

## Effects of Polyethersulfone Membrane Substrate on the Separation Performance of Thin Film Composite Membrane in Biorefinery

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This study was aimed to develop a customised thin film composite (TFC) membrane for the separation in biorefinery. After the biomass hydrolysis stage, sugars component (i.e. glucose and xylose) need further refinement to remove any inhibitor (i.e. acetic acid) that can decrease the yield of the product during the fermentation stage. Substrate layer properties and the condition of thin film formation during interfacial polymerisation (IP) influenced the performance of the TFC membrane. Not much attention is given on the effects of substrate membrane properties as most support membranes were purchased commercially. Polyethersulfone (PES) membrane substrate was fabricated in the current study at different PES concentration range of 15 wt% to 23 wt%. IP was performed using the piperazine and trimesoyl chloride monomers. As the PES concentration in the membrane substrate increased, the pure water permeability (PWP) decreased. The PWP of the membrane substrate prepared from 15 % PES and 23 % PES were  $231.67 \pm 16.59$  L/m<sup>2</sup>.h.bar and  $24.49 \pm 6.54$  L/m<sup>2</sup>.h.bar. After the IP, the PWP decreased to the range of nanofiltration. The PWP value were  $28.07 \pm 5.42$  L/m<sup>2</sup>.h.bar and  $3.94 \pm 1.21$  L/m<sup>2</sup>.h.bar for the TFC membrane prepared using 15 % PES and 23 % PES membrane support. TFC membrane prepared using 23 % PES showed the rejection value 24.07 ± 5.96 % of xylose, 47.56 ± 1.99 % of glucose and 2.67 ± 1.05 % of acetic acid. This is corresponding to the ideal separation factor of  $1.45 \pm 0.06$  for xylose/glucose,  $1.86 \pm 0.05$  for acetic acid/glucose and  $1.29 \pm 0.09$  for acetic acid/xylose.

### 1. Introduction

Biorefinery concept refer to the production of fuels and chemicals from biomass feedstock (He et al., 2012) that involves several processing routes such as biomass pretreatment, hydrolysis, separation and fermentation process (Binod et al., 2011). Biomass has been acknowledged globally as a potential alternative renewable resources to replace fossil fuels in industrial production (Cherubini, 2010). Through the hydrolysis process, fermentable sugar such as glucose, xylose and arabinose will be released from cellulose and hemicellulose fractions of lignocellulose biomass (Chenxi et al., 2013). Glucose and xylose are the main sugars that can be converted to wide variety of chemicals, bio-plastic, cellulosic ethanol and advanced bio-fuels like green gasoline, green diesel and bio-fuel. Other impurities such acetic acid were also formed during hydrolysis (Grzenia et al., 2008). This inhibitor will interferes the fermentation process and eventually lowering the product yield (Weng et al., 2009). An appropriate separation technology is required for the separation of individual sugar and for the removal of potential inhibitors in biomass hydrolysate.

Thin film composite (TFC) membrane bring an attractively attention in the separation process in biorefinery. Gautam and Menkhaus (2014) had evaluated a range of commercial reverse osmosis (RO) and NF TFC membrane for sugar concentration and inhibitor removal from model and real biomass hydrolysate solution. Careful selection of the TFC membrane and operating conditions are essential in the development a continuous

process for biomass hydrolysis (Malmali et al., 2014). TFC membrane is prepared by interfacial polymerisation (IP) technique to form a selective active skin layer on top of porous membrane substrate. TFC membrane can offer a better separation performance by optimising both characteristic of the membrane substrate and selective skin layer (Han, 2013). Among the important variables during the development of TFC membrane are monomer concentration, partition coefficient of the monomer, reaction times, post-treatment and properties of membrane substrate (Huang et al., 2015). Many studies focusing on the optimisation of IP process in order to produce high performance TFC membrane. Li et al. (2014) had compared four different types of water soluble monomer during preparation of TFC membrane. The tested monomers were diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA) and piperazine (PIP). Among all the TFC NF membranes, PIP based membrane displayed the highest permeability. Abu Seman et al. (2013) studied the effect of IP reaction time during production of TFC membrane from 6 % w/v of triethanolamine (TEOA) in aqueous solution and a solution containing trimesoyl chloride (TMC). Liu et al. (2012) investigated the IP preparation parameters including reaction time, pH of the aqueous phase solution, reactant concentration, as well as curing temperature, and time during preparation of polyvinylamine (PVAm) and TMC based TFC membrane.

A very limited research has been focused on the effect of membrane substrate on the TFC separation performance. Misdan et al. (2014) found that the separation performances of the poly(piperazine-amide) layer of the TFC membranes were altered when using different types and properties of the flat sheet membrane substrate. The substrates were made of three different polymer materials of polysulfone (PSf), polyethersulfone (PES) and polyetherimide (PEI). Hollow fiber TFC membrane was also affected by the properties of the substrate used as demonstrated by Kong et al. (2016). Membrane substrate has an important role during IP as it functions as a container for one of the monomer precursors, and provides the interface where the IP reaction will occur. Membrane substrate core structure and chemistry properties (e.g.: pore size, pore structure, pore length, hydrophobicity, and reactivity toward monomers) could influence the rate of polymerisation by controlling the amount of monomer reaching the reaction zone and the width of reaction zone (Jimenez-Solomon et al., 2013). The best membrane substrate should have a high mechanical stability with low resistance to permeate flow (Mansourpanah et al., 2011) and tolerates the formation of a defect-free thin top layer (Tiraferri et al., 2011). In the current study, five types of PES membrane substrate were prepared by varying the PES composition in dope polymer solution from 15 wt% to 23 wt%. IP was performed using the PIP and TMC monomers. The separation performances of TFC membrane prepared using different substrate properties were tested for xylose-glucose refinement and acetic acid removal.

## **2. Materials and Method**

### **2.1 Materials**

Polyethersulfone (Radel® A) was purchased from Solvay Specialty Polymers, USA. Pluronic 270 was purchased from Sigma-Aldrich (MO) to be used as a pore forming agent. N-methyl-2-pyrrolidone (NMP) was purchased from Merck, Darmstadt, Germany for use as solvent in dope polymer preparation. TMC and PIP were purchased from Sigma-Aldrich and were used as monomers. The solvent for monomer, hexane (reagent grade,) was purchased from Fisher Scientific, UK.

### **2.2 Membrane substrate preparation**

The dope polymer solution was prepared at constant Pluronic concentration of 10 wt%. Five types of membrane with different PES composition (15 wt%, 17 wt%, 19 wt%, 21 wt% and 23 wt% PES) were produced. The PES pellets and pluronic were dissolved in NMP at temperature 50 °C under stirring for about 8 h until homogeneous dope polymer solution was achieved. The polymer solution was treated in ultrasonic bath for about 2 h to remove bubbles and then was kept at room temperature for 24 h. The asymmetric UF membrane substrate was fabricated via phase inversion method using a semi-automated casting machine. The membrane was casted at 0.317 cm/s casting velocity, 250 µm membrane thickness and immersed immediately into deionised water coagulation bath at room temperature. The membranes were kept in deionized water for 24 h before use.

### **2.3 Interfacial polymerisation process**

Membrane sheets were cut into round shape with 49 mm in diameter for IP process. The membrane substrate was immersed in 0.2 %, w/v PIP aqueous solution for about 2 minutes. Excess monomer on the membrane surface was removed and the membrane was dipped in 0.2 %, w/v TMC in hexane for 2 min IP reaction time. Finally, the membrane was dried in air for 30 min and then was stored in deionised water overnight before use. All the experiment steps were performed at room temperature.

## 2.4 Dead end filtration performance

The performances of the membranes were measured using Sterlitech HP4750 (Sterlitech Corporation, USA) dead-end filtration cell with an effective membrane area of 14.6 cm<sup>2</sup>. The feed pressure was controlled using the compressed nitrogen gas connected to the liquid reservoir of the filtration cell. The membrane was first compacted using pure water at 6 bars to get a steady flux for 2 h. After that, the pure flux was recorded at three different pressures (5 bar, 4 bar and 3 bar) for 2 h. The pure water permeability (PWP) was calculated based on the slope of water flux vs. pressure plot. Water flux, ( $J_w$ ) was calculated by Eq(1)

$$\text{Flux } (J_w) = \frac{V}{A \Delta T} \quad (1)$$

where  $J_w$  is the permeation flux of the membrane (L/m<sup>2</sup>.h),  $V$  is the volume of permeate (L),  $A$  is the effective area of the membrane (m<sup>2</sup>) and  $t$  is the permeation time (h). The flux and rejection of single solution of 10 g/L of xylose, 10 g/L of glucose and 10 g/L of acetic acid were tested at 6 bars for 1 h. The concentration of solute in retentate and permeate were analysed to calculate the solute rejection ( $R$ ) using Eq(2) (Sjoman et al., 2007).

$$\text{Rejection } (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \% \quad (2)$$

where  $C_p$  and  $C_f$  are the concentrations of solute in permeate and feed solution, respectively (wt%). Based on the rejection value, the separation factor ( $X_{s1/s2}$ ) of solute 1 to solute 2 was calculated using Eq(3) (Sjoman et al., 2007).

$$X_{(s1/s2)} = \frac{1 - R_{s1}}{1 - R_{s2}} \quad (3)$$

where  $R_{s1}$  and  $R_{s2}$  is the retention of solute 1 and solute 2. The separation factor value bigger than one indicates that the separation process was achieved. The same membrane was used to filter different types of solute. The membrane was thoroughly rinsed with pure water at 8 bars after each of solute filtration until the original membrane water flux is restored. For each type of membrane prepared, at least duplicate membranes sample were tested in filtration experiment.

## 2.5 Solute concentration analysis

Xylose and glucose concentration were analysed using 3,5-dinitrosalicylic acid (DNS) method. Acetic acid concentration was analysed by Synergi 4U Hydro-RP 80A (Phenomenex) HPLC column (250 x 4.6 mm) using 0.7 ml/min 0.02 M potassium phosphate mobile phase with PDA detector at 211 nm wavelength.

## 2.6 Membrane porosity testing

Membrane porosity ( $\epsilon$ ) was calculated based on the mass fraction of water lost after drying of wet membrane. The membrane was incubated with water for 24 h and weighed as  $w_0$  (kg). The wet membrane was placed in an air-circulating oven at 60 °C for 24 h for drying and then was weighed as  $w_1$ , (kg). The porosity of the membranes was then calculated using Eq (4)

$$\epsilon = (w_0 - w_1) / \rho_w A l \times 100 \% \quad (4)$$

where,  $A$  is the membrane surface area (m<sup>2</sup>),  $l$  is the membrane thickness (m) and  $\rho_w$  is water density (kg.m<sup>-3</sup>). The average porosity based on triplicates membrane sample were reported.

## 3. Results and discussion

### 3.1 Pure water permeability of PES TFC membrane

Table 1 shows the PWP and porosity of the membrane substrate and TFC membrane. 15 % PES membrane substrate has the highest PWP of  $231.7 \pm 16.67$  L/m<sup>2</sup>.h.bar, which is more than ten times higher compare to other membrane substrate. As expected the PWP decreased with the increasing of polymer concentration in substrate, but the decrement of PWP for the membrane prepared within the PES concentration of 17 to 23 wt% was not very significant. The PWP value for this concentration range is within  $18, 84 \pm 1.94$  to  $24.83 \pm 5.09$  L/m<sup>2</sup>.h.bar. No linear relationship found on the porosity value of the substrate to the PES concentration in the substrate or to the PWP. It can be noticed that the porosity reduced significantly after the formation of TFC membrane. As for PWP, the size of pore in the skin layer effect significantly on the PWP rather than the total porosity measured in this study. After the IP, all the TFC membrane shows the PWP within the NF range. Based

on the PWP of several commercial NF membranes that had been used in biorefinery, the reported values are within 5.05 L/m<sup>2</sup>.h.bar to 17.1 L/m<sup>2</sup>.h.bar (Sjoman et al., 2007).

*Table 1: Pure water permeability (PWP) and porosity of membrane substrate and thin film composite membrane.*

Membrane	Membrane Substrate		Thin Film Composite Membrane	
	PWP (L/m <sup>2</sup> .h.bar)	Porosity, $\epsilon$ (%)	PWP (L/m <sup>2</sup> .h.bar)	Porosity, $\epsilon$ (%)
15 % PES	231.67 $\pm$ 16.59	69.59 $\pm$ 3.26	28.07 $\pm$ 5.42	34.46 $\pm$ 3.99
17 % PES	24.83 $\pm$ 5.09	97.57 $\pm$ 18.08	14.38 $\pm$ 7.75	35.02 $\pm$ 6.41
19 % PES	19.86 $\pm$ 0.24	69.99 $\pm$ 13.89	17.71 $\pm$ 3.25	37.55 $\pm$ 4.47
21 % PES	18.84 $\pm$ 1.94	87.89 $\pm$ 7.44	5.22 $\pm$ 1.82	40.29 $\pm$ 9.90
23 % PES	24.49 $\pm$ 6.54	65.10 $\pm$ 13.39	3.94 $\pm$ 1.21	29.08 $\pm$ 8.80

*Table 2: Flux, rejection, and separation factor of xylose, glucose and acetic acid for the TFC membrane prepared using different PES membrane substrate at 6 bars.*

Membrane	TFC membrane				
	15 % PES	17 % PES	19 % PES	21 % PES	23 % PES
<b>Flux (L/m<sup>2</sup>.h)</b>					
Xylose	3,032.11 $\pm$ 765.72	99.32 $\pm$ 10.66	40.41 $\pm$ 28.09	56.85 $\pm$ 24.22	17.30 $\pm$ 2.66
Glucose	2,164.37 $\pm$ 688.70	97.26 $\pm$ 7.75	33.56 $\pm$ 18.40	41.78 $\pm$ 10.66	21.58 $\pm$ 15.98
Acetic acid	2,038.68 $\pm$ 603.98	105.48 $\pm$ 3.88	71.23 $\pm$ 21.31	43.84 $\pm$ 17.44	19.52 $\pm$ 10.17
<b>Rejection</b>					
Xylose	26.22 $\pm$ 7.90	23.21 $\pm$ 1.22	9.25 $\pm$ 9.09	24.19 $\pm$ 14.30	24.07 $\pm$ 5.96
Glucose	33.91 $\pm$ 2.68	13.98 $\pm$ 3.30	25.49 $\pm$ 10.06	36.52 $\pm$ 21.47	47.56 $\pm$ 1.99
Acetic acid	1.23 $\pm$ 0.16	1.28 $\pm$ 0.04	1.26 $\pm$ 0.40	1.02 $\pm$ 0.78	2.67 $\pm$ 1.05
<b>Separation factor</b>					
Xyl/Glu	1.12 $\pm$ 0.07	0.89 $\pm$ 0.02	1.31 $\pm$ 0.21	1.23 $\pm$ 0.19	1.45 $\pm$ 0.06
AA/Xyl	1.35 $\pm$ 0.15	1.14 $\pm$ 0.13	1.09 $\pm$ 0.13	1.29 $\pm$ 0.13	1.29 $\pm$ 0.09
AA/Glu	1.50 $\pm$ 0.06	1.10 $\pm$ 0.01	1.27 $\pm$ 0.27	1.16 $\pm$ 0.13	1.86 $\pm$ 0.05

### 3.2 Filtration performance

The molecular weight cut off (MWCO) for TFC NF membrane usually ranges from 150 to 1,000 Da (Murthy et al., 2005). The MWCO for acetic acid, xylose, and glucose are 60.05, 150.3, and 180.6 g/mol. If the TFC membrane operated mainly based on the size exclusion, it is expected that the acetic acid will show the highest flux and lowest rejection percentage. Table 2 shows the flux, rejection, and separation factor of solutes for the TFC membrane prepared using different PES concentration in the membrane substrate. Almost all membrane showed high xylose flux compare to the glucose, except for the membrane of 23 % PES. The rejection of acetic acid is lowest in all membranes. High flux value of acetic acid only showed in the TFC membrane of 17 % PES and 19 % PES. This phenomenon occurred could be due to the charged dissociation of acetic acid, which has a low pKa value of 4.756. When the pH value was higher than pKa, acetic acid becomes negatively charged acetate. TFC membrane also had a negatively charged. This could lead to an increasing of electrostatic repulsion between the membrane and acetic acid molecule during the filtration. The flux and rejection on acetic acid is mostly influence by the membrane surface properties that determine the degree of electrostatic repulsion (steric hindrance) occurred during filtration.

Based on the size, the rejection for the solute should follow this trend: acetic acid < xylose < glucose. Acetic acid showed a rejection less than 2 % for all membrane. Most of the TFC membrane showed a rejection of xylose lower than glucose except for the 17 % PES membrane. The separation factor is calculated based on the rejection of solute. As shown in Table 2, the separation factor between the solutes does not change significantly compare to the flux changed when using different PES membrane substrate. The separation factor between xylose to glucose is bigger than one, except for 17 % PES membrane. The highest separation factor of 1.34 for xylose/glucose is comparable with the value reported by commercial RO98pHT (Zhou et al., 2013) and Desal-5 DK (Sjoman et al., 2008), which had a value of 1.56 and 2.00. The separation factor of acetic acid to sugar achieved is bigger than one for all the membrane. Although the acetic acid separation is feasible if the value is bigger than one, but the commercial membrane normally showed the separation value more than 200 (Zhou et al., 2013).

#### 4. Conclusions

This study showed that the TFC NF membrane prepared using different PES membrane support influences the separation performance of the membrane for biorefinery application. The membrane substrate had a significant effect on the membrane flux compare to the separation factor between the solutes. The best separation factor achieved in the current study for xylose/glucose, acetic acid/xylose, and acetic acid/glucose are  $1.45 \pm 0.06$ ,  $1.35 \pm 0.15$ , and  $1.86 \pm 0.05$ .

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