

SIMULTANEOUS METHYL ESTER PRODUCTION AND CAROTENE RECOVERY FROM CRUDE PALM OIL USING MEMBRANE REACTOR

I Gusti Bagus Ngurah Makertihartha^a, Khoiruddin Khoiruddin^a, Eryk Bone Pratama Nabu^a, Putu Teta Prihartini Aryanti^b, I Gede Wenten^{a*}

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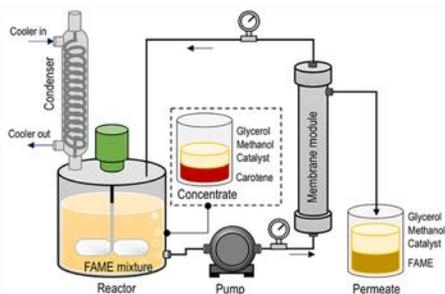
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^aChemical Engineering Department, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia

^bChemical Engineering Department, Universitas Jenderal Achmad Yani, Jl. Ters. Jend. Sudirman, Cimahi 40285, Indonesia

*Corresponding author
igw@che.itb.ac.id

Graphical abstract



Abstract

Fatty acid methyl ester (FAME) or biodiesel, which is considered as an alternative renewable fuel is usually produced via transesterification reaction of triglyceride from vegetable oil. Generally, there are two major challenges in the production of biodiesel i.e., reversible reaction of transesterification and immiscibility between oil and alcohol. Membrane reactor (MR), which combines reaction and separation, is an alternative process to overcome those challenges. The aim of the integrated reaction-separation process is to shift the equilibrium reaction, and to achieve a higher reaction conversion. The methyl ester that is produced may be separated to meet the biodiesel quality standards. FAME purification using membrane can be conducted without water washing (dry process), and this is interesting as the associated wastewater treatment step is eliminated. Another attractive feature of MR in esterification process is carotenoid recovery which is beneficial to improve the efficiency of the process. Several studies have indicated the efficacy of carotenoids recovery from methyl ester mixture. This paper reviews the use of MR for palm oil esterification. Membrane separation performances in methyl ester purification are also discussed. In addition, the potential of carotene recovery during esterification process is highlighted.

Keywords: Biodiesel, membrane, palm oil, transesterification, vegetable oil

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1.0 INTRODUCTION

Crude palm oil (CPO), one of the leading vegetable oils in the world market, cost less than other vegetable oils such as canola, rapeseed, and soybean oils [1]. Oil palm produces the highest yield of oil per area [2–6] and oil of high quality [7], which makes palm oil an attractive vegetable oil feedstock for esterification or production of methyl esters. Palm oil-based methyl esters can be used not only for biodiesel, but also as intermediate materials for producing oleo-chemicals

[8]. As can be seen in Figure 1, publication related to palm oil esterification, methyl ester, and biodiesel has been increasing since the year 2000.

Fatty acid methyl ester (FAME) is usually produced via transesterification reaction of triglyceride in vegetable oil or animal fats under acidic, basic, or enzyme catalyst. For biodiesel production, the purpose of reaction is to reduce oil viscosity in order to meet the specification of fuel [9]. In the conventional process, FAME production typically involves several

steps including transesterification reaction, neutralization, separation, and purification.

Generally, there are two major challenges in transesterification reaction i.e. reversible reaction and immiscibility between oil and alcohol [10]. Reversible reaction needs proper control to shift the equilibrium reaction towards the product in order to achieve a high yield. To achieve this purpose, methyl esters or glycerol should be separated from the reaction mixture. An incomplete reaction may result in low-quality methyl esters due to the presence of impurities (e.g., triglyceride, diglyceride, monoglyceride), and unreacted feed [11]. Alcohol may be added to the reactor to maintain reaction equilibrium. This, however, always increases the cost [11]. Another option is by washing the product (FAME). Unfortunately, this option requires an additional step for wastewater treatment [12]. Conducting reaction under an extreme condition, such as in a supercritical condition, may also be used but it will also consume high energy [13]. Meanwhile, immiscibility of alcohol and oil can reduce mass transfer, and limit the reaction rate. A high rate of agitation or additional solvent may overcome this problem. However, a high agitation rate increases energy consumption, while additional solvent results in a high operating and purification cost [13, 14].

Studies of membrane technology in vegetable oil are increasing, as they are driven by the attractive features offered by this technology [15, 16]. Membrane can produce high quality products with relatively low energy consumption, lower operating and investment costs, and operating flexibility [17–23]. It can be combined with other processes to reduce the processing steps [24–30]. In addition, since the separation is usually operated under mild operating conditions, it is beneficial for maintaining the quality of heat sensitive components [31–36]. Membrane reactors (MR) have been widely studied for biodiesel production as can be seen by the increasing number of publications related to this topic (see Figure 1). MR is used as an alternative process to solve problems encountered in conventional reactors. MR combines reaction and separation into a simultaneous process in a single unit. This is expected to maintain the reaction equilibrium and to achieve a high reaction conversion. Membrane also has potential to be used for separation of FAME products from glycerol. Biodiesel or FAME purification using membrane is interesting because the wastewater treatment step in the conventional washing process is eliminated. Another attractive feature of membrane in FAME production is carotenoid recovery. Since transesterification uses vegetable oil as feedstock, it provides an opportunity to recover unreacted components containing phytonutrients (e.g., carotenoids) which is beneficial to improve the efficiency of the process [37, 38].

Applications of membrane technology for biodiesel production and purification have been reviewed in the literature [39–41]. In this paper, membrane-based palm oil transesterification is reviewed including MR type, operational conditions, and performance.

Membrane performances in FAME purification are also discussed. In addition, potential application of MR for simultaneous FAME production and carotenoids recovery is highlighted. Therefore, this review complements previous reviews on transesterification of palm oil.

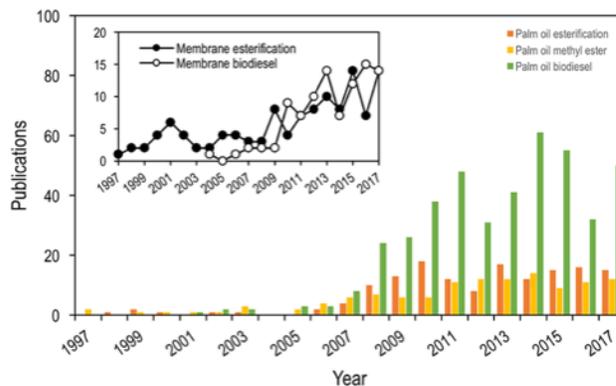


Figure 1 Number of publications related to “palm oil esterification, methyl ester, biodiesel” and “membrane esterification, biodiesel” indexed by Scopus

2.0 MR FOR VEGETABLE OIL ESTERIFICATION

A schematic illustration of FAME production with MR is shown in Figure 2(a). In a reactant mixture (containing oil, methanol, and catalyst), oil forms an emulsion or suspended droplet due to immiscibility of oil/alcohol mixture, and the presence of various surface tension. In a hydrophilic environment, oil tends to form droplets [10] (see Figure 2(b)). Esterification reaction occurs on the surface of these droplets [10]. As the membrane has a smaller pore size than the droplets, oil will not be able to permeate through the membrane [10, 12]. On the other hand, methyl ester can dissolve in methanol, and can thus be easily separated from the reactants mixture through the membrane. This also gives the possibility of obtaining high purity methyl ester even if the reaction is not complete.

Transesterification has two phases namely non-polar (i.e., triglyceride) and polar phases (i.e., methanol). The two-phase system is important to prevent triglyceride and unreacted reactants migrations to the product. Generally, transesterification consist of three reversible reaction steps. In the first step, triglycerides are transformed into diglyceride, monoglyceride, and glycerols. At each reaction step, one molecule of methyl ester is produced for one molecule of alcohol [42]. According to several reported studies, in a batch reactor, conversion of triglyceride to diglyceride is the limiting reaction and the determining step [43–46]. Meanwhile, conversion of diglyceride to monoglyceride is the fastest reaction step. Among those compounds, monoglyceride is the most unstable intermediate compound which will be directly converted to glycerol and methyl ester [47].

Kinetics of transesterification in a membrane is different from that in a conventional batch reactor. The determining step in membrane reactor is the conversion of diglyceride to monoglyceride, while the conversion of monoglyceride to monoglyceride is the fastest reaction step [48]. This is due to better mixing and separation between reactants and products provided by the membrane reactor. Moreover, it is associated with the higher molar ratio of oil and methanol used in the membrane reactor than in a conventional reactor.

2.1 Factor Affecting MR Performance

The performance of MR in FAME production is determined by several factors including molar ratio of methanol to oil, methanol recycling, temperature, reaction time, catalyst, and is specifically affected by feed flow rate, membrane type, membrane pore size, transmembrane pressure, and affinity [12].

In MR, two phases are formed during transesterification of vegetable oil. A high ratio of alcohol to oil is recommended to prevent phase

inversion of the oil phase to the continuous phase which can cause pore plugging [14]. Quantitatively, it can be estimated using the model proposed by Ho et al. [49] to express phase inversion point in a two-phase system:

$$\phi_1 / \phi_2 = 1.22 (\mu_1 / \mu_2)^{0.29}$$

where μ is viscosity of pure component and ϕ is volume fraction of the component. By introducing viscosity of oil and methanol at 65 °C into the equation, the value of ϕ_1 will be 0.31. Therefore, to keep methanol in the continuous phase, the minimum volume fraction of methanol should be 0.31 or the molar ratio of methanol to oil should be 11:1 [14,49]. MR can be effectively operated under a semi-continuous mode at a volume fraction of methanol/oil larger than 0.38 or the molar ratio of methanol to oil is about 16:1 [14]. The molar ratio used in MR is generally higher than that in a conventional batch reactor, i.e. about 16:1 to 24:1 for MR and 6:1 to 12:1 for the conventional batch reactor [10, 13, 44, 48, 50, 51].

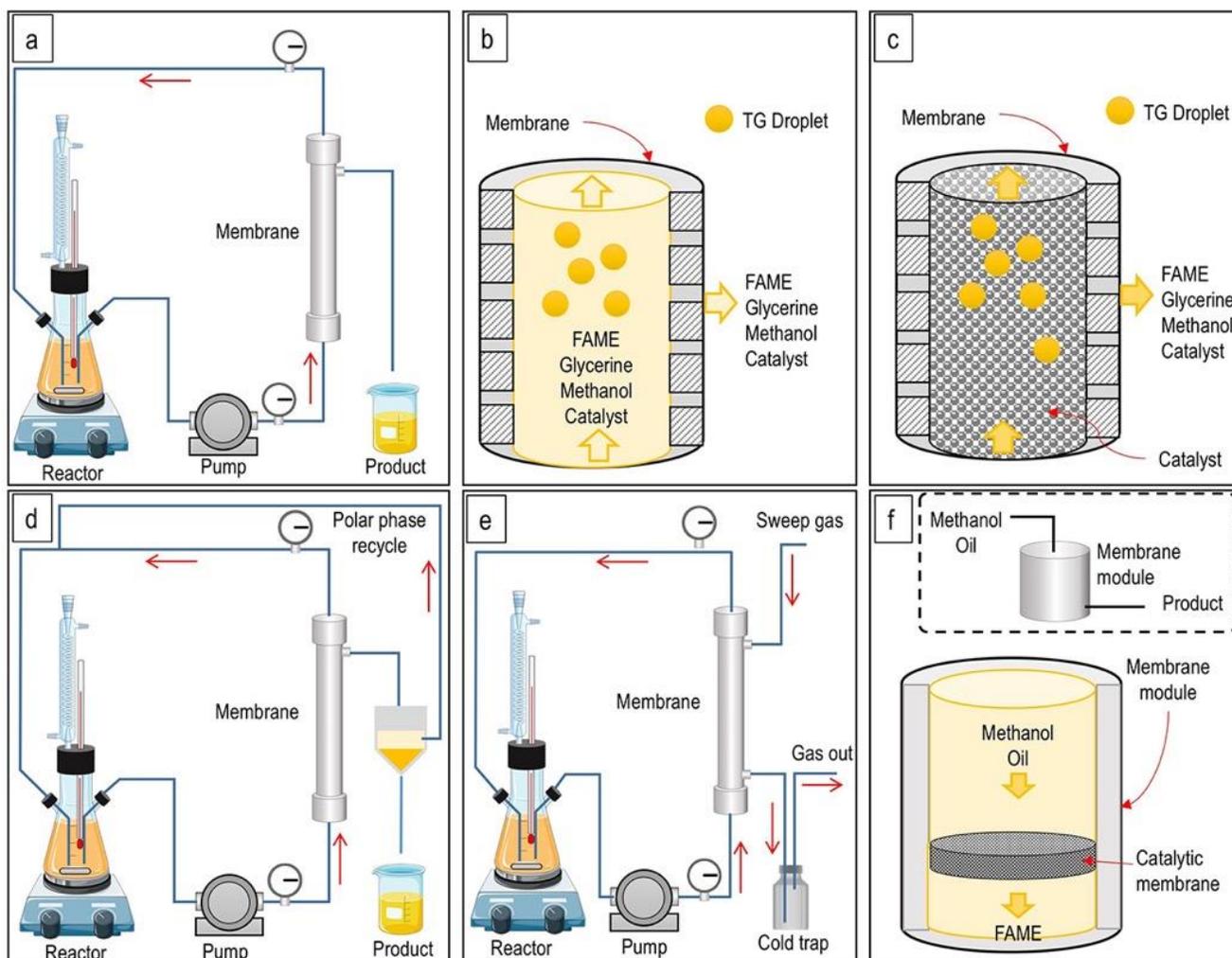


Figure 2 Schematic illustration of MR used in esterification. (a) MR system, (b) product separation in MR, (c) packed-bed MR, (d) MR with polar phase recycling, (e) pervaporation assisted MR, and (f) flow through catalytic MR

Table 1 Methyl ester production with membrane

Process	Operational conditions	Results	Ref.
MR	Carbon membrane (0.05 μm); Canola oil; Methanol/Oil = 2/1 (volume ratio); 65 °C; 1.4 bar; 6 h; Catalyst: H ₂ SO ₄ (2 Wt.%).	Conversion = ~85%;	[12]
MR	Carbon membrane (0.05, 0.2, 0.5, and 1.4 μm); Canola oil; Methanol/Oil = 11-46/1 (molar ratio); 65 °C; 2 bar; 2.5 h; Catalyst: NaOH (0.5 wt % by weight of oil).	Conversion = ~89-99%; Contained undetectable level of glycerol.	[14]
MR	TiO ₂ (300 kDa); Canola oil; Methanol/Oil = 23.9/1 (molar ratio); 65 °C; 2.75 bar; Continuous; t_r = 1 h; Methanol recycle = 75-100% ; Catalysts: NaOH (1 wt % by weight of oil).	FAME conc. in permeate > 85%	[10]
MR	TiO ₂ /Al ₂ O ₃ (0.05 μm); Palm oil; Methanol/Oil = 1/1 (volume ratio); 70 °C; Continuous; 1 h; Methanol recycle; Catalyst: KOH (1.12 wt % by weight of oil).	Conversion = 97%; Free glycerin = 0.009 wt.%	[52]
Catalytic MR	Zr(SO ₄) ₂ /SPVA; Acidified oil (with an acid value of 16.0 mg KOH/g and 0.03 wt.% water); Methanol/Oil = 6/1 (molar ratio); 65 °C; Continuous; atm; 2 h; Membrane/reactant = 4 wt%.	Conversion = 94.5%; Free glycerin = 0.009 wt.%.	[53]
Catalytic MR	Zr(SO ₄) ₂ /PVA; Acidified oil (with an acid value of 16.0 mg KOH/g and 0.03 wt.% water); Methanol/Oil = 6/1 (molar ratio); 65 °C; Continuous; atm; 2 h; Membrane/reactant = 4 wt%.	Conversion = 81.2%; Free glycerin = 0.009 wt.%.	[53]
Catalytic MR	SPES/PES/NWF composite membrane; Oleic acid; Methanol/oil = 3/1 (w/w); 65 °C; Continuous; Residence time = 210 s; Catalyst: Acid amount in membrane = 15.8 mmol (H ⁺).	Conversion >98% (continuous running for 500 h);	[54]
Catalytic MR	Cation ion-exchange resin particles (CERP)/PES catalytic membrane; Acidified oil from waste cooking oil; Methanol/Oil = 2/1; 60 °C; Continuous; 1.5 h; Microwave assisted; Membrane/oil = 3/20 (w/w).	Conversion = 97.4%;	[55]
Catalytic MR	CERP/PVA; Lauric acid; Methanol/oil = 18.75/1 (ml/g); 60 °C; Batch; 24 h; Membrane/oil = 1/8 (w/w).	Conversion = ~80%;	[56]
Catalytic MR	Sulfonated PES/PES; Oleic acid; Methanol/oil = 1/1 (w/w); 6 h; Catalytic membrane loading = 1.66 meq/g.	Conversion = 97.4%;	[57]
Catalytic MR	S-PES/ phosphotungstic acid; Acidic oil; Methanol/oil = 1/1 (w/w); 65 °C; 6 h; Catalytic membrane loading = 1.66 meq/g.	Conversion = 95.3 %	[58]
Catalytic MR	SO ₄ ²⁻ /TiO ₂ -ceramic catalytic membrane; Oleic acid; Methanol; Methanol/oil = 21/1 (molar ratio); 65 °C; 3 h; Catalytic membrane = 3 wt% (to oil).	Conversion = 97.63 %	[59]
Catalytic MR	Quaternized Psf membrane; Soybean oi; Methanol; Methanol/oil = 3/1 (w/w); 65 °C; Flow through; 2 ml/min; Membrane diameter = 68 mm.	Conversion = 98.2 %	[60]
Enzymatic membrane bioreactor	Ceramic membrane (zirconium on carbon support; 15 kDa ; Triolein; Alcohol/fatty acid = 1.6; 30 °C; Cutinase enzyme in reversed micelles; 0.5 – 1 mg/L.	Conversion = ~90%; $t = 24$ h (batch). Conversion = ~60% (continuous); Productivity = up to 500 g _{product} /day/ g _{enzyme}	[61]
Enzyme immobilized MR	PAN nanofibrous membrane; Soybean oil; Methanol/oil = 6.6/1; 30 °C; <i>P. cepacia lipase</i> (43 mg/g material).	Conversion = ~90%; $t = 24$ h.	[62]
Enzyme immobilized MR	PVDFP; 0.45 μm ; Activity = ~9 U/membrane; At 4 membranes per 0.5 g oil; Soybean oil; Methanol/oil = 4/1; 40 °C; 5.2% added water content; Lipase (from <i>Candida rugose</i>).	Conversion = 97.2%; $t = 33$ h;	[63]
Packed-bed MR	TiO ₂ /Al ₂ O ₃ (0.05 μm); Palm Oil; Methanol/oil = 1/1; 70°C; 1 h; KOH catalyst supported on activated carbon (157 mg/cm ³ of reactor).	Conversion = ~94%;	[64]
Packed-bed MR	Ceramic membrane (0.2 μm); Soybean oil; Methanol/oil = 24/1 (molar ratio); 70 °C; 0.5 bar; 2.5 h; 3.16 mL/min; 0.531 g/cm ³ catalyst amount; Catalyst: KF/Ca–Mg–Al hydrotalcite catalyst.	Yielding rate = 0.1820 g/min biodiesel.	[65]
Packed-bed MR	Ceramic membrane; Soybean oil; Methanol; Methanol/oil = 24/1 (molar ratio); 80 °C; 0.8 bar; Circulation velocity = 4.15 mL/min; 3 h; <i>p</i> -toluenesulfonic acid/MCM-41; 0.27 g/cm ³ of catalyst amount.	Biodiesel yield = 84.1%;	[66]
Packed-bed MR	Ceramic membrane (0.05 μm); Soybean oil; Methanol; Methanol/oil = 24/1 (molar ratio); 67 °C; 0.8 bar; Circulation velocity = 4.8 mL/min; 3 h; KF/Ca–Mg–Al hydrotalcite/honeycomb ceramic monolithic catalyst; Catalyst amount = 1.5 g.	Biodiesel yield = 91.7%;	[67]

In MR, product permeating through the membrane comprises of polar and non-polar phases which can be easily separated at room temperature.

The major fractions of the polar phase are methanol (70 wt.-%, glycerol, and catalyst). Meanwhile, the non-polar phase is mainly biodiesel [10]. Continuous

separation of these two phases gives the possibility to recycle polar phase into the reaction vessel [48]. The aim of polar phase recycling is to maximize methanol usage, to save catalyst consumption, and to keep the molar ratio of reactants. According to a study reported by Cao *et al.* [10], methanol recycling (50, 75, and 100%) reduced oil to methanol molar ratio from 1:24 to 1:10. The study indicated that the polar phase resulted from the membrane had a relatively high purity due to the low content of triglyceride, monoglyceride, and glycerol.

MR has been used to produce methyl ester from various oil feedstocks. It was reported that fatty acid composition of the feedstock affected methyl ester purity [13, 68]. Cao *et al.* [13] found that methyl ester produced from virgin soybean oil and virgin canola oil could meet ASTM specification without the water washing step. This was reported to be the effect of the fatty acid composition.

Operating temperature is also an important factor affecting MR performance in transesterification. It was reported that the optimum temperature was in the range of 55-70 °C [11]. At a temperature of 60 °C, oil may permeate through the membrane [69]. Those temperature ranges are similar to the operating temperatures used in conventional reactors which are 50-60 °C [70]. As in conventional reactors, a higher temperature leads to a higher reaction conversion, and the reaction becomes more temperature sensitive at high catalyst loading [12]. In a study reported by Dubé *et al.* [12], the highest conversion (90%) was at 70 °C. They also reported that the reaction became sensitive when the acid catalyst concentration was higher than 2 wt. % even though this resulted in an insignificant change of reaction conversion.

Operating temperature also influences membrane separation performance. The increase in temperature has a positive effect on membrane flux. As the temperature increases, viscosities of three components i.e. methanol, oil, and methyl ester, are reduced. Consequently, the diffusion coefficient is enhanced, and so is the permeate flux. The high temperature also affects the motion of polymer chain, and creates void fraction in the membrane matrix which then improves permeate flux [71].

As we know, reaction time is an important operating parameter of a batch reactor. Reaction conversion increases with the increase in reaction time. Usually, a maximum transesterification conversion is obtained at less than 90 minutes and is relatively constant for longer reaction times [72]. Several reported studies of transesterification with basic catalyst used 60-360 minutes reaction time [11, 48, 50, 51]. For basic catalyzed transesterification, the reaction time was around 6-60 hours depending on the type of alcohol used [10, 50, 73].

Similar to conventional reactors, basic catalyzed transesterification shows a higher conversion than acid catalyzed. This is due to the higher reaction rate of basic catalyzed transesterification [12]. Even though acid catalyst showed a slower reaction rate,

soap formation was not found [12]. The catalyst can be in either homogeneous or heterogeneous form. For basic catalyzed reaction, the catalyst is usually homogeneous. Meanwhile, for acid catalyzed reaction, the catalyst can be either in homogeneous or heterogeneous form. The heterogeneous catalyst is used in acid catalyzed transesterification to simplify catalyst separation and recycling, and also to prevent corrosion [74, 75]. The heterogeneous catalyst can be ion-exchange resins or catalytic membrane containing acid functional groups [75]. The concentration of basic catalyst is typically around 0.5-2 wt.%, while the concentration of acid catalyst is about 1-5 wt.% [12]. A higher reaction conversion is obtained at a higher catalyst concentration [12, 76]. However, Dubé *et al.* reported insignificant effect when the basic catalyst concentration was higher than 2% [12].

In transesterification, both organic and inorganic membranes have been used [77]. Polysulfone, polyacrylonitrile, poly(styrene sulfonic acid), polyvinyl alcohol, polyamide, polyimide, and PDMS are examples of organic membranes used in vegetable oil transesterification [74, 75, 78, 79]. Meanwhile, ceramic membrane is an example of inorganic membrane which is usually used for transesterification [13, 48, 80]. Several factors, such as thermal and chemical stability of the membrane, should be taken into consideration in membrane selection for transesterification reaction. Inorganic or ceramic membranes have the advantage of high stability in harsh conditions compared to polymeric membrane. They can withstand high operating temperature, and they have good stability toward chemical compounds such as organic solvent and catalyst (acid or basic) [77]. Inorganic membranes also have good mechanical properties, and are easy to clean. However, they usually have a higher production cost. Besides the type of membrane material, another important property is membrane pore size. The pore size will determine the efficacy of product separation from reactant mixture. The size of triglyceride is 1.5 nm to 12 µm [14]. Therefore, to prevent product contamination, a membrane with a smaller pore size than the size of triglyceride should be used.

2.2 MR Performances in Methyl Ester Production

Performances of MR in methyl ester production are summarized in Table 1. Generally, MR consists of a reactor where the reaction takes place, and membrane used to separate product from the reactants mixtures (Figure 1 (a) and (b)). In this type of MR, reactants and catalyst are mixed in the reaction vessel, and the membrane is solely used to separate the products. The catalyst can be acid, base, or enzyme. The various types of MR are shown in Figure 1.

Badenes *et al.* [61] used enzymatic membrane bioreactor for transesterification. In their study, cutinase of *Fusarium solanipisi* was encapsulated in sodium bis(2-ethylhexyl) sulfosuccinate

(AOT)/isooctane, reversed micelles which were used in the reactor. A tubular ceramic membrane with MWCO of 15 kDa was used to retain the enzyme. The productivity of the enzymatic membrane bioreactor was up to 500 g_{product}/day/g_{enzyme}. Another enzymatic membrane reactor for transesterification was investigated by Kuo *et al.* [63]. Unlike enzymatic membrane bioreactor studied by Badenes *et al.* [61]; Kuo *et al.* [63] studied immobilized Lipase on PVDF membrane. The enzyme immobilized membrane was then used as a catalyst in the reactor. They found that enzyme immobilized membrane offered several advantages over conventional beaded support that included the prevention of intra-particle diffusion, shorter axial-diffusion path, lower pressure drop, without bed compaction, and the easiness to scale up [63].

In MR, the catalyst can be mixed in the reactor containing reactant mixture, immobilized in the membrane matrix as reported by Kuo *et al.* [63], or packed inside the membrane lumen (Figure 1(b)). The last one is also known as packed-bed MR. In this type of reactor, the catalyst is immobilized onto the beaded support which is then packed in the membrane lumen [64]. The packed catalyst in membrane lumen improved the contact between catalyst and reactants. Simultaneous catalysis and separation occurred in the packed-bed MR. The heterogeneous catalyst used in packed-bed MR also offers the advantage of easy to produce high purity methyl ester without the additional separation steps and washing [64]. The catalytic membrane can also be used as a flow-through MR (FTMR) (Figure 1(f)). In FTMR, the catalyst is impregnated in the membrane pore [81], and the reactants are passed through the membrane. Here, the membrane acts as a catalyst carrier and separator in a single unit. The product is immediately separated after the reactants contact the catalyst in the membrane pores. Similar to packed-bed MR, FTMR may skip the product purification steps. However, it is difficult to control heating in the packed-bed MR compared to conventional reactor or vessel due to the presence of membrane. In addition, a high membrane surface is needed to obtain an adequate retention or reaction time.

Heating is another important factor of MR. Heating is needed to achieve the required reaction temperature, and also to increase the reaction rate. Saleh *et al.* [55] used microwave assisted MR for transesterification. Microwave assisted heating had a faster reaction time, lower reaction temperature, less energy consumption, and lower methanol additive [55]. Consequently, the cost of methyl ester production could be decreased.

3.0 METHYL ESTER PURIFICATION WITH MEMBRANE

In conventional FAME production, the produced FAME undergoes several purification steps to obtain a high purity or a high-quality product. The purification step is usually complicated and expensive [82]. In addition to its interesting function of both facilitating reaction and separating the product in a simultaneous process of MR, membrane technology was also studied for separation or purification of FAME produced from the conventional reactor (see Table 2 and Figure 3). Membrane is generally used to separate free glycerol in order to meet the ASTM D6751 and EN14214 standards of biodiesels quality [83]. Membrane is also used to remove residual catalyst [84]. The use of membrane as separation step is beneficial since it is a dry purification. Unlike conventional wet process which uses water to wash produced biodiesel, membrane separation requires no washing. Therefore, it prevents the formation of wastewater and also eliminates associated wastewater treatment. In summary, membrane-based FAME purification has several advantages over conventional washing process. They are easy to operate, better product quality, water-free or litter water usage, lower energy consumption, and no or less effluent [41].

It has been reported in several studies that the performance of membrane in biodiesel purifications are affected by several factors. One of the determining factors is water content. Saleh *et al.* [83] found that water contributed to glycerol size distribution. It was observed that water increased the size glycerol phase in untreated biodiesel. The increased size enhanced glycerol separation by ultrafiltration membrane [83]. The addition of acidified water (0.5% HCl) was also reported to improve the performance of membrane in biodiesel purification [85]. Most of the studies used inorganic or ceramic membrane for biodiesel purification. This is because the chemical and thermal stabilities of inorganic membrane are better than polymeric membrane. Therefore, in the separation of a mixture containing oil, an organic solvent, and acid or basic conditions, inorganic membrane is recommended. As can be seen in Table 2, purification was performed after the biodiesel evaporated. This was conducted to remove any residual methanol.

Membrane contactor can also be used in biodiesel purification. In membrane contactor, solvent extraction can be combined with a membrane. The membrane acts as a contacting device between FAME and solvent, and it provides non-dispersive contact between the two phases [86].

Amelio *et al.* [87] used membrane contactor as an alternative process for biodiesel purification. Membrane contactor was used to remove biodiesel impurities such as unreacted methanol and glycerol by using water as a solvent. Among the membranes studied (i.e., PES, MFP2, MFP5, PP, PVDF, and PTFE),

PTFE membrane was recommended due to its high chemical stability, breakthrough pressure, and flux

[87]. However, the use of membrane contactor in biodiesel purification is still limited.

Table 2 Membrane for biodiesel purification

Membrane	Feed	Operational condition	Results	Ref.
Cellulose ester; 0.22 μm	Pretreated biodiesel ^a	1-2 bar	J = 109-253 $\text{kg.m}^{-2}.\text{h}^{-1}$; Cg = 0.022-0.025 wt.%;	[88]
Cellulose ester; 0.30 μm	Pretreated biodiesel ^a	1-2 bar	J = 536-923 $\text{kg.m}^{-2}.\text{h}^{-1}$; Cg = 0.026 wt.%;	[88]
PES; 10 kDa	Pretreated biodiesel ^a	4 bar	J = 55 $\text{kg.m}^{-2}.\text{h}^{-1}$; Cg = 0.020 wt.%;	[88]
PES; 10 kDa	Pretreated biodiesel ^a + 0.1 wt.% water	4 bar	J = 40 $\text{kg.m}^{-2}.\text{h}^{-1}$; Cg = 0.010 wt.%;	[88]
PES; 30 kDa	Pretreated biodiesel ^a	4 bar	J = 120 $\text{kg.m}^{-2}.\text{h}^{-1}$; Cg = 0.031 wt.%;	[88]
$\text{Al}_2\text{O}_3/\text{TiO}_2$; 0.02 μm	Pretreated biodiesel ^b	2 bar; 40 $^{\circ}\text{C}$;	J = 9.08 $\text{kg.m}^{-2}.\text{h}^{-1}$; Cg = 0.006 wt.%;	[89]
$\alpha\text{-Al}_2\text{O}_3/\text{TiO}_2$; 0.02 μm	Synthetic biodiesel ^c	2 bar; 60 $^{\circ}\text{C}$;	J = 63.1 $\text{kg.m}^{-2}.\text{h}^{-1}$; Cg = 0.04 wt.%;	[80]
$\alpha\text{-Al}_2\text{O}_3/\text{TiO}_2$; 0.2 μm	Biodiesel + acidified water (0.5% HCl)	3 bar; 50 $^{\circ}\text{C}$;	J = 69.4 $\text{kg.m}^{-2}.\text{h}^{-1}$; Cg = 0.01 wt.%;	[85]
$\alpha\text{-Al}_2\text{O}_3/\text{TiO}_2$; 0.1 μm	Biodiesel + acidified water (0.5% HCl)	3 bar; 50 $^{\circ}\text{C}$;	J = 65.3 $\text{kg.m}^{-2}.\text{h}^{-1}$; Cg = 0.018 wt.%;	[85]
$\alpha\text{-Al}_2\text{O}_3/\text{TiO}_2$; 0.05 μm	Biodiesel + acidified water (0.5% HCl)	3 bar; 50 $^{\circ}\text{C}$;	J = 65.6 $\text{kg.m}^{-2}.\text{h}^{-1}$; Cg = 0.017 wt.%;	[85]
$\alpha\text{-Al}_2\text{O}_3/\text{TiO}_2$; 20 kDa	Biodiesel + acidified water (0.5% HCl)	3 bar; 50 $^{\circ}\text{C}$;	J = 70 $\text{kg.m}^{-2}.\text{h}^{-1}$; Cg = 0.014 wt.%;	[85]
$\alpha\text{-Al}_2\text{O}_3/\text{TiO}_2$; 0.1 μm	Biodiesel/ethanol/glycerol/oil	1 bar; 60 $^{\circ}\text{C}$;	J = 125 $\text{kg.m}^{-2}.\text{h}^{-1}$; Rg = 98.7 wt.%;	[90]
A modified PAN; 100 kDa	Biodiesel ^d + 0.2% water	5.5 bar; 25 $^{\circ}\text{C}$;	Cg = 0.013 wt.%;	[91]
Ceramic; 0.1 μm	Biodiesel ^d	1.5 bar; 60 $^{\circ}\text{C}$; VCR = 4;	J = 300 $\text{kg.m}^{-2}.\text{h}^{-1}$; Cg = 0.0108 wt.%;	[92]
Ceramic; 30 kDa	Biodiesel (from soybean oil)	3-4 bar; Dead-end mode.	J = 120 $\text{kg.m}^{-2}.\text{h}^{-1}$; Cg = 0.029-0.030 wt.%;	[93]
$\text{Al}_2\text{O}_3/\text{TiO}_2$; 0.05 μm .	Crude biodiesel (from palm oil; KOH catalyst) ^e	2 bar; 40 $^{\circ}\text{C}$;	$R_{\text{KOH}} = 93.7\%$;	[84]

^a Pretreated in vacuum evaporator; 90 $^{\circ}\text{C}$; 60 min; ^b The biodiesel sample was dried in rotary evaporation at 65 $^{\circ}\text{C}$ and 600 mmHg vacuum for 45 min for the recovery of the residual methanol; ^c 85% biodiesel, 10% glycerol, and 5% ethanol; ^d Vacuum treated FAME; ^e Pre-treated in rotary evaporator to remove methanol; J – stabilized flux of biodiesel; Rg – glycerol rejection

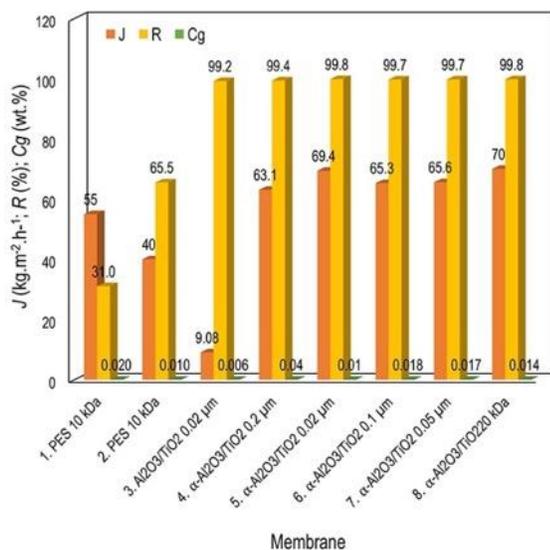


Figure 3 Membrane performance in biodiesel purifications (data from refs. [80,85,88,89,92]; J – flux, R – rejection, Cg – final concentration of glycerol; see Table 2 for operational conditions)

4.0 FAME PRODUCTION AND CAROTENE RECOVERY FROM PALM OIL

Fatty acid compositions of palm oil and palm kernel oil, the composition of FAME produced from palm oil,

and a photograph of FAME are shown in Figures 4 a-c. Palm oil contains a high concentration of palmitic acid (about 45-48%), and oleic acid (37-38%) (Figure 4(a)). In addition, the fatty acid content can be classified as saturated acid (50%), monosaturated fatty acids (40%), and polyunsaturated fatty acids (10%) [94]. The fatty acid composition of palm kernel oil is similar to coconut oil except that it has lower short-chain fatty acid content and higher oleic acid content [94]. Since palm oil has a high content of palmitic and oleic acid, the FAME produced from palm oil has a high concentration of methyl palmitate and methyl oleate [95] (Figure 4 (b)).

Several studies have successfully produced FAME from palm oil by using MR [13, 52, 64]. The properties of produced FAME can meet the ASTM standard of biodiesel quality (see Table 3). The produced FAME has free glycerine content of lower than 0.02%. Moreover, the viscosity of palm oil-based biodiesel is also within the range of ASTM standard requirement for engine performance. Palm oil based FAME can be a promising alternative to fossil fuels and is considered to be an attractive renewable fuel due to its characteristics and performance [6, 97].

Palm oil contains a considerable amount of phytonutrients which can be recovered as a valuable product (Figure 5 (a)). Carotenoids (provitamin A), tocopherols, and tocotrienols (Vitamin E) are the most valuable phytonutrients

(Figure 5 (b)). The carotenoids content is about 500–700 ppm of which 90% consists of α - and β -carotene [101, 102]. It was reported that palm oil carotene contains carotene isomers approximately 10 times higher than those in carrots [96]. Recovery of carotenoids is important due to its ability to improve vegetable oil stability and health benefit which gives added value for the palm oil industry. Example of carotene concentrate from FAME mixture is shown in Figure 5 (c).

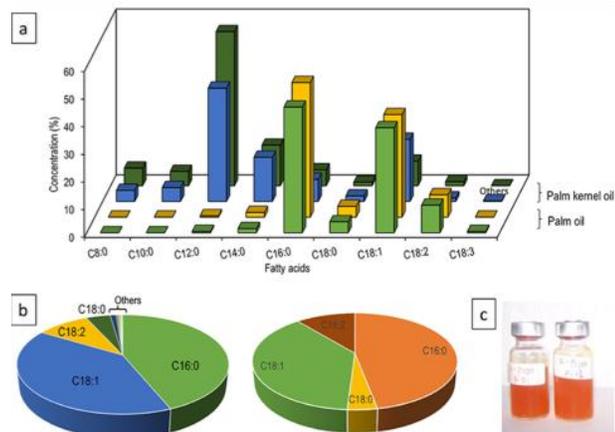


Figure 4 (a) Fatty acid compositions of palm oil and palm kernel oil (data from refs. [94,98,99]), (b) compositions of palm oil-based FAME (data from refs. [47,100] ; left : data in wt.-%; right : in mole-%), and (c) FAME from palm oil (authors results)

Table 3 Palm oil FAME produced by MR

Ref.	Results	Remark
[13]	Free glycerine = 0.0117%.	Meet ASTM standard (Max. free glycerine = 0.02%)
[64]	Free glycerine = 0.012%. Viscosity at 40 °C = 5.01.	Meet ASTM standard (Max. free glycerine = 0.02% max; Viscosity at 40 °C = 1.9-6.0)
[52]	Free glycerine = 0.009%. Viscosity at 40 °C = 4.64.	Meet ASTM standard (Max. free glycerine = 0.02% max; Viscosity at 40 °C = 1.9-6.0)

Recovery of phytonutrients from vegetable oil is quite challenging as they are heat, light and air sensitive, have different polarity, and differ in size or molecular weight [103]. There are two alternative routes for carotenoids recovery, namely direct separation of carotenoids from crude palm oil, and separation of carotenoids from methyl esters. The first route includes saponification, solvent extraction, supercritical fluid extraction, molecular distillation, and membrane filtration [32]. Molecular distillation [104–107] and solvolytic micellization [108] have been used for the second route. Although those processes can produce carotenoids with high concentration, excessive exposure to heat and chemicals reduce the activity of carotene. They also require high energy consumption.

Table 4 shows several studies on carotene recovery from palm oil. Darnoko and Cheryan [37] reported an approach of carotene recovery from fatty acid methyl esters which used three nanofiltration membranes. Carotene rejection of 68–80%, and flux of 0.5–10 LMH were obtained at TMP of 2.76 MPa and 40 °C. They also analyzed the economics of the carotene recovery process from a 10 tons/h of methyl ester. About 3.6 m³/h of carotene concentrate with 1.2 g/L of carotene was obtained using a three-stage separation process. The processing cost was estimated to be \$37/kg of pure carotene in concentrate. Chiu *et al.* [38] also studied the use of nanofiltration membrane to recover carotene from red palm ethyl ester. About 75% of carotene rejection with 7.5 LMH was obtained at 2.5 MPa and 40 °C. The findings from those studies indicate the possibility of carotene recovery during esterification. Since the triglyceride in palm oil is consumed in esterification reaction, the remaining unreacted component involving phytonutrients for example carotenoids can be easily recovered. Those studies also highlighted the possibility of performing transesterification of palm oil (or other vegetable oil), and carotenoids recovery using MR. Thus, MR not only reduces the processing steps of esterification and purification, but also provides the possibility of recovering some phytonutrients component.

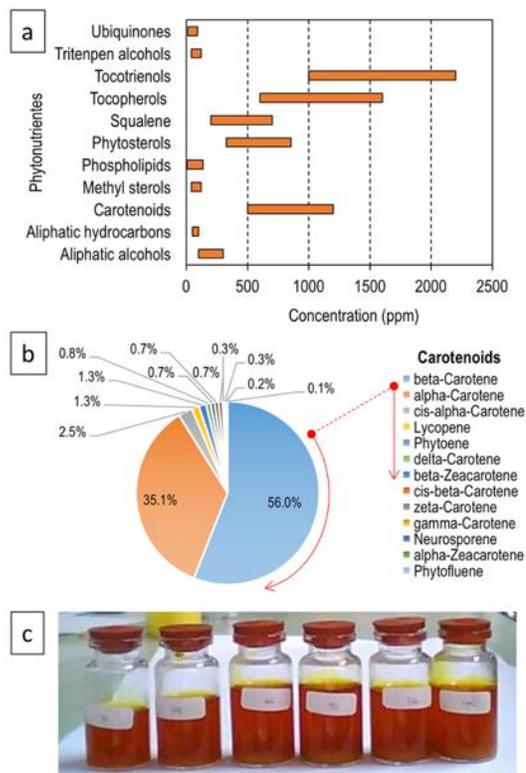


Figure 5 Phytonutrients and carotenoids in palm oil. (a) Concentration range of phytonutrients, (b) composition of carotenoids (data of (a) and (b) from references [101, 109, 110]), and (c) a photograph of carotene concentrates from FAME mixture (authors' result)

Table 4 Membrane performance in carotene recovery

Membrane	Feed	Operational conditions	Performance	Ref.
DS7	RPME; Cf = 0.45 g/L (β -carotene)	T = 40 °C; P = 2.76 MPa; VCR = 10;	J = 10 LMH; R = 65.3%;	[37]
MPF60; 400 Da;	RPME; Cf = 0.45 g/L (β -carotene)	T = 40 °C; P = 2.76 MPa; VCR = 10;	J = 1.7 LMH; R = 78.2%;	[37]
MPF44; 250 Da;	RPME; Cf = 0.45 g/L (β -carotene)	T = 40 °C; P = 2.76 MPa; VCR = 10;	J = 0.17 LMH; R = 78.2%;	[37]
NP10; PES; 2000 Da;	RPEE; Cf = 0.54 g/L (β -carotene)	T = 40 °C; P = 2.5 MPa; VCR = 2;	J = 7.5 LMH; R = 75.8%;	[38]
NTGS-2200; silicon/polyamide;	CPO/Hexane: 1/3; Cf = 0.87 g/kg (β/α -carotene = 2.6)	T = 40 °C; P = 2 MPa	J = 0.94 kg/m ² .h; R = 6.3%;	[111]
ES209; PES; 9000 Da;	CPO; Cf = 0.596 g/kg (β -carotene)	T = 63 °C; P = 2.6 MPa	J = ~1-5 LMH; R = 15.8%;	[112]
NTGS-2200	CSO; Cf = 0.047 g/kg (carotenoids)	T = 40 °C; P = 4 MPa	R = 79%;	[113]

CPO – crude palm oil; J – oil flux; R – carotene rejection; RPEE – red palm ethyl ester; RPME – red palm methyl ester

5.0 FUTURE PERSPECTIVE

Generally, the two major challenges in vegetable oil transesterification are reversible reaction and immiscibility between oil and alcohol. MR which combines reaction and separation is considered an alternative process to face those challenges. The aim of the integrated reaction-separation process is to shift the equilibrium reaction and to achieve a higher reaction conversion. The produced FAME may be separated to meet the biodiesel quality standards. The use of membrane for methyl ester purification (dry process) is interesting as it eliminates the wastewater treatment step in the conventional washing process. Another attractive feature of MR for FAME production from palm oil is carotenoid recovery. It is beneficial to improve the efficiency of the process and to give added value for palm oil industry. Several studies indicated the efficacy of carotenoids recovery from FAME mixtures. However, the membranes should be operated at a relatively high operating pressure. They also showed relatively low permeate fluxes. Therefore, a membrane with higher permeate flux and better carotenoid rejection needs to be developed for better performance.

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