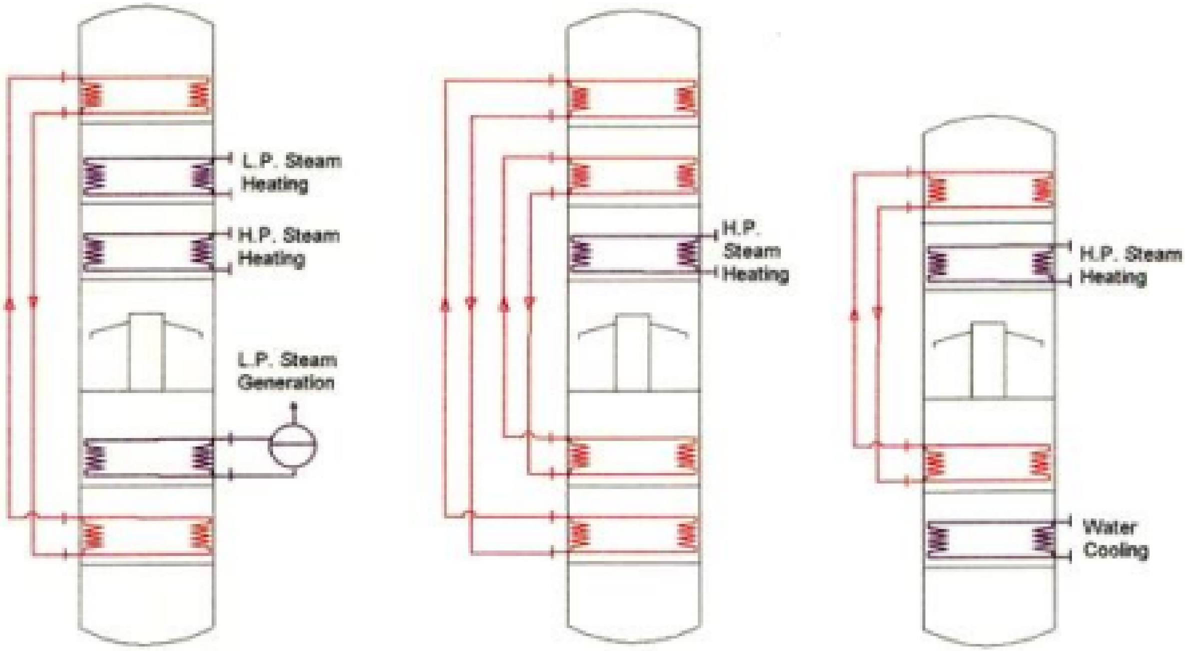
The batch process is used for small plants with <50 tpd or with plants operating on small batches of many different types of oils. The main features of the batch process are low capital cost for the setup of the plant and high flexibility towards the oil type and quality with every batch and minimal intermixing between the batches. The drawbacks of this process, which are the reason for its redundant use in larger plants are high operating costs due to more steam consumption, low heat recovery and longer process duration.

A semi-continuous process is a process employing the batch process for plants with a larger capacity that deals with different oils or oil products like margarine and shortening manufacturing plants. The heat recovery is done by the use of thermal siphoning, which is efficient than the batch process. The main advantages are low intermixing, short process time, and adaptability to feedstock changes.

For the high-capacity plants which operate only on one type of feedstock continuous process proves to be the best. The vertical tray deodorizing columns are the most common type of equipment used for continuous deodorization. This process employs a single column for all the steps in the refining of degummed and bleached oil, which allows easier installation, moderate costs, and low risk of air leakages. This is the process that most industries look up to for the physical refining of the oils.

The continuous deodorization process is a multi-step process starting from deaeration of the fat, to multi-stage heating, deodorization-deacidification, and multi-stage cooling of the oil. The oil from the bleacher is deaerated before physical refining to avoid oxidation or polymerization at high temperatures. This is accomplished either in a separate external vessel connected to the vacuum system of the bleaching equipment at 50 mbar or in an integrated vessel with the deodorizer, at even lower pressures [26].

The deaerated oil is heated usually in two or more stages. The first heating of the bleached and deaerated oil is done in the heat recovery compartment of the deodorizer by exchanging heat with the hot stripped oil. This method provides heat recovery up to 85% in the continuous deodorizer. The heat recovery can also be done in an external heat exchanger, but there is a risk of product intermixing, fouling, and loss of vacuum due to possible leakages.
Another method of heat recovery, mainly used for semi-continuous deodorizers in thermal siphon systems. This system also employs steam as the heating source, but there is a constant circulation of the steam in the equipment. The steam first heats the oil in the pre-heating section and gets condensed to water and flows down where it comes in contact with the hot deodorized oil and gets converted back to steam and reaches the top to heat the incoming oil. In this way, the steam flow in a loop system and provides heating and cooling functions with heat recovery of 45-75%. The heat recovery depends on the design of the system, with single or double loops, and the generation of low-pressure steam.



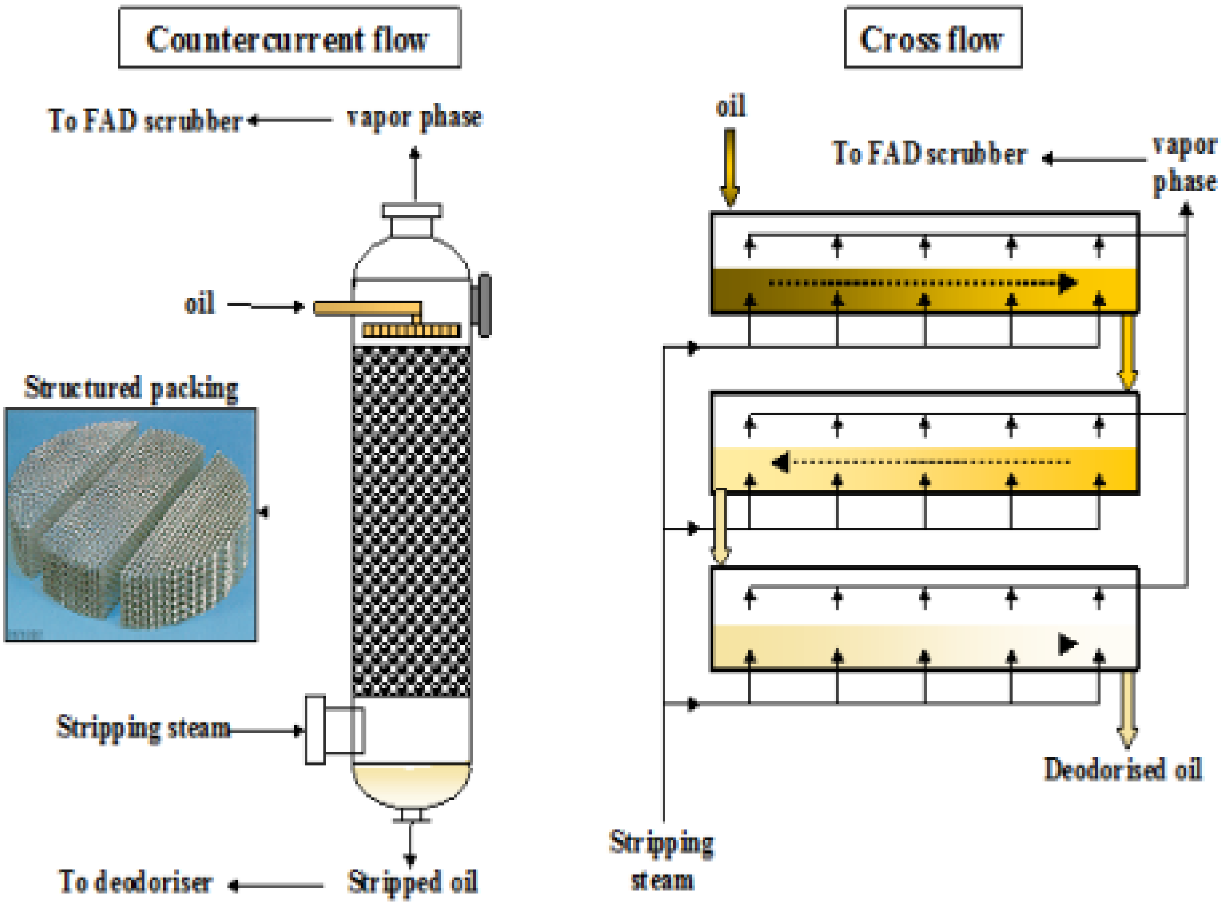
L.P. Steam Generation & Thermosyphon Heat Recovery 75%

Double Thermosyphon Heat Recovery 67%

Single Thermosyphon Heat Recovery 45%

After the oil has been heated to the desired temperature, it is transferred to the deodorizing compartment. To aid in the removal of volatile components, the stripping agent is injected into the stripping column. The most commonly used stripping agent is steam due to its economic feasibility. Nitrogen can also be used as the stripping agent and has been extensive, with low hydrolysis losses and higher quality of distillate as its advantages. But the fact that nitrogen is not condensable, while steam is, makes the removal of the stripping agent easy with a lower cost of the required vacuum system.

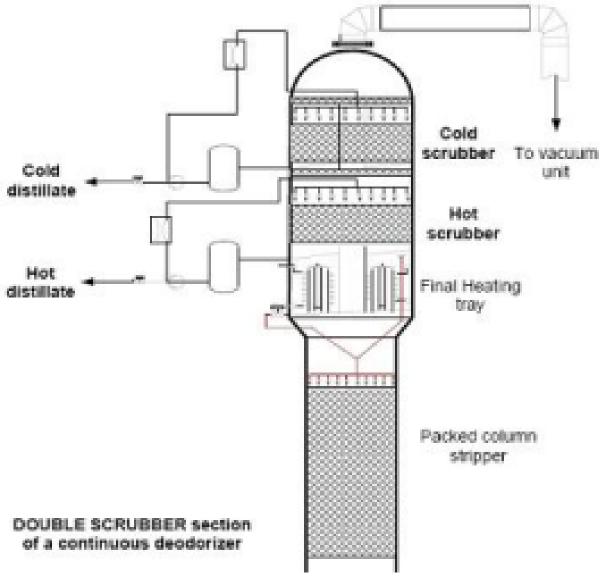
Modern deodorizers operate in a cross-flow or counter-current fashion by the use of trays or packings respectively for efficient stripping. Deodorization and deacidification carried out in a cross-flow regime employ the use of trays or compartments in which the steam is fed through the sparge coils with very fine orifices or by the steam lift pumps. The use of lift pumps provides excellent agitation of the oil, with frequent replacements of the top oil layer (the effective site of deodorization) and ensures high stripping efficiency. Using a packed column increases the efficiency of the process even further due to the higher surface area provided by the structured packings inside the column. A surface area as high as 250-350 sq.m/cu.m is available for the deodorization and deacidification process. Since there is no holding of the oil as in the case of trays, the duration of the process is very short. These types of strippers are in the application in the industry for many decades and are mainly used for increasing the capacity and throughput of the cross-flow deodorizers. The short residence time in the packed column is suitable for the stripping of heat-sensitive and highly unsaturated oils like fish oil and algal oils. But there is a drawback associated with this as shorter residence time will lead to incomplete deodorization, deacidification, and bleaching which has to be compensated for by employing an additional retention vessel before or after the packed column [26].



(25)

The last part of the deodorizer is the vacuum scrubber for the separation of the mixture of volatile components and steam. In the conventional deodorization process, which follows the chemical refining process, the vapour fraction consists of small amounts of volatile compounds like sterols, tocopherols, short-chain hydrocarbons, and some entrained glycerides which can be separated with a single scrubber and fetches higher value in the market due to the importance of the minor components of the oil. The price of natural tocopherols can vary from 20- 30 USD/ tonne of deodorized oil [28]. But in the case of physical refining, the vapour contains high amounts of FFA (about 85%) along with the minor components which have varied boiling points. This vapour mixture can only be separated into FFA and higher value minor compounds by employing a double scrubber. The FFA obtained from the distillate is used for technical applications like soap, biodiesel, and oleochemical production.

Condensation of the vapour and steam mixture



(25)obtained from the deodorizer is accomplished by creating a good contact and heat transfer between the hot vapours and cold distillate, recirculating over the scrubber. There is a packed bed of limited height in the scrubber on which the cold distillate is sprayed. To avoid any carryover of the fatty material to the vacuum system along with the steam, a demister is installed after the scrubber.

5.4. Limitations of Physical Refining

Although physical refining is a cleaner process than chemical refining, with a similar quality of refining achieved, there are still some drawbacks that lead to loss of the edible oil content and aesthetic appeal. For instance, the conversion of natural cis geometry of double bonds in the fatty acids to trans isomers at high temperatures while stripping, cause an increase in the trans fatty acid content in the oil which is harmful to health. Deodorization of soybean oil containing linoleic and linolenic acids, at temperatures of 240-290oC the formation of trans and conjugated fatty acids was observed 29. Degree of isomerization up to 35% can be observed when soybean and rapeseed oils are deodorized at 240oC, while at higher temperatures, polymerisation is also prevalent forming dimers at 0.32 to 2% 30,31. When oils rich in PUFA are heated to high temperatures, cyclic acids of 5-6 members are observed 32. The dimerization of sterols, which is a valuable minor component is also observed by the formation of ethers 33. The use of superheated steam and the application of an almost complete vacuum lead to higher costs of operation and the energy requirement is very high. These disadvantages or shortcomings of the physical refining process have searched for the novel, green processes for refining, especially deacidification, necessary. Due to the continuous work of the scientific community, there are some processes that have the potential to make the oil refining process cleaner and greener.

6. Green and Novel methods for Edible Oil Deacidification

There is no doubt that the conventional chemical refining and the later developed physical refining methods give the best quality of edible oils, with exceptionally low impurities, but the environmental effect, energy consumption and the waste which the processes lead to is of major concern, especially when climate change and waste reduction and recycling are the most trending issues in today’s time and date. Many researchers around the world are on the quest to find a novel and green process which would reduce wastage and energy consumption while providing a similar quality of edible oil. This is also necessary as there has not been any major change in the refining process, after the introduction of physical refining in the 20th century. This section will list the technologies that the scientists around the world have tried and will focus on a specific process which may be a potential process applied for refining; deacidification of the edible oils, as this is the process that leads to major losses and wastage.

One of the simplest methods is the re-esterification of the FFA present in the oil back to TAGs. Makasci et.al., performed the re-esterification of the degummed and dewaxed, high-acid olive oil by using enzymes. The lowest FFA content observed after the reaction was 3.7%. The reaction was sensitive to water content, as higher water content led the reaction in the reverse direction while less or no water present in the system affected the activity of the immobilized enzyme, Novozyme 435. The excess water was removed by maintaining a vacuum of 20 mm of Hg or by purging dry nitrogen gas in the mix, also providing agitation.

The optimum ratio of oil to the enzyme was 10:1 and the optimum water content is 1%. An amount of glycerol, equal or slightly lesser than the stoichiometric amount required by knowing the acid value, gives a very good reduction in FFA content. Some FFA was also consumed by the MAGs and DAGs present in the oil. The optimum temperature for the reaction was found to be 60oC, as higher temperatures, about 70oC led to enzyme deactivation 34. The use of enzyme is a green method, but the higher cost of the lipase enzyme and insufficient reduction of the FFA to the quality standards are of concern for the process to replace the conventional processes. Microorganisms were also suggested for deacidification of the oils, as they preferentially take up FFA for metabolic purposes. But the limitation here is the residual FFA like linoleic acid and fatty acids with less than 12 carbon, which is of no use to the microbes, and may act as a growth-inhibiting agent, and the higher cost of the microbial culture 35.

Apart from biological processes, chemical re-esterification is also possible. These re-esterification reactions are carried out in the presence of high temperature and inert atmosphere, with or without a catalyst 36. The FFA are consumed by the partial glycerides present in the oil, or by the addition of glycerol. The high temperature, up to 270oC, and inert atmosphere, makes the process expensive and energy-intensive 37.

Specific solubility of the FFA in some solvents can be exploited to deacidify the crude oils. One such approach was taken by Dunford and King 38, by using Supercritical CO2 in a column extractor with a temperature gradient, for deacidification of crude rice bran oil. The RBO can contain about 30-40% of FFA content as a result of the ill-processing of the bran. RBO is a valuable oil as it contains large amounts of phytosterols and oryzanol which are beneficial for health. About 50% of these valuable compounds are lost in the refining process, making an alternate process a mandate. The extract contains the FFA while the raffinate is the remaining neutral oil. FFA content retained in the oil is about 0.1%, which is equivalent to the conventionally processes oils, while giving sterol-ester enriched RBO. The sterol ester content in the oil was ~23% and oryzanol content was about 13.5%. The sterols and sterol-enriched products are obtained conventionally by extracting, esterifying, distilling, and crystallising free sterols from tall oil deodorizer distillate or soyabean oil. This makes the conventional process highly complicated and includes the use of chemicals. The SFF method, though expensive due to the pressure requirements, yields ultrapure products without the use of chemicals 38.

Solvent extraction is another such process that employs the use of short-chain hydrocarbons as selective solvents for FFA, to get neutral oil 39. The solvent extraction process can be considered superior to chemical or physical refining as the process is carried out at room temperature and atmospheric pressure. After extraction, the stripping of the solvent from extract and raffinate is performed at temperatures as low as 80oC and does not lead to any damage to the fatty materials because of a great difference in boiling points 40. A combination of extraction and alkali refining was suggested by van Dijck 41 in which, the FFA was neutralized by the addition of ammonia, forming ammonia soaps of fatty acids, which were extracted using ethanol. The FFA were neutralized selectively and the presence of ethanol inhibits emulsion formation, which resulted in lower oil loss. Cherukuri et. al. 42 separated the FFA from rice bran oil by using methanol, ethanol, and isopropanol. The process led to separation in two phases. The alcohol phase was distilled to recover the RBO enriched with tocols, tocotrienols, and gamma oryzanol. A similar approach was also adopted by Oezdikicierler 43 for the minimal refining of edible oils to preserve the bioactive compounds, which are lost or reduced in concentration during the conventional refining processes. As an improvement to the method suggested by 34, Durrani et. al. 44 went a step further in the re-esterification of the FFA present in degummed and dewaxed RBO. Since esterification by using the lipases from Rhizomucor miehei and Candida rugosa, the residual FFA content was not acceptable for edible purposes, this method employs the use of a mutated lipase (SMG1-F278N) from

Malassezia globose used in the immobilized condition, to get a better yield. Another important modification in this process is the use of ethanol to esterify the FFA. According to the experiments conducted, a 2:1 ratio of EtOH to FA was the optimum with a temperature of 30oC, for 6 hours. The reusability of the enzyme was also tested and up to 10 times of recycling is expected, with no effect on activity. For the scale-up, the RBO was suggested to be separated from the ethyl ester by molecular distillation at 120oC. The RBO obtained, contained 0.08% FFA (99.8% deacidification efficiency) and 27.7g/kg of gamma oryzanol which is excellent for edible purposes.

Another type of solvent used for deacidifying palm oil was Betaine Monohydrate-acetic acid or propionic acid 45. This is a Deep Eutectic Solvent that separated preferentially the fatty acids while enriching the palm oil with beta carotenes and alpha-tocopherols. The reaction was performed at 40oC at a 1:2 volume ratio of DES to Palm oil, for 2 hours. After phase separation, the extract enriched in palmitic acid was cooled to get solid palmitic acid.

A recent publication 46 shows the deacidification of high-acid RBO by using ethanolamine to get fatty acid ethanolamine, which is very beneficial and can compensate for the cost of the process. The reaction was performed with CaO as a catalyst for the amidation reaction. The residual FFA content in the RBO was 1.1% while retaining all the unsaponifiable in the oil. This method gives an easy, green, and industry applicable process for the deacidification of oils, and maybe an alternative to replace the conventional methods.

Membranes are also a good alternative to be used for deacidifying edible oils. The deacidification based on size exclusion is not a feasible option due to the small difference in the molecular weights of fatty acids (<300 Da) and TAG (>800 Da). Processing of undiluted oil with a nonporous membrane has shown some selectivity for FFA, but the effect is not prevalent when diluted oil is used 47. Some pre-treatment steps like the one suggested by Gupta and Bowden 48 consisted of the addition of tri-isobutylamine which formed salts with the fatty acids, resulting in increased cross-sectional area, facilitating membrane separation. Solvent resistant NF membrane was used to separate the cis fatty acids from saturated and trans fatty acids, using $CHCl_3$ and MeOH as solvents in a 3:1 ratio. Another method is the extraction of FFA with alcohols and obtaining FFA by nanofiltration, to separate the edible oil, FFA and the solvent for reuse 49. The progress in finding a suitable membrane for direct deacidification is not sufficient and processes other than direct deacidification have to be looked for.

7. Membrane Processing

Membranes are used for the separation of a mixture of two or more components, resulting in two output streams called permeate and retentate. The membranes are a kind of semi-permeable barrier which separate the feed based on some property. The feed is a fluid that can flow from the inlet to the outlet. The permeate contains the components which satisfy that property or condition, while the reject contains all the other components, which did not fulfil the set criteria. To maintain the performance of the membrane, the membrane material must not be damaged or get dissolved due to the feed or the solvent. The rejected components can be sent out of the membrane separation unit by using a sweep stream that carries the components by dissolving or suspending them. The sweep may be only used in cases where the stream has a high viscosity or greater interaction with the membrane material.

Traditionally, the membranes were of natural materials like cellulose, rubber, and their modifications. In modern times, synthetic polymers replaced natural materials as membranes. The polymers contained long linear chains like Polyethylene, branched chains like polybutadiene, or 3-D cross-linking like phenol-formaldehyde.

The linear polymers turn soft when the temperature is increased and are therefore known as thermoplastic, are soluble in organic solvents. The cross-linked polymers decompose at elevated temperatures and are insoluble in organic solvents. The glass transition temperature (Tg) and melting point (Tm) are of great importance for amorphous and crystalline polymers respectively. These are known as thermosetting polymers.

7.1. Types of membranes

Organic Membranes- Membranes made of polymeric material are called organic membranes. These include polytetrafluoroethylene (Teflon, PTFE), polyamide (PA), polyimide (PI), Polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), natural rubber, wool and cellulose. These membranes have sensitivity towards chemicals therefore should be used accordingly. The advantage is their lower cost and thinner layer required to withstand the pressures applied.

Inorganic Membranes- The membranes of this type can be made of many different materials. These membranes are thermally and chemically stable, inert to microbial damage, and offer ease of cleaning. Higher cost and thicker layers make them an expensive option.

Metallic membranes are made by depositing the powder of sintered metals like Tungsten, Palladium, or Stainless Steel, on a porous substrate. The disadvantage of these metals is the surface poisoning effect.

Ceramic membranes are another type of inorganic membrane made of metal or non-metals. They are mostly used in reactive environments, owing to their inert nature. They are highly sensitive to the temperature gradient, leading to cracking of the membrane.

Zeolites, which are highly porous can also be used as membranes, and are highly selective in gas separation, due to the uniform size of the pores. They can also be used in membrane reactors due to their catalytic properties. 50

7.2. Membrane Modules

Asymmetric thin-film polymeric membranes

Flat Sheet Membrane- 1000x1000x200 mm, 500-5000 Aothick. Also called Thin-film composite membranes. These are supported on a porous support layer.

Tubular Membrane- 0.5-5cm in diameter, and up to 6m long. Thin, dense layer on the inside or outside of the tube surface. The tube is mostly made of fibreglass.

Hollow Fibre, monolithic membranes- 0.3-0.6 cm in diameter, 20-40 mm thick membrane layer. The membrane is on the outer surface of the fibre.

Spiral-wound Membrane- 0.1-0.3 m in diameter, and 3 m long. Two membrane sheets separated by porous spacers are wound around a central perforated tube. The feed flows axially in the channels created between the membranes.

Plate and frame membrane- It is an extension of flat sheet membranes, where the sheets are separated by support plates that channel the permeate.

7.3. Regimes of Operation

There are four regimes of operation in the membrane processes, as shown in the figure. 1. Dead-end Filtration- The reject of the process is not sent out of the system until the feed is exhausted. Only permeate comes out of the system. It is a typical example of a batch process of membrane filtration. 2. Cross-flow – The direction of the feed and the permeate are mutually perpendicular to each other. It is operated in a continuous mode.

3. Co-current flow – The feed is fed in the module from one end, and the permeate and retentate are obtained from the other side. It is used in a continuous mode.

4. Counter-current flow – The inlet of the feed and the outlet of the permeate are on the same side of the module. The retentate comes out from the opposite side. It is used in continuous mode.

8. Use of Membranes in Edible Oil Deacidification

Membranes are also a promising alternative for the deacidification of the edible oil, and much research has been done to check the feasibility of the process, with various approaches and alterations and combination of membrane process with solvent extraction, and so on. The deacidification of oils by using membranes can be done at ambient temperatures, which help to protect the valuable compounds in the oil and prevent any oxidation of the oil. Membranes have been tried for all the processes that are included in the conventional refining process like degumming, dewaxing, deacidification, decolourization, and deodorization 51, and have shown moderate feasibility of their use for these processes, and this shows the huge potential of membranes for replacing essentially all the steps of refining and making edible oil refining a completely membrane-based process. There is no doubt that this will require immense research and optimization for all the processes, for them to be commercially viable and profitable. 47,51,52

8.1. Direct Deacidification using Membranes

Many researchers have tried their hand using direct deacidification with either undiluted or hexane/solvent diluted oil, with non-porous membranes in the past. One such research on crude groundnut and sunflower oil 53, and sunflower oil hydrolysate 54 resulted in a negative rejection of FFA from the oil, due to its preferential permeation, higher than the TAGs, leading to a permeate more concentrated in FFA, to the extent of -8 to -27%. In some other works also, non-porous membranes were seen to have lower selectivity of about 2 between FFA and TAGs, along with a lower flux which makes them unappealing to be used for direct deacidification in the industry. Furthermore, it was observed that the selectivity reduced, even more, when diluted oils were used for direct deacidification using non-porous membranes 55. The use of dense commercial RO membranes made of cellulose acetate and silicone polyimide showed excellent separation of FFA from high-oleic lipase hydrolysed sunflower oil with a solvent such as ethanol and hexane 56. The CA membrane in the hexane system and silicone-PI in the ethanol system showed very low flux and rejection, the reason being the difference in the polarities. The FFA separation was observed with CA membrane in ethanol system, with a TAG/FFA selectivity of 1.85, which was higher than silicone-PI composite membrane in hexane system, with a selectivity of 1.28.

Due to the infeasibility of non-porous membranes, the focus was now shifted to using porous ones, like the NF, UF, and MF membranes. When a model hexane miscella containing 20% soybean oil and 2% FFA was passed through an NF membrane, partial separation was obtained 57. The process involved simultaneous deacidification and solvent removal, leading to a 40% reduction in the FFA concentration while halving the energy requirement than that for the conventional miscella refining process. Krishna Kumar and Bhowmick carried out deacidification of oils with alcohol as the solvent, using both cellulosic and non-cellulosic types of membranes 58. The polyamide (PA) membranes with Molecular Weight Cut Off (MWCO) of 500-600 Da were more selective towards separating the fatty acids, than the cellulose acetate (CA) membranes with MWCO of 500 Da and polysulfone (PS) membranes with MWCO of 1kDa. This may be due to higher interactions of fatty acids with the polyamide membrane. The concentration of FFA increased to 86.8% from 61.7% in the feed, i.e., a selectivity of 4, by using a PA membrane. The total flux obtained was 67.4 L/m2h, with 5.2 L/m2has the oil flux. But, the long term stability of the membrane in the presence of the alcohol solvent can be a hurdle for its implementation in the industry.

Deacidification using laboratory-made NF membrane was also opted for and its feasibility was assessed 59. The NF membranes were stable in solvents like acetone, ethanol, 2-propanol, and hexane, containing a poly(amide-b ether) copolymer (PEBAX) or a cellulose type active layer for filtration. When operated in a dead-end filtration mode, sufficient rejection of TAG was observed, with a 10% lower rejection by the PEBAX membrane than the cellulosic one, while cross-flow operation in the total recycle mode, lead to 90% rejection of TAGs using PEBAX which remained constant. The selectivity between FFA and TAG was about 14, which shows its potential to be used in the industry, only if the flux is improved 55.

FFA separation from hydrolysate of partially hydrogenated soybean oil was conducted using both porous and non porous membranes with methanol and ethanol as solvents 60. Using ethanol assolvent, the highest flux (27 kg/m2h) was observed with regenerated cellulose PLAC membrane, while a flux of 10.1 and 5.7 kg/m2h was seen for PVA and PA membranes respectively with the same solvent. The solute rejections for PA were 95.9% TAG, 83.3% DAG, 87.7% MAG, and 22.9% FFA. When using the PLAC membrane, the FFA content was decreased from 25.7% to 6%, using ethanol as the solvent. When methanol has used a solvent, the flux increased to 40 kg/m2h for the PLAC membrane and zero flux with hexane as a solvent, which shows the dependency on the similarity between the properties of membrane and solvent. Despite these results, there is a need for improvement of the selectivity and flux which are the key issues. Improvement of stability of the membranes in various solvents will also play a major role for consistent performance in an industrial set-up, for the long term.

8.2. Deacidification with Pre-treatment

Due to the unsatisfying results of the direct deacidification process using membranes, another method for membrane deacidification requires the oil to be pre-treated before separation. Sen Gupta suggested and proposed a method in his patent based on the modification of the properties of FFA, by converting them into large micellar structures with pre-treatment and then separating them using ultrafiltration, in turn also removing some PL. FFA reduction of up to 90% was proposed by him. In this study on crude rice bran oil containing 8% FFA and 300mg/kg PL, a reduction to 1.3% FFA after neutralization with ammonia and UF, and to 0.4% FFA after the addition of 4% lecithin in the feed, due to lower PL content in the oil, was observed. The addition of lecithin improved the permeate flux. The effect of temperature on the process was also studied and it was found that the flux increased with temperature and so did the solubility of FFA in the RBO miscella, leading to lower rejection 61. In a simultaneous dewaxing, degumming, and deacidification study performed by Mutoh et. al. in their patent, on undiluted sunflower oil, using ETFE hollow fibre microfiltration membrane, 27.3% reduction in FFA was observed which improved to 95.4% when 0.05% phosphoric acid and 2% NaOH were added to the oil 62. A similar study was also conducted by Pioch et. al. where the concentration of NaOH was maintained below 30% to maintain the water content in the oil. 63. The filtration was carried out in a cross-flow mode with continuous recycling of the permeate to avoid the plugging of the membrane. The FFA of the sunflower oil reduced from 1.42% to 0.01%, which is superior to the alkali refined oils. The industrial application of this process needs further research and development, to replace the conventional processes. In a further study by this group with lampante olive oil 64, the use of less concentrated NaOH led to higher flux. The three membranes (200 nm, 500 nm, 800 nm) tested by the group showed a significant reduction in FFA with the membrane with 800 nm pore size showing excellent results with more than 94.14% deacidification and permeate flux of 220 L/m2 h. In a pilot plant study conducted in 2014 on similar lines 65, a low cost indigenously developed clay-alumina based ceramic MF membrane was used for the refining of RBO miscella. The FFA was reduced to 0.2% by using 10% excess of NaOH than stoichiometrically required along with oryzanol retention of 70% and negligible oil loss of about 2.6%.

The success and the feasibility of this method are close to that of the conventional refining processes and have a high potential for its use in the industry with more optimization of the scaled-up process. Despite this, the industrial acceptance and adoption of this process are feared to be a reality in the near future due to the argument that the method of oil deacidification with membranes, assisted by some pre-treatment methods is that the chemical refining step takes place in this method too, and the only modification is the separation of the soaps or FFA salts is to be done by using membranes, which is accomplished by a centrifugation step in the conventional alkali refining process. The industry is yet to realize the advantages of this method over conventional alkali refining regarding the negligible neutral oil and valuable micro-nutrient loss which was a major concern in alkali refining.

8.3. Deacidification using Solvent Extraction and subsequent Membrane Separation Apart from direct deacidification and deacidification with pre-treatment, research has led to a much more promising process, which has the potential for industrial adoption. This process is known as Deacidification with Solvent Extraction. The principle of this process is the selective solubilisation of FFA in an organic solvent over the TAGs, and subsequent separation of the dissolved FFA by using membranes, and de-solventization.

Keurentjes et. al. at Wageningen University researched the feasibility of membrane-based liquid-liquid extraction using hollow fibre membranes 66. The FFA containing oil was passed through the hollow tubes and the extractant 1,2-butanediol was passed over the outer surface of the tubes. The diffusion coefficients of the fatty acids differ largely, depending on the structure of the fatty acid. The main hurdle in this process is the requirement of a larger membrane area to facilitate efficient separation due to higher mass transfer resistance through the membrane. The variation in the mass transfer coefficients can be exploited in fractionating the fatty acids to get pure fatty acids for other applications.

Cheryan et al at the University of Illinois used membrane technology in combination with solvent extraction for the model crude rice bran oil 67. The principle of the process is based on the fact that due to the small difference in the molecular sizes of fatty acids and TAGs (of about 3 times) with respect to the membrane separation, as already evident from the direct deacidification process, the separation is difficult. Therefore, using a solvent that has a higher extraction coefficient for FFA and negligible extraction coefficient for TAGs will be a good choice. The mixture was then to be subjected to phase separation to get the two phases of oil and solvent containing FFA. The pure FFA were obtained by using a membrane that has good rejection for the FFA and allowance for the small molecules of the solvent to aid in efficient deacidification of the oil, with the solvent being recycled in each cycle, with lower losses. The membranes to be used in the process must be tolerant towards the solvent in use and must not wither away as time passes by. This process also removes the possibility of oil loss or soap formation due to the absence of alkali and can prove to be an important breakthrough in edible oil deacidification.

The group used methanol as an extraction solvent for the FFA because of its higher selectivity for it and smaller molecular size aiding in better membrane separation and higher flux. The separation was carried out using nanofiltration membranes with FFA rejection of more than 90% and flux of more than 25 L/m2.h.

In another study conducted 68 on crude Rice Bran Oil containing 16.5% FFA also used methanol for extraction. The extraction was performed in two steps with 1.8:1 and 1:1 ratios of methanol: oil by weight, reducing the FFA content to 3.7% and 0.33% respectively. The fatty acid and methanol solution was passed through nanofiltration membranes. The FFA rejection obtained by using DS-05 and BW-30 membranes was 93-96% on average, with a flux of 41 L/m2.h. This concentrated the FFA from about 4.7% to 20% in the retentate. The permeate contained about 0.4-0.7% FFA which was again nano-filtered with a flux of 67-75 L/m2.h to give a permeate stream containing about 0.13% FFA which can be recycled for FFA extraction. This two-stage membrane separation can give about 97.8% FFA removal from the oil, without any chemical processes, oil loss, soap formation and high energy requirement. Overall this process included a two-stage extraction and two-stage membrane separation. In a paper published in 2008, the use of subcritical CO2 with membrane was employed for vegetable oil deacidification 69. This was the first study to be conducted on vegetable oil refining using subcritical CO2. Due to the nature of selective solubility of polar compounds in the sub-CO2, the FFA from the oil is preferentially dissolved in the solvent and separated using FilmTec NF90 and FilmTec BW30 membranes. Soybean oil was used for deacidification. The solubility of oleic acid was 0.294 to 0.455 mg/ml and that of the oil was 0.066 to 0.139 mg/ml when tested individually. The best conditions for the separation were identified to be at 20oC and 68 atm pressure. The subcritical CO2 is much more inexpensive, and therefore feasible than supercritical CO2 due to the lower energy requirements, with many of the similar properties, which make their use feasible for the industry.

Pagliero et. al. in 2013 published a similar study on degummed soybean oil using ethanol for extraction 49. The soybean oil contained about 1.15% FFA before deacidification and was extracted using a 1.8:1 ratio of ethanol to oil for 30 minutes, followed by a 30 minute standing period for the separation of two phases. The oil phase was passed through an additional step of extraction under the same conditions to give an oil containing only 0.09% FFA. The ethanol and fatty acid solution were separated by nanofiltration using NF-99-HF membranes from Alfa Laval. The optimum operating conditions were 20 bar pressure and temperature of 35oC, giving a permeate flux of 28.5 L/m2.h and 70% FFA retention.

Pagliero et. al in 2013 also published 70 a comparative study of four tailor-made flat composite membranes of PVDF support with PDMS or CA coating and commercially available Solsep 030306 membrane to remove hexane and FFA from the hexane-oil miscella of soybean oil. The effects of the different conditions like transmembrane pressure, temperature, and feed oil concentration were also studied. The optimal conditions were at a feed concentration of 25%, the temperature of 30oC and transmembrane pressure of 20 bar with a flux of 20.3 L/m2.h, 80% oil retention and 58% FFA removal. The PVDF-12%siloxane appeared to be the best membrane being stable in hexane and providing efficient separation. An approach to deacidify palm oil was carried out in Malaysia in 2016 using a model oil system containing palmitic acid 71. From the solvents used like ethanol, hexane, and methanol, in a ratio of 2:1 solvent to model oil, ethanol emerged to be the most efficient in FFA extraction. The ethanol-FFA mixture was separated using NF membranes like Solsep (010206, 030306, 030705). The results showed that a combination of solvent extraction and membrane separation is a remarkably simple and waste-free technology for the deacidification of vegetable oils.

9. Conclusion

Edible oil is a basic source of fats which is among the three macronutrients, along with carbohydrates and proteins, and therefore will be used eternally. The production and purification of these oils are important processes that purify the crude oils obtained from plants and make them fit for consumption.

The free fatty acids present in the oils are a major hurdle physiologically if consumed, also accelerates the oxidation of the oil making it unfit for consumption, as well as industrially as the fatty acids may cause corrosion of the reactors and poison the bleaching earth, used for removing the colouring compounds. All these make the reduction of FFA content in oil extremely necessary.

The current processes of chemical and physical refining result in the best quality of oils but have some drawbacks which need to be tackled, and the best way to do that would be to find an alternate method that yields an oil fulfilling the same parameters as the conventional methods. Years of research, experimenting with a variety of different methods has generated a large amount of data which we can look at and try to adopt the best method among them.

According to the scope of this paper, the membrane processes are seen to have the potential to be used as an alternative method for edible oil deacidification, with lower oil loss and energy consumption than in conventional methods. The process of selective solvent extraction of fatty acids and then separating the fatty acid-solvent mixture by using membranes is the most optimum method, of the three methods discussed. The only drawback which this process has is that the industry is found to have reluctance against it by citing the opinion that already a large amount of hexane is used by the oils and oleochemicals industry and incorporating a new solvent as methanol will lead to an increased amount of solvent usage. The fact that methanol is poisonous also prevents its usage. But, the point that excess amounts of solvents would be used does not seem to be appropriate, since about 98-99% of the solvent is reused in every cycle of extraction and membrane separation. In the coming future, this technology has a good amount of potential, especially due to the increasing energy prices and a recent increase in the edible oil prices seen in India, as lower oil losses and energy consumption will have a great impact on the RBD oil sold in the market. Also, various other solvents apart from methanol have to be tested for their feasibility for the process and membrane have to be tested for the resistance towards these solvents.

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