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Conventional and advanced purification techniques for crude biodiesel – A critical review

Farwa Nadeem[1]*, Aimen Shahzadi[1], Asma El Zerey-Belaskri[2] and Zaheer Abbas[1]

[1]*Department of Chemistry, University of Agriculture, Faisalabad-38040-Pakistan and* [2]*Faculté des Sciences de la nature et de la Vie, Université de Sidi Bel Abbes, Algérie*

Abstract

With enormously increasing global population and rapidly depleting natural resources, there is an apparent demand for radical unprecedented innovation to satisfy the basic necessities of all living organisms. Hence, non-conventional and renewable biodiesel is gaining interest because of being a potential alternative, reliable source and ecofriendly future fuel. However, quality of biodiesel needs to be checked strictly in order to maintain the efficiency of fuel as several impurities like catalyst residues, free fatty acid contents, soap formation, monoglycerides, diglycerides and a significant amount of glycerol pose serious problems while using biodiesel in the engine. Conventional purification techniques including wet washing and deionized water washing are now being replaced by advanced purification methods such as adsorbents or membranes due to the generation of a huge amount of wastewater, large quantities of environment polluting agents and more consumption of energy. In this review, different purification methods and different adsorbent materials are discussed in detail among which magnesol and silica have shown better results than purolite and amberlite. Furthermore, some bio-adsorbents (sugarcane bagasse, OEPFB, eucalyptus pulp, cellulose, starch, and rice husk ash) along with pressurized CO_2 passage for purification of biodiesel are also being used nowadays. Commercially available cation and anion exchange resins are known to provide biodiesel purity level according to ASTM and ANP standards. Inorganic ceramic based membranes are better than organic membranes as they not only provide appreciable results but are also more durable and long lasting. PTFE membranes are preferred over all other characterized membranes for liquid-liquid extraction due to its high breakthrough pressure and contact angle value.

Keywords: Biodiesel, Purification Techniques, Biosorbents, PTFE Membranes, Magnesol, Silica, Purolite, Amberlite, Resins

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1. Introduction

Due to consistent depletion of naturally occurring resources of fossil fuels, efforts are being made to generate renewable fuel sources. Biofuel is the most prominent product of such efforts which is not only renewable but also environment-friendly, sustainable, reliable and highly promising. Chemically, it is alkyl ester of fatty acids obtained as a result of esterification reaction of oil and alcohol. This reaction can be carried out through different processes such as direct blending, transesterification and pyrolysis. The oil used for this purpose is obtained from plant sources and can be edible, non-edible or waste oil. To prevent the direct stress on the food industry and to control the economic factor, non-edible or waste seed oil is mostly preferred for the production of biodiesel. To produce biodiesel as an economically efficient and reliable fuel, it must meet certain quality parameters as prescribed by ASTM (American Standard for Testing Materials) and EU (European Union) according to which biodiesel fit for use in compression ignition engines should be 96.5% pure.

However, scientists are still struggling to cope with serious issues such as to improve the quality of biodiesel, to fabricate efficient and suitable catalyst for transesterification reaction, to truncate the manufacturing process at industrial level, to reduce the generation of large volumes of toxic and environmentally hazardous solvent wastes during the purification step of biodiesel and to control the cost of product at industrial level. The purification of biodiesel refers to the removal of unused methanol, diglycerides, monoglycerides, soap, free fatty acids, glycerols and catalyst residue etc. Great attention has been paid to draw an appropriate mechanism for the purification of biodiesel. Conventional techniques include washing of biodiesel using distilled water or deionized water. A study reports that at least 3 kg of fresh water is utilized to purify 1 kg of biodiesel which is a relatively high ratio. Purification can be categorically divided into wet washing and dry washing.

Different solvents which may be organic or inorganic in nature are used in wet washing.

Considerably large volumes of most of the commonly used solvents such as petroleum ether, n-hexane, cyclopentylmethyl ether (CPME), 2-methyltetrahydrofuran (2-meTHF) etc. are produced during purification of biodiesel even if the solvents are reused. Furthermore, these solvents are toxic in nature and are not environment-friendly. To solve this problem, green solvents have also been introduced but these are not cheap enough to be used freely at an industrial scale. Dry washing involves the use of different adsorbents which possess both acidic and basic adsorbing sites for the attachment of impurities. Although adsorbents are more efficient for purification, their usage still requires dealing with solid waste at the end of the process. Commonly used adsorbents are magnesol, bentonite, magnesium silicate, aluminium silicate, silica gel, activated carbon and activated clay etc. Recently, some bio-adsorbents have been used as sugarcane bagasse and oil free palm fruit bunch. These have shown considerably good results and are also environment friendly. Another method for the purification of biodiesel includes the use of oil-freepressurized passage of CO_2 from crude biodiesel.

Purification membrane is the most advanced method for purification of biodiesel that can be either organic or inorganic in nature. The basic purpose to use this membrane is to ensure pressure driven separation methodologies that can be via reverse osmosis, ultrafiltration and microfiltration. Initially, all the membranes used were cellulosic in nature nevertheless now-a-days, polycarbonate, polysulphone, polyamide and various other advanced polymers are also being extensively used. These artificially prepared polymeric membranes has shown better resistance and improved chemical stability towards microbial degradation. In addition to this, some recent researchers remarked that PAN is asymmetric and porous membrane that possesses high rate of permeation along with high selectivity. However, in the organic solvents, these polymeric membranes can swell thereby instantly or long term changing the pore size. Consequently, such types of polymeric membranes in number of solvent applications have significantly shortened the operating lifetimes. Nonetheless, much attention has been paid on different types of inorganic membranes owing to be superior then organic membranes in maintaining the thermal, mechanical and chemical stability, high flux, high porosity, resistance to microbial degradation, long lifetime, increased resistance to fouling and relatively a narrower pore size distribution. Thus, these porous inorganic membranes (like Al_2O_3, TiO_2, ZrO_2 and SiC) possess some extra practical advantages over polymeric ones such as higher mechanical strength and thermal and corrosive resistance among others.

Table 1 Impurities in biodiesel, their origin and technique for removal of impurities

Impurities	**Origin**	**Removal Method**
Methanol	It is the excess alcohol left unreacted at the end of transesterification	Water washing and evaporation
Glycerol	The by-product that is still present in trace amount	Water washing and adsorption
Soap	Produced through saponification of free fatty acids	Neutralization, distillation and water washing
Diglycerides and Monoglycerides	Produced in transesterification	Separate membrane and adsorption
Catalyst Residue	Mostly heterogenous catalyst residues in trace amounts	Water washing, separate membrane and adsorption

2. Wet Washing Process of Biodiesel Purification

Biodiesel has been most commonly purified by wet washing for which organic solvents, mineral acids or deionized water was used. Although wet washing results in high quality, purified biodiesel that meets the values specified by ASTMD6751 and EN14214 standards, but the generation of large volumes of environmentally hazardous wastewater, rise in cost and energy consumption, lowering of biodiesel yield and longer required production time questions its candidature for future usage [1]. Crude biodiesel contains impurities like unreacted alcohol, glycerol residue, catalyst residue and soap, out of which glycerol and alcohol are highly soluble in water and hence can easily be removed by extensive water washing. If a sodium based catalyst was used then it can also be removed simply by water washing. Excess alcohol can also be distilled or evaporated before washing step. The presence of moisture in a free fatty acid containing feedstock, during transesterification, leads to soap formation which not only consumes catalyst but also results in an extra unwanted layer of soap that needs to be removed to prevent the formation of an emulsion during washing. The moisture content of biodiesel is controlled either by drying over anhydrous sodium sulphate or molecular sieves followed by filtration or by stripping with a hot gas. Water washing has many advantages, but also it creates a number of problems, as evident in many research articles [2].

2.1 Washing with Deionized Water

Hot deionized water usually at 50-60ºC is used for purification of crude biodiesel for the separation of glycerol phase. Methanol, glycerol and catalyst residue can be completely eliminated from the final product. By now, the influence of water washing on the density, viscosity and acidity of the product has been studied by Gonzalo et al. [3]. A single water washing step with constant stirring in the reaction vessel for 30 minutes was reported for the crude biodiesel obtained from rapeseed oil or used cooking oil through acid catalyzed transesterification. The water content in the product increased with increasing the washing temperature and decreasing the amount of washing water. Coêlho et al. [4] reported the purification of biodiesel produced from castor oil by washing it at different temperatures (30°C and 70°C) and pH values (2 and 5). Acidified water was used to make emulsion containing 25% of crude biodiesel in the first wash. The amount of acidified water was decreased in the following washes. The emulsion was stirred and left to stand until the separation of these phases. The final purified product was obtained after centrifugation when the biodiesel attained a neutral pH value [4]. The most influential factor on the amount of washing water was pH, followed by interactions of the catalyst with pH and temperature. The amount of water increased with increasing the pH of the washing water from 2 to 5. The effects of temperature and catalyst type were found not to be statistically significant.

2.2 Washing with Green Solvents

Fewer green solvents have been reported for the purification of biodiesel which were organic and non-polar in nature. A purity level higher than recommended by ASTM and EU (96.5%) were obtained by using these green solvents, 2-methyltetrahydrofuran (2-MeTHF) and cyclopentyl methyl ether (CPME). A comparison with hexane solvent was also made which showed almost similar results. The usage of green solvents can provide an eco-friendly solution to avoid the use of toxic and environmentally hazardous acidic solvents. The product showed higher viscosities and densities as compared to other solvents but still fell in range prescribed by the ASTM and EU standards. However, the cost factor controls its implementation at the industrial level. At the laboratory level, liquid-liquid extraction and column chromatography techniques were used for the purification of algae biodiesel with green solvents. In liquid-liquid extraction, an extra washing step was needed in which the material was left for decantation for 24 h [5].

3. Dry Washing

Dry washing removes contaminants from crude biodiesel by adsorption or passing crude biodiesel through a bed of ion-exchange resin. Most operating procedures for dry washing are developed by trial and error. Different adsorbent materials fulfil for treating crude biodiesel, such as magnesium silicate (magnesol), calcium magnesium silicate and cheap biosorbents. The spent adsorbent can be disposed of to landfill or other uses might be invented. Also, different types of ion-exchange resins are applied for waterless refining of crude biodiesel. Usually, small styrene beads coated with polar functional groups are employed. The suppliers of these ion-exchange resins do not recommend regeneration of the spent material. Therefore, the main drawback of dry washing is to find a solution for the generated solid waste. Although the method using magnesol has a better effect on the removal of methanol than ion-exchange resins, the purified biodiesels from both processes might not fulfil the specifications of EN Standards. Dry washing refers to the removal of contaminants from biodiesel by using a bed of ion-exchange resin or adsorbent. It is a waterless purification method that involves treatment of crude product on the basis of trial and error. The adsorbent materials being used commonly for this purpose are magnesol (magnesium silicate), calcium magnesium silicate, amberlite, purolite; bentonite, hydrated magnesium silicate, silica gel, activated carbon and activated fibre and chamotte clay are also used as adsorbents [6].

3.1 Dry Washing by Using Adsorbent

Adsorbents are solid substances comprising of basic and acidic adsorption sites that attract oppositely charged incoming substances e.g. glycerol and methanol etc. In dry washing using adsorbents, diglycerides, triglycerides and free glycerols can easily be removed up to reasonable levels with zero wastewater generation and in comparatively lesser washing time. The procedure can easily be incorporated in the existing plant as it requires lower space and minimizes total surface area coverage of the wash tank. Dry washing using adsorbent materials is also reported by some scientists to be cost effective and efficient in terms of production time. Another benefit is that water content of pure biodiesel as specified by ASTMD6751 i.e. below 500 ppm is possible to achieve as no water is utilized in the washing of crude biodiesel. While in water washing, the addition of water removal step in the process makes it more complicated, costly and time consuming as water usually exceeds 1000 ppm concentration which is not acceptable.

A study reported commercial silica gel and rice hull ash for the removal of free fatty acid contents of the crude biodiesel under atmospheric conditions and the results showed silica gel to be a better adsorbent providing smaller loss of methyl esters. The content of methyl esters in the final product increased with increasing the silica gel dosage. Commercially synthesized silica gel has been used for purification of biodiesel obtained from different feedstocks using methanol and alkali catalyst. At first, methanol was removed from the crude biodiesel by vacuum evaporation. Then, the biodiesel was stirred with silica gel for 20 minutes and filtered to remove the silica gel. Finally, the filtrate was passed through a bed of sodium sulfate to remove traces of water. The canola methyl ester had physical and chemical properties similar to diesel fuels. The acid value of the final products was below the specified limit. The physicochemical properties of the purified biodiesel were according to ASTM standards.

Yori and coworkers used freshly prepared silica in the form of fixed silica beds for removing glycerol from purified biodiesel and glycerol mixtures which showed a better glycerol removal i.e. up to 0.13 gg^{-1}. Different factors such as feed rate, the concentration of glycerol and mass of adsorbent affected the breakthrough point of silica bed. Due to the coinciding saturation point and breakthrough point, maximum adsorption was attained when the particle size was 1-1.5 mm. With greater silica beads (1/8in), the breakthrough point was at about one-half of the time for full saturation because of internal mass transfer limitations. Treatment of used silica bed with methanol (4 bed volumes) followed by drying in a nitrogen stream for 1h can regenerate the adsorbent for reuse. The ability of adsorbent for glycerol removal is not affected by the presence of soap or small amounts of water. However, the saturation capacity decreases with increasing mono-acyl-glycerol and methanol levels in the crude biodiesel.

The activated bleaching earth is another adsorbent reported in the literature which was employed to palm oil derived biodiesel. The final reaction mixture of alkaline catalyzed ethanolysis of palm oil containing pure glycerol was heated for 1 minute at 70W in the microwave oven and then separated by gravity. The resulting layers were heated at 80°C for methanol removal. The adsorbent is then mixed and centrifuged where optimum concentrations of glycerol and adsorbent were 10% and 1.2% respectively. The resulting product purity lied within the specified range of ASTM standards. Same adsorbent material was also used for the purification of biodiesel obtained from Pollock oil through alkali catalyzed transesterification. The biodiesel to earth mass ratio of 1:10 was used. The results proved the activated bleaching earth to be an effective adsorbent for biodiesel purification.

Some scientists used a natural adsorbent prepared from clay material (i.e. natural silica-smectite mixture) for biodiesel obtained from soybean oil. Both free and total glycerol contents were reduced to appreciable levels in comparison with commercially manufactured synthetic magnesium silicate adsorbent. Some recent investigators showed that activated low silica bentonite (120–200mesh) was an efficient adsorbent for purifying biodiesel. The natural material was activated with 0.1M sulfuric acid at 100°C for 1h. Freundlich model was used to study the adsorption of impurities on the adsorbent. Activated silica bentonite provided 47% of glycerol removal when 5% of it was used.

A recent study reported the comparison of different adsorbents i.e. magnesol®, silica, amberlite BD10 DRY® and purolite PD 206® for their efficiency in the treatment of biodiesel obtained from soybean oil for impurities removal. The comparison was based on the amount of impurity like methanol, soap, residual water or potassium removed by that particular adsorbent. As a result, we observe that magnesol® and silica showed better adsorption properties than amberlite BD10 DRY® and purolite PD 206®, especially for removing soap, free and bonded glycerol and potassium. The main results found for these two adsorbents (magnesol®1% and silica 2%) were values below 0.17 mg KOH g^{-1} for acid number, 1 mg $kg^{-1}$of potassium, 61 ppm of soap, 500 mg $kg^{-1}$of water, 0.22% of methanol and 0.03% of free glycerol [7-8].

3.1.1 Chamotte Clay Adsorbent

Chamotte clay is a solid waste of red ceramic industry which was utilized as inorganic dry wash adsorbent for the removal of glycerol from crude biodiesel. Its structure and composition were studied by X-ray diffraction, FTIR and SEM to determine its capability to be used as adsorbent. Chamotte levels of 2.5 w/v% at 45°C maximized glycerol removal (1282 mg glycerol g^{-1}) with minimum loss of adsorbate. Biodiesel from palm kernel oil was used as a sample. After treatment with chamotte clay, significantly lower glycerol content (< 0.02 wt%) were found in comparison with crude biodiesel (0.29 ± 0.03 wt%). Monoacylglycerols and diacylglycerols were also reported to be removed by the adsorbent [9].

Table 2 Potential adsorbents and their uses

Adsorbents	Description	References
Chamotte Clay	Solid Waste from Red Ceramic Industry and Glycerol Removal	[9]
Magnesol	Metals, Alcohols, Diglycerides, Glycerol and Soap	[10]
Silica Gel	Alcohol, Water, Soap and Potassium	[10]
Hydrated Magnesium Silicate	-	[11]
Activated Carbon	-	[9]
Bentonite	-	[7-8]
Amberlite	-	[7-8]
Purolite	-	[7-8]

3.1.2 Activated Carbon

Activated carbon is another method of treatment for the purification of crude methyl esters. Activated carbon obtained from spent tea waste was compared with synthetic adsorbent silica gel and conventional water washing processes. The results proved the activated carbon to be better than the other two. Biodiesel not only resulted in higher yield but also showed better fuel properties. Moreover, the used activated carbon can be regenerated and reused. In another investigation, biodiesel was refined via activated carbon, activated clay, activated fibers and acid clay. It was reported that the grain size effects the purification of biodiesel as clay grain size that ranged between 0.1 mm and 1.5 mm gave better yield. The smaller grain size of clay particles helps to achieve better purification. However, the removal of spent adsorbent proves more cumbersome. When the size of clay grain is larger, the purification process is inferior but separation after the treatment becomes simple. Usually, activated carbons are mostly employed as an adsorbent for the removal of excess color in biodiesel [10].

4. Bio-Adsorbents Used for Purification

A number of adsorbent materials that are currently being used for purification of crude methyl esters are originated from plants that are organic in nature. These are usually extracted from plant materials and are either in the form of ashes, raw material, extracted cellulose or starch or fibrous material. These adsorbents usually have higher adsorption capacity, larger surface area and are even sometimes porous in structure.

4.1 Sugarcane Bagasse Bio-Adsorbent

Dry washing of crude biodiesel using bio-adsorbents is a new trend as these are inexpensive, biodegradable, non-toxic and easily available. However, research is being done to ensure biodiesel quality and process efficiency while using bio-adsorbents. Sugarcane bagasse has been proposed as a cheap adsorbent which was applied in its three different forms i.e. raw sugarcane bagasse (as received), steam explosion pre-treated bagasse and bagasse ash. An efficient glycerine removal was reported by adding only 0.5 wt% of sugarcane bagasse to gain 0.02 wt% of total glycerine content in purified biodiesel with 88.86 mgg^{-1} glycerine adsorption. Kinetic studies showed it to be a fast process where more than 70% of glycerol was removed in 10 minutes of the adsorption process. Sugarcane bagasse presented results for biodiesel purification similar to those for wet washing process or with magnesol®. Thus, dry purification with sugarcane bagasse is a suitable alternative for biodiesel treatment at a low cost and efficient process [12].

4.2 OPEFB Bio-Adsorbent

A naturally extracted bio-adsorbent was fabricated by pressing and shredding oil palm empty fruit bunch and used to remove impurities from crude biodiesel obtained after transesterification of waste cooking oil. The operating procedure involved the implication of 5 different wt% concentrations of bio-adsorbent under continuous stirring at 500 rpm for 1 h. For 5 wt% loading concentration of bio-adsorbent, 89.7% of residual methanol, 81.7% of water, 36.7% of free fatty acid and 98.6% of potassium removal was obtained which met European standards for biodiesel (EN14214). In comparison to commercial adsorbents and the water washing method, purification using oil palm empty fruit bunch derived bio-adsorbent resulted in higher removal of free fatty acids, potassium, water impurities and a smaller loss of fatty acid methyl esters. The bio-adsorbent is not only renewable but also provides the ease of operations and considerably efficient results for the treatment of crude biodiesel.

4.3 Coco Coir as Bio-Adsorbent

Coco coir is a heterogeneous natural fibre consisting of coco pith, coco fibre and coco chips, collected from coconut husks. Chemically, it is cellulosic fibrous material whose sponge like pith is known to participate in ion exchange reactions. It is studied in research as a readily available, cheap, durable, renewable and biodegradable dry wash adsorbent material that can be effective for the removal of contaminants from biodiesel. The ability of coco coir bio-adsorbent to separate soap, methanol and free glycerol from crude biodiesel was examined along with its long term stability and efficiency. The results proved that coco coir bio-adsorbent is not only stable enough to last for a time period greater than 5 years but also provides biodiesel qualities as required i.e. it lowers soap concentrations up to 3000 ppm in a single column pass, removes free glycerol, free fatty acids and methanol up to satisfactory levels even when large volumes of raw biodiesel are treated at industrial scale. Moreover, it did not show any increase in Ca^{2+} or Mg^{2+} in the treated product [13].

4.4 Starch and Cellulose as Bio-Adsorbents

Natural adsorbents are usually non-toxic, biocompatible, renewable and easily degradable in nature which generate minimal waste at the end of the process. Cellulose and starch have been reported for their use in the purification of fatty acid methyl esters obtained from sunflower oil. Cellulose and starch used for this purpose were extracted from potato starch, corn starch, rice starch, cassava starch and eucalyptus bleached kraft cellulose. An industrial adsorbent select 450 was also employed in the study in order to make a comparison. Different concentrations of selected adsorbents were chosen 1%, 2%, 5% and 10% (w/v) at 25°C for 10 min. For the evaluation of the efficiency of the adsorbent chosen, different parameters such as acidity index, combined alkalinity, free glycerine and turbidity of biodiesel were determined. All the selected adsorbents showed considerably good results regarding the purification of biodiesel which proved the future usage of natural adsorbents promising enough to be employed at an industrial scale [14].

4.5 Eucalyptus Pulp as Bio-Adsorbents

Biodiesel produced from sunflower oil and recycled cooking oil was treated with different techniques to study their efficiency in metal removal (mainly Fe, Mn and Cu) from crude biodiesel. Biodiesel treated with cellulosic adsorbent resulted in the removal of 13–81%, 35–84% and 40–74% of Fe, Mn and Cu while when washed with deionized water, it removed 4–40%, 10–47% and 4–19% of Fe, Mn and Cu. So and cellulosic are not only much more efficient but are also eco-friendly, non-toxic, renewable and biocompatible in nature. Moreover, the adsorbent can be regenerated. On the other hand, waste deionized water containing metal ions have to be treated before its disposal.

This study also provided results for the removal of Fe, Mn, Cu and Pb from fatty acid methyl esters obtained from sunflower oil and residual cooking oil using kraft pulp eucalyptus fibres. The cellulosic fibres have great potential for adsorption of metals as these possess active hydroxyl groups that can attach metal ions. The efficiency of regenerated cellulose was also discussed as it gave 62%, 84% and 70% removal of Fe, Mn and Cu from biodiesel [15].

4.6 Rice Husk Ash

A comparison of rice husk ash, commercially available magnesol (1% w/w) and conventionally used acid solution (1% aqueous H_3PO_4) was made for the purification of biodiesel obtained through transesterification of waste frying oil. Rice husk ash is a by-product of rice processing and was used as bio-adsorbent for the removal of glycerol from the crude biodiesel. Different concentrations i.e. 1%, 2%, 3%, 4% and 5% w/w were used in the process. The 4% concentration provided the best results as compared to other concentrations. This result was because of the presence of high silica content as well as the structure which comprised of meso and macropores in the rice husk ash. Hence, rice husk ash appears to be effective bio-adsorbent for the treatment of crude biodiesel [10].

Table 3 Impurities removed by some effective bio-adsorbents

Bio-Adsorbents	Description	Impurities Removed	References
OPEFB	Tertiary Industrial Waste, Pressed and Shredded Oil Palm Empty Fruit Bunch	FFA, Methanol, Water and Potassium	[16]
Coco Coir	Heterogeneous Natural Fiber Collected from Coconut Husks	Soap, Methanol and Free Glycerol	[13]
Eucalyptus Pulp	Cellulosic Adsorbent containing Kraft Pulp Eucalyptus Fibre	Metals like Fe, Mn and Cu	[15]
Cellulose and Starch	Obtained from Natural Sources like Rice, Corn, Potato and Cassava	Metal, Turbidity, Glycerine and Alcohol	[14]
Sugarcane Bagasse	Used as Bagasse Ash	Free Glycerine	[12]
Rice Husk Ash	Obtained from Agro-Industrial Waste and Natural Cellulosic Adsorbent	Glycerol	[15]

5. Dry Washing by Using Ion Exchange Resins

Anion and cation exchange resins have been used for biodiesel purification for many years. These may be used as a bed of adsorbent or in form of column. Ion exchange resins are also used for the catalysis of oil for the synthesis of biodiesel. However, much work is needed to be done to fabricate simultaneous transesterification and purification to obtain a cleaner biodiesel product from feedstock oil [17]. SP112H and GF101 were reported to treat crude biodiesel for its free fatty acid component as well as mono-acyl-glycerol, di-acyl-glycerol and tri-acyl-glycerol, water and glycerol. Results were satisfactory for their use in further studies [18]. The cation exchange resin, "diaion PK208LH", and the anion-exchange resin, "diaion PA306S" were reported by [19]. The methanol content which was 1.0 wt.% in the effluent was reduced to 0.2 wt.% by evaporation under pressure. Most of the impurities like free fatty acid content, soap, glycerol, total water content and mono and di glyceride contents fell into the specific range as prescribed by (EN14214) and the USA (ASTM D6751).

6. Membrane Technology

Membranes are selectively permeable barriers that can separate the constituents of a mixture by restricting or allowing its passage through the porous structure of the membrane. Separation of a mixture component can occur due to the phenomenon of convection or by diffusion. This chosen phenomenon can be driven by applying external electric field, pressure or temperature gradient. In nature, a membrane can be charged, neutral or bipolar with a symmetric or asymmetric and homogeneous or heterogenous structure. For the separation of non-aqueous fluids, the membrane usage is not quite common as it has been commonly used for commercial applications of water purification, protein separations and gas separations. Membrane technology is emerging in biodiesel purification where chemically different components of the crude biodiesel i.e. glycerol, methanol and soap can be removed across the membrane structure. Recently, the membrane is being functionalized with catalytic entities such that the catalysis and purification of biodiesel occur simultaneously. Various factors like particle size, shape and molecular weight of constituents affect the interaction of that particular component with the membrane material. The performance of membrane separation is significantly affected by membrane composition, pressure, temperature, velocity of flow and interactions in between components of the feed with the membrane surface.

Module configurations include tubular, hollow fiber, spiral wound and rotating devices along with flat plates. Tubular modules are commonly applied where it is beneficial to have a turbulent flow regime, for instance, in the concentration of high solid content feeds. The membrane is cast inside of a porous support tube which is often housed in a perforated stainless steel pipe. Individual modules contain a cluster of tubes in series held in a stainless steel permeate shroud. The tubes are generally 1–6 m in length and 10–25 mm in diameter. Tubular modules are cleaned without difficulty and a good deal of operating data exists for them. Their major disadvantages are the fairly low membrane surface area. The separation of solution components via membrane is achieved by restricting the passing of unwanted material via a semi-permeable barrier in a selective manner. The transportation using membrane is affected by diffusion of individual molecules, temperature or pressure gradient and concentration difference.

6.1 Organic Membranes

Traditionally, most of the organic membranes were cellulosic in nature but recently polyamide, polysulphone, polycarbonate or some other synthetic or natural polymeric materials are also in use. The synthetic polymeric material is now being preferred for membrane synthesis as these are more stable, chemically improved and resistant to microbial degradation. The separation usually occurs through microfiltration (MF), ultrafiltration (UF) and reverse osmosis (RO). Selectivity, permeation rate, symmetry and porosity are some of those factors which decide the appropriate selection of membrane for a particular separation procedure. However, the major disadvantage of using organic membranes is that these may swell resulting in an instant or long-term pore-size changes. Consequently, in several fruitful solvent applications, these polymeric membranes are known to have shorter operating lifetimes.

6.2 Hollow Fibre Membrane

Polysulphone based organic membranes with hollow fibre modulation was used for the purification of fatty acid methyl esters (biodiesel) with dimensions: length 1 m, diameter: 1 mm was filled with distilled water and immersed into the reactor at a temperature of 20°C. Crude biodiesel is passed through the membrane at a low rate of 0.5 ml/min and the pressure was kept 0.1 MPa. It is then treated with heated sodium sulphate and then filtered. The level of purity of biodiesel obtained was up to 90% and other physicochemical properties were found within the specified range of ASTM standards. Moreover, the use of membrane has also decreased the loss of yield as well as controlled emulsification process during the washing step. The results supported the idea of using membrane technology for the removal of contaminants from crude biodiesel which requires no water washing. It is not only environmentally friendly and effective but also provides solutions to many ecological problems commonly faced during the refining of crude biodiesel [10].

6.3 Polyacrylonitrile Membrane

A synthetic organic polymer polyacrylonitrile (PAN) based membrane was utilized at 25°C in order to eliminate glycerol, methanol, water and soap from crude biodiesel. Appreciable removal of glycerol (as low as 0.013 mass%) from crude biodiesel was obtained by using this membrane. This value was significantly lower than the value (0.020 mass%) specified by ASTM D6751 standard. The characterization suggested that polyacrylonitrile (PAN) is an asymmetric and porous membrane which joins high permeation rate and high selectivity, but polymeric membranes may swell up, which result in either instant swelling or long-term pore-size changes. Therefore, the application of polymeric membranes in the solvent system could lead to short life span [10].

6.4 PTFE Membranes

Polytetraflouroethylene (PTFE) membranes are already being used at industrial scale for liquid-liquid-extraction based biodiesel purification as its breakthrough pressure and contact angle values fall well within the range prescribed by ASTM standards. Studies presented the characterization of a number of commercially available membranes as candidates for biodiesel purification but PVDF was the only that can be used for this purpose due to its high breakthrough pressure and contact angle but the efficiency of the membrane started decreasing rapidly after 1 hour. So, PTFE which survived such limitations was preferred over PVDF membranes [20].

6.5 Inorganic Membranes

Currently, organic and inorganic membranes are used for the purification of biodiesel. Inorganic membranes (Al_2O_3, TiO_2, ZrO_2 and SiC) are preferably used for this purpose such as ceramic membranes have gained great attention toward aiding purification processes due to increased resistance to fouling, long lifetime, narrower pore size distribution, mechanical, thermal and chemical stability and resistance to microbial degradation, high flux and high porosity. The organic membranes include polysulfone, polyamide, polycarbonate and a number of additional highly developed polymers. Most of these synthetic polymers comprised of improved resistance to microbial degradation and chemical stability but quite reduced mechanical stability as these swell up and the pore size and internal configuration changes [10].

6.6 Ceramic Membranes

Ceramic membranes are more prominent and promising candidates for the purification process of biodiesel due to their superiority to organic membranes in terms of mechanical, thermal and chemical stability, refined pore size distribution, high reflux and immunity to fouling and microbial degradation. Thus, practically ceramic membranes are more advantageous over organic ones. Porous ceramic membranes are normally prepared by sol-gel or hydrothermal methods and have high stability and durability in high temperature, harsh impurity and hydrothermal environments. Multilayer configuration with asymmetric pore size has also been studied and is preferred due to high performance which is the result of permeation flow and mechanical resistance. In the development of the multilayer configuration, the phenomenon of microfiltration occurs in the inner layer while ultrafiltration takes place in the top layer. Configuring a suitable support material is also required to support it. Multilayer asymmetric membranes usually consist of perm-selective material as a thin film on one or a series of porous supports, which provide the required mechanical stability without dramatically reducing the total transmembrane flux. Tsuru et al. stated that one indicator of molecular size is molecular weight as molecular sieving effect. Therefore, the interaction between solutes and membrane appears to be important. The effect of interaction between solutes and membrane surface would be more pronounced in nano-filtration membranes having pores approximately 1 nm than for ultrafiltration and micro-filtration membranes having much larger pores.

Ceramic membrane separation system was developed to simultaneously remove free glycerol and soap from crude biodiesel. Crude biodiesel produced was ultra-filtered by a multichannel tubular membrane of the pore size of 0.05m. The effects of process parameters: transmembrane pressure (TMP, bar), temperature (°C) and flow rate (L/min) on the membrane system were evaluated. The best retention coefficients (%R) for free glycerol and soap were 97.5% and 96.6% respectively. Furthermore, the physical properties measured were comparable to those obtained in ASTMD6751-03 and EN14214 standards.

A multi-channel tubular-type Al_2O_3/TiO_2 ceramic membrane was used for the experiments. The total filtration area is 0.031 m^2. The membrane with the pore size of 0.05 m was purchased from Jiangsu Jiuwu Hitech CO., China and the module was fabricated in-house. The key operating parameters evaluated for the membrane separation method are transmembrane pressure, temperature and flow rate. The values of operating parameters were varied as follows: transmembrane pressure (1–3 bar), temperature (30–50°C) and flow rate (60–150 L/min). Additionally, the content of free glycerol was expressed as a percentage, the content of soap as part per million (ppm), and the unit of the permeate flux as kg/m^2 hr [1].

7. Ultrafiltration

Ultrafiltration is an important process while using membrane technology for the purification of biodiesel. A study reported an evaluation made on the effect of using ultrafiltration for glycerol separation from produced biodiesel obtained through ethylic transesterification of soybean and canola oils. The experiments were carried out with tubular α-Al_2O_3/TiO_2 membranes with average explore diameter of 0.05 mm and 20 kDa, varying the transmembrane pressure and the concentration of the feed mixture. The ultrafiltration was efficient in removing glycerol since the highest glycerol content in permeate was 0.013 wt%. This novel refining process of biodiesel showed the advantage of not requiring early decantation to separate two phases obtained after transesterification and the reduction in the amount of water used in the washing steps. The properties of the biodiesel produced, which were evaluated, meet the ANP biodiesel standards required for marketing the final product.

The ultrafiltration of mixed products from refined canola oil whose acidity was lower than commercially evaluated oils was not found to be so efficient in the separation of glycerol that is the major byproduct. While taking into consideration the stoichiometry of the reaction, the amount of glycerol in the feed stream varied from 6% to 7% depending upon the amount of water added. For all the evaluated conditions, dispersed phase constituting glycerol readily permeated via a membrane and its percentage in permeate varied from 1% to 44%. These experimental results were also justified by the presence of high acidic contents in the soil that prevented the agglomeration of the dispersed phase in the final mixture. Various scientists studied the membrane process for purification of biodiesel and showed that at lower soap concentrations, increasing the amount of water generally increases the glycerol contents in product. Soap formation takes place when a relatively large amount of free fatty acids are found in oil along with various salts. After that, neutralization with acidified water tends to contribute to the information of dispersed phase constituting glycerol that can be preferably retained by different types of membrane filters [21].

Conclusion

Refining crude biodiesel to maintain quality standards is mandatory to guarantee efficient usage. The methodology adopted to address this issue has evolved magnesiafrom the use of simple distilled water to separate membranes. Distilled water can purify the biodiesel products having a huge amount of toxicants thereby polluting the environment. Therefore, wastewater and higher energy consumption rates compelled researchers to look for other options such as adsorbents and membranes etc. Different bio-adsorbents and inorganic adsorbents have been explored for this purpose. Research has shown that silica gel and magnesol are efficient than ambulate and purolite, etc. Chamotte clay has also provided the required results. Recently, oil palm empty fruit bunch derived bio-adsorbent and sugarcane bagasse, eucalyptus pulp, coco coir and rice husk ash bio-adsorbents were reported which gave appreciable results and are also cost effective. The use of CO_2 under high pressures is a new trend. The organic and inorganic membranes are used for the removal of impurities like glycerol, soap and methanol etc. based on pore size and flux speed. The inorganic membranes are more promising as compared to organic membranes due to high flux speed, resistance to fouling and narrower pore size distribution. For industrial scale, liquid-liquid extraction is least efficient in comparison with PTFE which proved highly effective owing to high breakthrough pressure and suitable contact angle values.

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