

Refining technologies for the purification of crude biodiesel

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ABSTRACT

In biodiesel production, downstream purification is an important step in the overall process. This article is a critical review of the most recent research findings pertaining to biodiesel refining technologies. Both conventional refining technologies and the most recent biodiesel membrane refining technology are reviewed. The results obtained through membrane purification showed some promise in term of biodiesel yield and quality. Also, membranes presented low water consumption and less wastewater discharges. Therefore, exploration and exploitation of membrane technology to purify crude biodiesel is necessary. Furthermore, the success of membrane technology in the purification of crude biodiesel could serve as a boost to both researchers and industries in an effort to achieve high purity and quality biodiesel fuel capable of replacing non-renewable fossil fuel, for wide range of applications.

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Contents

1. Introduction	4239
2. Biodiesel separation technologies	4240
3. Biodiesel wet washing technologies	4241
3.1. Dionized water washing technology	4242
3.2. Acids and dionized water washing technology	4243
3.3. Organic solvents washing technology	4244
4. Dry washing technologies	4244
4.1. Magnesol	4245
4.2. Washing with ion exchange resins	4245
4.3. Washing with other dry washing agents	4246
5. Biodiesel membrane refining technology	4246
5.1. Organic membranes	4246
5.2. Ceramic membranes	4246
5.3. Prospects of biodiesel membranes refining technology	4246
6. Advantages and disadvantages of biodiesel refining technologies	4248
7. Conclusions and recommendations	4249
References	4249

1. Introduction

Today, continuous increase in World energy consumption, fuel price hike, depletion of non-renewable fossil fuels and global warming effects are among the greatest challenges facing the globe [1]. Also environmental concerns have drastically increased globally over the past decade, particularly after the Earth Summit '92

[2]. Thus, the most viable approach to meet this rising demand, decrease greenhouse gas emissions and minimize the effects of fossil fuels depletion is by exploring alternative renewable energy sources [3–5]. Biofuels, particularly biodiesel is such a fuel that shows great potential to replace petro-diesel [6–8]. Biofuels are commonly known to offer several advantages over fossil fuel such as sustainability, biodegradability, lower greenhouse gas emissions, regional development, social structure and agriculture development, and fuel security supply [9,10]. Further, replacing petro-diesel with biodiesel fuel could reduce the accumulation of

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Table 1
Negative effects of contaminants on biodiesel and engines.

Contaminants	Negative effect
Methanol	Deterioration of natural rubber seals and gaskets, lower flash points (problems in storage, transport, and utilization, etc.), Lower viscosity and density values, Corrosion of pieces of Aluminum (Al) and Zinc (Zn)
Water	Reduces heat of combustion, corrosion of system components (such as fuel tubes and injector pumps) failure of fuel pump, hydrolysis (FFAs formation), formation of ice crystals resulting to gelling of residual fuel, Bacteriological growth causing blockage of filters, and Pitting in the pistons
Catalyst/soap	Damage injectors, pose corrosion problems in engines, plugging of filters and weakening of engines
Free fatty acids (FFAs)	Less oxidation stability, corrosion of vital engine components
Glycerides	Crystallization, turbidity, higher viscosities, and deposits formation at pistons, valves and injection Nozzles
Glycerol	Decantation, storage problem, fuel tank bottom deposits Injector fouling, settling problems, higher aldehydes and acrolein emissions, and severity of engine durability problems

green house gases such as CO₂ in the atmosphere [11,12]. Also biodiesel fuel has been commonly found to offer similar engine performance to that of petro-diesel fuel, whilst reducing engine emissions of particulates, hydrocarbons and carbon monoxide [13].

Biodiesel fuel is usually produced from virgin and used vegetable oils and animal fats [10,14]. Presently several efforts are made to produce biodiesel from microalgae. Microalgae clearly offers a few advantages among others include: much higher biomass productivities than land plants (doubling times may be as short as 3.5 h), some species can accumulate up to 20–50% triacylglycerols, while no high-quality agricultural land is necessary to grow the biomass, and even no land at all, offshore microalgae farming could be a reasonable alternative [15]. Conventionally, the triglycerides of fats and oils are transesterified using short-chain alcohol such as methanol and ethanol in the presence of alkali catalysts. Also, acid catalysts are used for the transesterification reaction [16,17]. Transesterification reaction is the most adopted process for biodiesel production [18,19].

At the end of transesterification, biodiesel is mostly separated via gravitational settling or centrifugation. The crude biodiesel is then purified and dried to meet the stringent international standard specification provided by EN14214 [20]. Otherwise the contaminants could reduce biodiesel quality and affects engine performance as shown in Table 1. The production of biodiesel using alkaline catalysts such as sodium and potassium hydroxides (NaOH and KOH), and sodium and potassium methoxides (CH₃ONa and CH₃OK), could provide higher biodiesel yield (>98%), but the process of biodiesel refining is complicated [21,22]. This is due to soaps formation associated with alkaline catalyst [23]. Further, the formation of soap decreases biodiesel yield obtained after the clarification and separation stages. As well, the dissolved soaps increase the biodiesel solubility in glycerol, an additional cause of yield loss [3]. However to mitigate the problems faced with the use of homogeneous alkaline and acid catalysts, heterogeneous catalysts such as solid and enzymes catalysts are developed and used during biodiesel production process [24,25].

The purification of crude biodiesel is usually achieved via two notable techniques; wet and dry washings. Conventionally wet washing is the most employed technique to remove impurities such as soap, catalyst, glycerol and residual alcohol from biodiesel. However, the major disadvantage in the use of water to purify biodiesel is increase in cost and production time [26]. Besides, separation of biodiesel phase from water phase is difficult and produces large amount of wastewater. Thus for each litre of biodiesel, close to 10 L of wastewater is produced [27]. Refining of crude biodiesel alone accounts for 60–80% of the total processing cost [28].

Furthermore, dry washing technique (ion exchange resins and magnesol powder) was introduced to substitute water washing to remove biodiesel contaminants. This technique is also employed in commercial plants to purify biodiesel [29]. However, the understanding of the chemistry of dry washing substances is still skeletal [30].

The difficulties regarding operation of wet and dry washing processes for the purification of crude biodiesel have derived the discussion on the use of membrane technology to purify crude biodiesel. Biodiesel purification via membrane has so far shown to provide promising results, in addition to less water utilization [31]. In view of the above, more efforts need to be made to explore and exploit better purification processes such as membranes to effectively replace conventional biodiesel separation and washing techniques. Thus, this study critically examines and reports on the refining technologies employed to purify crude biodiesel.

2. Biodiesel separation technologies

The first step usually employed to recover biodiesel after transesterification reaction is separation of crude biodiesel from by-product, glycerol. The fast separation of biodiesel and glycerol is as a result of differences in their polarities and also significant difference in their densities. The density of biodiesel and glycerol are 0.88 gm/cc and 1.05 gm/cc or more respectively. The density of glycerol is dependent on the amount of water, catalyst and methanol present in it. This density difference is sufficient to employ simple gravity separation technique to separate biodiesel phase from glycerol phase [23]. However, the separation process between biodiesel and glycerol can be difficult in the presence of soaps formation, which mostly solidifies and form a semi solid substance [32]. This problem is usually circumvented using heterogeneous catalysts [33,34]. Chew and Bhatia [24] stated that separation cost of homogeneous catalyst and high consumption of energy and has pinched the need for the growth and development of heterogeneous catalysts for the production of biodiesel. Heterogeneous catalysts are simply estranged from the crude biodiesel product and recyclable. Sharma et al. [22] stated that several researchers have tried heterogeneous catalysts to circumvent the problem of time and water consumption encountered during alkali-biodiesel refining process. Table 2 presents reduced biodiesel water washing process using heterogeneous catalysts in biodiesel production [35]. Zabeti et al. [36] reviewed biodiesel production via heterogeneous catalysts (solid catalysts). The authors noted that heterogeneous catalysts are not dissolved or consumed during transesterification, therefore they are easily separated. This characteristic limits impurities and reduces cost of final biodiesel product separation. Additionally, the catalysts can be regenerated and re-used and as added advantage, the catalysts are environmentally friendly since the need to use acids, solvents and water during separation stage is minimized. Also, Shimada et al. [33] reviewed enzymatic alcoholysis for biodiesel fuel production. Production of biodiesel via enzymes could alleviate separation difficulties commonly encountered with alkaline catalyst. The authors noted that application of enzymes also minimizes large quantity of wastewater generated via use of homogeneous catalyst. As well increase in purity of biodiesel above 90% is achievable.

Consequently, feedstocks with high amount of water and FFAs molecules could easily interfere with the transesterification reaction resulting in soaps formation, thereby affecting the purification of crude biodiesel and lowering the yield of alkyl esters as shown in Figs. 2 and 3 [38]. Therefore to meet international standard specification of high purity requirements for biodiesel fuel as provided by European standard (EN 14214) and the American standard for testing materials (ASTM D6751) as shown in Table 4 [41], it is necessary to extensively purify crude biodiesel. Traditionally until recently the commonest effective technique to remove glycerol and methanol from biodiesel product mixture is by water washing, since both glycerol and methanol are highly soluble in water [26]. Sandra and Dejan [57] reported that use of hot water washing can provide ester yield of 86% and high purity of 99%. The authors stated that to meet either EN 14214 or ASTM D6751-07, biodiesel should contain 96.5 wt.% Fatty acid methyl esters (FAME).

Biodiesel wet washing technique involves addition of certain amount of water to crude biodiesel and agitating it gently to avoid formation of emulsion. The process is repeated until colorless wash water is obtained, indicating complete removal of impurities. Wet washing processes usually requires a lot of water [27,58], approximately water wash solution at the rate of 28% by volume of oil and 1 g of tannic acid per liter of water [59]. The use of large quantity of water generates huge amount of wastewater and incur high energy cost [60–62]. Jaruwat et al. [63] reported that Thailand is producing about 350,000 L/day of fatty acid esters (biodiesel), resulting

to no less than 70,000 L/day of contaminated wastewater. The authors noted that the wastewater disposed is at a high pH due to significant levels of residual KOH and hexane-extracted oil, high solid content and low nitrogen concentration, besides higher concentration values of BOD, COD, oil and grease, etc. as shown in Table 5. These components were found to inhibit the growth of microorganisms, making it difficult for the wastewater to naturally degrade [63].

Wet washing is mostly conducted through washing with dionized water, washing with acid (5% phosphoric acid) and water and washing with organic solvent and water as discussed below:

3.1. Dionized water washing technology

Water washing has been traditionally used to purify crude biodiesel after its separation from glycerol [50]. Demirbas [59] reported that air was cautiously introduced into the aqueous layer, while gently stirring the mixture of crude biodiesel and water. This process was continued until the ester layer became cleared. In addition, after settling the aqueous solution was drained and water alone was added at 28% by volume of oil for the final washing process [59]. Van Gerpen [55] noted water washing to be the most problematic step in biodiesel production. The author reported that although water washing involves heated, softened water, wastewater treatment and water/methanol separation. But the process of water application provides an avenue for the addition of acid to neutralize the remaining catalyst and remove the salts formed. Further, excess alcohol sometimes needs to be removed before the washing step. This usually prevents the addition of alcohol to the wastewater effluent. In some cases the alcohols is removed with the wastewater and then later remove from wastewater. The application of distilled water (120–140 °F) couple with gentle water washing eliminates precipitation of saturated biodiesel and prevents the formation of emulsions [55]. Balat and Balat [21] remarked that after transesterification, crude biodiesel and glycerol can be phase separated within the first 10 min and a complete separation could be achieved in 2 h after stirring is stopped. Also alcohol can be removed through distillation and evaporation and that care must be taken to ensure zero water accumulation in the recovered alcohol stream. The authors reported that after phase separation dionized water is added to crude biodiesel at the rate of 5.5% by volume of the feedstock and the mixture stirred for a period of 5 min and allowed to settle for glycerol removal. The removal of complete glycerol is an indication of high-quality biodiesel production. Also, Fangrui et al. [64] noted that washing two times is enough to get rid of impurities from the methyl esters. The crude methyl esters produced was washed and distilled under vacuum at 30–80 °C and 133 pa. The product was then dried at 80 °C for 10 min to remove traces of moisture and the methyl ester yield was found to be 97–99%. Chongkhong et al. [42] stated that after transesterification, 10.24 wt.% of 3 M NaOH–H₂O solution was used to neutralize crude biodiesel product containing residual FFAs of about 1.4 wt.%. The crude biodiesel and the solution of NaOH–H₂O were mixed and stirred at a temperature of 80 °C for 20 min. The biodiesel phase was removed from the top of the separator whilst soap was taken from the bottom. The final biodiesel product was then heated in an evaporator to remove the residual water in the product.

Furthermore, Saifuddin and Chua [65] washed esters phase separated from the mixture by placing the esters on a glass cylinder and spraying water on top of the cylinder at low velocity. Both catalyst and alcohol were separated through the cylinder via percolation process. They used microwave heating power (750 W) for 3–4 min to speed up the separation process and the cylinder was then left to stand for 10 min after irradiation. Consequently a clear esters phase at the top was obtained and the residual alcohol and catalyst

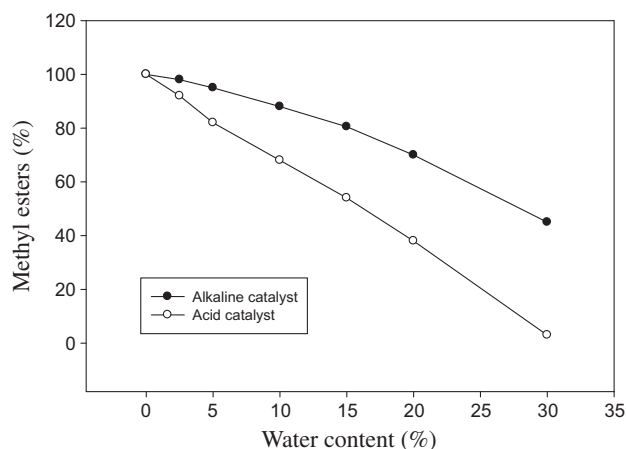


Fig. 2. Graph of yield of methyl esters against water content in transesterification.

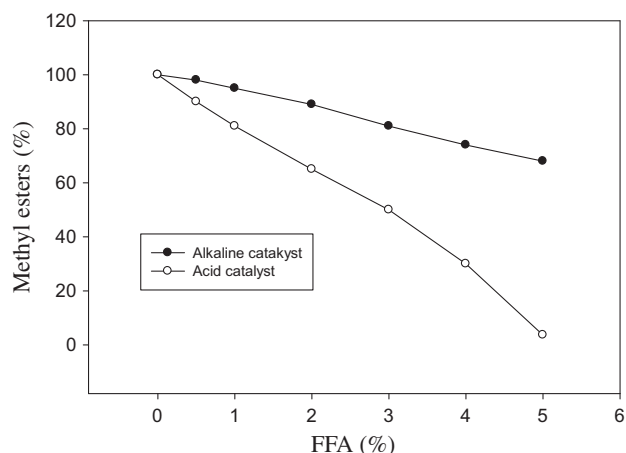


Fig. 3. Graph of yield of methyl esters against FFAs in transesterification.

Table 4
International biodiesel standard specifications [41].

Properties	Units	ASTM Method	EN14214
Ester content	% (m/m)	–	96.5
Flash point	°C	130 min.	>101
Water and sediment	vol.%	0.050 max.	0.05
Kinematic viscosity, 40 °C	mm ² /s	1.9–6.0	3.5–5
Sulfated ash	% (m/m)	0.020 max.	0.02
Sulfur	mg/kg	–	≤10
S 15 grade	ppm	15 max.	–
S 500 grade	–	500 max.	–
Copper strip corrosion	rating	No.3 max.	class1
Cetane	–	47 min.	≥51
Cloud point	°C	Report	–
Carbon residue 100% sample	% (m/m)	0.050 max.	–
Acid number	mg KOH/gm	0.50 max.	0.50 max.
Triglyceride	% (m/m)	0.20 max.	0.20 max.
Free glycerin	% (m/m)	0.020 max.	0.02 max.
Total glycerin	% (m/m)	0.240 max.	0.25 max.
Phosphorus content	mass%	0.001 max.	0.001 max.
Methanol content	% (m/m)	–	0.20 max.
Distillation temperature, atmospheric equivalent temperature, 90% recovered	°C	360 max.	–
Sodium/potassium	ppm	5 max. combined	5 max.

Max: Maximum.

Min: Minimum.

Table 5
Chemical and physical properties of raw biodiesel wastewater.

Parameters	Thailand standard [63]	Values of raw biodiesel wastewater [63]	Biodiesel waste water [26]
pH	5.5–9	9.25–10.76	6.7
COD (mg/L)	≤400	312,000–588,800	18,362
BOD (mg/L)	≤60	168,000–300,000	–
Oil and grease (mg/L)	≤5	18,000–22,000	–
TKN (mg/L)	≤100	439–464	–
Conductivity (Scm ⁻¹)	–	–	1119
TSS ^a (mg/L)	–	–	8850
VSS ^b (mg/L)	–	–	8750
MSS ^c (mg/L)	–	–	100

TKN: Total Kjeldahl Nitrogen.

^a Total suspended solids.^b Volatile suspended solids.^c Mineral suspended solids.

were collected from the bottom. The final ester product was dried using anhydrous sodium sulfate (Na₂SO₄). The authors remarked that agitation during water washing could lead to high ester losses as much as 18% due to formation of an emulsion. They stated that the amount of water needed in the purification of biodiesel could be minimized, if refined raw materials, moderate catalyst amount and lower alcohol ratios are employed. In another study, Suprihas-tuti and Aswati [66] reported that to achieve low glycerol content in biodiesel as stipulated by ASTM D6751 and EN14214, the washing should be done in multistage process. The authors noted that water washing could significantly affect the extraction of glycerol. They added that during water washing process, higher temperatures gives more glycerol extraction. The authors experimented different washing times and remarked that for washing time more than 20 min and at room temperature and by using esters to water volume ratio of 1:3, the glycerol content in esters was reduced from 0.9331% to 0.0423% and the pH was down to 7.3. Although, the glycerol value obtained was higher than the allowable value for international standards.

3.2. Acids and dionized water washing technology

Acids such as phosphoric acid, sulfuric acid and hydrochloric acid are mostly used in the purification of crude biodiesel. This

process is followed with use of distilled water to completely remove biodiesel impurities. For the purpose of immediate use on diesel engines and long term storage, purified biodiesel is properly dried. Cayli and Kusefoglul [67] noted that after one-step transesterification reaction, the crude methyl esters produced was purified with hot water at 70 °C, and 5% H₃PO₄ (aq) at 50 °C. The authors dried the methyl ester layer in a vacuum and checked with ceric ammonium nitrate reagent for glycerol removal. Hass et al. [13] stated that water have to be reduced to a limit of 0.050% (v/v) to meet the ASTM D6751 standard specification. The authors washed biodiesel with water of pH 4.5. The process helped in neutralizing the catalyst and converting the soap formed to FFAs, thus reducing its emulsifying tendencies. Further, vacuum dryer was used to reduce the residual water from the initial value of 2.4% to final value of 0.045%. The water removed via drying was recycled into washing operation. As well, to reduce the cost of production, the glycerol produced was also refined to a concentration level suitable to the market value (80w/w%). Karaosmanoğlu et al. [68] investigated refining of crude biodiesel via neutralization with Sulfuric acid (1:1). Two processes were explored: use of catalyst in solid form and use of catalyst dissolved in methanol. In the case of refining technique for catalyst in solid form, decantation was used to remove the catalyst and the product was transferred into a separatory funnel to separate biodiesel from glycerol. Sulfuric

(1:1) was then applied to reduce the pH from the initial 11.92 to a pH of 7.0. The biodiesel phase was then separated via centrifugation and the water content of biodiesel fuel was removed overnight by leaving the product over heated Na_2SO_4 (25% of the quantity of biodiesel). For the case of catalyst dissolved in methanol containing pH of 13.07, the pH was reduced to neutral pH value of 7.0 with similar refining approach as that of catalyst in solid form being adopted. In addition, Faccini et al. [69] thoroughly washed crude biodiesel using 10% acid water at 55 °C. The acid water was prepared by adding 2% (v/v) H_3PO_4 to distilled water. This washing step was conducted in the same transesterification reactor with constant stirring over 5 min, maintaining the temperature at 55 °C. Subsequently, the mixture of wastewater and biodiesel was separated using separatory funnel. The wastewater (bottom layer) was removed and the biodiesel was washed three times with portions of 10% (v/v) hot water (55 °C). The upper layer, containing the purified biodiesel, was dried and stored for further analysis.

Furthermore, Srivastava and Verma [70] stated that separation of glycerol was achieved after the product mixture was allowed to stay for 8 h. The upper layer of crude biodiesel was purified via bubble washed technique using 10% H_3PO_4 . The product was purified by passing air by aquarium stone for at least a day. The product was finally washed with distilled water to remove the dissolved impurities such as catalyst, soap and alcohol. The product was then transferred into a separatory funnel and allowed to stay for half an hour. The final biodiesel with much lighter color was obtained and stored in container for use. This method of biodiesel purification is efficient for a small biodiesel installation [71]. However, this technique is not employed by any large biodiesel purification facility. In another study, He et al. [51] used HCl (pH = 1) to treat crude biodiesel at room temperature (20 °C). The product was then washed twice with deionized water at a volume ratio of 1:1. The final biodiesel product was placed over heated Na_2SO_4 (10% of the amount of biodiesel) for a period of 12 h to remove biodiesel water content and the product was filtered. Similarly, Atapour and Kariminia [72] employed 35 mL of hot distilled water to wash the biodiesel produced. In order to neutralize the residual catalyst and decompose the soaps formed, the product was treated with 35 mL of HCl (0.5%). Further the product was washed three times with 35 mL of hot distilled water. They observed that successive rinses successfully removed contaminants such as methanol, residual catalyst, soaps and glycerol. Finally the biodiesel obtained was then dried using manganese sulfate and filtered under vacuum conditions to eliminate manganese sulfate crystals. Also, Qiu et al. [10] reported that the upper layer containing biodiesel, traces of the catalyst, *n*-hexane and residual methanol was thoroughly cleaned by washing with deionized water to eliminate the contaminants such as catalyst, *n*-hexane and residual methanol. They used rotary evaporation at 70 °C to remove *n*-hexane and the residual methanol from the product. The final biodiesel product was then washed twice with HCl solution (0.5 mol/L) until a clear phase (biodiesel) was achieved. In another investigation, Tint and Mya [73] used stainless steel tank having 45 gallons capacities to separate biodiesel and glycerol. The crude biodiesel was washed using phosphoric acid followed by multiple water washings to achieve pH of 7. The authors stated that repeated water washing is necessary to achieve clear biodiesel layer free from methanol, residual catalyst and soap. Thus, after water washing the final biodiesel product was sent to the sand stainless steel filtration tank. The tank was open at the top containing 100 mesh size stainless steel screen supported by steel frame. The sand consisting the size of (-20 + 60) mesh was put over the 100 mesh size screen. After filtration, a clear amber-yellow liquid biodiesel with a viscosity comparable to that of petro-diesel was obtained.

In additional, Van Gerpen [55] noted that to eliminate magnesium and calcium contamination and neutralize the remaining

base catalysts, softened water (slightly acidic) is usually applied. Similarly, copper and iron ions removal eradicates the sources of catalysts that decreases the fuel stability and minimize the tendency for the fuel to be out of specification. Finally, the refined biodiesel is dried using vacuum flash technique, sent to storage unit and made available for diesel engine consumption [55].

3.3. Organic solvents washing technology

Organic solvents such as petroleum ether have been used to purify crude biodiesel. This process is usually followed with the use of large amount of demineralized water to remove residual soap and catalyst. Wang et al. [74] distilled fatty acid methyl ester (FAME) under vacuum (40 ± 5 mmHg) at 180 °C. When the temperature reached 240 °C (40 ± 5 mmHg), the distillation was assumed to be completed. The crude FAME was separated after acidic transesterification and then purified with petroleum ether and washed with hot water (50 °C) until the washing reached a neutral pH. *n*-Hexane was also used for the extraction of crude biodiesel at a 1:1 ratio at room temperature. The mixture was washed three times using distilled water and the final yield obtained was 93.0 wt.%. Soriano et al. [75] reported that after transesterification, the residual alcohol and the tetrahydrofuran (THF) were removed via vacuum distillation followed by extraction with petroleum ether. The residual catalyst was then removed by filtration process. The final biodiesel product was achieved by using vacuum distillation.

Furthermore, Fangrui et al. [64] reported that methyl esters were washed with petroleum ether, and glacial acetic acid was added to adjust the pH to 7. The authors revealed that the products obtained were further purified by washing three times with water. The products were then dried over anhydrous magnesium sulfate, filtered and the solvent removed by evaporation. Karaosmanoğlu et al. [68] used petroleum ether to refine crude biodiesel. The process was employed after biodiesel and glycerol were separated via decantation. The catalyst was removed in solid form from the reacting vessel while rotary evaporator under vacuum was used to remove the methanol. The crude biodiesel was then poured into a separatory funnel and then petroleum ether and distilled water were added, the pH of the mixture was adjusted by adding acetic acid. To further purify the product, water washing was repeated three times and the final biodiesel was heated via Na_2SO_4 overnight and separated. The separation of petroleum ether was achieved via rotary evaporator under vacuum.

4. Dry washing technologies

The dry washing technique commonly employed to purify crude biodiesel is usually achieved through the use of silicates (Magnesol or Trisyl), ion exchange resins (Amberlite or purolite), cellulose, activated clay, activated carbon, and activated fiber, etc. These Adsorbents consist of acidic and basic adsorption (binding) sites and have strong affinity for polar compounds such as methanol, glycerin, glycerides, metals and soap [76]. This technique is followed with the use of a filter to enable the process to be more effective and efficient as shown in Fig. 4. Dry washing is usually carried out at a temperature of 65 °C and the process is mostly completed within 20–30 min [77]. Therefore during washing process, the amount of glycerides and total glycerol in crude biodiesel are lowered to a reasonable level. Besides, the process has the advantage of being waterless, strong affinity to polar compounds, easy to integrate into existing plant, significantly lower purification time, no wastewater, total surface area coverage of wash tank is minimized, solid waste has alternate uses, saves space, and improves fuel quality [76]. Dugan [78] have discussed

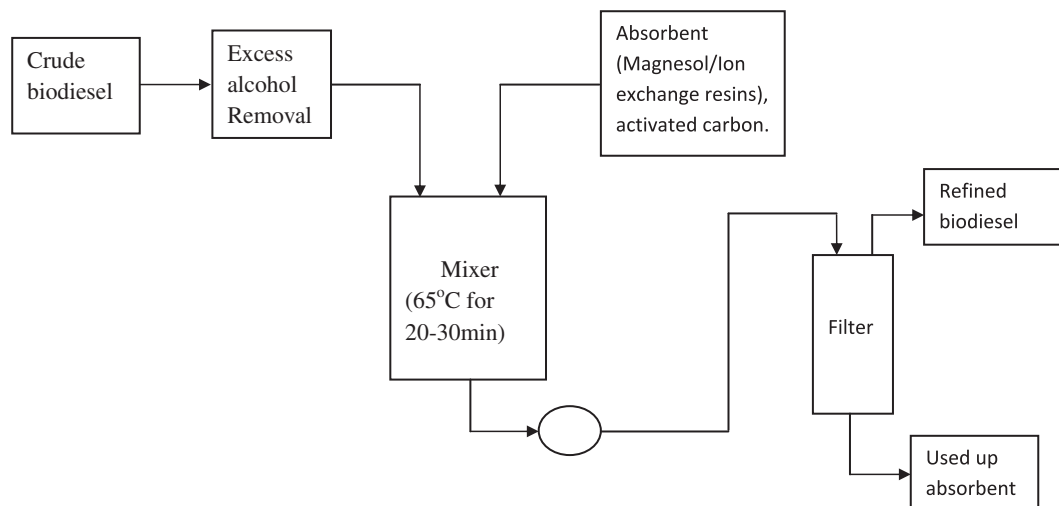


Fig. 4. Schematic diagram of biodiesel dry washing process.

the process of dry washing technique to purify biodiesel, and noted the process to decrease production time, and lower cost of production. The author stated that dry washing provides high-quality fuel and since water is not added, it is possible to achieve less than 500 ppm water content as stipulated by ASTM D6751. However in wet washing, the water content of the fuel is usually above 1000 ppm, which makes its removal difficult, time-consuming and costly [78].

The use of magnesol, ion exchange resin, and other adsorbents such as activated clay, activated carbon, and activated fiber are discussed as follows.

4.1. Magnesol

Cooke et al. [79] remarked that water washing is being substituted by dry washing (magnesol powder or an ion exchange resin) to neutralize impurities. The authors reported the adoption of both dry washing techniques in industrial plants. The treatment of crude biodiesel with magnesol, a synthetic magnesium silicate, requires 1.5–3 wt.% of biodiesel and need to be thoroughly mixed. The mixture is filtered using cloth filter of size 5 μm and 1 μm nominal filter is used to conduct final filtration process. The final product is polished through a filter with sizes 0.45 μm or 0.55 μm before being used as fuel. The process of magnesol biodiesel purification was experimented and the results obtained were comparable to those provided by ASTM D6751 and EN14214 [30]. Also, Bryan [80] have experimented use of magnesol on both soybean and grease biodiesels and the physicochemical properties met both EN 14214 and ASTM D6751. The author stated that magnesol has a strong affinity for polar compounds, thereby actively filtering out metal contaminants, mono and di-glycerides, free glycerin, and excess methanol as well as free fatty acids and soap.

Furthermore, Faccini et al. [69] studied different types of dry washing techniques. The adsorbent experimented showed good performance, the results from the two best adsorbents (Magnesol 1% and silica 2%) are 0.17 mgKOHg^{-1} for acid number, 61 ppm of soap, 500 mg kg^{-1} of water, 0.22% of methanol and 0.03% of free glycerol. Although the value of the free glycerol obtained exceeded the minimum glycerol requirement as stipulated by ASTM6751 standard. Similarly, Berrios and Skelton [26] experimented use of magnesol of varying concentrations: 0.25, 0.50, 0.75 and 1.00% at 60 °C, using a batch reactor with sample size of 200 mL fitted with a variable speed agitator and immersed in a water batch to purify

crude biodiesel. Samples were also taken at 10 and 20 min, although the standard washing time is 30 min. A vacuum filtration using a Büchner funnel and water ejector was employed to separate the final product. Also, a centrifuge was used to remove the intermediate product. The authors noted that since magnesol is hygroscopic the bag was opened with care and re-sealed as tightly as possible. They suggested use of mask before handling magnesol, since the powder is very fine. At the end of the purification process, biodiesel containing methanol content of 0.51%, and free glycerol content of 0.03% were obtained. However the major limitation about use of magnesol is that little is known about the process, its catalytic efficiency and performance intricacies [76].

4.2. Washing with ion exchange resins

Ion exchange resin is an insoluble matrix (or support structure) normally in the form of small (1–2 mm diameter) beads, usually white or yellowish, fabricated from an organic polymer substrate [81]. The application of ion exchange resins as a dry washing agent is being promoted by the resins manufacturers; Purolite (PD206) and Rohm and Haas (BD10 Dry). Purolite (PD206) is a dry polishing media specifically formulated to remove by-products remaining after production of biodiesel [82]. Although being sold as ion exchange materials, but none of the suppliers advocates its regeneration because of being acting as adsorbents. Berrios and Skelton [26] studied the effects of ion exchange resins on the purification of crude biodiesel. The authors reported that the feed were passed through a column of resin supported in a glass tube and metered pump was used to control the flow, and restricted outlets were employed to ensure a liquid head above the resins. They noted that initial loading and flows of the resins were based on the recommendation of R&H trade literature. The authors analyzed the samples at interval of 2 h for methanol and glycerol and demonstrated that ion exchange resin has the capability to reduce glycerol to a value of 0.01 wt and considerably remove soap, but could not successfully remove methanol. They obtained methanol content of 1.14%, which is far above EN14214 standard specification. More so, the adsorption of little soap indicates a constraint for feed containing high soap content [76]. Additionally, ion exchange resins offers good performance and provide cost benefits in the removal of glycerin and water, removal of salts, soap, and catalyst and also eradicate water washing [83]. However, it has less effect on the removal of methanol [8].

4.3. Washing with other dry washing agents

Dry washing agent such as activated carbon is commonly used to remove biodiesel excess color. Thus for effective dry washing of crude biodiesel, the adsorbent is channeled into a paddle type mixing tank and thoroughly agitated. Hayafuji et al. [84] experimented use of activated fibers, activated carbon, activated clay and acid clay to purify biodiesel. Further, glycerin was also used as a solvent to wash impurities. The authors noted that clay; especially acid clay treated with sulfuric acid is a preferable, which is superior in the aspects of dealkaline effect, deodorant effect and decoloring effect. Also clay grain size ranging from 0.1 mm to 1.5 mm is more suitable for effective biodiesel purification. They stated that clay with smaller grain size provides superior purification process, but separation after the purification treatment is more difficult. However, when the clay grain size is larger, separation after the treatment becomes easier, but purification process is inferior.

5. Biodiesel membrane refining technology

Basically, membranes are semi-permeable barriers that separate different species of solution by allowing restricted passage of some component of mixture in a selective manner [85]. A membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid, and can carry a positive or negative charge or be neutral or bipolar. Transport through a membrane can be affected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient [86]. Membrane based separations are well-established technologies in water purification, protein separations and gas separations. However, commercial applications of membrane technologies are limited to separations involving aqueous solutions and relatively inert gases. Thus the use of membranes to treat non aqueous fluids is an emerging area in membrane technologies [53]. Lin et al. [52] reported that membrane separation is primarily a size exclusion-based pressure-driven process. Therefore, different components are separated according to their particle sizes and shapes of individual components or molecular weights. The mode of components' operation is somewhat dependent on their interactions with the membrane surface and other components of the mixture. Also, performance of membrane separation is affected by membrane composition, pressure, temperature, velocity of flow and interactions between components of the feed with membrane surface [52].

5.1. Organic membranes

The membranes used for the pressure driven separation processes, are microfiltration (MF), ultrafiltration (UF) and reverse osmosis (RO). Initially most of such membranes were cellulosic in nature. These are now being replaced by polyamide, polysulphone, polycarbonate and several other advanced polymers. These synthetic polymers have improved chemical stability and better resistance to microbial degradation [87]. Additionally, Salahi et al. [88] remarked that polyacrylonitrile (PAN) is porous and asymmetric membrane which combines high selectivity with high permeation rate. However in organic solvents, polymeric membranes may swell, resulting to instant and/or long-term pore-size changes. Consequently, polymeric membranes in solvent applications have shorter operating lifetimes [89].

5.2. Ceramic membranes

Ceramic membranes have great potentials and represent a distinct class of inorganic membranes. Much attention has been

focused on inorganic membranes for their superiority than organic ones in thermal, chemical and mechanical stability, high porosity, high flux, long life time, resistance to microbial degradation, increased resistance to fouling, and a narrower pore size distribution. Thus, porous inorganic membranes (e.g. Al_2O_3 , TiO_2 , ZrO_2 , SiC) possess some practical advantages over the polymeric ones such as higher mechanical strength, thermal and corrosive resistance among others [90]. In addition to membrane material, pore size influences membranes and small pore sizes give more stable membranes [91]. 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 [92]. Saffaj et al. [93] reported that using asymmetric multilayer configuration, ceramic membranes with high performance parameters such as permeation flow and mechanical resistance can be achieved. The development of such a multilayer configuration includes: shaping of a suitable support material, formation of a microfiltration interlayer and synthesis of an ultrafiltration (UF) top layer. Multilayer asymmetric membranes usually consist of permselective 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 [94]. Tsuru et al. [95] state that one indicator of molecular size is molecular weight, i.e. a 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 nanofiltration membranes having pores approximately 1 nm than for ultrafiltration and microfiltration membranes having much larger pores.

5.3. Prospects of biodiesel membranes refining technology

The criteria for selecting membranes are complex and this depends on the application. Important considerations on productivity and separation selectivity, as well as the membrane's durability and mechanical integrity at the operating conditions must be balanced against cost issues in all cases. The relative importance of each of these requirements varies with the application. However, selectivity and permeation rate (permeances) are clearly the most basic properties of a membrane. The higher the selectivity, the more efficient the process, the lower the driving force required to achieve a given separation. The higher the flux, the smaller the membrane area is required [93]. Further the driving force is often pressure or concentration gradient across the membrane. Additionally, an authoritative outline of basic concepts and definitions for membranes is obtained in a report of International Union of Pure and Applied Chemistry [92]. Usually, membranes are applied for different purposes. Thus, Table 6 compares polymeric and inorganic membranes features. Thus, inorganic membranes favor applications under higher temperature and chemical conditions, whereas polymeric ones have the advantages of being economical. The successful application of membrane technology to purify crude biodiesel has re-ignited the interest in the struggle to develop commercial biodiesel production. Table 7 shows that membrane biodiesel purification could provide high purity and quality biodiesel comparable to those obtained via conventional wet and dry washing techniques. Contrary to both wet and dry washing techniques, membrane biodiesel purification process does not require both water and absorbent [62]. Membrane processes are usually based on the theory that higher permeates fluxes are followed by lower selectivity and higher selectivity is followed with lower permeates fluxes. Fig. 5 shows ceramic membrane biodiesel purification process.

Cao et al. [61] stated that maintaining a separate lipid phase is a key factor to assure high-quality biodiesel production with the membrane reactor system. The membrane used had a 300 kDa

Table 6

Comparison of polymeric and inorganic membranes [92].

Membrane	Advantages	Disadvantages	Current status
Inorganic	<ul style="list-style-type: none"> • Long term durability • High thermal stability (>200 °C) • Chemical stability in wide pH • High structural integrity 	<ul style="list-style-type: none"> • Brittle (Pd) • Expensive • Some have low hydrothermal stability 	<ul style="list-style-type: none"> • Small scale applications • Surface modifications to improve hydrothermal stability
Polymeric	<ul style="list-style-type: none"> • Cheap • Mass production (larger scale) • Good quality control 	<ul style="list-style-type: none"> • Structurally weak, not stable, temp. limited • Prone to denature & be contaminated separation (short life) 	<ul style="list-style-type: none"> • Wide applications in aqueous phase, and some gas

Table 7

Comparison of biodiesel purification of different types of refining techniques.

Refining techniques	Methanol (wt.%)	Glycerol (wt.%)	Triolein (wt.%)	FAME (wt.%)	NaOH (wt.%)	Water/sediment (wt.%)	Ester loss (wt.%)	Cloud point (°C)	Cetane number	Density @ 15(°C) (kg/m ³)	Viscosity @ 40°C (mm ² /s)	Flash point (°C)	Ref.
Wet washing	0.5	0	4.02	95.34	0.14	0.6	0.0	–	–	–	–	–	[57]
	–	–	–	99.6	–	0.03	–	–	–	879	4.87	180	[42]
	–	0.201	–	97.1	–	<0.01	–	1.0 ± 0.1	–	887	4.90 ± 0.20	170.0 ± 3.0	[47]
Dry washing	<0.001	0.196	–	–	–	0.0	–	–	55.9	–	4.207	163	[79]
	1.40	0.11	0.43	95.3	–	–	–	–	–	–	–	–	[26]
	0.11	0.45	0.2	98.5	1	0.18	–	–	55.2	881.2	4.91	132	[30]
Membranes	0.011	0.191	–	–	–	0.04	–	–	51.3	–	4.097	200	[79]
	–	–	–	99.0	–	0.042 ± 0.004	8.1 ± 0.2	–	–	876 ± 7	3.906 ± 0.006	–	[51]
EN14214	0.20 max	0.25 max	0.20 max	96.5	–	0.05	–	–	≥51	–	3.5–5	>101	[41]

MWCO. This property provided an exceptional means of retaining emulsions formed. Table 8 compares glycerin purification results obtained from membrane and conventional refining technologies. In the case of batch reaction, the total glycerin and free glycerin were approximately twice that obtained from the membrane system. Wang et al. [62] have experimented use of inorganic (ceramic) membrane to purify biodiesel from impurities such as; glycerol, soap and catalyst. The authors explored micro-filtration technique using different membrane pore sizes (0.6, 0.2 and 0.1 µm) at temperature of 60 °C and pressure of 0.15 Mpa. The removal of glycerol was less difficult due its formation of reverse micelle with soap forming molecule size of 2.21 µm which was analyzed by zeta potential analyzer and showed to be bigger than that of biodiesel molecule, and therefore was easily removed by membrane. However, great caution is required during membrane refining process to achieve biodiesel with glycerol content of 0.02 wt.%. They also showed that ceramic membranes can considerably reduce biodiesel metal contents as depicted in Table 9. The removal of biodiesel metal contents automatically limits the presence of soap [62]. Also, Cheng et al. [96] have purified crude biodiesel using a membrane separator integrated with liquid–liquid extraction for the oil–FAME–MeOH system. They used porous ceramic disk membranes (47 mm in diameter) with an effective membrane area of 13.1 cm², the pore size of 0.14 µm, and the molecular weights cut off (MWCO) of 300 kDa. The membrane active layer consisted of zirconia oxide supported on carbon. The authors noted that the tested modified UNIFAC models are not adequate for simulating the phase behavior of the oil–FAME–MeOH system and envisage exploration of different models using the results of liquid–liquid extraction (LLE) obtained.

Furthermore, He et al. [51] conducted experimental studies on membrane extraction using hollow polysulfone and polyacrylonitrile fiber membranes and the conventional extraction techniques to purify crude biodiesel. The biodiesel obtained from polysulfone fiber membrane gave purity of 99%, besides properties such as kinematic viscosity (3.906 mm²/s²) density (0.876 g/cm) and water content (0.042 wt.%) met the ASTM D6751 standard specification.

The authors remarked that, these results were possible due to the absence of emulsion formation, zero density difference between fluids for hollow fiber membranes, and high interfacial area [51]. The membrane purification provided better results in terms of low water requirement, zero emulsion and less wastewater discharges than the conventional methods such as water washing, which produce significant amounts of wastewater containing impurities. This results in an economic gain and the avoidance of a serious environmental disposal problem [97]. In another study, Low and Cheong [31] used polymeric membrane system to purify crude biodiesel and reported improved biodiesel yield and less water consumption. They have experimented different types of membranes such as: PAN membrane, hydrophobic polypropylene 0.2 µm, 0.2 µm polyethersulfone membrane, flat PVDF 0.2 µm membrane, 0.2 µm ceramic tube membrane, 0.45 µm polysulfone membrane, and 0.2 µm flat mixed cellulose acetate membrane. The water discharged from the membranes was slightly basic and only contained trace of oil content. This effectively reduced the environmental impact, and the cost of wastewater treatment. The authors demonstrated that refining of methyl esters by membrane method may reduce water consumption by 75% in volume, save oil losses up to 44%, achieve high yield and low effect of environmental pollution. In addition, Saleh et al. [27] used modified polyacrylonitrile (PAN) membrane, with 100 kD molecular weight cut-off to remove glycerol from fatty acid methyl esters (FAME or biodiesel). The experiments were conducted at a temperature of 25 °C and operating pressure of 552 kPa. Using gas chromatography according to ASTM D6584, the free glycerol content in permeate, retentate and feed, of the membrane system was analyzed. The experimental results revealed low concentrations of water had a considerable effect in removing glycerol from the biodiesel even at approximate value of 0.08 mass%. The authors noted that conventional water washing requires 10 L of water per litre of treated biodiesel, whereas membranes need only 2.0 g of water per litre of treated biodiesel. They achieved 0.02 wt.% glycerol content in biodiesel at FAME + 0.1 wt.% water, and FAME + 0.2 wt.% water respectively.

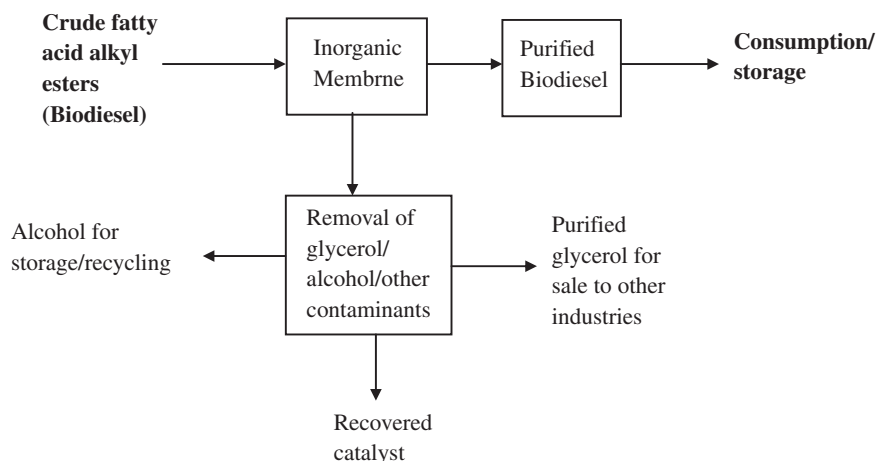


Fig. 5. Schematic diagram for biodiesel purification process.

Table 8

Comparison between different refining techniques for the removal of glycerin from biodiesel.

Lipid feedstock	Biodiesel from membrane reactor (w%)		Biodiesel from batch reaction (w%)		Ref.
	Total glycerin	Free glycerin	Total glycerin	Free glycerin	
Canola	0.0712	0.00654	0.131	0.0124	[61]
Yellow grease	0.0989	0.00735	0.685 ^a	0.0234 ^a	[61]
Brown grease	0.104	0.0138	0.797 ^a	0.0171	[61]
Palm oil	–	0.0152 ± 0.0074	–	0.0179 ± 0.0067	[62]
Canola oil	–	0.013 ^a	–	–	[54]
Soybean oil	–	0.04 ± 0.004 ^a	–	–	[45]
–	–	–	–	0.03 ^{a,b}	[26]
–	–	–	–	0.03 ^{a,c}	[26]

^a Does not meet the ASTM standard for glycerin in biodiesel (0.02 wt.%).

^b Ion exchange resin.

^c Magnesol.

Table 9

Contents of metals in the permeates and the retentate by membrane [62].

Component	Metals content (mg/kg) ^a			
	Potassium	Sodium	Calcium	Magnesium
Feed biodiesel	160 ± 19	8.98 ± 1.52	1.45 ± 0.36	0.33 ± 0.12
The permeate (0.6 μm):	4.25 ± 0.37	0.68 ± 0.15	0.70 ± 0.24	0.25 ± 0.11
The permeate (0.2 μm):	2.20 ± 0.42	0.88 ± 0.23	0.55 ± 0.25	0.26 ± 0.16
The permeate (0.1 μm):	1.70 ± 0.31	1.36 ± 0.34	0.95 ± 0.38	0.15 ± 0.07
Biodiesel by water washing:	2.46 ± 0.41	1.41 ± 0.35	0.64 ± 0.29	0.18 ± 0.08

^a Results are means ± SD (n = 5).

Demirbas [98] reported that alcohols such as ethanol forms azeotropes with water during transesterification reaction and most often cannot be completely recovered during purification process. However, it was noted that pervaporation, a membrane process is a promising technique in removing ethanol from alkyl esters [99].

6. Advantages and disadvantages of biodiesel refining technologies

The refining of crude biodiesel is primarily done to achieve high purity and quality biodiesel products that can be used in compression-ignition (diesel) engines [100]. Furthermore, refining of crude

biodiesel is a key factor to its commercial production and application. Thus continuous development of these refining technologies to purify biodiesel has raised hope for biodiesel industrial production and practical usability. Furthermore, achievement of high-quality biodiesel fuel could provide the following benefits: reduction in elastomeric seal failures, decrease in fuel injector blockages and corrosion due absence of glycerol, catalysts and soaps, reduces degradation of engine oil thereby providing high engine performance, better lubricant properties and better quality exhaust emissions. In addition, generation of high-quality biodiesel could also lead to elimination of fuel tanks corrosion effects, eradication of bacterial growths and congestion of fuel lines and filters, and annihilation of pump seizures emanating owing to higher viscosity at

Table 10
Advantages and disadvantages of different refining techniques.

Technique	Advantages	Disadvantages	Ref.
Wet washing	– Excellent methanol removal	– Emulsion formation, wastewater treatment, no effects on glycerides, and drying of final product	[26]
	– Can reduce methanol, soap and free glycerol levels below the amount needed by EN14214, with biodiesel purity of 99%	– Consumption of water and Na ₂ SO ₄ , high biodiesel products drying cost long time for water washing and the process is less ecologically viable	[77,81,100]
	–	Considerable loss in product due to formation of soap and emulsion, and treatment could incur high energy cost	[101,102]
Dry washing	– Magnesol can remove free and bonded glycerol, soap and potassium.	–	[69]
	– Magnesol is efficient and has the Ability to replace water washing	– Information regarding the chemical composition of the resin is difficult and little effects on methanol	[26,80]
	– Can effectively remove residual methanol, catalyst traces	–	[103]
	– Can augments the stability of bio-diesel in the oxidation process, besides it ability to remove sulfur	–	[104]
	– Can save time, lower energy, save capital cost, and lead significant disposal cost reduction	Involve highly consumable incurring expensive, require significant resources, larger size of powder grains making them exceedingly difficult to remove, and this caused an abrasive contaminated fuel	[79,81]
Membrane purification	– Provided good yield, high purity and quality finished products that are comparable to the conventional diesel fuels, simple, with less energy consumption, provide enormous environmental benefits and energy savings	–	[31,51,52]
	– Reduction in separation and purification costs, improved fuel quality, and high recovery of valuable products	– Organic membranes are less stable and easily get swollen in organic solvent	[27,31,53,54,105]
	– Zero waster washing with no waste discharges, and provide biodiesel with less glycerol content	– No large-scale industrial applications	[61,62,106]

low temperatures [26]. Table 10 summarizes the advantages and disadvantages of refining techniques used to purify crude biodiesel.

7. Conclusions and recommendations

Based on the foregoing the following conclusions and recommendations were made:

1. Wet refining technologies were reported to meet EN14214 in terms of methanol and free glycerol level required in biodiesel fuel, but the process is associated with wastewater discharges, which leads to environmental pollution, thus raising environmental concerns.
2. It was reported that separation of glycerol is critical to achieved high-quality biodiesel fuel.
3. It was found that dry washing process (using magnesol and ion exchange resins) does not meet EN14214 in terms of methanol required in biodiesel fuel.
4. It was also discovered that with little addition of water, membrane process could provide biodiesel with 0.013 wt.% glycerol, a value below the level stipulated by both ASTM D6751 and EN14214.
5. Membrane biodiesel refining proved to be less energy consuming and generate almost zero wastewater. These advantages makes membrane refining technology to be more environmentally friendly compared to wet water washing technology.
6. The significant effects of membrane on the removal of triglycerides and residual glycerol placed it at an advantage compared to some dry washing processes.
7. Development of membrane technology is necessary to exploit its inherent characteristic of operating under moderate conditions.
8. Application of adsorbents to overcome problems of wet refining was noticed to result in spent adsorbents that are not regenerated and cannot be re-used.
9. Wet biodiesel refining need to be completely discouraged for its high energy and water consumption and considerable wastewater discharges.

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