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Physico-chemical characterization, morphology and performance of polyethersulfone based membrane for glycerol removal from biodiesel produced through trans-esterification of waste cooking oils

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Abstract−In the current research, the biodiesel purification was by use of poly ether sulfone based membrane. The biodiesel was produced from waste cooking oils by trans-esterification. Membranes were fabricated by solution casting through phase inversion method. The effect of PES concentration in the casting solution on physico-chemical characteristics, morphology and performance of membranes in glycerol removal from produced biodiesel was studied. SEM and AFM analysis have been utilized for the membrane morphological characterization. SEM images showed uniform surface for the membranes. AFM analysis revealed that the membrane surface roughness was decreased by increase of polymer concentration. The membrane flux, water content and porosity were also decreased by increase of PES concentration. Moreover, obtained results showed that membrane glycerol rejection and mechanical strength were improved by increase of polymer binder concentration. The prepared membrane with 16%wt PES showed more appropriate performance compared to others.

Keywords: Biodiesel Production, Transesterification, PES Membrane, Fabrication/Characterization, Glycerol Removal

INTRODUCTION

Energy consumption has increased widely due to tremendous growth of transportation and industrial sectors, so attention has been directed to looking for alternative fuels. Biodiesel is being considered as one of the most promising integrative fuels. It is nontoxic, renewable, biodegradable and safe environmentally compared to petroleum fuel. The emission of carbon monoxide, particulates, unburned hydrocarbons and SOx is much lower for biodiesel fuel compared to others. Biodiesel is produced from renewable sources such as vegetable oils or animal fats through different techniques, such as micro-emulsion, pyrolysis and transesterification [1-9]. However, the most notable method for biodiesel fuel production is transesterification. Transesterification is defined as reaction of triglycerides with low molecular weight alcohols such as methanol and ethanol in presence of catalyst [2,5,6,9-15].

Non-purified biodiesel contains impurities such as glycerol, unreacted methanol, residual catalyst, un-reacted triglyceride and small amounts of soap and water, which should be removed because of their effect on engine performance [1].

Different methods have been used for biodiesel purification, such as water washing, acid washing, solvents extraction, adsorption by solid adsorbents. Membrane technology also is well known as new method for biodiesel purification [9]. Energy saving, resource recovery and pollution control are the main reasons for the membranes development and application. It can also be easily scaled-up and combined with other processes, besides having a low operating cost.

Earlier researches reported the biodiesel purification by ceramic membranes. The ceramic membranes showed high thermal, chemical and mechanical stabilities besides their disadvantages compared to polymeric membranes such as high cost [16].

Peyravi et al. [16] prepared nanocomposite PI membranes with different concentration of MWCNTs loadings ratio via phase inversion method to biodiesel purification. The synthesized membranes showed behavior in good glycerol removal without significant decline in flux permeation.

Gomes et al. [17] also used commercial tubular α-Al_2O_3/TiO_2 membranes for biodiesel purification. The influence of ethanol concentration in the feed solution on membrane performance was studied. Low flux and high glycerol rejection were achieved for the feed solution containing 5%wt ethanol.

Alves et al. [4] also used micro and ultrafiltration membranes for biodiesel purification. Results showed best performance for 10 KDa ultrafiltration membrane compared to others. Also, the addition of water in crude biodiesel improved the glycerol removal by membrane filtration.

Saleh et al. [6] designed a membrane system by using of ceramic membrane for removal of glycerol from crude FAME. In other research, Saleh et al. [7] studied performance of modified polyacrylonitrile (PAN) membrane with 100 KDa molecular weight cut-off.

The reported researches showed that the membrane separation process is a suitable alternative for biodiesel purification. In the current research, poly ether sulfone membranes were prepared by phase inversion method through immersion precipitation for separation of dispersed free glycerol from crude biodiesel. We found a few researches for fabrication of PES membrane for biodiesel purifica-

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tion. The biodiesel was produced from waste cooking oils by transesterification method using alkaline catalyst. The effect of PES concentration in the casting solution on physico-chemical property, morphology and performance of prepared membrane for glycerol removal/biodiesel purification was studied.

MATERIALS AND METHOD

1. Materials

Poly ether sulfone (PES Ultrason E6020P with MW=58,000 g/mol) was used as membrane base binder. Dimethyl acetamide (DMAC) by Merck was also employed as solvent. Polyvinyl pyrrolidone (PVP, 25,000 g/mol, Merck) was used as pore former. Methanol (99.9% purity) and sodium hydroxide (NaOH) were supplied from Merck for biodiesel production.

2. Biodiesel Production

Biodiesel was produced from waste cooking by transesterification method. The kinematic viscosity and density of used cooking oil were measured 46.59 (mm^2/s) and 0.92 (g/mL), respectively. Before transesterification reaction, the cooking oil was filtered to remove the residues and precipitates. The oil was heated to 60 °C for 10 min for water removal. The transesterification reaction was in a glass reactor that contained a thermometer to control the temperature, a reflux condenser to prevent the methanol lossing and a mechanical stirrer to constant agitation. The reactor was also supported by heating mantle to control the temperature around 60 °C. The waste oil was fed into the reactor and preheated before sodium hydroxide (catalyst) and methanol addition. The molar ratio of methanol to waste cooking oil was adjusted (9 : 1). The reaction time was also 2 h and the amount of used catalyst was 1.5%wt.

The yield of transesterification reaction was measured as 92.5 percent. The yield of biodiesel production was calculated as follows [4]:

$$\mathrm{Yield}(\%) = \frac{m_{biodiesel}}{m_{raw\ oil}} \times 100 \tag{1}$$

where $m_{biodiesel}$ is the crude biodiesel quantity after transesterification reaction and $m_{raw\ oil}$ is the quantity of used cooking oil as feedstock.

The products were allowed to settle for 8 h. The lower phase/polar glycerol layer was removed and the upper phase/non-polar layer was neutralized with sulfuric acid and then used as membrane feed. The glycerol mass percentage in the cell feed was measured 0.0604 mg glycerol/mg biodiesel.

3. Preparation of Membrane

PES membranes were prepared by phase inversion through immersion precipitation. The homogenous solution containing PES, DMAC (solvent), and PVP (pore former) was cast by a casting knife with 200 µm thickness on a glass plate. The prepared films were then immersed in non-solvent bath for precipitation. The immersion process was at ambient temperature. Distilled water was used as non-solvent in coagulation bath. The prepared membranes were washed and stored in distilled water for one day to remove residual solvent completely. The composition of used casting solution is shown in Table 1.

4. Membrane Test Cell

The separation performance of prepared membranes was studied by using a dead end cell (Fig. 1). The membranes were located at the end of cell and fed by produced biodiesel. The fluid passed through the membrane and collected. The driving force for separation process was provided by nitrogen gas. The applied trans-membrane pressure was 2.5 bar.

Table 1. Composition of casting solution for the preparation of home-made membranes

Samples	PES (wt%)	PVP (wt%)	DMAC (wt%)
1	16	2	82
2	18	2	80
3	20	2	78

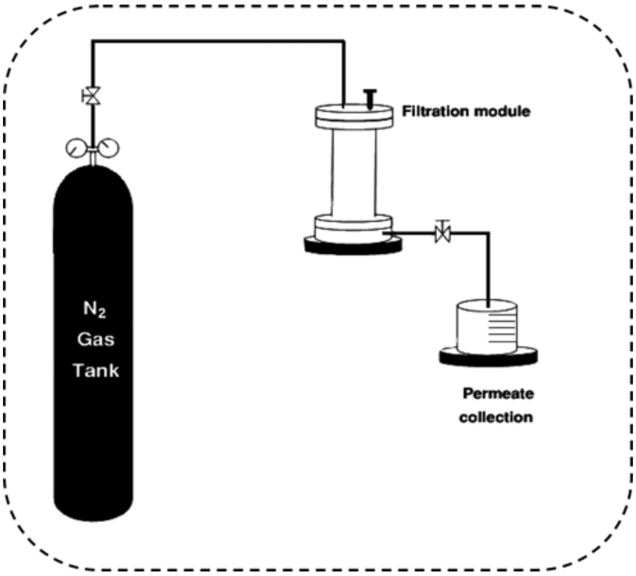


Fig. 1. Schematic diagram of used filtration module.

MEMBRANE CHARACTERIZATION

1. Membrane Flux (J)

A self-made dead end cell was used to measure the flux of the membranes. The flux (J) is measured as amount of permeant (ΔV) per unit area of membrane surface (A) and time (Δt). The flux is calculated as follows [18,19]:

$$J = \frac{\Delta V}{A\Delta t}\left(\frac{m^3}{m^2 \cdot h}\right) \tag{2}$$

2. Membrane Rejection

The glycerol concentration in feed and permeant was measured with UV-Visible instrument [20]. Measurements were made according to yellow complex formation, which is proportional to the amount of free glycerol in the sample. The yellow compound has a maximum absorbance peak at 410 nm. Five samples containing 0.00, 0.25, 0.50, 0.75 and 1.00 mL of 0.036 mg/mL glycerol solution were prepared through dissolution of glycerol in water. Then, samples were diluted by solvent (mixture of distilled water and ethanol; (1/1) (V/V)) to get a final volume of 2 mL. The samples were used as standard solutions.

For the membrane rejection measurement, 0.5 g of permeated biodiesel was dissolved in 4 mL of hexane in a glass tube. Then 4 mL of working solvent (mixture of distilled water and ethanol; (1/1) (V/V)) was added. The tube was shaken vigorously for 5 min. After 24 h, the upper layer/phase was removed by Pasteur pipette. Then, 0.5 mL of lower layer/remaining section was poured into a glass tube and mixed with working solvent to get the final volume of 2 mL. All standards and biodiesel samples were treated by 1.2 mL of 0.01 M sodium periodate solution. Each solution was then treated with 1.2 mL of 0.2 M acetyl acetone solution. The samples were placed in water bath at 70 °C for 1 minute and stirred vigorously. The solutions were immediately placed in cold water to stop the reaction. The sample absorbance was finally measured by UV-Visible spectrophotometer. The calibration curve obtained from absorbance of standard samples at 410 nm versus the mg glycerol in standards samples. As a result, by use of calibration curve and the rate of absorption for the biodiesel samples, free glycerol concentration in biodiesel was determined [20]. Finally, the value obtained from the graph, Will be announced as mg glycerol/100 mg biodiesel.

The membrane glycerol rejection is calculated as follows [18-20]:

$$R\% = \left(1 - \frac{C_P}{C_F}\right) \times 100 \tag{3}$$

where (C_F) is glycerol concentration in feed and (C_P) is glycerol concentration in permaete stream.

3. Water Content

The water content was measured as the weight difference between the dried and swollen membranes. The wet membrane was weighed (OHAUS, Pioneer^{TM}, readability: 10^{-4} gr, OHAUS Corp.) and then dried in oven at 60 °C until constant weight was obtained. Following equation [21-25]:

$$\text{water content } \% = \left(\frac{W_{wet} - W_{dry}}{W_{dry}}\right) \times 100 \tag{4}$$

where W_{wet} is the weight of wet membrane and W_{dry} is the weight of dried membrane. To minimize the experimental errors, measurements were carried out three times for each sample, then their average value was reported.

4. Membrane Porosity

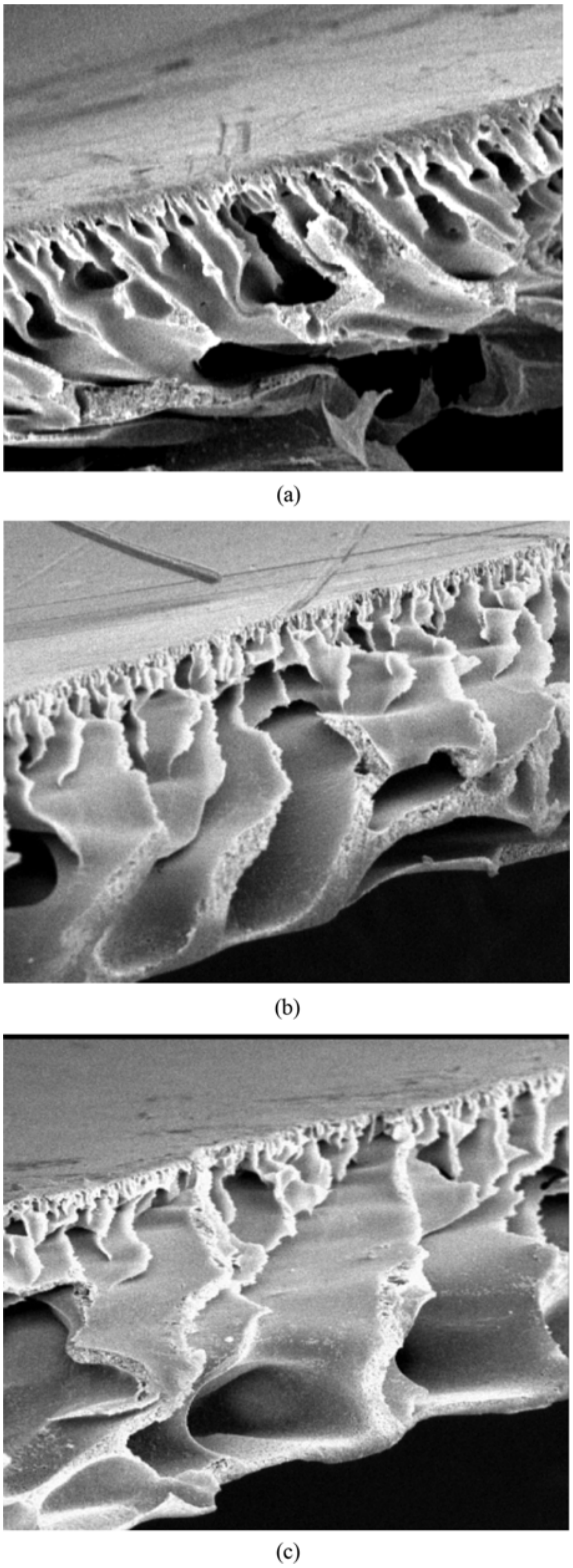
Porosity (Pr, %) was measured as a function of the membrane weight as follows [26]:

$$P_r = \left(1 - \frac{m}{s \times d \times \rho}\right) \times 100 = \left(1 - \frac{m}{s \times d \times \rho}\right) \times 100 \tag{5}$$

where m is membrane weight, s is membrane area, d is the thickness and ρ is membrane density, which is determined by multiplying active surface to sample's thickness. The thickness was measured by a digital caliper device (Electronic outside Micrometer, IP54 model OLR, China). To minimize the experimental errors, measurements were made three times for each sample, then their average value was reported.

5. Scanning Electron Microscope (SEM)

The surface and cross-section of prepared membranes was studied by scanning electron microscope (SEM, Cambridge 360) with an accelerating voltage of 15.0 kV. The membranes were cut into small sizes pieces that were then immersed in liquid nitrogen and frozen. Frozen fragments of the membranes were broken and kept in air for drying. The dried samples were sputtered by gold for elec-



(a)

(b)

(c)

Fig. 2. SEM cross section images of prepared membranes with different concentration of PES: (a) 16%wt; (b) 18%wt; (c) 20%wt.

tric conductivity producing.

6. Atomic Force Microscopy (AFM)

The surface roughness of prepared membranes was characterized by atomic force microscopy (AFM, Auto Pro CP, American). The samples were cut into 1 cm^2 pieces and fixed on glass substrate. The membrane surfaces were imaged in a scan size of 5 μm×5 μm by contact mode.

7. Mechanical Strength

The tensile stress of prepared membranes was investigated by Universal Testing Machine (UTM, SDLATAS, M 350-5 KN, 1 mm/min, at ambient temperature). The sample's size was 80 mm×15 mm. Measurements were done three times for each sample and then their average was reported in order to minimize the experimental errors.

RESULTS AND DISCUSSION

1. Scanning Electron Microscopy (SEM)

The SEM cross-sectional images of prepared membranes are shown in Fig. 2. SEM images showed relatively uniform surfaces for the prepared membranes. Also, images exhibited a asymmetric structure with dense top layer, porous sub-layer and fully developed macro-pores for the prepared membranes. As seen in cross-sectional SEM images, increase of polymer concentration in the casting solution caused a decrease of finger-like pores in membrane sub-layer. Moreover, SEM images showed a dense sub-layer for the

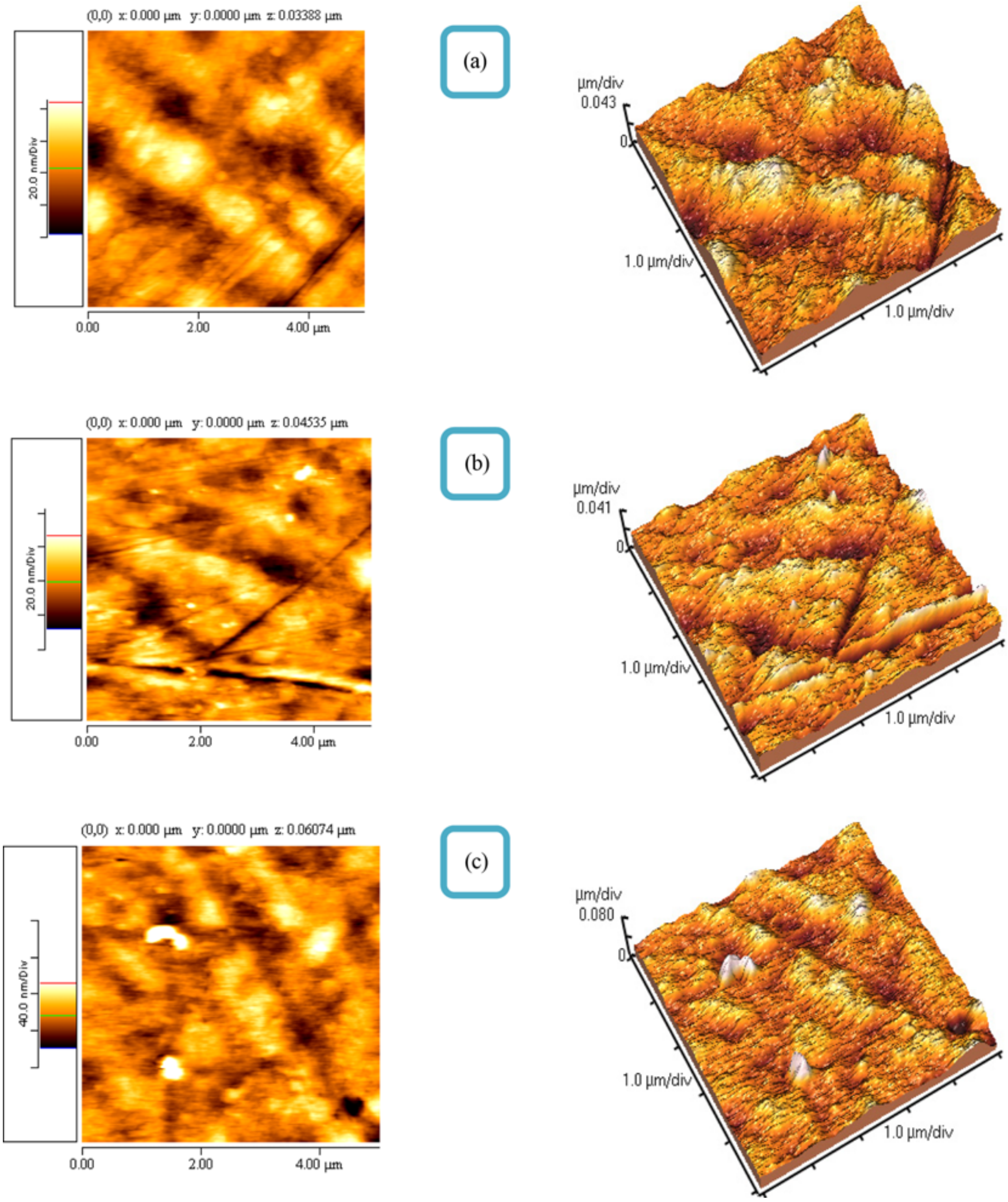


Fig. 3. AFM analysis of prepared membranes with different polymer concentration: (a) 16%wt; (b) 18%wt; (c) 20%wt.

Table 2. The surface roughness parameters for the prepared membranes

PES concentration (wt%)	Average roughness (nm)
16	12.86
18	11.52
20	9.02

membranes containing more PES content ratio. This may be attributed to increase of casting solution viscosity, which decreases the exchange rate between solvent and non-solvent during phase inversion process [27-29].

2. Atomic Force Microscopy (AFM)

The surface roughness of prepared membranes was examined by Atomic force microscopy (AFM). In the AFM images (Fig. 3), dark and bright areas refer to valleys and peaks, respectively. AFM results showed that membrane roughness was decreased by increase of polymer concentration. The calculated roughness parameters for the prepared membranes are presented in Table 2. Results indicated that membrane roughness was decreased from 12.86 to 9.02 nm by increase of polymer concentration from 16 to 20%wt in the casting solution. This may be attributed to decrease of exchange rate between solvent and non-solvent at high polymer concentration during phase inversion process. Also, at high polymer concentrations, increase of casting solution viscosity hinders the exchange rate between solvent and non-solvent, which leads to formation a membrane with smooth surface, smaller pore size and denser structure [28,29]. Membrane with low roughness has more antifouling ability.

3. Water Content and Porosity

Water content was measured as 128, 116 and 102% for the prepared membranes (samples 1 to 3). Results revealed that increase of polymer concentration in the casting solution led to decrease of membranes' water content. This may be due to decrease of voids/cavities in membrane matrix at high PES content, which results in less water accommodation. Low amount of water content for the membranes causes to less transfer channels for the membranes. This decreases the membrane flux. The overall porosity for the homemade membranes was also measured as 54, 46 and 32%, respectively. The increase of PES concentration in the casting solutions caused a decrease of membrane porosity. This is due to decrease of exchange rate between solvent and non-solvent during fabrication process, which makes the porosity of prepared membranes decline [30]. Increase of casting solution viscosity by increase in polymer concentration also decreases free spaces in the membrane matrix [28,29]. Note that measurements were made three times for each sample, and then their average value was reported in order to minimize the experimental errors.

4. Mechanical Strength of Prepared Membranes

The effect of polymer binder concentration on tensile stress behavior of prepared membranes was studied by Universal Testing Machine. The mechanical stability was measured 11.7, 15.5 and 16.7 (N/μm) for the membranes (sample 1 to 3), respectively. The increase of membrane mechanical stability by increase of polymer concentration is due to decrease of membrane porosity and greater links between polymer chains at high PES concentration, which leads to mechanical property improvement.

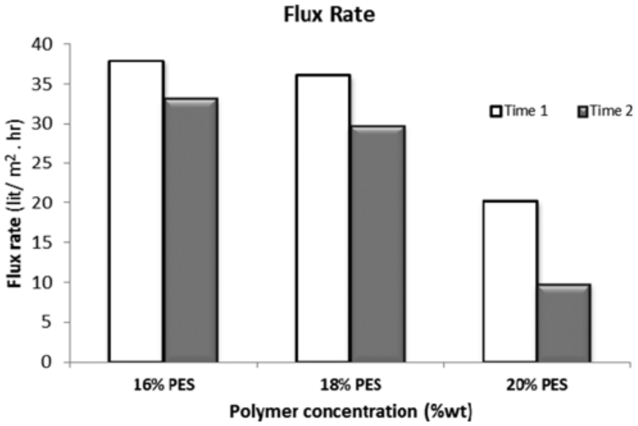


Fig. 4. The effect of PES concentration and time on membrane flux.

5. Flux Rate and Glycerol Rejection

Fig. 4 presents the flux rate of prepared membranes. The flux was measured as the amount of collected permeate's volume per unit area of membrane surface and time. The membrane flux was collected two times similarly. The required time to collect the first volume sample was named as Time 1 and the second as Time 2.

The obtained results (Fig. 4) revealed that that membrane flux was decreased by increase of PES concentration in casting solution. This may be due to decrease of membrane porosity, which makes difficult the fluid passage through the membrane and so decreases the flux. Also, results showed that membrane flux declined with time, which is assigned to membrane fouling phenomenon.

The glycerol mass percentage in the permeate section was measured as 0.0421, 0.0402 and 0.0354%wt for the prepared membranes containing 16%wt, 18%wt and 20%wt PES concentration, respectively. By using additional membrane separation steps, the amount of glycerol in biodiesel can be reduced to standard percentage: 0.02%wt.

The separation efficiency for the prepared membranes also is shown in Fig. 5.

As seen, separation efficiency was enhanced by increase of polymer concentration. This may be due to decrease of membrane surface roughness, which decreases the possibility of stagnant layer

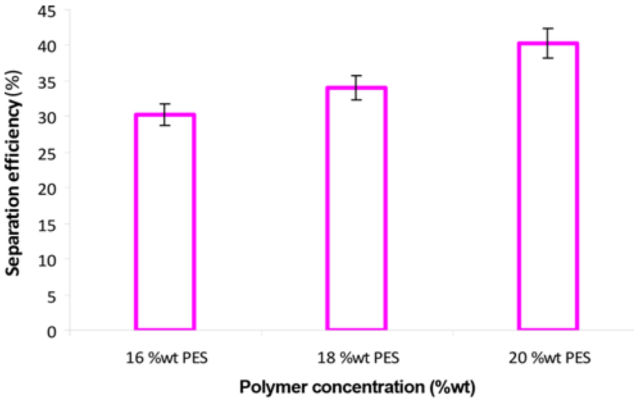


Fig. 5. The separation efficiency of prepared membranes with different PES concentration.

formation on membrane surface and improves the membrane rejection.

Among the prepared membranes, the membrane containing 16%wt PES, with high flux, suitable separation efficiency and physico-chemical characteristic showed more appropriate performance compared to others.

CONCLUSIONS

Biodiesel from waste cooking oils was purified by using poly ether sulfone based membrane. The used biodiesel was produced from waste cooking oils by trans-esterification method. Membranes were prepared by solution casting through phase inversion. The SEM images showed relatively uniform surface for the prepared membranes. Results showed that membrane selectivity was improved by increase of PES content in prepared membranes. Opposite trend was found for membrane flux. AFM images revealed that membranes' average roughness was decreased by increase of PES concentration in the casting solution. The membrane porosity and water content was also decreased by increase of polymer concentration in the casting solutions. Furthermore, the mechanical stability of prepared membranes was improved by increase of PES concentration. Among the prepared membranes, the prepared membrane containing 16%wt PES showed appropriate performance compared to others.

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