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Effect of Polyethylene Glycol Membrane on the Separation of Biodiesel from Palm Oil

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Abstract: Transesterification of methyl ester is a reversible reaction and requires excess methanol to drive the reaction forward. In this study, Polyethylene Glycol (PEG) membrane reactor was used to separate glycerol during reaction, to attain high conversion of palm oil at lower methanol to oil ratio. Thus reduces the amount of methanol used. The transesterification of palm oil was performed using base catalyst. Experiments were performed in the membrane reactor in batch mode at different catalyst concentrations and different molar ratio (methanol/oil). Asymmetric polyethersulfone ultrafiltration flat sheet membranes with Polyethylene Glycol (PEG) of different molecular weight as additive were prepared by phase inversion process from casting solution containing Polyethersulfone (PES) as polymer, N,N-porylydone (NMP) as solvent and PEG of different molecular weights namely PEG 200, PEG 300 and PEG 400 as additives. The results show that PES with different PEG as additive are suitable for separation of glycerol during the reaction.

Key words: Biodiesel, membrane reactor, palm oil, PES, PEG

INTRODUCTION

Biodiesel, known as either methyl-ester or ethyl-ester, is derived from naturally occurring vegetable oils or animal fats that have been chemically modified (esterified) to run in a diesel engine. Currently, the biodiesel is produced by the transesterification of palm oil. In South East Asia, Malaysia has rich oil palm industry that generates excess Crude Palm Oil (CPO), in vast quantities for consumption. CPO is one of the four leading vegetable oils traded on the world market. It is also cheaper than other vegetable oils such as soybean oil, sunflower oil and rape seed oil (Freedman et al., 1984, 1986). Membrane technology offers several advantages to drive the reaction toward the equilibrium in short time. To tackle the challenges and other processes in the biodiesel production, membrane technology has been given significant attention by researchers worldwide. These problems were solved through the use of a membrane reactor (Dube et al., 2007, Krishnaiah et al., 2007).

Removing reaction products as they are formed drives reactions to very high conversions that cannot be reached in conventional reactors. To date, much effort has been spent on membrane reactors involving easily separated mixtures such as hydrogen and methane (Armor, 1998; Hsieh, 1991; Saracco and Specchia, 1994; Zaman and Chakma, 1994). In this investigation, flat sheet membranes with Polyethylene Glycol (PEG) of different molecular weight as additives were investigated.

MATERIALS AND METHODS

Materials: Methanol and sodium hydroxide purchased from lab-scan used as alcohol and catalyst in methyl ester production and commercial edible grade palm oil (Cooking Oil Cap Buruh) supplied Lam Soon Oil Sdn Bhd was used as vegetable oil. Anhydrous sodium sulphate supplied by Sigma-Aldrich used to remove moisture and powder activated carbon supplied by Hann to remove color and odor methyl esters. The solvent used in H^{1}NMR analysis was Chloroform CDCl$_3$ 99.8% and the NMR tubes, 5 mm 600 MHZ, 7 in, Norell were supplied by Sigma-Aldrich. Methyl oleate ≥99% purity purchased from Sigma-Aldrich used as a standard biodiesel. All chemical used were analytical reagent grade.

In membrane preparation, Polyethersulfate (PES) supplied by Sigma-Aldrich was used as polymer in preparation of membrane casting solution. Polyethylene Glycol (PEG) with molecular weight PEG200, PEG400 supplied by Fluka and Sigma-Aldrich were used as additives in the casting solution. PEG 35000 supplied by Fluka used for preparation as aqueous solution to investigate rejection membrane. Lastly, solvent used to dilute the polymer to prepare dose solution was reagent

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grade 1-methyl-2-pyrrolidone (NMP) supplied by Riedel-de Haen. Purified distilled water was used as the main non-solvent in the coagulation bath.

Preparation dope solution: Dope solution was prepared by dissolving polyethersulfone in Methyl-1 pyrroidone-2 and stirred until the polyethersulfone completely dissolve at 70°C. Then, the additive was added and with continuous stirring at 70°C until the solution is completely mixed. The resultant polymer solution was kept in glass bottle and left it for one day to eliminate the bubble in dope solution. The weight percentage NMP solvent, polymer PES and additive PEG used to prepare the dope solution were 83, 15 and 2% which are corresponding to 83 g NMP solvent, 15 g polymer PES and 2 g additive for one batch preparation.

Membrane casting: The dope solution was poured onto clean glass plate at room temperature and it was casted on a glass plate using a casting knife. Immediately after casting, the glass plate with the casted film was dipped into the distilled water at room temperature. The membrane separated out of the glass plate after sometime. The membrane was washed with distilled water and kept in the distilled water for one day. Before the membrane used to biodiesel separation, the membrane must be kept in distilled water to protect the quality membrane (Idris, 2001).

Experimental method: Experiments were carried out by using a membrane reactor. The effective membrane area was 8.66×10^{-3} m^2. Membrane PES placed in membrane reactor and distilled water charged into membrane reactor. Then, inert gas used to provide pressure in whole separation system. Same procedure was used in rejection experiments. The 10w/w% PEG35000 aqueous solution prepared with mixed 10 g of PEG 35000 and 90 g distilled water. The operating pressure was maintained at 2.5 bars and room temperature.

Membrane performance evaluation: Membrane characterization of Pure Water Permeation (PWP) for the PES ultrafiltration membrane was calculated from the Eq. 1:

$$PWP = \frac{Q}{A \times \Delta t} \qquad (1)$$

where, Q is volume of the permeate (l), A is membrane surface area (m^2) and Δt is permeation time (hour). The rejection percentage of the membrane was given by Eq. 2:

$$R (\%) = \left[1 - \left(\frac{C_p}{C_t} \right) \right] \times 100 \qquad (2)$$

where, C_p is solute concentration in permeate and C_f is solute concentration in feed.

Membrane analysis: The structure and pore size of the prepared membranes was estimated with scanning electron microscopy (JEOL, Japan). For this purpose, the standard procedure of this model SEM was used. All samples were cut into 10×10 mm and dried in a freeze drier Model DW6-55-1 supplied Heto RYWINNER manufactured by Heto-Holten A/S Gydevang 17-19 DK-3450 Allerod Demark. After plated with platinum, the structure and pore size was evaluated with SEM microscope.

Production of biodiesel with membrane reactor: The methyl ester productions were started with pre-mixed or dissolve sodium hydroxide in methanol. Then, the mixture sodium hydroxide-methanol and palm oil were charged into external reactor and started the stirring about 15 min. Later, the methyl ester discharged from the external reactor charged into membrane reactor. Then, the inert gas started and discharged into the membrane reactor with the desired pressure. In this research, there were three parameters attempted to study, include molar ratio of methanol to palm oil and concentration of sodium hydroxide. The optimization of membrane extractive reactor for biodiesel production was focused on the additive used to produce membrane and the pressure used to separate glycerol and biodiesel. The experiments were carried out at 1, 2 and 3 bar pressure. For optimization of biodiesel production, three different molar ratio of methanol to palm oil 4:1, 5:1 and 6:1 were investigated for their effect on biodiesel yield, which corresponded to 33, 42 and 49 mL of methanol per 200 mL palm oil. The concentrations of sodium hydroxides used to produce biodiesel were 0.25% (0.45 g), 0.5% (0.9 g), 0.75% (1.35 g) and 1% (1.80 g).

For purification methyl ester, 50 mL of methyl esters were collected at the end of the experiments and then the sample washed immediately an equivalent volume of hot distilled water (60°C) and shaken by hand gently for a few minutes. The mixture left a while for separation and the water layer removed. At least three times washing process was done. These steps served to stop any further reaction in the sample. Besides this, it also removes the catalyst and glycerol if resented on it. The moisture is removed by using anhydrous magnesium sulphate and filtered it. Lastly, the activated carbon was mixed in the methyl ester

to remove the color and odor. Then, methyl ester was analysed with hydrogen nuclear magnetic resonance (H[1] NMR).

Analysis methods: The yield biodiesel investigated with H[1] NMR ECA with 600MHz (JEOL, Japan) spectroscopic method used to quantify the yields of methyl ester. Solvent used for H[1] NMR analysis was chloroform. (CDCl$_3$) The conversion of methyl ester was determined by the ratio of the signal at 3.68 ppm (methoxy groups of the methyl ester) and 2.30 ppm (α-carbon CH$_2$ groups of all fatty acids) as described by Wenlei Xie *et al.* (2006).

RESULTS AND DISCUSSION

Biodiesel production: Glycerol and methyl ester was able to form and were separate manually. No soap found during reaction for each molar ratio of methanol:oil at 4:1, 5:1 and 6:1. Measurement of glycerol and methyl ester volume for each molar ratio of methanol: oil show decreasing value. Catalyst effect at different concentration of 0.125, 0.25, 0.5, 0.75 percentage increase the volume of glycerol and methyl ester product in every molar ratio methanol to oil ratio.

Determination of biodiesel yield: The signal due to methylene protons adjacent to the ester group in triglycerides appears at 2.3 ppm and after the reaction of methoxy protons of the methyl esters appeared at 3.7 ppm. We used the areas of the signals of methylene and methoxy protons to monitor the yield of transesterification using Eq. 3 as shown below (Knothe, 2000):

$$C_{me} = \frac{2 \times I_{ME}}{3 \times I_{a-CH_2}} \times 100 \qquad (3)$$

Table 1, we determined the indices of methyl ester using refractive meter and calculated the conversion percentage. The results were compared with ^{1}H NMR result in 3rd column of Table 1. The agreement between the conversions determined by 1H NMR spectra data and those determined by the refractive index gives the differences of <4%.

As illustrated in Fig. 1, there is a linear correlation between the conversion of palm oil and the refractive index. Conversion of methyl ester using molar ratio methanol:oil of 6:1 at different catalyst concentration gives the above result.

Pure water flux (PWF): The steady-state value of PWF for each membrane corresponding to the applied pressure (2 kPa) is found to increase with molecular weight of PEG for the solvents as shown in Fig. 2. The steady state flux for PEG 200 increases from 0.23 -0.35 L m^{-2} min for and 0.64 L m^{-2}.min for PEG 600. The increase in flux with increase in molecular weight of PEG is due to the increase in porosity.

Membranes with PEG 200 have the highest membrane resistance of 5.92×10^{10} m^2 kg^{-}.[1] The lower water permeability and higher membrane resistance are because the lower porosity. The result clearly indicates that addition of PEG with different molecular weights influence the formation of pores in the membranes, which affect the permeability as the latter is conceptually related to its pores for UF membranes.

The rejection of the membranes with different additives is shown in Table 2. The high rejection and
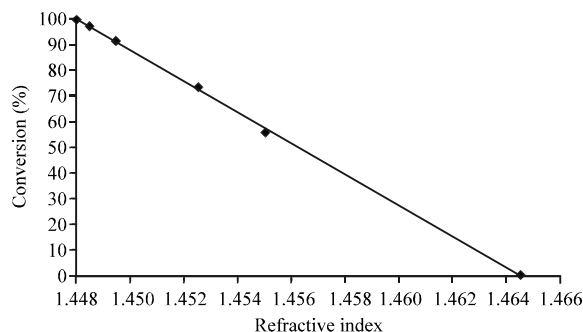

Fig. 1: Relationship between the refractive index of product and the conversion
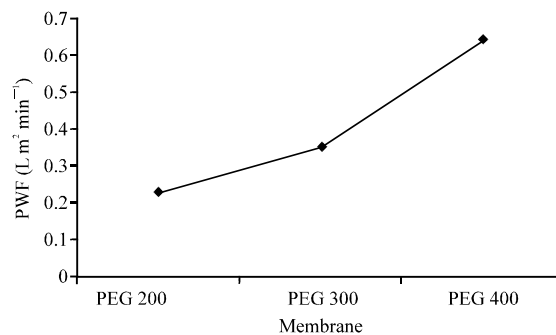

Fig. 2: Pure water flux at steady state for membranes with different additively

Table 1: Conversions of palm oil determined by different analytical methods

Entry	Refractive index (RI)	Conversion (RI) (%)[a]	Conversion (^{1}H NMR) (%)[b]
1	1.4645	0.00	0.00
2	1.4550	57.58	55.30
3	1.4525	72.73	73.10
4	1.4495	90.91	90.98
5	1.4485	96.97	96.47
6	1.4480	100.00	100.00

[a]Conversion (RI), determined by refractive index, [b]Conversion (H NMR), determined by ^{1}H NMR spectroscopy
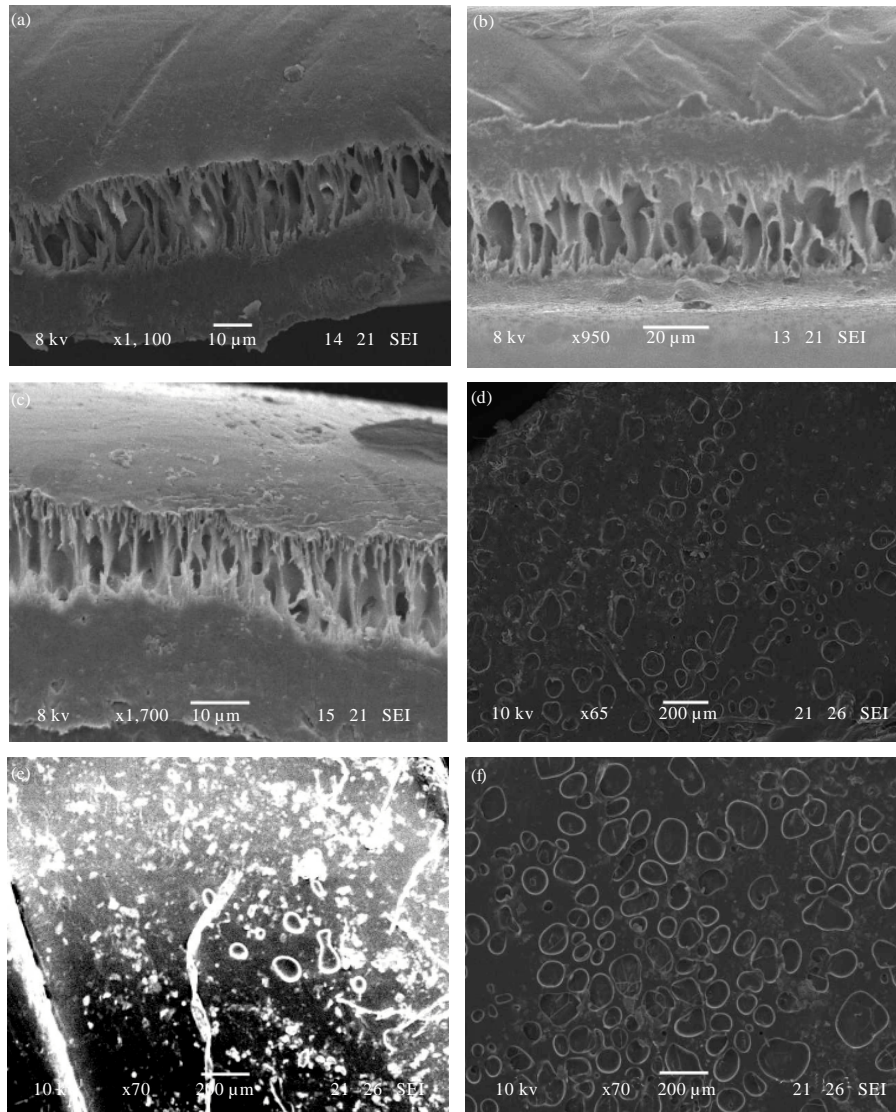
Fig. 3(a-f): (a), (b) and (c) Cross sectional area membrane with PEG 200,300 and 400 (d), (e) and (f) Surface area of membrane with PEG 200, 300 and 400

comparatively low flux with PEG 400 membranes was explained by the porosity. The thin asymmetric layer probably explains for the improvement in the rejection rate while the thick sponge-like sub layer offers resistance resulting in rather low flux and high rejection. Generally, the higher permeability means the number of pores inside the membrane is more.

Membrane forming mechanism: Figure 3 shows the morphological structure of PEG 200, 300 and 400 membranes by SEM. Cross sectional area of

Table 2: Rejection of the membranes with different additives by molecular weight cut off of PEG 35000

Additive	Rejection (%)
PEG 200	85.7
PEG 300	85.7
PEG 400	100.0

membranes (a), (c) and (e) show that the porosity increases as the concentration of PEG increases. The difference in the structure is due to the freezing and cutting process of the membrane during the SEM experiment. Figure 3b, d and f represent the surface

Table 3: Flux permeation of different constituents using membranes with different additives

	Flux (kg m⁻² min⁻¹)			
	PEG 200	PEG 300	PEG 400	Viscosity, cP
Methanol	2.78	4.67	6.44	12.2
Oil	0.15	0.16	0.20	192.3
Glycerol	0.13	0.19	0.20	63.4

Table 3: Flux permeation of different constituents using membranes with different additives — column header units: Flux (kg m^{-2} min^{-1})
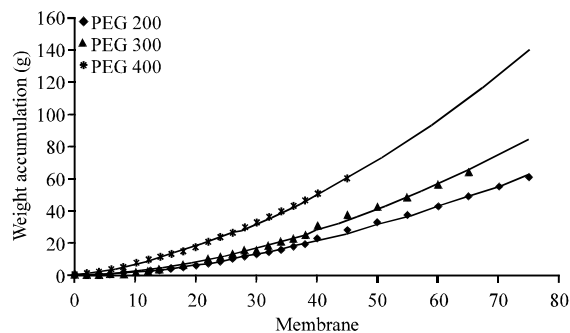

Fig. 4: Weight accumulation of glycerol and methyl ester with respect to time using membranes with different additives

morphology of PEG 200, 300 and 400 membranes. It can be seen that the porous structure decreased as the PEG concentration increased.

Membrane reactor and separation: Separation of biodiesel was conducted in the membrane reactor. In the case of membrane separation which is based on the molecular size of the components and the membrane, the separation rate of the selective molecule is also encouraged by applying different operating conditions (pressure and temperature) of two separated environment. Most of the membrane processes are pressure driven. As two main liquid phases are needed to be separated in the process of biodiesel production which is methyl ester (biodiesel) and glycerol, pressure driven liquid filtration can be applied.

Flux improvements: Flux is an important performance parameter besides membrane selectivity in determining the suitability of membrane processes for industrial adoption. Methanol gave a highest flux of 2.78-4.67 kg m⁻² min and 6.44 kg m⁻² min with respect of different PEG additive in membrane as shown in Table 3. Flux for glycerol has almost similar result to oil flux despite the difference in viscosities. Variances in viscosities between oil, glycerol and methanol results in more flux difference with oil being the viscous liquid. The results also can be explained in terms of molecular weight for oil, methanol and glycerol. Methanol with smaller molecule can pass through the membrane and the flux increases with the increase in PEG molecular weight.

Biodiesel separation: Biodiesel separation in the membrane reactor is shown in Fig. 4. The weight of glycerol and methanol was collected in the permeate side with respect to time. Due to the pressure driven in the membrane reactor and glycerol is denser than methyl ester, it will pass through the membrane followed by methyl ester. No rejection was found in the retentate side which means 0% rejection.

The permeation and rejection of glycerol and methyl ester from biodiesel solution did not preferentially happened in the membrane reactor as was expected based on the studies. This may be due to unsuitable selectivity of membrane used which is polyethersulfone ultrafiltration flat sheet membranes with Polyethylene Glycol (PEG) of different molecular weight as additives and N,N-porylydone (NMP) as solvent.

Large pore size of PES membrane was proved not able to retain molecule of FAME as it permeates along with glycerol through the membrane. The present work illustrates that oil and methanol can readily co-exist in the reactor at a volume ratio of 4:1, 5:1 and 6:1 without plugging the membrane pores. No soap was found in the permeate and retentate side. Flux for methanol, oil and glycerol increases with the addition of PEG at different molecular weight. This shows that with the increase of PEG number, the pore sizes becomes the limiting factor in glycerol/FAME separation.

CONCLUSION

In this study, in the range studied, the pure water flux increases linearly with respect to PEG molecular weight. The flux of methanol, oil and glycerol increases with PEG molecular weight. The permeate consisting of glycerol and FAME increased with PEG molecular weight. However, to separate glycerol and to retain biodiesel, further investigation required in terms of thickness of membrane, analysis with time and pressure.

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