

## Fabrication of Asymmetric Nanofiltration Flatsheet Membrane for the Separation of Acetic Acid from Xylose and Glucose

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Malaysia palm oil based industries generate a huge amount of lignocellulose biomass wastes. These wastes can be utilized to produce chemicals and fuel. Lignocellulose biomass consists of hemicelluloses, cellulose and lignin. Cellulose and hemicelluloses portion need to be hydrolysed to release fermentable glucose and xylose for further processing. Biomass hydrolysis using acid is a simple method, but it also produces acetic acid inhibitor that can inhibit the microorganism during fermentation. In order to increase the yield of product as well as to elevate the rate of product, there is a need to remove this acetic acid inhibitor from the biomass hydrolysate. In the current study, asymmetric nanofiltration (NF) flat sheet membrane was fabricated for acetic acid removal. Five types of asymmetric NF membranes were produced with different formulation in term of polymeric material (polysulfone (PSf) and polyethersulfone (PES)), types of solvent (N-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), ethanol, dimethylacetamide (DMAc)), and types of additive (polyvinylpyrrolidone (PVP), polyethylene glycol (PEG)). The best separation factor of acetic acid over glucose (1.1607) and acetic acid over xylose (1.2985) were showed by the asymmetric membrane produced from 19.6 wt% PSf/ 74.8 % DMAc/ 5.6 % ethanol and 21 % PSf/ 55.3 % NMP/ 23.7 % THF.

### 1. Introduction

Lignocellulosic biomass residues such as frond, trunk and empty fruit bunch (EFB) are among the bio-waste produced by Malaysia palm oil industry. Without proper handling, this waste can bring pollution to the environment. This lignocellulosic waste however can be converted to the useful products such as biofuel (Lee et al., 2014), chemicals (Nataraj et al., 2009) and biofertilizer (Gautam and Menkhaus, 2014). Hemicellulose, cellulose, and lignin are the main constituent in the lignocellulose biomass (Grzenia et al., 2010). Fermentable sugars such as xylose and glucose can be released from this hemicellulose and cellulose by using selected pretreatment and hydrolysis process. Hydrolysis of lignocellulose with dilute sulphuric acid produces high yield of sugar but at the same time releases an acetic acid as the byproduct (Grzenia et al., 2008). Acetic acid can inhibit the microorganisms uses in the fermentation process. Acetic acid decreases the water activity and creates a stress environment for the microorganism to grow (Palmqvist and Hahn-Hagerdal, 2000). It is important to remove this acetic acid prior to the fermentation in order to increase the yield of product (Grzenia et al., 2008). Nanofiltration (NF) process has been considered for the removal of acetic acid from the biomass hydrolysate (Zhou et al., 2013). NF gives effective separation and simple process compared with other unit operations. NF membrane is normally applicable for the separation of the solutes within the range of 150 – 1,000 g/mol (Weng et al., 2009). Acetic acid which is 60 g/mol molecular weight is expected to permeate freely through NF membrane compared to the xylose (160 g/mol) and glucose (180 g/mol) (Teella et al., 2011). Malmali et al. (2014) had used commercial NF270 (Dow) and RO99 (Alfa Laval) NF membrane for sugars concentration and acetic acid removal from model hydrolysate solution. Desal-5 DK (GE Osmonic) NF membrane showed a separation factor of 5.4 for acetic acid to xylose using model solution (Weng et al., 2010). Zhou et al. (2013)

also used Desal-5DK (GE Osmonic) NF membrane for acetic acid removal from a ternary solution of glucose, xylose and acetic acid. The separation factors of acetic acid to xylose and acetic acid to glucose were 8.87 and 56.5. DSS-HR98PP (Microdyn-Nadir) and NF97 (Dow Filmtec) NF membrane showed an acetic acid rejection of 84 % and 77 %, respectively (Afonso, 2012). More than 80 % of glucose rejection and less than 15 % of acetic acid rejection were achieved using Koch MPF34 NF membrane (Teella et al., 2011).

Most NF membranes used in above studies were commercially purchased and were based on the thin film composite (TFC) NF membrane. TFC membrane is normally produced by interfacial polymerization process by forming a dense skin layer on the top of porous membrane support. Compared to the TFC membrane preparation, asymmetric NF membrane is simpler to produce. Both top dense skin layer and porous support of asymmetric membrane are produced from the same material. High performance NF asymmetric membrane can be produced by carefully control the design parameters and fabrication parameters involve in the phase inversion process. In the current study, flat sheet asymmetric NF membranes were produced from five established dope formulation found in the literature. The performance of the asymmetric NF was tested for the removal of acetic acid from the xylose and glucose.

## 2. Methodology

### 2.1 Material

Polysulfone (PSf, Udel P-3500, Solvay) and polyethersulfone (PES, Radel® A, Solvay) were used as the base polymer in dope solution. The solvent used in dope formulation were N-methyl-2-pyrrolidone (NMP, Merck), dimethylacetamide (DMAc, Fisher), tetrahydrofuran (THF, Fisher), and ethanol (Fisher). Polyethylene glycol (PEG) of average molecular weight 200 Da and polyvinylpyrrolidone (PVP K30) were used as additive and were purchased from Sigma Aldrich. The tested solutes were acetic acid (Merck), glucose (Sigma) and xylose (Sigma). All chemicals were of analytical grade and used without further purification.

### 2.2 Fabrication of Membrane

Table 1 shows the dope polymer composition for making asymmetric NF membrane. The polymers and additives were dissolved in the solvents under continuous stirring at room temperature. Then, the homogeneous dope solution was left for 24 h in tight container so that air bubbles can be released. It is then degassed in ultrasonic bath for 3 h. Based on the phase inversion process, flat sheet membrane was casted on the glass plate using semi-automatic casting machine with constant thickness of 250  $\mu\text{m}$ . The membrane gel was immersed immediately to the water coagulation bath at room temperature after casting process to form a solidified membrane. The membrane was then left for 24 h in tap water to fully remove any residual solvent and finally dried in open air for another 24 h.

Table 1: Composition of dope polymer solution based on the weight percentage

Membrane	Polymer	Solvent	Additive	Reference
A	19.6 % PSf	74.8 % DMAc 5.6 % Ethanol	-	(Ismail and Hassan, 2006)
B	21 % PSf	55.3 % NMP 23.7 % THF	-	(Hołda et al., 2013)
C	21 % PSf	51.8 % NMP 22.2 % THF	5 % PEG 200	(Hołda and Vankelecom, 2014)
D	23.1 % PSf	70.6 % DMAc 6.3 % Ethanol	-	(Ismail and Hassan, 2006)
E	20.34 % PES	71.51 % NMP 3.15 % Water	5 % PVP K30	(Ismail and Hassan, 2007)

### 2.3 Dead End Filtration

The performances of the membranes were tested using Amicon stirred cell (Model 8200) operated as dead end filtration with an effective membrane area of  $3.15 \times 10^{-3} \text{ m}^2$ . Nitrogen gas was used to compress the feed liquid to pass through the membrane and collected as permeate. The stirring speed was kept constant at 300rpm and filtration was run for 90 minutes. The water flux at pressure of 3, 3.5 and 4 bar were tested and calculated using Eq(1) in order to calculate the pure water permeability (PWP).

$$J = \frac{V}{A\Delta t} \quad (1)$$

where  $J$  is pure water permeability,  $V$  is volume of permeated pure water (L),  $A$  is effective membrane area ( $m^2$ ) and  $t$  is a permeated time (s).

The solute filtration experiment was conducted at 4 bars for 90 min using single solution of 15 g/L acetic acid, 15 g/L xylose, and 15 g/L glucose respectively. The membrane was flushed with water for 60 min before change to the new feed solution. The concentration of solute in the retentate and permeate sample were analyzed to calculate the solute rejection ( $R$ ) using Eq(2). The separation factor for acetic acid to xylose or acetic acid to glucose were calculated using Eq(3). All experiments were carried out in duplicate and data were expressed in average value.

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

where  $R$  is rejection,  $C_p$  is concentration of permeated solution and  $C_f$  is concentration of feed solution

$$\alpha_{A/B} = \frac{1 - R_A}{1 - R_B} \quad (3)$$

where,  $\alpha_{A/B}$  is a separation factor of solute A over solute B,  $R_A$  is rejection or retention of solute A and  $R_B$  is a rejection or retention of solute B.

#### 2.4 High Performance Liquid Chromatography Analysis

Water Acquity Ultra Performance Liquid Chromatography (UPLC) system was used for HPLC analysis of the sample concentration. Glucose and xylose concentration were both measured using Rezex RHM Monosaccharide (7.8 X 300 mm) (Phenomenex) HPLC column with refractive index detector. As for the mobile phase, ultrapure water was used with flow rate of 0.6 ml/min and injection volume of 0.6  $\mu$ L. Acetic acid was analysed using SYNERGY (3.9 x 300 mm) (Phenomenex) HPLC column with PDA detector at 211 nm wavelengths. 0.02 M potassium phosphate was used as the mobile phase at 0.7 ml/min with a sample injection volume of 10  $\mu$ L.

#### 2.5 Porosity and Pore Size Determination

Overall porosity ( $\epsilon$ ) was calculated by Eq(4). The wet weight of the membrane ( $\omega_1$ ) was obtained after immersion of the membrane with water overnight. The dry membrane ( $\omega_2$ ) was weighted after the wet membrane was oven-dried at 60 °C for 24 h.

$$\epsilon = \frac{\omega_1 - \omega_2}{Al\rho} \quad (4)$$

Where  $\omega_1$  &  $\omega_2$  is weight (kg) of the wet and dry membrane,  $A$  is effective membrane area ( $m^2$ ),  $\rho$  is density of water (998 kg/ $m^3$ ), and  $l$  is membrane thickness.

The Guerout–Elford–Ferry (Vatanpour et al., 2012) equation was used to determine the mean pore radius ( $r_m$ ) of the membrane using pure water flux and porosity data. The equation is as shown in Eq(5).

$$r_m = \sqrt{\frac{(2.9 - 1.75\epsilon) \times 8\mu l Q}{\epsilon A \Delta P}} \quad (5)$$

where  $\mu$  is viscosity of water (8.9 x 10<sup>-4</sup> Pa.s),  $Q$  is volumetric flow rate of the permeated water ( $m^3/s$ ), and  $\Delta P$  is operating pressure (Pa).

### 3. Results and Discussions

The parameters that are important during manufacturing of NF membrane can be group into design parameter and fabrication parameter. This study focused on the design parameter which involves type and composition of polymers, type and composition of solvents, and type of additives in membrane dope solution. Table 2 and Table 3 summarized the properties and performance of asymmetric flat sheet NF membrane prepared using different dope formulation, respectively.

Based on Table 2, the highest water flux is exhibited by membrane E (16.553 L/ $m^2$ h), followed by membrane A (13.377 L/ $m^2$ h). Meanwhile, membrane C shows the lowest water flux of 1.983 L/ $m^2$ h. PVP additive in dope solution produced high porosity (44.93 %) of membrane E since the PVP is a pore forming agent (Wang et al., 2006). In addition to the above, the present of water in the dope solution can result in membrane with spongy structure (Ahmad et al., 2013) and improved hydrophilicity of the PES membrane (Khulbe et al., 2010), thus contribute to the high water flux in Membrane E.

Table 2: Properties of asymmetric flat sheet NF membrane

Membrane	Water Flux (L/m <sup>2</sup> h)	PWP (L/m <sup>2</sup> .h.bar)	Porosity (%)	Pore Radius (nm)
Membrane A	13.3772±9.6633	5.2932±1.4972	5.6764±0.0003	24.6655±9.6044
Membrane B	2.1173±1.0888	0.4331± 0.4764	3.2758±0.0058	15.1536±5.20513
Membrane C	1.9825±1.5516	0.5486±2.2457	7.0783±0.0111	9.3718±3.1968
Membrane D	4.7446±0.1769	0.5389±0.0544	4.7692±0.0200	17.1840±3.4974
Membrane E	16.5531±1.6332	5.7743±1.0888	44.9296 ± 0.0052	9.7879±0.4073

Table 3: Separation performance of asymmetric flat sheet NF membrane

Membrane	Rejection			Separation Factor	
	Glucose	Xylose	Acetic Acid	Acetic Acid/ Glucose	Acetic Acid/ Xylose
Membrane A	17.1431±9.8478	4.9115±0.9011	4.7772±4.5273	1.1607±0.1926	1.0017±0.0571
Membrane B	7.5504±2.4192	24.2184±16.5939	3.6037±3.2565	1.0426±0.0079	1.2985±0.2414
Membrane C	2.7374±2.1736	11.9474±7.4239	5.5855±4.4221	0.9705±0.0238	1.0740±0.0403
Membrane D	13.5151±5.6932	17.6288±18.5103	1.9270±0.0450	1.1364±0.0743	1.2214±0.2739
Membrane E	6.0418 ±5.3113	4.6356 ±4.5858	1.5843±0.2423	1.0490±0.0567	1.0331±0.0471

Even though, PEG200 was added to the dope solution of Membrane C, the water flux is low compared to the Membrane B (2.117 L/m<sup>2</sup>h) that used the same system of PSf/NMP/THF but without PEG additive. Based on Holda and Vankelecom (2014), an interaction between PEG and PSf caused delayed demixing that made the polymer solution to become more viscous and thus decrease in water flux exchange during phase inversion. This can shrink the pore size of the membrane formed (Ghosh, 1996). It can be seen that Membrane C exhibits the smallest pore radius (9.372 nm) compare to the Membrane B (15.153 nm). Depending on the polymer system, PEG can be functioned as macrovoid suppression (Chakrabarty et al., 2008) or macrovoids formation (Idris et al., 2007).

Based on the analysis, Membrane A and Membrane D produced with the same polymer system but with different PSf concentration. Membrane A that is produced using 19.6 % PSf concentration, showed a higher water flux compared to Membrane D that is produced using 23.1 % PSf concentration. The water flux of Membrane D (4.744 L/m<sup>2</sup>h) is almost three times lower than that of Membrane A. High polymer concentration can also be related to the delayed demixing that allow only a small amount of coagulating agent to penetrate and also decrease the precipitation rate (Amin et al., 2015). The increment of the polymer concentration can also lead to the decrease of the surface porosity and the pore size of the membrane (Sotto et al., 2011). It can be seen that membrane A that produced from the lowest polymer concentration showed the largest pore radius of 24.666 nm.

In term of membrane performance, the highest rejection of glucose (17.143 %), xylose (24.218 %), and acetic acid (5.586 %) were showed by the Membrane A, Membrane B, and Membrane C, respectively. Membrane A has the highest separation factor of acetic acid over glucose with a value of 1.1607 and membrane B shows the highest separation factor of acetic acid over xylose with a value of 1.2985. If the separation factor is more than one, the separations between these two solutes were feasible. In this analysis, all the membranes shows the separation factor larger than one for acetic acid to glucose or acetic acid to xylose except to the Membrane C. Nevertheless, the separation factor values produced by asymmetric membrane in this study are still low and not comparable with the commercial NF membranes tested in the previous studies which is higher. As an example, the separation factor for Desal-5DK (GE Osmonic) NF membrane for acetic acid over xylose and acetic acid over glucose were determined as 8.87 and 56.5 (Zhou et al., 2013).

#### 4. Conclusion

Based on the value of pure water permeability and separation factor of the membranes, Membrane A was considered as the best asymmetric NF membrane produced from this study. Membrane A had a separation factor of 1.1607 and 1.0017 for acetic acid to glucose and acetic acid to xylose, respectively which is better compared to Membrane B, Membrane C, Membrane D, and Membrane E. It is expected that further improvement of the asymmetric NF membrane performance can also be made by investigation the fabrication parameters involve during casting process. These improvements are expected improve the performance of the membranes.

## Acknowledgement

The authors are grateful for the research financial support by the Ministry of Higher Education Malaysia under the Fundamental Research Grant Scheme (FRGS RDU140144) and Long Term Research Grant Scheme (LRGS- UKM on Future Biorefineries – RDU140901), and Universiti Malaysia Pahang under Research University Grant Scheme (RDU140337). Author, Wan Hairani Wan Na'aman thanks the sponsorship given by Ministry of Higher Education under MyBrain15 (MyMaster) scheme and Universiti Malaysia Pahang under Graduate Research Scheme (GRS 1403179) during her Msc. The authors would also like to acknowledge all researchers that have contributed to the research.

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