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Latest advances in degumming feedstock oils for large-scale biodiesel production

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Abstract: The removal of gummy or mucilaginous substances from vegetable oils, commonly known as degumming, is required for the use of crude vegetable oils as the feedstock for biodiesel production. These gums reduce the rate of transesterification reactions by deactivation of the catalyst and they hinder the separation of the glycerol phase from the biodiesel. They also cause the deposition of carbon particles within engine machinery and affect performance. To take care of these issues, gums should be separated from the oils to make the oils suitable for use as fuel. Chemical treatment, membrane separation, and biological separation processes have been reported in the literature for this purpose. In the chemical treatment process aqueous solutions of chemicals like acids, bases, ethylenediamine-tetraacetic acid (EDTA), and water are used for separating gums. The membrane separation process is based on size exclusion, and polymeric, ceramic, and inorganic membranes are used to separate gums from oil. In biological degumming, phospholipase groups of enzymes are used. These enzymes hydrolyze gums into fatty acids and lipophilic substances. Enzyme degumming also enhances oil-phase yield. This paper reviews the chemical nature of gums and presents a comprehensive critical summary of different degumming technologies, their specific features, effecting parameters, advantages and disadvantages, and industrial uses. © 2018 Society of Chemical Industry and John Wiley & Sons, Ltd.

Keywords: chelating agent; degumming; immobilization; inverse micelle; phospholipids; vegetable oils

Introduction

The increasing world population, increasing industrialization, the deteriorating environment, and the energy security situation have generated global interest in the exploration of various renewable energy sources based on green technologies.[1–4] Biodiesel, in particular, has attracted substantial academic and commercial research interest due to its biodegradability, availability, and high energy returns (~90%).[5,6] Biodiesel, an alternative to petroleum diesel fuel, is a clean-burning, oxygenated, sulfur-free fuel.[7,8] It can be used in existing internal combustion diesel engines for transport and power generation with or without minor engine modifications.[9] Biodiesel is a mixture of long-chain fatty acid alkyl esters, which are produced from vegetable oil via transesterification reactions with alcohols (also called alcoholysis). Depending on their availability, various edible or non-edible vegetable oils like soybean, rapeseed,

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palm, karanja, jatropha, and animal fats, algae, and waste cooking oil have been used as feedstocks for biodiesel production in different countries.[10] At present, high-quality, food-grade vegetable oils are the most commonly used feedstocks, which result in higher production costs. This is the main barrier to the commercialization of biodiesel. The feedstock cost contributes up to 85% of the biodiesel production cost. Consequently, the use of low-value oils (waste cooking oils and animal fats) or unprocessed, crude edible or non-edible oils (also known as non-degummed oils) is one of the ways to reduce the production cost of biodiesel.[11] Crude vegetable oil is expelled from seeds by mechanical extraction, solvent extraction, and enzymatic oil extraction or a combination of these. This crude oil contains largely triglycerides and some other minor impurities that can be categorized into two classes: oil soluble and oil insoluble. Seed fragments, meal fines, free water, resins, waxes and higher hydrocarbons are present in oil as the insoluble impurities that can be purged by filtration. Free fatty acids (FFA), phospholipids (PLs), pigments, glycolipids (GLs), organic compounds of trace metals, etc., are oil-soluble impurities (approximately 1–3 wt%). The concentration of these minor constituents in crude vegetable oil varies with the kind of oil, the nature and quality of oil-bearing seeds, preconditioning of seeds prior to oil recovery, the oil recovery procedure, and the operating temperature (Table 1).[12]

Gums are any viscid defilements in crude oil and are mostly PLs.[20–22] They lead to several problems when unprocessed oil is used for biodiesel production. Some of them are listed below:

- Metallic species attached with phosphatides as trace amount impurities in oil cause catalytic oxidation and polymerization reactions in oil, resulting in the formation of aldehydes, ketones, acids, and alcohols that are

Table 1. Triglyceride and phospholipid content in some crude vegetable oils.

Type of feedstock	Triglyceride content (%)	Phospholipid content (%)	References
1. Soybean oil	90–93	1.0–3.0	12
2. Canola oil	94.4–99.1	1.25–2	13,14
3. Rapeseed oil	98.5	1.25	15
4. Palm oil	~90.35	0.03–0.1	16
5. Cotton seed oil	92–98	0.7–0.9	17
6. Rice bran oil	81.3–84.3	3.6–6.0	18
7. Sunflower oil	98.0–99.5	0.5–1.3	19
8. Corn oil	-	0.7–2.0	19
9. Ground oil	98.0–99.7	0.3–0.7	19

pro-oxidant in nature. These alter the chemical composition of oil, which affects its shelf life, quality, color, odor, and the oxidation stability and shelf life of the biodiesel produced.[23,24]

- Gum may combine with the catalyst during transesterification because of its adhesive nature and block the active catalyst sites by changing the catalyst structure, which results in a lower conversion rate.[25,26] Deactivation of catalyst can be correlated with gum concentration linearly by the following relation (according to Maxted *et al.*):[27]

$$A = A_0 - xC_p \qquad (1)$$

Here A and A_0 are the activities of the catalyst after and before poisoning, respectively; C_p is the concentration of poison, i.e. gum, and x is a constant. With increasing gum concentration, catalyst deactivation enhances linearly.[27]

In enzymatic biodiesel synthesis, process gums, mainly PLs, function as inhibitory substances that bind to immobilized enzymes, causing interference in the interaction of lipase enzymes with reaction substrates, resulting in the lower conversion efficiency of biodiesel.[28]

- Phospholipids present in gums are emulsifying and are problematic in the separation of biodiesel and glycerol phase, after the transesterification reaction, resulting in a noticeable reduction in the biodiesel yield. The presence of gums in oil also leads to an increase in viscosity by forming aggregates of oil molecules. The viscosity of oil in the area of biodiesel production and food industry is an important consideration when deciding the technology and design of processing.[29]
- In engine machinery, gum causes the deposition of carbon particles in the combustion chamber, choking filters, lines and injectors, plugging the carburetor, and contaminating lubricants during the combustion of biodiesel. These lead to a decrease in engine efficiency by rotation restrictions.[21,25]

To overcome these problems, the removal of PLs and mucilaginous impurities – a process known as 'degumming' – is imperative before unrefined vegetable oils are used as an alternative for diesel fuel.[20] According to ASTM standard D6751 and the EN 14214 specifications for biodiesel (B100), the phosphorus and metal (group II) content should not exceed 10 and 5 ppm, respectively, to sustain fuel quality.[30]

The recovery of lecithin is another advantage of this gum removal procedure. Lecithin is a desirable food additive and a commercially important compound, which increases the cost-effectiveness of the degumming process. Lecithin

is not only a mixture of phospholipids but also consists of triglycerides and other non-phospholipid compounds.[31] Consequently, this review article suggests that partially refined vegetable oils, i.e. degummed oils, should be considered as an alternative solution for economically viable biodiesel synthesis. Research has suggested that partially refined (degummed) vegetable oils can produce high-quality biodiesel similar to refined vegetable oil, so degummed vegetable oils can be promising feedstocks for the commercialization of biodiesel production.[11]

The PLs and their constituents

The PLs are diacyl surfactants and are amphiphilic in nature because they have hydrophobic fatty acid groups and hydrophilic glycerol phosphate moieties.[32] When water is added to crude vegetable oil containing PLs, oil-insoluble lamellar liquid crystals (gum/micelle) form, which can be separated from the oil by centrifugation. Phosphatidylcholine (PC), phosphatidylinositol (PI), phosphatidylserine (PS), phosphatidic acid (PA) and phosphatidylethanolamine (PE) are found as major components of PLs and lysophosphatidylcholin (LPC), lysophosphatidylethanolamine (LPE) are minor components. The major components of PLs are categorized into two groups: hydratable (HPLs) and non-hydratable (NHPLs) depending on their interaction with water. The HPLs PC, PI and PS form insoluble hydrates in the presence of water while PA and part of PE present as Ca and Mg salts do not form hydrates.[33,34] The nature and structure of phospholipid components are given in Table 2.

Phospholipid detection

The PL concentration is determined using the American Oil Chemists' Society (AOCS) method Ca 12-15 and absorbance is read at 650 nm using ultraviolet–visible (UV-VIS) spectroscopy (Shimadzu, Tokyo, Japan).

Phosphorus content is determined by analysis using the standard curve of NaH_2PO_4. The elemental phosphorus is then converted into total PL using factor 26 for the calculation of PLs ($mg\ kg^{-1}$) from P ($mg\ kg^{-1}$). The metal (calcium, magnesium, and iron) concentration is analyzed by inductively coupled plasma (ICP) optical emission spectroscopy following AOCS method Ca 17-01.[38]

Degumming process

Oil impurities, mainly gums, can be removed by simple gravity settling. Gums have a higher density than oil molecules and settle at the bottom of the storage tank over a period of time. The resulting settlings can be removed by a simple filtration process. However, the settling of gums takes a long period of time and the process is ineffective for total gum removal. A number of degumming techniques, e.g. water degumming, acid degumming, TOP degumming, soft degumming, membrane techniques and enzyme degumming processes have consequently been examined by researchers for gum separation in a short time span.[36]

The selection of an appropriate degumming process depends on the nature of the PLs. Most of the PLs present in oil are hydratable and can be removed easily by water treatment. During water degumming, HPLs aggregate into bigger particles – oil-insoluble liquid crystals – which have higher densities and can be separated by centrifugation. Non-hydratable PLs in oil are present as a complex unit with metallic species like calcium, magnesium, and iron. So the addition of chemical reagents is required to hydrolyze them into HPLs and metallic cations, which are further removed by the water degumming process. These chemical reagents may be acids, such as citric acid, phosphoric acid, etc., alkalis, and chelating agents like ethylenediaminetetraacetic acid EDTA, as well as enzymes. To select an appropriate degumming technology or a combination of these technologies, it is essential to know the chemicals forming gums in the oil.

Table 2. Nature, percentage, and structure of phospholipids in crude vegetable oils.[29,35–37]

Structure of phospholipids	Constituents of phospholipids			
	Name of constituents	Structure	Nature	Percentage*
	1. Phosphatidylcholine (PC)	$X = CH_2-CH_2-N^+(CH_3)_3$	Hydratable	29.0–39.0
	2. Phosphatidylinositol (PI)	$X = C_6O_5H_{11}$		13.0–17.5
	3. Phosphatidylserine (PS)	$X = CH_2-CH(COO^-)NH_3^+$		5.9–6.3
	4. Phosphatidic acid (PA)	$X = $ Hydrogen	Non-hydratable	5.0–9.0
	5. Phosphatidylethanolamine (PE)	$X = CH_2-CH_2-NH_3^+$		20.0–26.3

*The percentage of phospholipid constituents varies with the kind of oil as well as the nature and quality of oil-bearing seeds. In Table 2 soybean oil is used as reference for the percentage of constituents.

Degumming techniques are broadly divided into two categories on the basis of the nature of PLs:

- hydratable gum-removal processes; and
- non-hydratable gum-removal processes.

The basic steps for all degumming techniques include the micellization of phospholipids in the presence of polar solvents, prompt hydration of PLs at increased temperature, and acidulation followed by neutralization to convert NHPL to HPLs.[37]

Hydratable gum removal process

For degumming of vegetable oil, hydratable gum removal processes are applied first because they provide additional assistance in the removal of non-hydratable phospholipids. Hydratable phospholipids are removed by a simple water-degumming technique. The addition of water to crude oil results in the formation of a ternary phase system of the water-phospholipid-oil molecules and hydration of hydratable phospholipid occurs as a result of the weak dipole-dipole interaction (hydrophilic) between the polar head group of PLs and the water molecules. This interaction results in phase transitions, i.e. oil-soluble PL aggregates transform into oil-insoluble lamellar liquid crystals (gum).

The relative affinity of PL species with water is called 'hydratibility' (Table 3). The higher the hydratibility, the higher is the water affinity.[12]

Table 3 indicates that PC has the highest hydratibility compared to other PL species. Higher hydratibility results in higher emulsifying power – i.e. PC is easily separated out in less time than other PLs species by the water degumming process.

Water degumming method

These are the traditional degumming processes in which water is used as a hydrating agent for the hydration of PLs.

Table 3. Relative rate of hydration of phospholipid species.[12]	
Phospholipid species	Relative rate of hydration
1. Phosphatidylcholine (PC)	100
2. Phosphatidylinositol (PI)	44
3. Phosphatidylinositol (PI)-(calcium salt)	24
4. Phosphatidylethanolamine (PE)	16
5. Phosphatidic acid (PA)	8.5
6. Phosphatidylethanolamine(PE)-(calcium salt)	0.9
7. Phosphatidic acid (PA)-(calcium salt)	0.6

Only HPLs can be removed by these techniques, leaving NHPLs intact. Water or steam is finely dispersed into preheated (80 °C) oil and sufficient contact time is allowed with stirring. Hydratable PLs in oil interact with water at an increased temperature. Oil-insoluble gums are separated from this by settling, filtering, or centrifuging. These gums are processed for commercial lecithin by removing water, oil, and other components. Oil is dried by vacuum drying.[20,39] List et al.[40] proposed two basic processes for the industrial-scale degumming of oils: batch degumming and continuous centrifugal degumming. The batch-degumming method, in which tanks are used to agitate oil with water followed by centrifugal separation, is most popular in the USA. In the continuous centrifugal degumming method, preheated oil and water are metered into a continuous indwell pipeline agitator. After holding for a short period it is then pumped into a centrifuge. This process is extensively used in Europe (Fig. 1).

Variations in water concentration, temperature, agitation speed, and contact time have been studied by researchers, as these affect the extraction efficiency, purity and color quality of lecithin. Indira et al.[41] critically examined the effects of these variables on gum removal in rice bran oil with the help of Response Surface Methodology (RSM). Eshratabadi[35] also demonstrated the effects of these variables on extraction efficiency. List et al.[40] suggested that the efficiency of gum removal significantly depends on water concentration rather than other variables like time, agitation speed, and temperature. Higher temperature and increased agitation speed cause a darkening of the lecithin's color.[40] Water concentration plays a critical role in the hydration of gums. On increasing water concentration, hydration increases and results in the formation of more emulsions, which enhance extraction efficiency. At lower water concentration, hydration would be carried out in an appropriate manner. About 95–98% extraction efficiency was observed by List et al.[40] during the optimized water degumming process. Further increasing water concentration above certain limits favors the entrainment of an excessive amount of oil in gums, which results in high oil loss and a decrease in gum extraction efficiency. Regarding results observed by researchers, a water level closer to the PL content of crude oil is considered to be the optimal water concentration.[42]

The effect of the degumming temperature on PL removal has been studied by varying it from 25 to 90 °C[41,42] and relatively little effect has been observed. Increasing the temperature from 25 to 75 °C has a positive effect on gum removal efficiency but beyond 75 °C gum-removal efficiency decreases. At an increased temperature, the color of lecithin darkens. On increasing the temperature, the
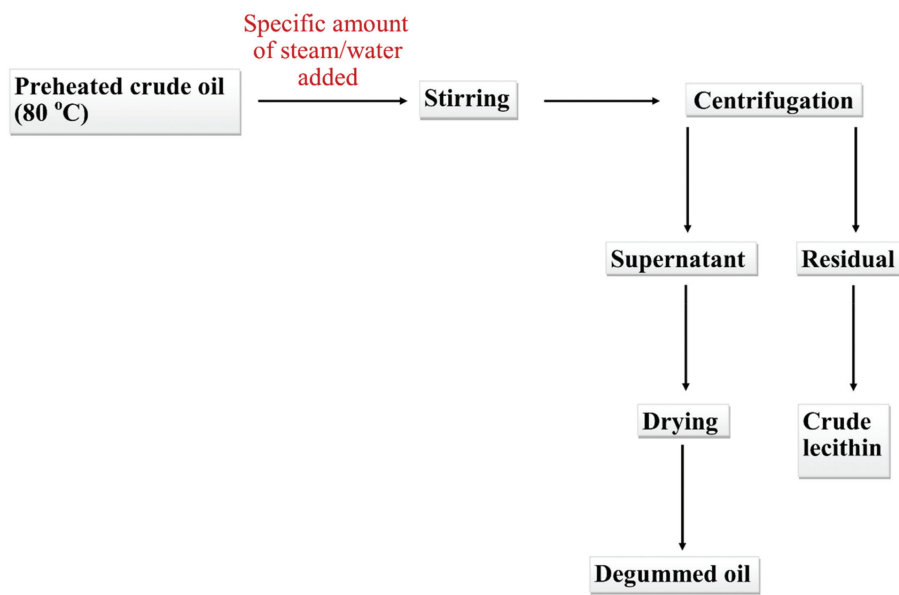
Figure 1. Water degumming process.

retention of waxes that are present increases, which also facilitates gum retention. A temperature of 60 °C is optimal for higher gum-removal efficiency with lecithin quality retention. A higher degumming temperature causes some disadvantages, such as a propensity for oil to oxidize into unfavorable compounds, formation of free fatty acids in oil as well as lecithin, and decreased lecithin viscosity.[42] The speed of agitation has minor but a positive linear relationship with the removal of phospholipid in gums. High agitation speed is apparently desirable because it facilitates more aggregate formation while at lower agitation speed more oil is entrained in the gums causing oil loss.[40,41] Agitation time also affects the degumming efficiency marginally positively. However, allowing a long time for degumming enables gums to re-enter the oil phase. Prolonging the agitation time also has a negative effect on lecithin color.[40,41] Moreover, degumming is a stepwise process and has a complex mechanism. Indira et al.[41] have suggested that process variables do not function individually and the combined effect of variables significantly increases the gum extraction efficiency.

Non-hydratable gum-removal processes

Non-hydratable PLs are salts of Ca, Mg and Fe of PA and PE. They are not hydratable with water so cannot be precipitated out from the oil phase. Complex processes, such as the use of acids, bases, complexing agents and enzymes, are needed to remove non-hydratable phospholipids.[37]

These processes can be broadly grouped as chemical, physical, and biological methods, depending on the chemical reagents added, the size difference between PLs and triglycerides, and the nature, quantity, and structure of PLs in feedstock oil.

1. Chemical degumming methods
   - Acid degumming.
   - TOP degumming.
   - Soft degumming.
   - Dry degumming.
2. Physical degumming methods
   - Membrane separation.
3. Biological degumming methods
   - Enzyme degumming.

Chemical degumming methods

Chemical degumming involves the addition of chemical reagents. These chemicals liberate PA from NHPLs. Citric acid forms a complex with Ca and Mg ions present in NHPLs and phosphoric acid forms a precipitate with these metal ions. Alternatively, EDTA is also used as a chelating agent.

1. **Acid degumming techniques.** During acid degumming, the hydratibility of phospholipids is raised by the addition of an acid. All organic and inorganic acids may be used that have a pH of at least 0.5 as measured at 20 °C in one molar aqueous solution. Edible acids such as acetic acid, citric acid, and tartaric acid are preferred, and toxic or corrosive acids are avoided. The application of organic acids is named as the super degumming process. Citric acid is the most commonly used acid.[43,44]

(a) Citric acid degumming (super degumming). In this process, dilute citric acid (30%) is dispersed onto oil by 2% v/v at an increased temperature (70 °C) and is stirred for 20 min. The oil-acid mixture is cooled to a temperature below 40 °C and a small amount of distilled water (0.5–3 wt%) is thoroughly mixed for a period of 0.2–5 h. The amount of acid added varies with oil weight and PL content. Citric acid decomposes the PL-metal complex into insoluble metal salt and PA. Here citric acid has additional advantages: it is a weak organic acid and can function as a chelating agent to bind metal ions; it also prevents the oxidation reaction in the oil produced by metal during the heating process.[45] Addition of some amount of water forms gel by hydration of phosphatidic acid. Formed gel and metal salt is removed by centrifugation at 4000 rpm for 45 min (Fig. 2).[44]

(b) Phosphoric acid degumming. In this process, 14% diluted phosphoric acid is added to the oil (by 0.5% volume) at elevated temperature (70 °C) and stirred for 10 min followed by mixing with water (1% volume). Phosphoric acid forms precipitates with metals and releases phosphatidic acid by decomposing the PL-metal complex, which is removed by centrifugation at 4000 rpm for 45 min.[39] A comparison of the citric and phosphoric acid degumming processes is depicted in Table 4 for *Pongamia pinnata* oil (Fig. 3).

A limitation of acid degumming is the migration of some decomposed phosphatic acid into the oil phase

because of the soluble nature of phosphatic acid. Lowering of the solution pH by the addition of acid makes NHPLs decomposition process reversible. It inhibits the complete removal of phosphatides from the oil. This method has been further improved and is known as TOP degumming.

2. **TOP degumming process.** TOP is a Dutch acronym that means 'total degumming process'. This is a two-step process. The first step involves dispersion of 14% phosphoric acid into the water-degummed oil or crude oil in 0.1 wt% ratio at an increased temperature for the decomposition of phosphatide metal complexes. The second step involves the addition of a diluted base, e.g. NaOH, Na_2CO_3 or Na_2SiO_4, in an adequate amount to prevent migration of decomposed phosphatic acid by the acid-base neutralization process after a certain contact time, but in an insufficient amount to form soap. This neutralized acid and metal complex is removed by centrifugation for 45 min and oil with a low PL content is obtained.[46–48]

Table 4. Comparison of citric and phosphoric acid degumming of *Pongamia pinnata* oil.[39]

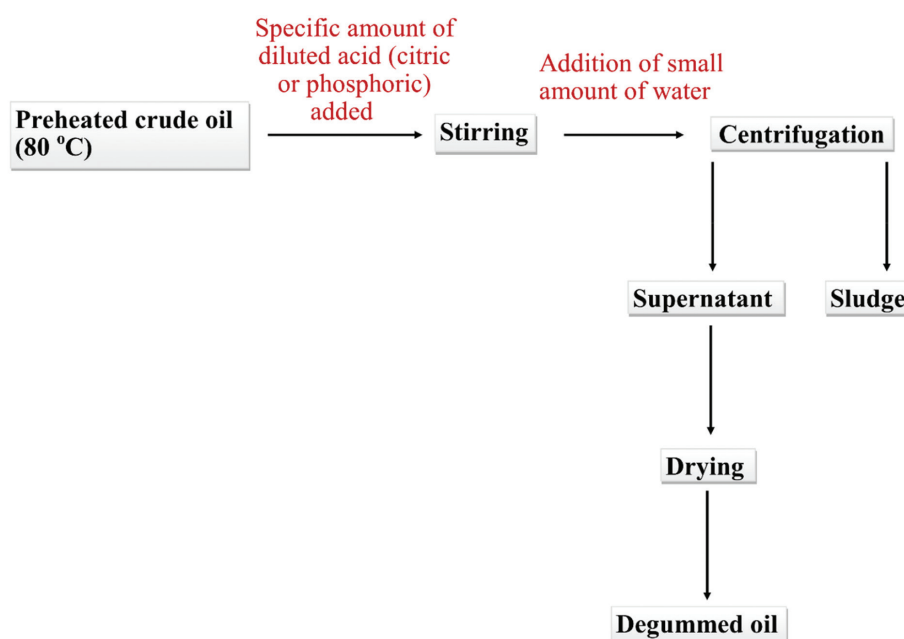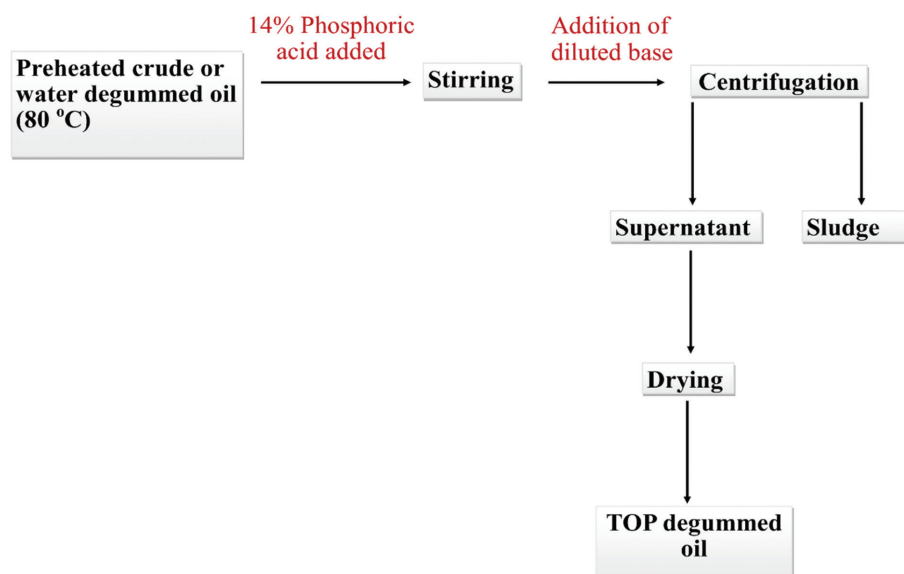|	Crude *Pongamia pinnata* oil	Citric acid degummed oil	Phosphoric acid degummed oil
Phosphorus content (ppm)	810	22	31
Phosphorus reduction percentage	—	97.28	96.17

Figure 2. Acid degumming process.

Figure 3. TOP degumming process.

Table 5. Comparison of water, acid and TOP degumming processes used for sunflower oil.[46]

	Phosphorus (mg per kg)	Percentage phosphorus removal	Ca (mg per kg)	Mg (mg per kg)
Crude vegetable oil	95.7	—	26	18.4
Water degummed oil	50.1	47.64	12.9	6.5
Acid degummed oil	7.1	92.58	4.1	2.3
TOP degummed oil	4.5	95.29	0.9	0.5

Typical results for water, acid, and TOP degumming processing of pressed crude sunflower oil are presented in Table 5.[46]

In crude sunflower oil, high levels of of PLs (expressed as mg of phosphorus per kg of oil), Ca, and Mg are present. From Table 5 it may be seen that the TOP technique is the most efficient method for removing gum-forming species. Another advantage of TOP degumming is that no oil loss occurs during the process.[13]

3. **Soft degumming process.** This is the latest degumming technique developed by Deffence (1999). It uses the unique complexing power of EDTA. The EDTA chelating agent or its salts are used in the presence of an emulsifying agent for the degumming of crude oil. The EDTA reacts with NHPLs present in the crude oil because it has a greater affinity for metals and forms a metal-EDTA complex by chelation. In chelation with central metal ion, two nitrogen of amines and four carboxylates oxygen participate and form four three dimensional five-member metal-EDTA complexes. The formation of these complex entities is represented by the pK value of the complex as shown

Table 6. Comparison of pK values of EDTA and PA-metal complexes.

Metal complex	pK	Metal complex	pK
Ca-PA complex	4.6	Ca-EDTA complex	10.7
Mg-PA complex	4.0	Mg-EDTA complex	8.7
Fe-PA complex	14.3	Fe-EDTA complex	25.1

in Table 6. The higher the pK value, the more stable the complex will be; thus Ca-EDTA and Mg-EDTA complexes are more stable than Ca-PA and Mg-PA complexes. Non-hydratable PLs are decomposed into metal complexes and PA, which forms an emulsion in the presence of a chelating agent, which is removed by centrifugation.[43]

Deffence advocated that, in the soft degumming process, the aqueous solution of EDTA (5 wt%) and an emulsifying agent should be added to crude or water-degummed oil at an elevated temperature (75 °C) and homogenized for 1 min. The EDTA converts non-hydratable phospholipids into hydratable phospholipids by forming a 3D metal-EDTA complex. The formation of the complex depends

upon contact between the oil-soluble phospholipid phase and the water-soluble EDTA phase; the formation of the water-in-oil emulsion is imperative. Sodium dodecyl sulfate (SDS), as an emulsifying agent, facilitates contact between these two phases. The emulsion is separated by centrifugation (Fig. 4).[43]

Choukri et al.[49] studied the soft degumming process in detail, including factors affecting the gum-removal process, and they reported that the concentration of PLs was reduced to less than 5 mg L^{-1} using this technique. They also indicated that the efficiency of the process depends on the degree of dispersion and contact between the chelating agent (EDTA) and NPLs, which can be increased by four factors: the concentration of EDTA and emulsifying additives, the aqueous/oil phase ratio, incubation time, and operating temperature. It has been noted that increasing the concentration of sequestrate and emulsifier enhances dephospholipidization. Choukri et al.[49] mentioned that increasing EDTA concentration from 2 to 50 mmol L^{-1} and then 200 mmol L^{-1} results in the complete removal of PLs. This is because by increasing the EDTA concentration, the formation of metal-complexes is enhanced, and with increasing emulsifier concentration dispersion and stabilization is enhanced. Phospholipids can thus be easily separated out. By increasing the aqueous/oily phase ratio, the contact between EDTA containing water with the oil phase is increased and the degumming is significantly increased. Allowing sufficient contact time for hydrating NHPLs into hydratable form also plays a significant role in the soft degumming process – a minimum 20 min are required for phase reaction time.[43] The degree of degumming has a direct relationship with the temperature. By increasing the operating temperature, the PL concentration decreases linearly, ensuring a more rapid and effective contact between the phases involved in the process. Above 65 °C, the PL concentration remains lower than 10 ppm.[50]

This is the best method for degumming because it decreases the PL concentration to less than 10 ppm but

it has not been possible to industrialize it due to the high cost of EDTA. This method becomes less effective when oil has high phosphorus content.

4. **Dry degumming process.** This is essentially a modified acid degumming process and it is based on the fact that strong acids displace weaker acids from their salts. In this method, oil is treated with stronger acids (than PA) such as phosphoric acid (0.05–0.1%). This is followed by mixing with 1 or 2% acid-activated bleaching earth under a vacuum at a temperature of 80–120 °C. After a certain contact time, the spent earth is removed by filtration. As cited earlier[50] phosphoric acid decomposes NHPLs into HPL and metallic species, which are chemisorbed on the acidic sites of the bleached earth and removed. Sulfuric acid or nitric acid can also be used but these acids have disadvantages such as their corrosive nature and side reactions with oil molecules. They can only be used for oil with low PL content.[50]

5. **Physical degumming method.** All chemical degumming methods (water, acid, bleaching earth, and chelating agents) consume a large number of chemical additives and energy. They cause thermal degradation of the oil and generate effluents that are heavily contaminated with oil, soap, and alkali, with sizeable oil losses. To reduce energy needs and effluents, membrane-based technology has been applied for oil degumming.[51]

Membrane degumming

This technique is somewhat superior to chemical degumming methods and is able to replace conventional degumming processes fully or partially. Its advantages are:[52]

- no polluted effluent is generated and it does not require the addition of chemical reagents;
- no oil losses occur by trapping with gums;
- it requires milder operating conditions and hence operates with lower energy consumption;
- it is effective in total gum removal; and
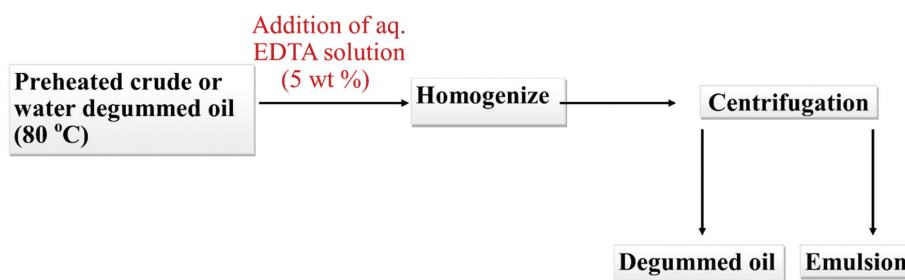- it requires fewer processing steps.

Figure 4. EDTA degumming process.

Gum separation by membrane technology is a size-exclusion-based, pressure-driven process.[53,54] In the crude vegetable oil, the sizes of the triglyceride and phospholipid molecules are 1.5 and 1 nm, and molecular weights are 900 and 700 Da, respectively.[25] These small differences in size and molecular weight cause difficulties in separation using membranes.[23] Phospholipids are natural surfactants and form reverse micelles in non-aqueous media, encapsulating a number of non-lipid molecules, e.g. the metal ions, free and bound sugars, peptides, and glycosides. In reverse micelles, polar head groups have an inward orientation, interacting with other polar compounds, while non-polar hydrophobic groups orient outward. This reverse micellization process occurs above a PL monomer concentration known as the critical micelle concentration (CMC). The reverse micellization process is enhanced by the addition of non-polar solvents like hexane, or benzene. Sen Gupta reported[55] that the molecular size and molar mass of reverse micelles are 18–200 nm and < 20 kDa, respectively. These reverse micelles are larger in dimensions than triglyceride molecules; thus they can be removed effectively by ultrafiltration (UF) or nanofiltration (NF) membranes with an appropriate molecular weight cut off (MWCA) (20 kDa).[54,56–58]

Koris et al.[56] studied phospholipid removal from crude soybean and sunflower-seed oil by three polymeric membranes: microdyne polypropylene tube membranes (surface area 54 cm^2), mavibran FP055A flat-sheet membranes (surface area 100 cm^2, MWCA 55 kDa), and mavibran SP015A flat-sheet membranes (MWCA 15 kDa, surface area 100 cm^2). The maximum phosphorus retention achieved was 77% with the SP15A membrane at 5 bar pressure.[56] Pagliero et al.[52] synthesized polyvinyliden fluoride (PVDF) polymeric membrane in the laboratory for degumming studies of soybean oil and membrane separation process yielded phospholipids retention values higher than 95% at 2 bar pressure. The degumming of soybean oil was performed using a polyethersulfone (PES) (MWCO 101.9 kDa) ultrafiltration membrane by de Moura et al.[54] and the removal of 89% of phospholipids was achieved. Ochoa et al.[59] used four different ultrafiltration polymeric membranes – PVDF, PES, PSf, and PVP – for the degumming of vegetable oils. They also compared membrane permeation flux, and phospholipid retention and stability in hexane and concluded that PVDF showed maximum phospholipid retention – over 98% – with maximum fouling stability and flux.[59] Pagliero et al.[58] performed a degumming study of crude soybean oil by two ultrafiltration polymeric membranes: PVDF and PI. The test membranes gave suitable results for removing phospholipids within

the temperature range and trans-membrane pressure used. Polymeric membranes have offered a promising solution for the degumming of oil but problems associated with the stability of the extraction solvent have delayed application at industrial scale. Microbial degradation and shorter life are other limitations of polymeric membranes. Marenchino et al.[60] proposed inorganic membranes to treat crude oil miscella in a laboratory-scale ultrafiltration module because of higher temperature durability, wide pH tolerance, sufficient mechanical strength, chemical inertness, and solvent resistance. A tubular inorganic membrane composed of ZrO_2 was used and 93.4% rejection was achieved at 3 bar trans-membrane pressure.[58] Wibisono et al.[25] used a tubular ultrafiltration inorganic membrane made from the ATZ (alumina/titania/zirconia) support layer and titania as filtrate layer for corn-oil degumming for biodiesel production. Inorganic membranes are reported to be expensive and brittle in nature, so composite membranes have recently been used as a promising solution to the above problem. Manjulata[57] investigated the nonporous polymeric composite hydrophobic membrane polydimethylsiloxane as an active layer and polyimide as a support layer for phosphorus rejection in hexane-diluted systems (82–99%). Subramanian et al.[36] reported polymeric composite membrane NTGS-1100 and NTGS-2100 with silicon as an active layer and polysulfone and polyimide as support layers in the study of soyabean and rapeseed oil degumming. The rejection of PLs was above 93% and 96%, respectively. The NTGS-1100 membrane was more stable in its rejections during operating conditions. These authors also investigated the differential permeation of oil constituents using NTGS-2200 membrane.[61]

Four major types of membrane modules have been studied: plate and frame, tubular, spiral-wound, and hollow fiber. Operating trans-membrane pressure and temperature ranges, chemical stability of the membranes, and sanitation requirements decide the membrane module selection.[23,62] In the membrane separation process an oil-hexane mixture is allowed to pass through an ultrafiltration or nanofiltration membrane.[60,63,64] This membrane acts as a selective semi-permeable barrier, which allows the passage of certain components and the retention of others. Hexane, triacylglycerol, free fatty acid, and other small molecules constitute permeate flux while all PLs in the form of reverse micelles are retained on the membrane.[64] The performances of the membrane process are expressed in terms of the permeate flux rate and retention coefficient. High permeate oil flux and high PL retention on the membrane indicates greater efficiency of the membrane separation process. The performance of these membranes

depends on many variables like membrane composition, shape, and configuration of membranes, temperature, trans-membrane pressure, feed flow, and tangential velocity conditions.[65–68]

Permeate flux rate is the volume of permeate during the filtration process per unit of area (m²) of membrane per unit of time (t). The flow rate of permeate (J) through the pores of the membrane is a function of mean pore diameter (d_p), numbers of pores (N), porosity ($\mathcal{E}$), pressure applied (P_T), solvent viscosity (μ) and membrane thickness (Δx) and is expressed as[58]

$$J = \mathcal{E}.d_p^2.P_T/32\,\Delta x\,\mu \qquad (2)$$

An oil-hexane mixture is passed through membrane filtration modules using dead-end and cross-flow filtration. In the dead-end filtration module higher permeate flux is initially observed but, after a certain time, there is a drastic fall in permeate flow because of concentration polarization. Concentration polarization is due to the accumulation of larger dimension particles, like PLs and colloids, on the surface of the membrane. These accumulated species form a second layer on the membrane known as a 'polarized gel layer', which reduces permeate flow. Accumulated particles are adsorbed on the membrane and cause fouling of the membrane.[64,66–70] Fouling is the result of interaction between constituents of the membrane and the accumulated particles, which further increases the resistance to permeation. These interactions may be through chemical bonding, van der Waals' forces, electrostatic forces, and Lewis acid-base reaction. To prevent the concentration polarization effect on the membrane, greater turbulence

at the feed-side filter surface by magnetic or mechanically sheer stress is preferable. But adverse effect of sheer stress was observed on membrane life. Application of tangential velocity (cross flow) conditions in place of conventional perpendicular (laminar) flow conditions (see Fig. 5) is one of the solutions to regulate deposition of solutes on the membrane. Majulata et al.[23] suggested that in cross-flow filtration 3–5 times greater flux was obtained than with dead-end filtration.

In tangential velocity condition, oil-hexane solution is allowed to flow parallel to the membrane surface. Accumulated reverse micellar particles are thus washed away due to the velocity effect and the thickness of the polarized gel layer is reduced. The permeate flux rate in tangential velocity conditions is enhanced by stimulating greater turbulence and expressed by the following equation:[26]

$$J = \Delta P/(R_M + R_C)\,\mu \qquad (3)$$

Here J refers to liquid flow in tangential condition, ΔP trans-membrane pressure, R_M membrane resistance (related to porosity), R_C membrane cake (related to fouling), and μ is liquid viscosity.[26]

Besides this, fouling is a function of pH of oil-hexane-emulsion. At higher pH levels (~10 pH) the functional group of oil changes – carboxylate ions form instead of a carboxylic acid functional group – leading to more stable emulsion formation. This carboxylate ion emulsion is attached to the membrane surface causing fouling, whereas in acidic media less fouling is observed because there is less interaction between carboxylic acid emulsion and the membrane.[63]
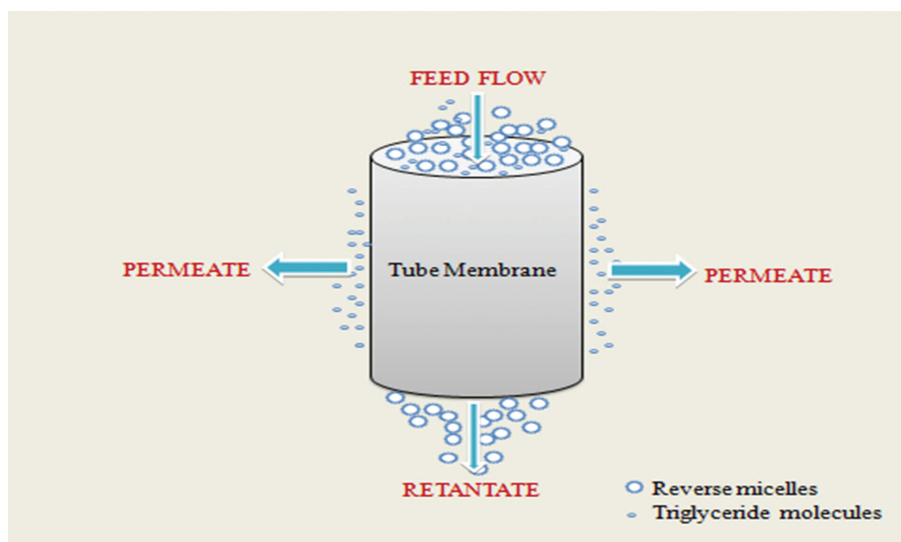

Figure 5. Tangential flow in hollow tube membrane.

Solute concentration also influences the permeate flux of hexane-oil miscella as well as oil flux. Saravanam *et al.*[71] reported that, at constant trans-membrane pressure, increasing oil dilution from 1:0 to 1:3 ratio increased the oil flux by nearly 15-fold. Dilution with hexane significantly reduced the viscosity of feed (by ~50-fold at 1:3 dilution) and was responsible for increased flux.

Higher flux rate is observed with increasing temperature. Temperature accretion lowers the viscosity and increases diffusivity – both of which increase permeate flux linearly. It should be noted that temperature should not exceed 60 °C. Above 60 °C vaporization of hexane takes place, which adversely affects the separation process. Subramanian *et al.*[61] reported that when the temperature was increased from 20 to 50 °C at constant pressure and feed concentration, flux increased from 64.4×10^{-3} to 246×10^{-3} kg m^{-2} h^{-1}. Temperature also decreased the kinetic constant, i.e. less fouling occurred and as a result higher flux was obtained.[60,72]

High trans-membrane pressure has positive effect on high permeate oil flux following Darcy's behavior. Ribeiro *et al.*[65] observed that on increasing the trans-membrane pressure from 1 to 2 bar, permeate flux increased linearly from 21.5 to 40 5 kg m^{-2} h^{-1}. At lower pressures, flux is pressure controlled and it shifts to mass transfer controlled at higher pressure. At higher pressure, polarized gel layer formation on membrane surface takes place and flux becomes less sensitive to pressure.

The **retention coefficient (R)** is a measure of the rejection of PL by a membrane during the filtration process. It is expressed as

$$\%R = [1 - (C_P/C_F)]\ 100 \qquad (4)$$

Here C_F and C_P are the concentrations of phospholipids in feed oil and in the permeate oil flow, respectively. In membrane separation, both HPLs and NHPLs are retained in the form of micellar molecules.[58,60] The rejection of PLs is affected by membrane type, size, and concentration of solute, temperature, and tangential flow velocity.

Rafe *et al.*[73] studied the effect of temperature on PL retention by membranes. Increasing temperature decreased retention; this might be due to the dissolution of the PLs or disruption of the reverse micellar structure. Rejection by membrane is a negative function of the trans-membrane pressure without agitation. This influence is diminished with agitation. This is due to a higher micellar solute concentration at the membrane surface.[58] Membranes with smaller pore diameters show higher rejection. Carvalho *et al.*[72] reported that membrane M1 (pore size 0.01 mm) presented higher retention than membrane M5 (pore size 0.05 mm) (Table 7).

Degumming by membranes is a promising technology. As reported, the membrane degumming process improves two important fuel properties: kinematic viscosity and carbon residues. These are another advantage of the membrane-separation technique.[20]

Biological degumming method

Enzyme degumming. In this method, the phospholipase group of enzymes is used. This is a complex and important group of enzymes, which are hydrolytic in nature and can hydrolyze the ester bonds in PLs, releasing a variety of substances like lysophospholipids, free fatty acids, diacylglycerols, choline phosphate, and phosphatides without affecting the triglycerides in oil. This is the best method

Table 7. Comparison of the advantages and disadvantages of ceramic, polymeric, and polymeric composite membranes.

Membrane	Composition material	Advantages	Disadvantages	Perspective application	References
1. Ceramic membrane	Al_2O_3, TiO_2, ZnO_2, SiC etc.	Higher mechanical strength, higher thermal stability, corrosive resistant, Higher structure integrity	Brittle, expensive, some are low hydrothermal stable	Small-scale application	60, 70, 72
2. Polymeric organic membrane	PVDF, PI, PSf, PC, PES etc.	Cheap, easy to synthesize, good quality control,	Short life, pore size changed by swelling in presence of organic solvent, microbial degradation, prone to denature and be contaminated	Large-scale application in food and beverage industry	56, 58, 60, 64
3. Polymeric composite membrane (modified organic membrane)	PVDF with nano-sized TiO_2/Al_2O_3 etc.	Physically and chemically very stable	Expensive	Small-scale application	63

for the reduction of PLs in oil to a level below 10 mg kg^{-1}. It is an eco-friendly and green technique that enhances the oil phase yield to 0.2–1.9 mg kg^{-1} in form of free fatty acid compounds in vegetable oil and has low process steps with the reduced use of acid-base and reduced effluents generation.[76]

Enzyme degumming is the latest technique and has been developed by the German engineering company Rohm GmbH (now Lurgi). It has been named the EnzyMax process and patented by Aalrust in the 1990s. Lurgi also developed another seed pre-treatment process prior to oil extraction known as the ALCON process. This reduces the NHPL content in extracted oil. The enzymes for the conversion of HPLs to NHPLs are deactivated by heat-moisture treatments.[74]

Phospholipase groups of enzymes fall into four major classes – A, B, C, and D – on the basis of the sites of hydrolysis in the phospholipid molecule as shown in Figure 3. Phospholipase A1 (PLA1) hydrolyzes the phospholipids at the SN-1 acyl chain and A2 (PLA2) hydrolyzes them at the SN-2 acyl chain, releasing fatty acid and lysophospholipid. Phospholipase B causes a cleavage of both SN-1 and 2 acyl chains, resulting in the formation of phosphoglycerate. Phospholipase C catalyzes the hydrolytic cleavage of the phosphate-glycerol bond, releasing diacylglycerols and the phosphate group, and phospholipase D hydrolyzes the PLs phospholipase D hydrolyses the PLs next to the phosphate group releasing phosphatidic acid and alcohol (Fig. 6).[75,76]

Several researchers have described in detail a number of methodologies for enzyme degumming. The common method for enzyme degumming involves:[74]

- Attainment of optimal reaction variables such as pH value and temperature for an enzyme reaction in oil.
- Addition of the aqueous solution of enzyme in the appropriate concentration into the oil.
- The enzymatic reaction at a high shear rate.
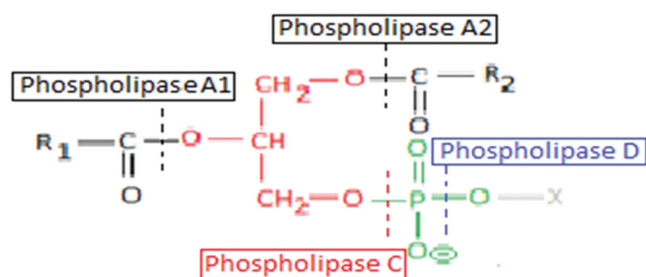- Separation of gums from the oil in the form of an emulsion.

Figure 6. Phospholipase cleavage sites in phospholipid. (Note: Phospholipase B displays activity on both phospholipase A1 and phospholipase A2 sites)

The selection of an enzyme among the various types of enzymes depends upon the PL content in the oil, the availability of enzymes (sources of different PLs are shown in Table 7),[77] enzymatic activity, and the purpose of the procedure.

Lamas et al.[78] evaluated different degumming processes using phospholipase A1, A2, and water degumming of crude sunflower oil. The PL content was reduced from 544.51 to 63.21 mg kg^{-1} in water degumming and to 3.02 and 5.81 mg kg^{-1} using phospholipase A1 and A2 respectively. They also reported that enzyme PLA1 was more efficient than PLA2. The reaction time for PLA1 was 60 min and more than 120 min for PLA2 to achieve less than 10 mg kg^{-1} phosphorus in degummed oil. In soybean oil, PLA2 needed a 5 h reaction time to reach the phosphorus content of 10 mg kg^{-1}. The differences in efficiency of both enzymes could be due to the preferential hydrolysis of phospholipid present in the oil phase by PLA1 and in the aqueous phase by PLA2. They also reported improved physicochemical properties of enzyme-degummed oil – i.e. lower viscosity and density due to separation of viscid impurities, but increased acid value due to the liberation of fatty acids by hydrolysis of ester bonds. Similar acid value results were observed by Jiang et al.[79] in the enzymatic degumming of soybean, rapeseed, and peanut oil by novel phospholipase B from Pseudomonas fluorescens BIT-18. As mentioned above,[75,76] PLB releases two FFAs from one phospholipid molecule, resulting in an approximately 0.2% increase in FFAs. The FFA content of soybean, rapeseed, and peanut oil using PLB was increased to 1.37%, 2.39%, and 2.26% from 1.27%, 2.31%, and 2.18%, respectively. Jiang et al.[76] studied the degumming efficiency of the PLA1 and PLC enzymes on a variety of citric-acid-treated oil samples and reported that PLA1 significantly reduced the phospholipid content below 10 mg kg^{-1} and that PLC enhanced the oil-phase yield. They concluded that the combined action of both PLC and PLA1 could efficiently reduce the phosphorus and diacylglycerol (DAG) content with minimal oil yield loss. Ye et al.[80] reported that PLC degumming is more efficient than water degumming in terms of phosphorus removal and contributed to the oil-phase yield by liberating DAG as a part of the oil from the PLs. They observed that coloring matter was also reduced in the PLC degummed oil by entrainment into colloidal particles of PLs.

A simple enzyme degumming method was not preferable for high PLs containing oil. A modified methodology for enzyme degumming was proposed by Yang et al.[81] to efficiently reduce high PL content. Citric acid (45%) solution was added into preheated oil (80 °C) and mixed at a higher shear rate. After 20 min contact time, NaOH (16%) solution was added to the oil to adjust to the required pH 3–6

of the above mixture. The appropriate amount of enzyme solution was then added at 50 °C and sheared at a high rate. After an incubation time of 5–6 h, the mixture was centrifuged for 10 min and both aqueous and sludge phases were separated. They also optimized the above process using three parameters: enzyme dosage, temperature, and pH. The phosphorus content was decreased with increasing enzyme dosage. They reported that the residual phosphorus content was nearly 20 mg kg^{-1} when no enzyme was added and 36.9 mg kg^{-1} enzyme dosage reduces phosphorus content to 3.1 mg kg^{-1}. The lowest phosphorus content was observed at a lower pH of 4.9 and a high temperature of 48 °C. This might have occurred due to maximum activity of phospholipase rather than that of lipase at lower pH and high temperature maximum activity. The effect of temperature and pH on Lecitase® Ultra was studied by Yang et al.[82] When the temperature was over 40 °C and there was slight acidity of pH ~5.0, the enzyme exhibited phospholipase activity predominantly, and the lipase activity was suppressed (Figs 7 and 8; Table 8).

In the commercialization of enzyme degumming, high enzyme cost, and lack of separation and reusability of enzymes, are major limiting factors. The immobilization

of enzymes on solid supports has proven to be an excellent alternative due to their stability, reusability, and lower operating costs. The key point of the enzyme degumming process is the adjustment of the optimal conditions for the enzyme reactions – i.e. optimal pH and temperature. Immobilization also reduces the sensitivity of enzymes to pH and temperature. Immobilized enzymes also exhibit better catalytic activity and stability during storage and use. The solid supports used are mainly nano-materials like nano-particles of polymers, because they provide a larger surface area for enzyme attachment, which enhances enzyme activity (U).

Yu et al.[90] considered the effects of pH and temperature and the relative activity of magnetic immobilized phospholipase A2 (Fe$_2$O$_3$/SiO$_x$-g-p GMA) for soybean oil degumming. The magnetic immobilized enzyme had shown a broader pH (4.0–5.5) and temperature (50–70 °C) operating profile. The enzyme retained more than 80% of its initial activity after five cycles of enzymatic process. Sheelu et al.[91] also observed that immobilized lecitase in gelatin hydrogel had been used effectively without loss of enzyme activity for up to six cycles of degumming reaction. Li et al.[92] had proposed the application of bio-imprinted
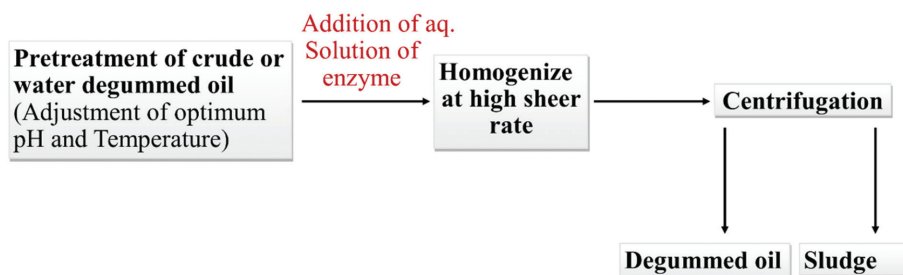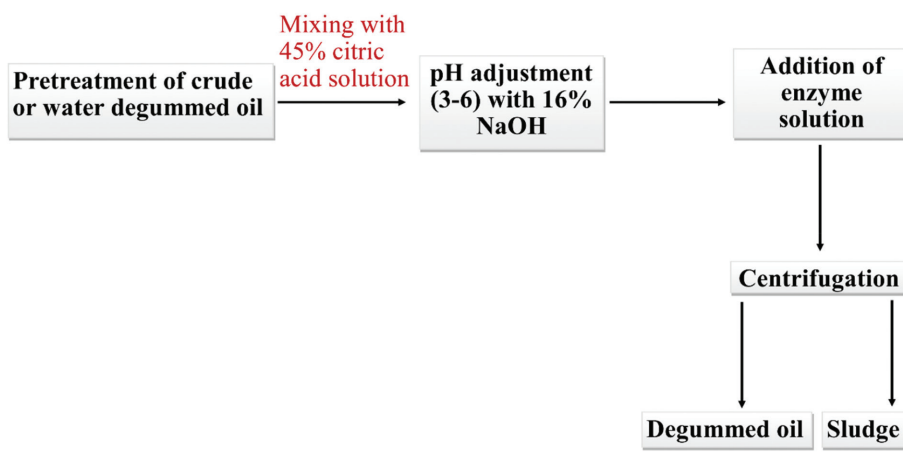

Figure 7. Enzyme degumming process.

Figure 8. Modified enzyme degumming process.

Table 8. Types of phospholipase and their sources.

Types of phospholipase enzyme	Sources	References
Phospholipase A1	Mammalian cells such as plasma of rat livers and bovine brain and micro-organisms like yeast, *Sachharomyces cerevisiae*, as well as fungi, *Fusarium oxysporum, Aspergillus oryzae* etc.	83, 84
Phospholipase A2	Mammalian tissues, porcine pancrease as well as insect and snakes venom and *Streptomyces violaceoruber* bacteria	85, 86
Phospholipase B	Snake and bee venom, *P. fluorescens* BIT-18	72
Phospholipase C	Mammalian tissues and bacteria like *Staphylococcus aureus, Pseudomonas aeruginosa, Clostridium perfringens* etc.	87, 88
Phospholipase D	Mammalian tissues, virus and plant cells, e.g. cottenseed, rice.	89

enzymes in the area of enzyme degumming. Bio-imprinted enzymes exhibit non-aqueous system tolerance, super activation, high constancy, substrate selectivity, enantioselectivity, and reusability. Bioinformatics techniques and protein engineering of phospholipase enzymes to improve activity were recently explored areas. Some mutants of PLA1 were designed by An *et al.*[95] using bioinformatics and these were applied in soybean oil degumming and resulted higher phospholipase activity.

As mentioned earlier, the PL enzyme degumming reaction takes place at the interface area of the aqueous phase containing enzyme and oil phases, which means that the reaction is very slow. By increasing the interfacial area the rate of this reaction can be increased. The kinetics of this reaction have also been studied taking interfacial area into account. Jiang *et al.*[94] advocated ultrasound irradiation to enhance the interfacial surface area as an alternative to mechanical stirring. Ultrasound irradiation causes cavitations in water/oil emulsion. When cavitation bubbles collapse near the phase boundary, the resultant shock wave provides a very efficient mixing of the two immiscible liquids. Jiang *et al.* also compared mechanical-stirring systems with ultrasound assisted mechanical stirring and reported that less time and water were needed in the

ultrasonic-assisted system. They reported that the quality of degummed oil in terms of oxidation stability was also reduced because of oxidation acceleration by cavitations.

Enzyme degumming is a superior method and has the following advantages:

- No oil loss occurs during enzyme degumming and it enhances the oil phase yield. In this process, soap stock is not produced, therefore no oil loss is caused by soap stock separation.
- Oil with a very low phosphorus level is obtained after enzyme treatment. The phosphorus level of oils can be less than 10 ppm, making them suitable for biodiesel production.
- It is an environmentally friendly process, as waste products are formed after degumming except 1–2% wastewater.

Enzymes provide significant degumming of crude oil for biodiesel production but there are some drawbacks. It affects the quality of oil, with decreased oxidation stability, increased peroxide values, etc., with the result that a less stable oil is produced. Contact with light, oxygen, and oxidized compounds should be avoided during and after the degumming process.[95] The oxidation stability of oil is very crucial quality when oil is used in biodiesel production, so more attention should be paid to this area.

Comparison of various degumming techniques

The various degumming techniques and their advantages and disadvantages are presented in Table 9.

Two conventional methods – water and chemical degumming, especially using citric and phosphoric acid – are currently quite popular for degumming vegetable oils. In water degumming, lecithin recovery is a beneficial aspect but the major drawback of the technique is its lower efficiency. In phosphoric acid degumming, the high phosphatide content can be reduced by up to 90% and this process is used in industrial procedures for the degumming of crude vegetable oils.[26,96]

Economic assessment of the degumming process

The economic assessment of various degumming techniques for vegetable oils is crucial for industrial-scale application. The economics of degumming methods should consider the number of operations performed as

Table 9. Advantage and disadvantage of various degumming techniques.

Types of degumming techniques	Advantages	Disadvantages
1. Water degumming	Ecofriendly; No chemical effluents generation; lecithin recovery	Only applicable for removal of HPLs removal; less efficient
2. Chemical degumming	Better efficiency	Use of chemicals; Temp can alter the degummed oil quality; Chemical effluent generation; Huge water consumption
3. Membrane degumming	Better efficiency	Expensive; time consuming; use of organic solvents; membrane fouling
4. Enzyme degumming	Eco-friendly; not-polluting; efficient	Not applicable for high gum amount; slower process; cost ineffective

well as the degummed oil quality. The water degumming process is the most economic method in terms of the least number of operations during phospholipid removal. However, the gum-removal efficiency of water degumming is lower than other degumming techniques. Chemical degumming methods include the utilization of chemicals such as citric acid, phosphoric acid, and EDTA. The use of acids effectively removes the gums from vegetable-oil feedstock. The treatment of waste effluents is also an important aspect of chemical degumming. With the membrane degumming technique, the use of expensive solvents, membrane fouling, poor permeate flux rate, etc., are major challenges to the industrialization of the process. With the enzyme degumming approach, the phospholipase group of enzymes is used. These enzymes are very efficient in removing PLs from oil, with oil phase enhancement. The high cost of enzymes, no-reusability, and number of operational processes makes enzyme degumming techniques uneconomical. Reviewing the literature regarding the various degumming techniques, it was concluded that each technique has its own limitations and disadvantages, which provides scope for research to make the degumming process economical.[97]

Concluding remarks

The removal of gums – mainly PLs that are mucilaginous and amphoteric molecules – is considered to be an important process for obtaining fuel-grade biodiesel. Degumming improves the oxidation stability of biodiesel, minimizes yield loss, reduces the viscosity of oil, and results in the higher conversion rate of biodiesel. After water degumming, a large amount of PLs remained, which decreased the conversion rate of biodiesel and caused yield loss. Although chemical methods of degumming reduce

PLs adequately, they generate chemical effluents and are energy intensive. The membrane and enzyme degumming methods reduce PLs to very low levels, but these methods are very costly at an industrial scale. Degumming is still an area that needs intensive research. Newer degumming methods should be discovered that are eco-friendly, energy intense, cost effective, with low requirements for time or chemicals, and they should reduce the PL and metal content to meet international standards for biodiesel.

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