Membrane Performance on Biodiesel Production and Purification: A Review

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Abstract: Biodiesel is considered as a renewable and cleaner fuel compared to the equivalent fossil fuels. However, the conventional methods of biodiesel production as well as its purification processes present economic and environmental limitations. Membrane based systems can significantly improve biodiesel yield retaining the unrecovered feedstock and recycle it to the reactor for further esterification/transesterification. Moreover, the simultaneous removal of byproducts leads in high purity and quality biodiesel production. The current study presents recent experimental and modeling results based on a PRISMA literature review analysis. Several membrane-based catalytic systems were categorized by their performance and stability on biodiesel production as well as by their biodiesel purification for glycerol removal. Findings indicated that high biodiesel yield can be achieved by using catalytic synthesized membranes of different materials; while their stability presents high rate after several runs in batch mode or continuous running mode. In the purification process, glycerol removal over filtration membrane systems seems to be a viable solution for obtaining high quality biodiesel and avoiding wet washing methods that result in wastewater generation. Membrane technology contributes in biodiesel production and purification processes enhancing cost reduction and environmental protection. Nevertheless, more research is required for further industrialization.

Keywords: Membranes, Biodiesel production, Membrane reactor, Catalytic activity, Catalytic stability.

INTRODUCTION

Global environmental concern, energy crisis and human growth population combined with depletion of fossil fuel recourses have turned the attention to the production of alternative renewable fuels. Toward this direction, biodiesel is considered as one of the most promising alternatives to fossil fuels. However, conventional methods for biodiesel production present several drawbacks in processes, such as saponification, removal of catalyst, separation of glycerol, wastewater disposal, etc. After reaction, glycerin is separated from esters phase while purification of crude biodiesel is essential in order to meet the ultimate fuel specifications according to ASTM 6751 and EN 14214 standards [1, 2]. Typical downstream purification methods involve wet and dry washing. However, huge water consumption, high energy demand, wastewater treatment and increased cost are the main drawbacks. Hence, the integration of reaction-separation processes can reduce the overall cost and improve the reaction conversion. Inhibitory compounds are removed and the equilibrium is shifted towards the products side in accordance with Le Chatelier's Principle. Moreover, methanol and glycerol recycling reduces the total methanol to oil ratio [3, 4].

In recent years, membrane technologies have been developed for a range of applications including biofuels production and purification. Membrane systems play a dual role; on one hand membrane can transesterify triglycerides to biodiesel and on the other hand separation of impurities, such as catalysts, soap, glycerol, remaining alcohol and unreacted triglycerides can be achieved. In fact, membrane acts as a selective barrier and separates glycerol from the product steam, so that the triglycerides are retained within the membrane (Figure **1**). Membrane performance depends on its selectivity that presents towards compounds of interest, its composition, temperature, pressure, flow velocity, pore size, etc. [3, 5, 6].

Catalytic membranes (organic, inorganic, or both) are more efficient for biodiesel production compared to non-catalytic ones in terms of Fatty Acid Methyl Esters (FAME) yield and removal of undesired byproducts. Bio-derived polymers, like chitosan, comprise promising materials in membrane preparation and have been used for several processes, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), pervaporation (PV) etc. [7]. Moreover, functionalization of polymeric membranes, such as polysulfone, is able to improve membrane separation

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along with physicochemical properties of synthesized membranes [8].

Membrane reactors (MRs) are novel structures that combine in a single unit both reaction and separation processes providing high biodiesel selectivity and yield.. Types of MRs include catalytic membrane reactors (CMRs), pervaporation catalytic membrane reactors (PVCMRs), membrane bioreactors (MBRs) and inert membrane reactors [1, 9, 10]. Moreover, reverse membrane bioreactors (rMBRs) could be a promising combined technology merging conventional MBR and cell encapsulation techniques that could be more efficient than conventional pressure driven MBRs, mainly for bioconversion of complex substrates [11]. Synthetic membranes comprise a capable support for enzymes immobilization in a membrane bioreactor resulting in coupling of chemical reaction and separation process [12]. However, application of MRs and MBRs on industrial scale still remains challenging, due to high capital cost and challenges linked with membrane long term stability under real operational conditions, membrane fouling etc. [13, 14].

Sustainable valorization of increased waste production combined with fossil fuels depletion has gained attention of circular economy perspective. Waste disposal reduction and improvement of current technologies to circulate raw materials for biofuels production are of great significance. Towards to this direction, membrane reactors can reduce energy and economic requirements as they combine production and separation processes in one unit. Utilization of waste materials as feedstock could be an alternative solution for cost reduction, but even in that case pretreatment cost has to be taken under serious consideration. In case of lignocellulosic biomass, which is considered as an abundant renewable carbon source for biofuel production, the economic viability of hydrolysis pretreatment using membrane processes, such as reactive membrane extraction, nanofiltration, reverse osmosis and pervaporation, is uncertain and the development of robust low cost membranes is essential [15, 16].

Furthermore, the use of waste cooking oil (WCO) as an alternative feedstock for biodiesel production by CMRs has high potential, robustness and more efficient glycerol separation compared to conventional reactors. Specifically, Monte Carlo simulation indicated that CMR process was at least 50% more profitable than conventional one in all potential scenarios from different compositions of WCO [17].

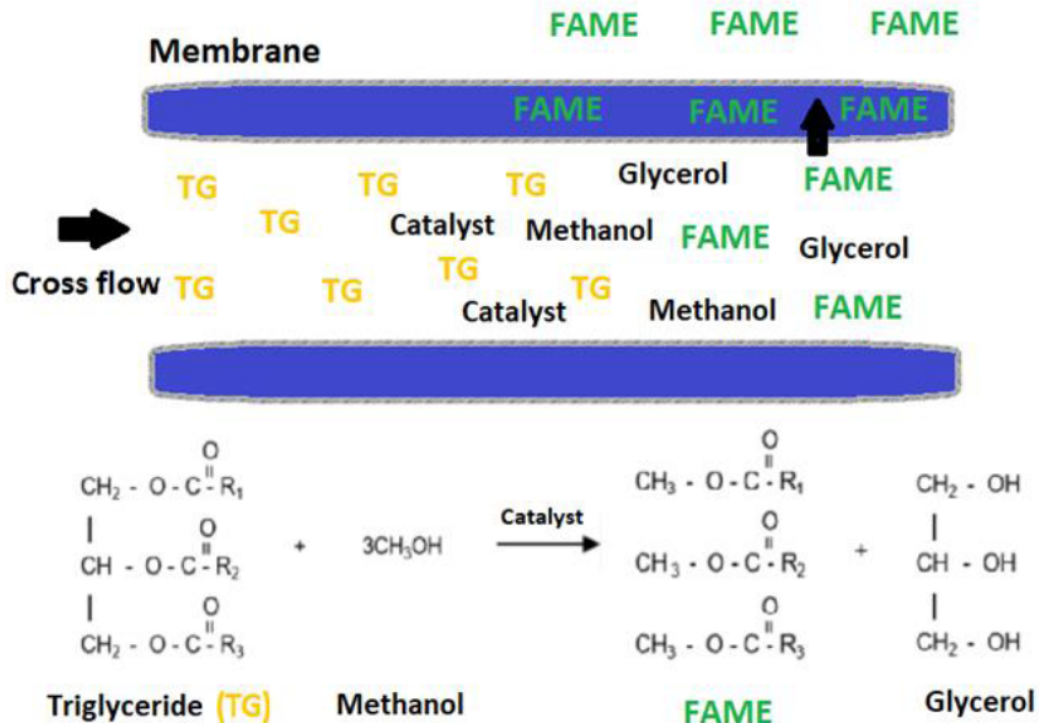However, the application and sustainable performance of membrane technologies for biodiesel

Figure 1: Schematic of membrane application in biodiesel production via transesterification and separation of byproducts.

production on industrial scale is still challenging and under improvement [2]. In this study, recent experimental and modeling results were presented based on a systematic literature review.

REVIEW METHOD

A systematic review was conducted by following the reporting checklist of the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) (Figure **2**) [18]. Scopus database was used for searching literature. The search in database took place from February 1, 2022 to March 1, 2022 and was performed within article title, abstract and keywords having publication dates between 2013 and 2022. The words that have been identified as keywords were the following: "membrane* AND biodiesel" AND "production OR upgrading". Advanced search was also limited to articles and reviews in English language on final publication stage at the subject areas of "Energy" and "Chemistry". Inside the full text, the following keywords or phrase have also to be included: "Biodiesel" OR "Biodiesel Production" OR "Biofuel" OR "Membranes" OR "Bioreactors". In total, 166 papers were found and exported from Scopus database to a digital spreadsheet categorized by document title, abstract, authors and year. Records removed before screening were 35 as ineligible document type. After the identification process, the record screening began by reviewing each accessible manuscript. From 131 screened files, 15 records did not reflect the subject of the request. Thus, 110 papers were considered to
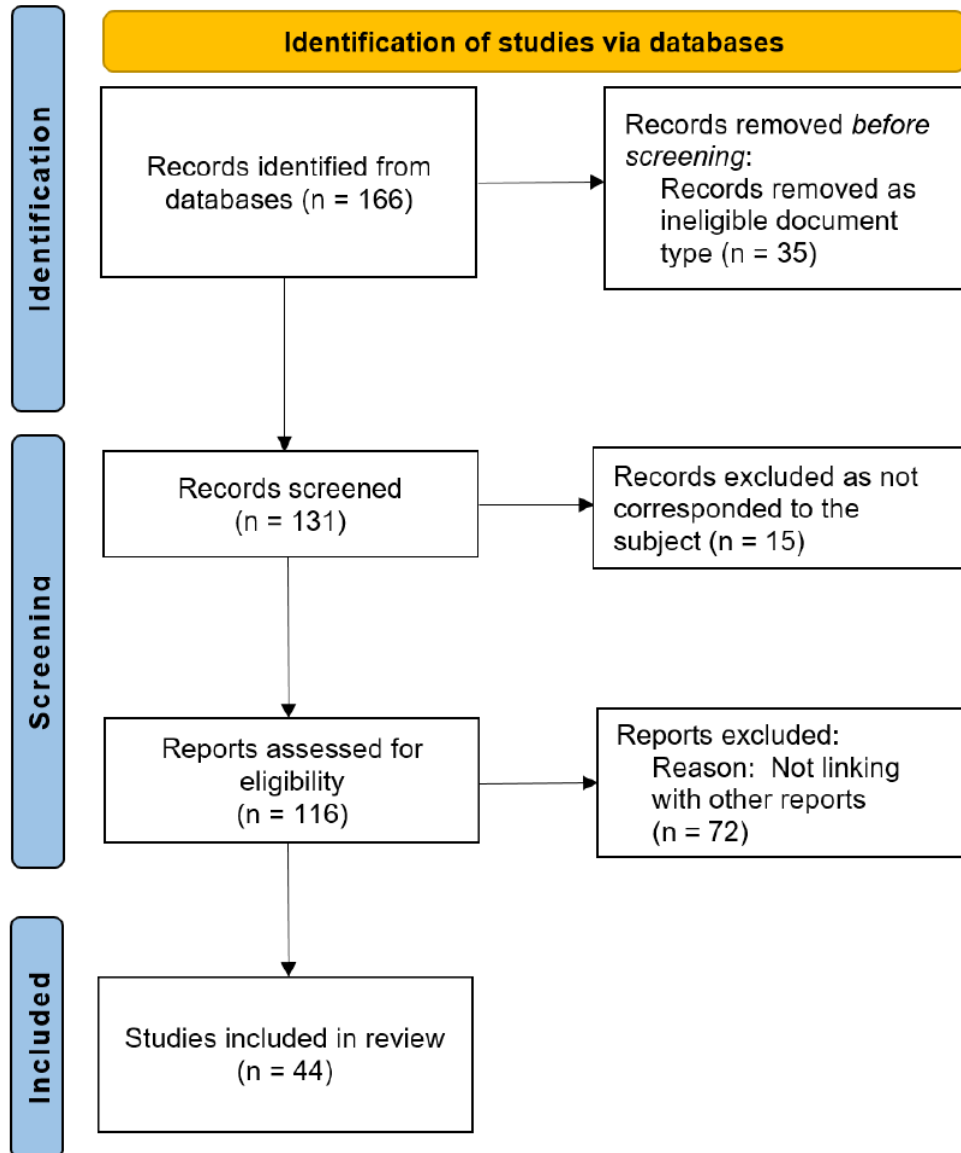

Figure 2: PRISMA flow chart of the systematic review study.

correspond to the topic of current review and they were thoroughly investigated. After a comprehensive analysis, it was determined that 44 papers fully matched with the subject of the current study, while 72 records excluded as their results could not be comparable to the reported ones.

DISCUSSION

In this section, recent experimental findings regarding biodiesel production through esterification or transesterification reaction from several oil feedstocks with different synthesized membrane catalysts and membrane reactors were presented (Table **1**). In all cases, feedstock, membrane material, optimum reaction conditions, remarks as well as production yield and reusability of membranes were further analyzed. Biodiesel yield (%) is described by the following formula:

$$Biodiesel\ yield = \frac{mass_{biodiesel}}{mass_{lipid}} \cdot 100 \qquad \text{(Eq. 1)}$$

In Table **2**, biodiesel purification and glycerol removal efficiency of several membranes were discussed, where various feedstocks for biodiesel production and transesterification reaction conditions were presented. The glycerol rejection rate was calculated by division of the difference between the initial and final glycerol content divided by the initial glycerol content.

Traditional catalysts for biodiesel production from transesterification of oils or esterification of fatty acids with lower alcohols include mainly homogeneous alkalis and acids, respectively. However, many researches focused on heterogeneous catalysts, due to several disadvantages that homogeneous ones present such as saponification, removal and recyclability [19]. Saengprachum et al. [20], prepared an acidic chitosan membrane (ACM) by crosslinking deacetylated chitosan with sulfosuccinic acid (SSA) for biodiesel production from oleic acid (OA). Owing to its high acidic side density (4.62 mmol/g) and swelling capacity (10.92 g/g), ACM exhibited high catalytic activity with the conversion of OA reaching 99.25% via single factor experiment and response surface modeling (RSM). However, reusability of ACM declined sharply after six runs and the OA conversion was 54.92%, because of the inability of ACM to adsorb more water. OA conversion was also investigated by Tian et al. [21], who prepared a Graphene oxide (GO)/Polyethersulfone (PES) catalytic membrane for biodiesel production.

Under optimal esterification reaction conditions that detected, the conversion of OA reached 94% after eight hours, showing excellent catalytic stability with 8% deactivation after six runs. Moreover, several parameters such as GO/PES ratio, temperature, membrane thickness and dosage and methanol/OA mass ratio were evaluated for their effects on biodiesel production. However, continuous esterification for catalytic stability assessment is required.

Recently, Zhang et al. [22] tested the catalytic performance of synthesized polyphenylene sulfide catalytic membrane (PPSCM) for OA continuous esterification with methanol in a flow-through mode membrane reactor. Under optimal conditions, the conversion reached 98% and PPSCM exhibited good catalytic stability with a conversion over 95% after 50h of continuous running, rendering PPSCM as a promising solid catalyst for biodiesel production. Continuous esterification of OA with methanol in a flow-through mode membrane reactor with a prepared composite catalytic membrane (CCM) from sulfonated polyethersulfone (SPES) and PES blend supported by non-woven fabrics was also investigated by Shi et al. [23]. Their findings indicated the significant effect of membrane's structure on the acid conversion. Catalytic activity and stability were very high, as OA conversion was above 98% after 500h of continuous running. Moreover, effects of membrane porosity, thickness and reaction temperature obtained by the predicted model was found in agreement with experimental results. A recent interesting study for membrane reactors potential design and evaluation was conducted by Hapońska et al. [24], who investigated the performance of several membrane reactors combined with heterogeneous catalysts. The innovative inert membrane reactor with strontium oxide catalyst (SrO) on a feed side (IMRCF) provided the proper conditions for sunflower oil conversion combined with high selectivity and a steady state yield of more than 90%. Simultaneous occurrence of reaction and separation could be possible by continuous recirculating the test fluid in the membrane module. Moreover, Handayani et al [25], found that high quality of biodiesel can be produced from sunflower's transesterification using MBR with immobilized Mucor miehei lipase on aminated polyethersulfone (PES-NH$_2$) membrane under optimum reaction conditions and proper enzyme loading. On the same investigation, results indicated that glycerol was not detected on LC-MS chromatographs showing that it was retained on membrane's filter; while the addition of glutaraldehyde improved efficiency of biodiesel conversion.

Table 1:   **Biodiesel Production from Several Feedstocks over Membrane Catalysts**

Feedstock	Catalyst	Experimental Conditions (optimal) for esterification or transesterification reaction	Remarks	Biodiesel Yield (%)	Catalytic stability after several runs	Ref.
Oleic acid (OA)	Synthesized acidic chitosan (ACM)	Amount of catalyst: 10.18 wt% Time: 120 min Temperature: 69.15^oC Methanol to OA ratio: 22.53:1	ACM performed high catalytic activity, due to high acidic site density swelling capacity.	98.76	After 6 runs: 54.92%	[20]
Oleic acid (OA)	Synthesized Graphene Oxide (GO)/Polyethersulfone (PES)	Amount of catalyst: 4g Temperature: 65^oC Time: 8h Methanol to OA ratio: 2:1	GO/PES also showed excellent catalytic stability with only 8% deactivation after 6 runs.	94	After 6 runs: 85.7 %	[21]
Oleic acid (OA)	Polyphenylene sulfide (PPS)	Amount of catalyst : 6 pieces of PPSCM into membrane reactor Time: 50h Temperature: 65^oC Methanol to OA ratio: 3:1	PPSCM performed good catalytic activity and stability.	98	After 50 h of continuous running: >95%	[22]
Oleic acid (OA)	Catalytic composite membrane (CCM) with non-woven fabrics as catalyst	CCM: round sheet of 68mm diameter Circulation flow rate: over 1.2 mL/min Temperature: 65^oC Methanol to OA ratio: 3:1	1. High catalytic activity and stability. 2. Part of adsorption water by the membrane did not affect the FFAs conversion for the long run.	98.2	After 500 h of continuous running: >98%	[23]
Sunflower Oil	Immobilized SrO on Polysulfone (PSf) membrane	Amount of catalyst: 2 wt% Time: 40 min Temperature: 65^oC Methanol to oil ratio: 12:1	Inert membrane reactor with catalyst on a feed side (IMRFC) improved the catalytic performance and selectivity.	>93%	-	[24]
Sunflower Oil	Immobilized Mucor miehei lipase on aminated polyethersulfone (PES-NH_2) membranes (PESNH2-10 D5 P8)	Sunflower oil: 25g n-butanol: 150mmol Time: 24 h Temperature: 50^oC	1. Glutaraldehyde as a cross-linker performed excellent enzyme loading value and increased biodiesel conversion efficiency. 2. Glycerol was retained on the filter membrane.	Abundance of methyl palmitate reached 100%	Continuous running	[25]
Soybean Oil	KF/Ca–Mg–Al hydrotalcite/honeycomb ceramic monolithic catalyst	Amount of catalyst: 1.5 g Time: 3 h Circulation velocity: 4.8 mL/min Temperature: 67^oC Methanol to oil ratio: 24:1	RSM 3D plots indicated that temperature had a positive effect on biodiesel yield, whereas high catalyst amounts and circulation velocities resulted in yield reduction.	91.7	After 3 runs: 87%	[26]
Soybean Oil	Al_2O_3 with KF/Ca–Mg–Al hydrotalcite as catalyst	Amount of catalyst: 10 wt% Time: 3 h Circulation velocity: 3.16 mL/min Temperature: 70 °C Methanol to oil ratio: 24:1	Models used indicated that oil content was very low and negligible in practical operation when the conversion was less than 50%.	95%	-	[27]

Soybean Oil	Alkalized polysulfone (APSF)	Amount of catalyst: 2.5 g Time: 10 h Temperature: $45^{o}C$ Methanol to oil ratio: 1:1 Co-solvent: n-hexane (50 wt%)	Effect of water (below 5%) and FFAs (below 2.5%) content on conversion were not obvious	95.3	After 5 runs: 93.2%	[28]
Soybean Oil	Synthesized crosslinked PVA-88-SSA PVA-99-SSA and PAAc-BDSA	Amount of catalyst: 4.39 wt % Time: 400 h Temperature: $60^{o}C$ Methanol to oil ratio: 60:5	1. Diffusion was found at least 4 to 6 times faster in PAAc-BDSA membrane than in PVA-88-SSA and PVA-99-SSA. 2. Lower biodiesel yield in PAAc-BDSA is due to a lower IEC and the presence of carboxylic groups in the polymer matrix.	92% for PVA-99-SSA 73% for PAAc-BDSA	-	[29]
Soybean Oil	Synthesized guanidinylated chitosan (GCS)	Amount of catalyst: 20 wt % Time: 6 h Temperature: $60^{o}C$ Methanol to oil ratio: 2.5:1	1. The conversion declined only 2.2% after five times. 2. Transesterification mainly took place on the surface of the catalytic membrane.	98.8	After 5 runs: 96.6%	[30]
Soybean Oil	C. rugosa lipase-immobilized PVDF	Amount of catalyst: 4.3 pieces Time: 33 h Temperature: $40^{o}C$ Methanol to oil ratio: 4:1	1. Immobilized lipase remained stable through a long-term hexane and methanol exposure. 2. Highest yield found with a water content of 5.2%.	97.2	After 5 runs: 90%	[31]
Eruca sativa Gars (ESGs) oil	$H_3PW_{12}O_{40}$/agarose membrane	Amount of catalyst: 5 wt% Time: 12 h Temperature: $65^{o}C$ Methanol to oil ratio: 95:1	1. In membrane reactor the reaction rate increased almost two folds compared to batch reactor. 2. Decrease in water content or glycerol from the reaction mixture.	97.2	After 10 runs: Negligible loss	[32]
Palm fatty acid distillate (PFAD)	Cross-linked 6FDA-NDA/DABA with s-MWCNTs as catalyst	Amount of catalyst: 3 wt% Time: 10 h Temperature: $135^{o}C$ Methanol to PFAD ratio: 20:1	1. Pervaporation membrane reactor improved FAME yield. 2. High removal percentage of water from the reactant mixture.	68.8	-	[33]
Pretreated acidified oil from WCO	Synthesized A-15/PVA membrane	Batch mode: Acidified oil: 20 g Amount of catalyst: 4g Time: 8 h Temperature: 65oC Stirring rate: 360 rpm Methanol to oil ratio: 29:1 Continuous mode: Acidified oil: 100 g A-15/PVA: 25 g Temperature: $65^{o}C$ Methanol to oil ratio: 29:1 Flow rate 1.2 mL/min	1. PVA could enhance the reusability of A-15/PVA in recycle runs by adsorbing the produced water. 2. High-quality biodiesel with pleasant emission characteristics. 1. Potential of A-15/PVA in the large scale and continuous production of biodiesel.	97.75 >98	After 6 runs: 87.2% After 120 h of continuous running: >98%	[35]

WCO	Synthesized crosslinked PPS:S-PPS 30:70 (MD 3C)	Amount of catalyst: 7 wt% Time: 250 h, Temperature: 60°C Methanol to oil ratio: 60:5	1. Larger IEC and controlled swelling increase conversion of TG to biodiesel. 2. Crosslinking by thermal treatment impedes the weight loss due to a high methanol solubility.	86	Not recovered	[36]
Pretreated WCO	KOH catalyst over a $TiO_2/Al2O_3$ membrane	Amount of catalyst: 1.24 wt% Time: 60 min Circulation flow rate: 18.78 mL/min Temperature: 58.5°C Methanol to oil ratio: 9:1	1. RSM 3D plots indicated that temperature, circulation flow rate and catalyst concentration had positive effects on biodiesel yield. 2. Catalyst concentration presented the highest positive effect on biodiesel production.	94.03	After 2 runs: no significant difference	[37]
Chicken Fat/ Oil	Catalytic composite membrane (CCM) for esterification of FFAs and sodium methoxide as catalyst for transesterification	Amount of catalyst: 1 wt% Time: 500 h Temperature: 69.85°C Oil to methanol ratio: 1:1	1. The CCMs presented high FFAs conversion and stability. 2. Part of adsorption water by the membrane does not affect the FFAs conversion for the long run.	>98.1	After 500 h of continuous running: >92%	[38]
Chicken Feet Oil	Filtanium ceramic membrane	Amount of catalyst: 1 wt% Oil to methanol ratio: 1:12 Ultrasonic frequency: 45kHz Time: 15 min Temperature: 68°C	1. Membrane system improved biodiesel's production rate and decreased six times the reaction time. 2. Membrane effect was prominent at greater frequencies.	88.8	-	[39]

Table 2:   Biodiesel Purification for Glycerol Removal with Membrane Filtration

Biodiesel feedstock	Transesterification conditions	Membrane	Amount of free glycerol	Amount of glycerol after filtration	Glycerol Rejection Percentage	Ref.
Calophyllum inophyllum (CI) Oil	0.01 mol of CI oil Mix of methanol (0.3 mol) and NaOH NaOH to oil ratio: 2.5 Temperature: 59.85°C Time: 3h	Glutaraldehyde-crosslinked chitosan	0.3014±0.05%	0.1429±0.09%	52.58%	[40]
Soybean Oil	KOH amount: 0.75 wt% Methanol to oil ratio: 4:1 Temperature: 40°C Time: 3h	PES ultrafiltration	0.029 wt %	0.019 wt %	34.48%	[41]
Sunflower Oil	225 g of sunflower oil 27.97 g of methanol 22.5 g of Lipolase Temperature: 40°C Time: 48 h	Polyacrilonitrile (PAN)	0.068 ± 0.002 wt. %	0.006 ± 0.001 wt %	91.48 ± 1.32%	[42]

WCO	KOH: 2–3 wt % Methanol to oil ratio: 6:1 Temperature: 60±3°C Time 1.5 h	Electrospun ABS–bamboo fiber (BF)	0.072 v. %	0.02 v. %	72.2%	[43]
WCO	KOH: 2–3 wt % Methanol to oil ratio: 6:1 Time 1.5 h Temperature: 60±3° C	Electrospun PU-MWCNT	0.08 v. %	0.02 v. %	75%	[44]
WCO	NaOH: 1.5 wt % Methanol to oil ratio: 9:1 Time 2 h Temperature: 60 °C	Polyethersulfone (PES)	0.0604 wt %	0.0421 wt %	30.2%	[45]

Coupling of transesterification reaction and membrane separation was also tested by Xu *et al*. [26], by using KF/Ca–Mg–Al hydrotalcite/honeycomb ceramic monolithic catalyst in a bench-scale membrane reactor for biodiesel production from soybean oil with methanol. RSM model was used to determine the optimum level of each parameter for maximum response where the highest biodiesel yield reached 91.7% and in case of fresh catalyst the yield was found 87% after three runs showing a reasonable stability. Soybean transesterification with methanol in a bench membrane reactor catalyzed by KF/Ca-Mg-Al hydrotalcite was further examined by Gao *et al*. [27], whose findings indicated that membrane reactor can shift equilibrium to products side by simultaneously removing the products. Validation of developed mathematic and UNIUAC models occurred and results showed that biodiesel yield increased under the same time with temperature increase. Moreover, as oil content was very low, it can be neglected when conversion was less than 50%.

Furthermore, in regards to transesterification of soybean oil, polymeric synthesized alkalized polysulfone (APFS) membrane was investigated by Shi *et al*. [28] for biodiesel production. Addition of co-solvents improved reaction yield, where n-hexane was found to be the most suitable for transterification (95.2% yield). APFS membrane exhibited good catalytic performance after five runs with a small decline in conversion rate and the effects of FFAs (below 2.5%) and water (below 5%) in the feedstock were not obvious on transesterification reaction. On another study [29], a novel catalytically active membrane from polyacrylic acid (PAAc) crosslinked with 4,40-diamino-2,20-biphenyl sulfonic acid (PAAc-BDSA) was performed for biodiesel production from transterification of soybean oil in comparison with other

catalytic membranes. Conversion rate (73%) was found to be less, as the ion exchange capacity (IEC) value was lower in case of PAAc-BDSA membrane, however due to its high hydrophilicity membrane had higher swelling degree in water, methanol and soybean oil, it could be applied for low quality feedstocks. A high conversion of soybean oil (98.8%) was obtained by transesterification with methanol using guanidinylated chitosan (GCS) as heterogeneous catalyst during the experimental investigation that conducted by He *et al*. [30]. Under optimum reaction conditions, catalytic stability was proven high as conversion was 96.6% after five runs and transesterification took place basically on the membrane surface. Moreover, a synthesized biocatalytic membrane with immobilized lipase Candida rugosa on polyvinylidene fluoride (PVDF) has been tested for transesterification of soybean oil with methanol in n-hexane by Kuo *et al*. [31]. Under optimum predicted condition, biodiesel yield reached 97.2% with water content 5.2 wt%; then, the batch immobilized lipase was used for five runs with the yield remaining at 90%. Another important investigation conducted by Hou *et al*. [32], who studied the transesterification reactions of Eruca sativa Gars (ESGs) oil not only in a batch reactor but also in a HPW/agarose membrane reactor comparing the reaction rates between them. In case of membrane reactor application, the reaction rate was almost double compared to batch reactor, due to the removal of glycerol from the reaction. Finally, an integrated pervaporation membrane reactor that combined both esterification reaction of palm fatty acid distillate (PFAD) and separation into one unit was investigated by Shuit *et al*. [33]. Their findings indicated that cross-linked 6FDA-NDA/DABA polyamide membrane with sulfonated multi-walled carbon nanotubes (s-MWCNTs) as catalyst in pervaporation membrane reactor

exhibited higher biodiesel yield (68.8%) compared to batch reactor (58.45) under the optimum conditions. In addition, high removal percentage of water from the reactant mixture was observed in membrane reactor, resulting in the equilibrium shift towards the products.

However, instead of edible oils as feedstocks for biodiesel production, utilization of non-edible oils and waste cooking oils (WCO) have been widely investigated as they are considered as promising feedstocks, because of their lower cost and contribution to the reduction of disposal waste [34]. Zhang *et al*. [35], investigated the catalytic performance of synthesized Amberlyst-15/ Poly (vinyl alcohol) membrane (A-15/PVA) on both batch and continuous esterification of acidified oil (WCO) with methanol. Under optimum conditions, high quality biodiesel production was achieved and A-15/PVA membrane exhibited excellent catalytic performance and stability for both esterification applied modes. Moreover, engine test was performed for biodiesel as well as for four blends with diesel, demonstrated pleasant emission characteristics. Another recent investigation was conducted by Gomez-Trejo-Lopez *et al*. [36], who prepared and tested catalyzed by polyphenylsulfone (PPS) and sulfonated polyphenylsulfone (S-PPS) blend membranes (PPS:S-PPS) for biodiesel production from WCO with high content in triglycerides. Membrane MD 3 C (PPS:S-PPS 30:70 blend) with the best balance of Ion Exchange Capacity (IEC), methanol swelling and weight loss was identified and used for transesterification reaction. Biodiesel yield (86%) that was achieved in less time compared to other sulfonic acid membranes could provide a suitable option for WCO transesterification. However, reusability of these kind of membranes has to be studied in order to evaluate their feasibility for continuous biodiesel production.

Evaluation of the interaction among several parameters in biodiesel production with membrane technology is very important. Thus, Moyo *et al*. [37] used RSM to investigate the effect of temperature reaction, catalyst amount and circulation flow rate in a membrane reactor for biodiesel production from pretreated WCO over a TiO_2/Al_2O_3 membrane and KOH as catalyst. Under optimal experimental conditions, biodiesel yield reached 92.6 mole%; while upon membrane optimization, it reached 94.03 mole% under lower temperature, circulation flow rate and catalyst amount.

Moreover, Shi *et al*. [38] investigated a two-step process for biodiesel production from waste chicken fat through an integrated catalytic process of composite membrane (CCM) and sodium methoxide. Continuous esterification in a membrane reactor was first applied for FFAs conversion, which reached 92.8% under the optimum conditions. Then, transterification of triglycerides (TGs) conversion took place with sodium methoxide addition and the maximum conversion of TGs reached 98.1%. Catalytic stability and activity of CCM was really high after 500h of continuous running. FFAs conversion was above 92%. It was also observed that part of adsorption water by the membrane does not affect the FFAs conversion for the long run. Chicken waste as feedstock for biodiesel production though a two-step esterification-transesterification mechanism using ultrasonic bath and a membrane system was also examined by Haghighi *et al* [39]. Their findings indicated that membrane system performance, which was evaluated by modeling, exhibited efficient TG conversion under optimum conditions and biodiesel blend decreased the reaction time to six times shorter (15 min) than the conventional method (1.5 h). Moreover, membrane approved more effective at higher frequencies than at lower ones.

The conversion rate and the biodiesel yield of membrane-system catalyzed esterification of fatty acids as well as transesterification of plant oils and animal fats revealed the efficiency of membranes presenting high selectivity and stability after certain runs, even in case of continuous running in membranes reactors for many hours. Furthermore, reactions took place under mild conditions in the membrane reactors with a simultaneous separation of water or glycerol that moves the equilibrium to the products side. Continuous mode under optimum operational conditions presented high membrane catalytic stability with small reduction in conversion rate or biodiesel yield [9, 10]. Characteristic examples are oleic acid esterification with methanol in a flow throw membrane reactor in the presence of PPSCM membrane where conversion rate retained above 95% for 50 h of continuous running [22], as well as the esterification of waste chicken oil with methanol under novel sulfonated polyethersulfone (SPES)/PES/Non-Woven Fabric (NWF) catalytic membrane, which exhibited great stability after 500h of continuous running in a membrane reactor [38].

However, after transesterification reaction, biodiesel purification is crucial in order to meet ASTM and EN requirements [5]. According to ASTM D6751 and EN14214, the maximum limit of total free glycerol in

biodiesel B100 is 0.03 v. % and 0.02 wt %. In Table **2**, membrane filtration systems were reported for their efficiency in biodiesel purification. Wafiroh *et al*. [40] investigated a synthesized glutaraldehyde-crosslinked chitosan membrane to improve biodiesel quality. Glutaraldehyde was added to promote the mechanical properties of chitosan membrane. During purification process addition of water in biodiesel mixture was important for lowering glycerin content. Their findings indicated that membrane reduced efficiently the glycerol content (52.8%). On the other hand, Alves *et al*. [41] compared several microfiltration and ultrafiltration membranes for their efficiency in glycerol removal from biodiesel produced by transesterification of soybean oil. Even if microfiltration membranes presented higher fluxes, the filtered biodiesel contained glycerol amount above the accepted limit (0.02 wt %). Only ultrafiltration process with 10 kDa molecular weight cut-off membrane was able to achieve glycerol content that meet standard specifications (free glycerol content after filtration equal to 0.019 wt %).

Another recent investigation regarding biodiesel purification was conducted by Sokác [42], who evaluated the performance of four different membranes on glycerol removal from biodiesel produced by lipase catalyzed transesterification of sunflower oil. Their findings have shown that among other membranes used, polyacrylonitrile membrane exhibited the highest glycerol removal (91.48%) without loss of its performance for six times.

Chingakham *et al*. [43] examined the filtration of biodiesel produced by coconut oil based WCO using a superoleophilic and hydrophobic synthesized nano-bamboo fiber (BF)-reinforced acrylonitrile butadiene styrene (ABS) electrospun membrane. Measured properties of membrane revealed that it was effective for biodiesel filtration and the concentration of glycerol in biodiesel decreased from 0.072 to 0.02 v.v % after the filtration. Moreover, as filtration process is aided by gravity, less power consumption was achieved. Recently, Chingakham *et al*. [44] investigated a hydrophobic multi-walled carbon nanotube (MWCNT) reinforced polyurethane (PE) electrospun membrane for biodiesel purification. MWCNT loading on PE membrane improved its mechanical strength. Glycerol rejection percentage reached 75% and the filtered biodiesel satisfied ASTM standards. Purification of WCO was also investigated by Farahani *et al*. [45] using prepared PES membranes

for biodiesel filtration. Results indicated that membrane containing 16 wt% preformed higher removal rejection compared to the others. After filtration glycerol mass percentage in permeate section was 0.042 wt%, where initially free glycerol content in biodiesel was 0.0604 wt%.

Consequently, purification of produced biodiesel from several feedstocks and under different transesterification conditions was conducted through several synthesized membranes presenting efficient rates of rejection removal. In all cases, filtered biodiesel was in accordance with ASTM standards for free glycerol content. Especially, in case of biodiesel produced by sunflower oil glycerol, the removal percentage reached approximately 91.48% indicating that ultrafiltration PAN membrane was really efficient even after six runs [43]. Moreover, superoleophilic and hydrophobic nanofibrous membranes, that used for filtration of WCO, showed efficient glycerol removal demanding less power consumption [43, 44].

CONCLUSIONS

Energy and fuel supply concerns along with environmental protection measurements have paved the way for alternative biodiesel production and purification methods that can eliminate the drawbacks of conventional ones. Towards this direction, membrane science becomes more attractive over the years. Membrane reactors with catalytic ceramic and polymeric membranes, as well as membrane bio-reactors result in high product yields of esterification/transesterification reactions for biodiesel production from a variety of feedstocks. Simultaneous separation of water and glycerol byproducts move the equilibrium towards the product side. Hence, high quality of biodiesel can be obtained, while minimization of separation and purification costs are also advantageous. Moreover, utilization of waste feedstocks and sustainable recycling of raw materials can reduce operational cost and chemicals usage. Results indicated that under optimal operational conditions high quality biodiesel could be produced over different synthesized membranes. Their catalytic stability presented small reduction in conversion rate/biodiesel yield during esterification/-transesterification reactions of several oil based feedstocks under certain running cycles. Nevertheless, more research and development are required in order membrane materials to be cost effective and to meet industrialization requirements and purposes.

LIST OF ACRONYMS

ABS	Acrylonitrile butadiene styrene
ACM	Acidic chitosan membrane
APSF	Alkalized polysulfone
BF	Bamboo fiber
CCM	Composite catalytic membrane
CI	Calophyllum inophyllum
CMR	Catalytic membrane reactor
ESGs	Eruca sativa Gars
FAAE	Fatty acid alkyl esters
FAME	Fatty acid methyl esters
FFAs	Free fatty acids
GCS	Guanidinylated chitosan
GO	Graphene oxide
IEC	Ion exchange capacity
LC-MS	Liquid chromatography-Mass spectrometry
MF	Microfiltration
MR	Membrane reactor
MWCNT	Multi-walled carbon nanotube
NF	Nanofiltration
NWF	Non-Woven Fabric
OA	Oleic acid
PAN	Polyacrylonitrile
PES	Polyethersulfone
PES-NH$_2$	Aminated polyethersulfone
PPSCM	Polyphenylene sulfide catalytic membrane
PRISMA	Reporting Items for Systematic Reviews and Meta-Analyses
PV	Pervaporation
PVCMR	Pervaporation catalytic membrane reactor
PVDF	Polyvinylidene fluoride
rMBR	Reverse membrane bioreactor
RSM	Response surface modeling
SrO	Strontium oxide
SPES	Sulfonated polyethersulfone
SSA	Sulfosuccinic acid
UF	Ultrafiltration
WCO	Waste cooking oil

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