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Thin Film Composite Hollow Fiber Membrane for Separation in Biorefinery

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One of the newest applications of the membrane technology is for the separation of sugar component and inhibitor removal during biomass processing in biorefinery. Most of the membranes used in biorefinery were commercially purchased and not specifically customise for the biomass hydrolysate processing. In the current study, a series of thin film composite (TFC) hollow fiber membranes were fabricated to tailor the performance toward xylose/glucose refinement and acetic acid removal in biomass processing. Polysulfone (PSf) hollow fiber membrane support was prepared using 20 wt% PSf, 2 wt% polyvinylpyrrolidone K30 (PVP K30) and 78 wt% dimethylformamide (DMF) through dry/wet spinning process. Three types of aqueous monomers were studied in interfacial polymerisation process, which are piperazine (PIP), triethanolamine (TEOA) and polyethyleneimine (PEI). TFC hollow fiber membrane prepared using TEOA monomer showed the best performance for separation of biomass hydrolysate component. It exhibited rejection value 50.98 ± 4.11 % of xylose, 71.72 ± 3.92 % of glucose and 5.45 ± 1.93 % of acetic acid. This is corresponding to the ideal separation factor of 1.75 ± 0.10 for xylose/glucose, 3.42 ± 0.54 for acetic acid/glucose and 1.95 ± 0.20 for acetic acid/xylose.

1. Introduction

Bioconversion of lignocellulosic materials into useful products has received a great attention recently due to its vast resource and renewability characteristics. In Malaysia, the abundance of wastes and residues generated from oil palm industries can be utilised as the potential source of lignocellulose biomass. The conversion of lignocellulose into targeted products consists mainly of polysaccharide hydrolysis, fermentation and purification step. Sugar components such as glucose, xylose, arabinose, mannose and galactose were released during dilute acid hydrolysis. Others impurities such acetic acid were also formed in the hydrolysate solution (Grzenia et al., 2008). This inhibitor will interferes the fermentation process and eventually lowering the product yield (Weng et al., 2009). Individual sugar components in biomass hydrolysate can be further fractionated in order to convert it into specific product such as gluconic acid, levulinic acid, xylitol and furfural (Wettstein et al., 2012). Purification and separation of lignocellulose hydrolysate solution is the most essential processes to the key successful of product development in lignocellulosic biorefinery.

Membrane technology has expanded and drawn industrial attention due to the various benefits compare to conventional separation method especially with regard to the energy saving. Reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) are the types of pressure-driven membrane processes developed for industrial applications. Application of NF and RO membrane has emerged in various fields in biorefinery such as for sugar concentration and fractionation, and inhibitor removal from biomass hydrolysate. Typical NF membranes that have been tested for biomass hydrolysate processing are Alfa Laval-NF (Alfa Laval), Desal-5 DK (GE) (Zhou et al., 2013a), Desal-5 DL (GE) (Sjoman et al., 2007), NTR729 (Nitto-Denko), PZ (Fluid Systems) (Han and Cheryan, 1995) , NF90 (Dow), and NF270 (Dow) (Malmali et al., 2014). For RO process, the following membrane has been used; RO90 (Alfa Laval), RO98pHt (Alfa Laval), RO99

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(Alfa Laval) (Malmali et al., 2014), FT30 (Dow), TLC (Fluid Systems), and NTR759 (Nitto-Denko) (Han and Cheryan, 1995).

Most of the membranes applied in biorefinery are commercially purchased. Commercial membrane normally prepared through interfacial polymerisation (IP) and known as thin film composite (TFC) membrane. Active thin film layer is formed on the membrane substrate in IP process by reacting an organic-soluble monomer with water-soluble monomer. The properties of the TFC membrane can be manipulated by controlling the IP process parameter. Commercial membranes have a fixed pore properties and the only option available for optimisation is the filtration operating parameters such as pressure, flow velocity and feed properties. In the current study, IP was used to fabricate TFC hollow fiber membranes to tailor the performance toward xylose/glucose refinement and acetic acid removal in biomass hydrolysate processing. Up to date, there are still lack of studies that have been conducted to customise the properties of TFC for specific uses in biomass hydrolysate processing. Three different types of aqueous monomers were used during preparing TFC membrane, which are piperazine (PIP), triethanolamine (TEOA) and polyethyleneimine (PEI). The performance of the membrane was evaluated with aqueous solution of xylose, glucose and acetic acid.

2. Materials and Methods

2.1 Materials

Polysulfone (PSf, Udel P-3500) (Solvay) as a base membrane polymer, polyvinylpyrrolidone (PVP K30) (Sigma-Aldrich Inc, MO) as an additive and dimethylformamide (DMF) (Merck, Darmstadt, Germany) as a solvent, were used for the preparation of PSf hollow fiber substrate. The chemicals used in IP were n-hexane (Merck) as a organic solvent, piperazine (PIP) (Merck), triethanolamine (TEOA) (Sigma-Aldrich) and branched polyethyleneimine (branched PEI) (Sigma-Aldrich) as an organics monomers, and trimesoyl chloride (TMC) (Sigma-Aldrich) as an aqueous monomer. Glucose (Sigma-Aldrich), xylose (Sigma-Aldrich) and acetic acid (Fisher Scientific, Malaysia) were used in the performance test of the TFC membrane. All the chemicals used were of analytical grade. Milli-Q water was used for the measurement of pure water permeability (PWP) of the membranes.

2.2 Membrane fabrication

PSf hollow fiber substrate was prepared based on the UF dope formulation developed by Maurya et al. (2012). It has the composition of 20 wt% PSf, 2 wt% PVP K30 and 78 wt% DMF. The mixture was continuously stirred at constant stirring speed (1,400 rpm) at about 80 °C for several hours until all polymer pellets were completely dissolved. The homogenous dope solution was kept in air tight bottle and left at room temperature for 24 hours to remove the air bubbles. Dry-jet wet spinning process was used to prepare the PSf hollow fiber membrane substrate. The detail of spinning condition was summarised in Table 1. The hollow fiber membrane was immersed in water at room temperature for 72 h to remove residual solvent. The hollow fiber was then preserved for one day in 10 wt% glycerol and dried at room temperature for a week. Five fibers, approximately 30 cm long, were bundled and glued into a stainless steel tube module (Li et al., 2004) using Loctite E30CL epoxy resin. The membrane area for one module is 8.80 x 10^{-3} m^2.

Table 1: Spinning parameters in dry-wet spinning process.

Parameter	Value
Dope composition (wt%)	PSf/PVP K30/DMF (20 : 2 : 78)
Dope flowrate (mL/min)	7.33
Bore fluid	Water
Bore fluid flowrate (mL/min)	19.48
Air gap distance (cm)	9.5
External coagulant type	Water
External coagulant temperature	Room temperature
Take-up speed (cm/s)	15.71
Spinneret dimension (mm)	i.d./o.d. (2.0/2.6)

2.3 Interfacial polymerisation

The detail condition of the IP process was selected based on the established method found in literature as shown in Table 2. The hollow fiber membranes were flushed with water in crossflow mode for half an hour to remove the glycerol in the membrane pores. The IP was performed in the lumen side of the fiber by pumping the aqueous monomer for certain duration and followed by purging with nitrogen gas to remove the excess monomer. TMC in hexane solution was then introduced to the fibers to complete the IP process and formed a thin film on the membrane. The TFC membrane was dried at room temperature for certain duration and then kept in deionised water before used for further testing and characterisation.

Table 2: Interfacial polymerisation procedure for different types of aqueous monomer.

TFC membrane	Monomer	Concentration	Time	Reference
TFC-PIP	PIP	2 wt%	2 min	Zhu et al., 2015
	TMC/n-hexane	0.1 wt%	1 min	
	Curing [a]	-	5 min	
	Drying [b]		2 h	
TFC-PEI	PEI	0.75 wt%	10 min	Wei et al., 2014
	TMC/n-hexane	0.5 wt%	20 s	
	Drying		2 h	
TFC-TEOA	TEOA	0.6 % w/v	30 min	Jalanni et al., 2013
	TMC/n-hexane	0.15 % w/v	15 min	
	Drying		24 h	

[a] Dried in an oven (UF 55, Memmert, USA) at 80 °C.
[b] Drying is done at room temperature.

2.4 Cross flow filtration

The performance of the TFC membranes were tested in crossflow filtration system as shown in Figure 1. Water flux (L/m^2.h) was measured at three different pressure of 1 bar, 2 bars and 3 bars. The flux, J_w, was calculated using Eq(1). The PWP was determined based on the slope of water flux versus pressure plot.

$$J_w = \frac{\Delta V}{A\,\Delta t} \tag{1}$$

where ΔV is the permeate collected (L), A is the effective membrane surface area (m^2) and Δt is the sampling time (h).

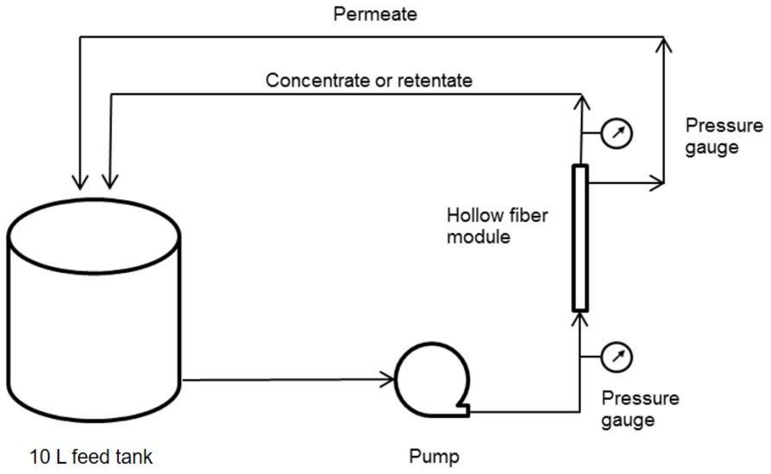

Figure 1: Schematic diagram of laboratory scale crossflow filtration system

The performance of the TFC membranes were evaluated using single solution of 10 g/L glucose, 10 g/L xylose and 10 g/L acetic acid. Three litres of feed solution was circulated through the membrane for 1 h at 3 bars by returning back the retentate stream to the feed tank. The permeate flux was measured using Eq(1). The concentration of permeate and retentate solution were measured. The rejection and separation factor were calculate using Eq(2) and Eq(3) (Zhou et al., 2013a).

$$R\,(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100\ \% \tag{2}$$

$$X_{s1/s2} = \frac{C_{p(s1)}/C_{p(s2)}}{C_{f(s1)}/C_{f(s2)}} \qquad (3)$$

where R is the rejection of solute (%), C_p and C_f are the concentrations of solute in permeate and feed solution, s1 and s2 are the solute 1 and solute 2, and $X_{s1/s2}$ is the separation factor of solute 1 to solute 2.

2.5 Sample analysis

The concentration of glucose and xylose were measured by 3,5-dinitrosalicylic acid (DNS) (MIiller, 1959). The absorbance of the samples were measured at 540 nm using Hitachi Ratio Beam Spectrophotometer U-1800 uv-vis spectrophotometer. The concentration of acetic acid was assayed using Synergi 4U Hydro-RP 80A (Phenomenex) HPLC column (dimension of 250 x 4.6 mm). The column was attached to the Waters Acquity UPLC H-class system with the Acquity refractive index detector and was measured at 211 nm. The column was run using 0.02 M potassium phosphate mobile phase at flowrate of 0.7 mL/min.

2.6 Porosity

The porosity of the membrane was determined by Eq(4).

$$\varepsilon = \left(\frac{W_1 - W_2}{\rho_w A t}\right) \times 100 \% \qquad (4)$$

W_1 is the weight of the wet membrane (kg) after 24 h soaked in the water. W_2 is the weight of the dry membrane (kg) after dried in oven at 50 °C for 24 h. A is the membrane effective area (m^2), t is the membrane thickness (m) and ρ_w is the density of water (1,000 kg m^{-3}).

3. Results and discussion

3.1 Flux and porosity

Table 3 shows the pure water permeability (PWP), porosity and permeate flux of water, xylose, glucose, and acetic acid of the PSf substrate and the TFC membrane after the IP process. The PWP of PSf substrate membrane was 4.01 ± 1.63 L/m^2.h.bar, which is within the NF membrane range between 1.5 to 30 L/m^2.h.bar (Van Der Bruggen et al., 2003). After the IP, the PWP of all TFC membranes reduced to RO range which has typical value of 0.05 – 1.5 L/m^2.h.bar (Van Der Bruggen et al., 2003). The degree of PWP reduction for the TFC-PIP membrane is less than PWP reduction for TFC membrane from PEI and TEOA. The total porosity value reported in Table 3 is not correlated well with the value of PWP obtained. PWP not only depends on the membrane total porosity but more significantly depends on the pore properties of the membrane skin layer formed at the lumen side of TFC hollow fiber membrane. Concentration of monomers and contact/reaction time are important parameters that influence the skin layer properties (Fang et al., 2013). TFC-PIP membrane had lowest contact time (i.e. 2 min) and probably produces less dense and thin skin layer, as demonstrated by highest PWP (4.01 ± 1.63 L/m^2.h.bar) compares to others TFC membrane. Although longer contact time of 30 minutes used during making TFC-TEOA membrane compared to 10 minutes for TFC-PEI, the PWP of TFC-TEOA is still bigger than the PWP of TFC-PEI. This might be contributed to the good compatibility of PEI monomer with TMC during IP process which leads to the formation of very thick and dense skin layer. The trend of the solute flux for the TFC membranes follows the same pattern as PWP value. Solute flux for TFC-PIP > TFC-TEOA > TFC-PEI. The degree of flux is correlated well the solute molecular weight and size. Flux for acetic acid > xylose > glucose in most of the membrane except for TFC-PEI membrane where flux for glucose is higher than xylose.

3.2 Solutes rejection and separation factor

Two main mechanisms for separation in TFC membrane are size exclusion and Donnan effect. For the uncharged molecules such as xylose and glucose, size exclusion was the main factor influencing retention. Table 4 show the rejection of xylose, glucose, and acetic acid for three types of TFC membrane, respectively. The chemical and structural changes occurring during IP process determines the rate of reaction of TFC membrane as well as the separation and flux performance (Ahmad and Ooi, 2005).

TFC-TEOA membrane possessed higher rejection of xylose (50.98 ± 4.11 %), glucose (71.72 ± 3.92 %) and acetic acid (5.45 ± 1.93 %). This is corresponding to the ideal separation factor of 1.75 ± 0.10 for xylose/glucose, 3.42 ± 0.54 for acetic acid/glucose and 1.95 ± 0.20 for acetic acid/xylose. Although the PWP of TFC-PIP membranes shows the highest water flux, its low rejection (41.11 ± 17.38 % for xylose, 23.63 ± 12.55 % for glucose and 0.68 ± 0.29 % for acetic acid) and separation factor (0.75 ± 0.10 for xylose/glucose, 1.34 ± 0.22 for acetic acid/glucose and 1.85 ± 0.54 for acetic acid/xylose) was not favourable in monosaccharide separation due to the loss of large amount of glucose and xylose during the filtration (Zhou et al., 2013b). The separation is achieved if the separation factor bigger than one. The TFC-TEOA membrane produced during this study showed a competitive performance for xylose/glucose separation compared with commercial RO98pHt and RO99 membrane (Zhou et al., 2013b). However, its performance for acetic acid separation is extremely low compares to the commercial membrane. Further optimisation of the IP process parameters might be necessary in order to improve the performance of this TFC membrane.

Table 3: Pure water permeability, porosity, and permeate flux of water, xylose, glucose and acetic acid of the membrane.

Membrane	PSf substrate	TFC-PIP	TFC-PEI	TFC-TEOA
PWP (L/m^2.h.bar)	4.01 ± 1.63	1.75 ± 0.16	0.59 ± 0.15	0.78 ± 0.04
Porosity, ε (%)	81.51 ± 1.01	69.36 ± 9.62	68.09 ± 5.32	83.79 ± 1.27
Water flux (L/m^2.h) [a]	9.19 ± 4.40	3.15 ± 1.70	1.64 ± 0.41	2.30 ± 0.14
Xylose flux (L/m^2.h) [a]	-	2.61 ± 1.30	1.23 ± 0.30	1.56 ± 0.22
Glucose Flux (L/m^2.h) [a]	-	2.29 ± 1.24	1.34 ± 0.27	1.16 ± 0.16
Acetic acid flux (L/m^2.h) [a]	-	3.25 ± 1.17	1.63 ± 0.49	1.73 ± 0.02

[a] Measured at 3 bar

Table 4: Rejection and separation factor of membranes.

Author	Membrane	Xylose rejection (%)	Glucose rejection (%)	Acetic acid rejection (%)	Sep. factor Xyl/Glu	Sep. factor AA/Glu	Sep. factor AA/Xyl
This study	TFC-PIP	41.11 ± 17.38	23.63 ± 12.55	0.68 ± 0.29	0.75 ± 0.10	1.34 ± 0.22	1.85 ± 0.54
	TFC-PEI	47.77 ± 1.30	66.47 ± 0.16	2.89 ± 0.92	1.56 ± 0.03	2.90 ± 0.04	1.86 ± 0.06
	TFC-TEOA	50.98 ± 4.11	71.72 ± 3.92	5.45 ± 1.93	1.75 ± 0.10	3.42 ± 0.54	1.95 ± 0.20
Han and Cheryan (1995)	NTR729	-	99	40	-	6	-
Weng et al. (2009)	Desal-5 DK	28 – 81[a]	-	-6.8 – 90[a]	-	-	5.4 (max.)
Zhou et al. (2013a)	RO98pHt	99.75	99.84	44.21	1.56	223.16	348.69
	RO99	99.73	99.75	47.51	1.08	209.96	194.41
	Desal-5 DK	89.05	98.28	-	6.37	-	-
	Alfa Laval-NF	82.25	96.26	-	4.75	-	-
Zhou et al. (2013b)	RO98pHt	99.73	99.75	42.90	1.08	228.4	211.5

[a] Depending on the solution pH and pressure

Xyl – xylose, Glu – glucose, AA – acetic acid

4. Conclusions

TFC membrane produced based on the TEOA – TMC monomers give the best performance for separation of component in biomass hydrolysate. It showed a competitive performance for xylose/glucose separation (1.75±0.10) compared with commercial RO98pHt (1.56 and 1.08) and RO99 membrane (1.08) (Zhou et al., 2013a). This TEOA based TFC membrane is acceptable to be used for xylose/glucose separation, but a further improvement is requires for acetic acid separation.

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