

## Removal of Acetic Acid from Aqueous Solution by Polyethersulfone Supported Liquid Membrane

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Lignocellulosic biomass can be converted to biofuel, which is one of the renewable energy. To achieve this purpose, acid hydrolysis was used to hydrolyse lignocellulosic materials to fermentable sugars. However, acetic acid, a major inhibitory compound was released during the acid hydrolysis process. Existence of acetic acid significantly suppressed fermentative organisms and decreased the production of ethanol. It is necessary to remove acetic acid inhibitor from biomass hydrolysate prior to the fermentation process. Selective removal of acetic acid from aqueous solution was attempted by using supported liquid membrane (SLM) system based on tri-n-octylamine carrier and sodium hydroxide stripping phase. Polyethersulfone (PES) membrane was prepared by vapour induced phase separation method and used as a matrix support in SLM process. Effects of PES membrane thickness, types of diluent, and flow rate of feed phase were tested. Under favourable condition, almost 86 % of acetic acid was successfully removed from the aqueous solution. The PES SLM system remained stable for 8 h of extraction without any breakage.

### 1. Introduction

Meeting the world's demand for fuels and value-added chemicals required the resources to be abundant and inexpensive to produce. Lignocellulosic biomass was pointed out to be one of the most promising alternative source. Almost 200 x 10<sup>9</sup> t of lignocellulosic biomass are readily available annually for conversions to the value-added product (Chandel and da Silva, 2013). Biomass is the only sustainable source of organic carbon in earth for the production fuels and fines chemical with net zero carbon emission. Pre-treatment and hydrolysis of lignocellulosic biomass was required in order to release the fermentable sugars for subsequent bioconversion to bioethanol. Inhibitor was also produced which directly restricted the microorganism activity during fermentation process (Lee et al., 2013). The fermentation inhibitors that were commonly found in lignocellulosic hydrolysates are aliphatic acid (acetic acid, formic and levulinic acid), furaldehydes, aromatic compounds, and extractives (Lee et al., 2014). Among them, acetic acid was the most serious inhibitor present in large amount in lignocellulosic biomass hydrolysate, thus it is necessary to be removed from the biomass hydrolysate before fermentation.

Various detoxification methods have been used to remove acetic acid inhibitors from simulated and real biomass hydrolysate. Lee et al. (2014) used electrodialysis (ED) to remove acetic acid and formic acid from the biomass hydrolysate of mushroom waste medium. Only 40 % of acetic acid was successfully removed by using ED method. Malmali et al. (2014) had separated acetic acid from clarified biomass hydrolysate using nanofiltration membrane. Kim et al. (2012) had proposed a lime addition-capacitive deionisation method for removing acetic and sulphuric acid from model hydrolysate solution containing glucose, xylose, acetic acid, and sulphuric acid. Another potential method that can be used for selective removal of acetic acid was by using supported liquid membrane (SLM) process.

In liquid membrane system, a carrier that can selectively extract the solute from the feed phase was dissolved in suitable diluents to form an organic liquid membrane phase. This organic membrane phase was incubated within the pore of the membrane support and placed between feed phase and stripping phase. Extraction and stripping can be performed in a single step in SLM process. This will provide maximum driving force for the separation of desired solute, leading to high extraction and recovery rates. The advantages of SLM process over conventional solvent extraction process was due to its highly selective separation, simplicity of process, minimal used of carrier and low operating cost (Harruddin et al., 2015). The performance of the SLM system can be influenced by several parameters such as concentration of carrier, concentration of feed phase, type of diluents, thickness of membrane support, and flow rate of feed phase. In this work, the effects of PES membrane thickness, types of diluent in organic membrane phase, and flow rate of feed phase were investigated on the removal of acetic acid from the aqueous solution using SLM system. The membrane support was fabricated by vapour induced phase separation (VIPS). Membrane fabrication using VIPS method is versatile, simple and effective in producing microporous membrane for used as support in SLM (Caquineau et al., 2003).

## 2. Methodology

### 2.1 Material

To fabricate a microporous membrane, PES (Radel® A, Solvay, USA) was used as a polymer for microporous membrane. Dimethylacetamide (DMAc) and polyethylene glycol (PEG 200) were used as diluents and pore forming agent and were supplied by Sigma Aldrich (MO). Tri-n-octylamine (TOA) was supplied by Sigma Aldrich and used as the carrier in organic liquid membrane phase. 2-ethyl-1-hexanol, kerosene, 5 % octanol in kerosene, toluene and sunflower oil were tested as diluents in liquid membrane formulation. All diluents were purchased from Sigma-Aldrich except the sunflower oil was purchased from the local shop. Acetic acid and sodium hydroxide were obtained from Merck (Darmstadt, Germany).

### 2.2 Membrane Fabrication

The flat sheet PES membrane was prepared by vapour induced phase separation (VIPS) method using 15 wt% PES, 42.5 % PEG 200, 42.5 % DMAc dope polymer solution. The PES pellet was dried in an oven at 100 °C overnight. PEG 200 was mixed with DMAc and then PES was dissolved in the mixed solution at room temperature. Using semi-automatic casting machine, the polymer solution was casted onto glass plate at different thickness (300 µm, 350 µm, 380 µm, 400 µm) and be exposed to air environment for 30 s (Li et al., 2008) at room humidity of 86 %. The cast film was then immersed into water coagulation bath at temperature of 40 °C to induce complete solidification process. 30 min later, the solidified membrane was transferred to another water coagulation bath for one day and dried at room temperature for 48 h.

### 2.3 Supported Liquid Membrane Process

Supported liquid membrane was prepared by submerging the PES membrane support in liquid membrane solution for 24 h. The organic liquid membrane phase was formulated by dissolving 0.5 M TOA carrier in different types of diluent. The tested diluents were 2-ethyl-1-hexanol, kerosene, 5 % octanol in kerosene, toluene and sunflower oil. The schematic diagram for SLM system is shown in Figure 1. The membrane cell was made of two Teflon compartment of equal size with the dimension of 16.5 cm x 10 cm. The supported membrane (10.5 cm x 4 cm) was placed between these two compartments. 10 g/L acetic acid solution and 0.5 M NaOH solution were used as the feed and stripping solution, respectively. The solutions were circulated into the membrane cell by two channel peristaltic pump. The concentration acetic acid was detected by Synergy Hydro C18 column (150 mm x 4.6 mm x 4 µm) connected to Waters Acquity UPLC system. 0.02 M potassium dihydrogen phosphate was used as mobile phase and acetic acid was detected by UV detector at 221 nm wavelength.

### 2.4 Acetic acid removal percentage

The percentage of removal acetic acid during the SLM process was calculated using Eq(1).

$$\text{Removal (\%)} = \frac{[AA]_{fi} - [AA]_{fo}}{[AA]_{fi}} \times 100\% \quad (1)$$

Where,  $[AA]_{fi}$  is the initial concentration of acetic acid ions in the feed phase and  $[AA]_{fo}$  is the final concentration of acetic acid ions in the feed phase

## 2.5 Scanning Electron Microscope

The membrane morphology was observed by using Scanning Electron Microscope (SEM) ZEISS EVO 50. Membrane was fractured in liquid nitrogen and coated with gold-palladium before examined in SEM machine.

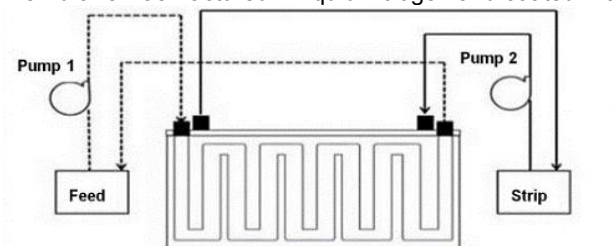


Figure 1: Schematic diagram of supported liquid membrane system

## 3. Results and discussions

### 3.1 Morphology of membrane support

Figure 2 shows the SEM photograph of cross section and upper top surface of PES membrane support prepared VIPS method. As shown in Figure 2(a), PES membrane shows a symmetrical structure with cylindrical microvoids that uniformly distributed throughout the cross section of membrane. Compared to the asymmetric morphology, symmetric membrane was more suitable for the SLM process because it had better stability (Scott and Hughes, 1996). The forces exerted on both sides of the symmetric membranes were likely to be almost the same thus there was possibility of improving the SLM process stability (Lv et al., 2007). Figure 2(b) showed the upper surface of PES membrane. It can be seen that no obvious pores were detected on the top surface of membrane. This surface characteristics will help the organic liquid membrane phase to be retained inside the membrane pore and prevent any leakage of the liquid membrane during SLM process (Dzygiel and Wieczorek, 2010).

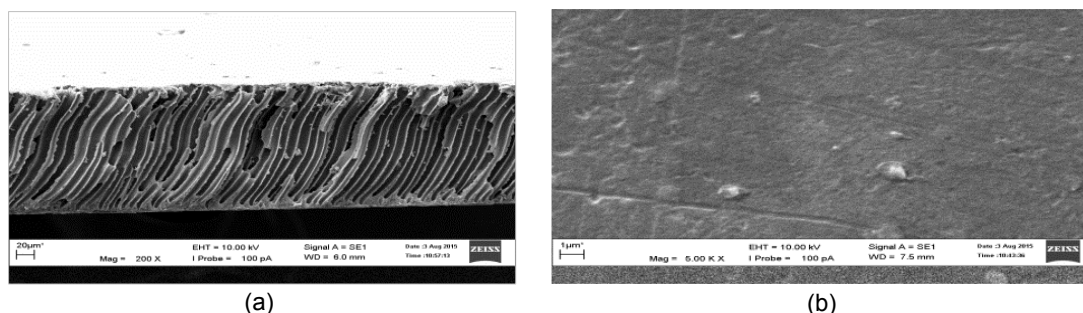


Figure 2: SEM photograph of PES membrane, a) cross section and b) upper surface

### 3.2 Effect of membrane support thickness on acetic acid removal

Membrane support properties such as hydrophobicity (Curcio et al., 2016), thickness, and pore structure played a key role in the transport and separation efficiency of SLM. All these properties were related to the physical stability of the support and the rate of the mass transfer (i.e. solute flux) through the membrane during SLM process (Dzygiel and Wieczorek, 2010). Not much studies were done on the effect of membrane thickness on SLM process due to the most of the membranes support used were based on commercial microporous membrane. Ideally, the support should be as thin as possible to reduce the solute diffusion pathway, hence enhancing the solute flux (Dzygiel and Wieczorek, 2010). However, the thickness of the membrane is limited by the mechanical stability of the support and physical stability of the organic liquid membrane contained within the membrane pores. The effect of membrane support thickness from 300  $\mu\text{m}$  to 400  $\mu\text{m}$  on the removal of acetic acid was shown in Figure 3. A membrane support thickness of 380  $\mu\text{m}$  increased the amount of acetic acid removed from an aqueous solution to the value 86 %. Further increment to 400  $\mu\text{m}$  membrane thicknesses reduced the value of acetic acid removal to 79 % which was higher than the membrane of 300  $\mu\text{m}$  and 350  $\mu\text{m}$  thickness. Optimum membrane support thickness will provide high stability and durability against physical stress in SLM process and this was proven by membrane at 380  $\mu\text{m}$  thickness (Dzygiel and Wieczorek, 2010). Very thick membrane can contain high volume of organic liquid membrane phase which was expected to extract more solute, but sometimes accommodation can be a problem. Solute

can be easily accumulating in the membrane pore due to long diffusion pathway taken to cross from the feed side to the strip phase. Extraction rate will be reduced due to this slow diffusion of carrier –solute complex and the release of solute to the stripping side will be delayed (Ho and Zydney, 1999).

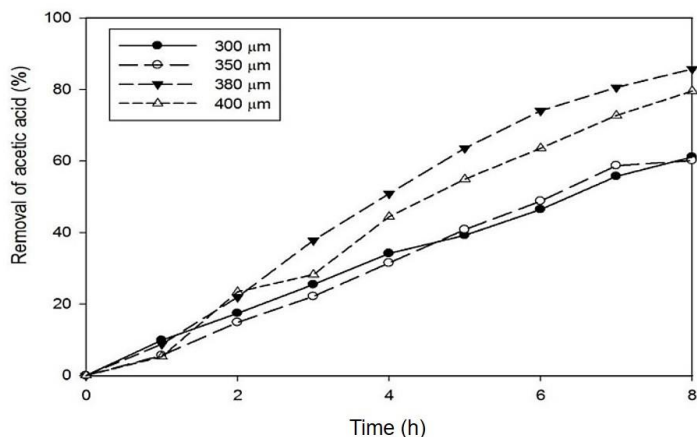


Figure 3: Effect of membrane support thickness from 300  $\mu\text{m}$  to 400  $\mu\text{m}$  on the removal of acetic acid

### 3.3 Effect of diluents in liquid membrane on the removal of acetic acid

Types of diluent significantly affected the solvation and specific interaction between carrier-diluent, hence exhibiting different extraction efficiency. High extraction power and maximum distribution coefficient of TOA can be achieved by selecting the right diluents. Diluent used in SLM process can be categorised as polar, nonpolar, and combination of both. Organic diluent such as vegetable oil had been proposed by previous researcher (Narayanan and Palanivelu, 2008). The effect of using different types of diluents on the acetic acid removal was shown in Figure 4. It can be seen that the highest removal of acetic acid was achieved by using 2-ethyl-1-hexanol diluent with 86 % of removal. The rest of diluents exhibited acetic acid removal percentage less than 30 %. 2-ethyl-1 hexanol is a polar diluent that can enhance the extracting power of nonpolar amines (i.e TOA) by providing additional solvation effect which can improve the formation of acid-amine complexes in the organic liquid membrane phase (Yang et al., 2013). Solubility of acid-amine complexes could be increased as the polarity of diluent increases (Sahin et al., 2010). Low extraction efficiency was shown using nonpolar diluent of kerosene and 5 % octanol in kerosene. Since kerosene is a nonpolar solvent, TOA has low solubility in kerosene and is difficult to form acid-amine complex during SLM process. Organic sunflower oil was found not suitable for dissolving TOA in the current SLM formulation. Poor performance of sunflower oil can be related to the high viscosity of the oil which reduced the diffusivity of acid-amine complexes within the membrane support (Parhi, 2013). Although the toluene was commonly used as diluent in the SLM process, it was not compatible with the PES membrane support used in this study. The breakage of PES membrane support occurred after 5 h of SLM process. Toluene is a carcinogenic solvent that can cause adverse health effect and its usage should be avoided.

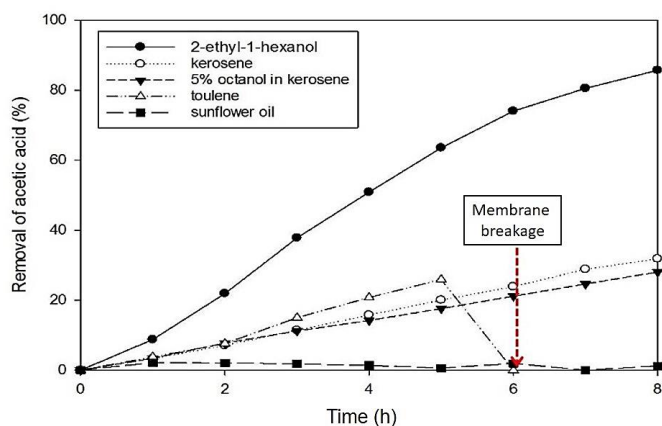


Figure 4: Effect of diluents in liquid membrane on removal of acetic acid

### 3.4 Effect of flow rate of feed phase

Flow rate of feed phase was an important parameter during solute permeation through liquid membrane phase (Manna et al., 2014). Feed flow rate greatly influenced the thickness of the aqueous boundary layer near the membrane-feed interface (Ata andÇolak, 2005). The effect of feed phase flow rate had been stressed in many studies in order to determine the optimum feed flow rate. Optimum feed flow rate can minimise the aqueous boundary layer thickness to achieve highest separation and avoid liquid membrane phase forced out from the support. Figure 5 illustrates the effect of feed flow rate on the removal of acetic acid from 50 mL/min to 125 mL/min. Highest removal of acetic acid of 86 % was achieved at a flow rate of 75 mL/min. An increment of feed flow rate up to 100 and 125 mL/min significantly reduced the acetic acid removal performance to 67 and 64 %. Feed flow rate operated higher than the optimum value can create high turbulence near the membrane support and affect the stability of the organic liquid membrane phase in the support. This finding agrees with the research of Surucu et al. (2012) and Amiri et al. (2008), who stated that further increase in the flow rate at high level decreases the solute transport efficiency due to high turbulence which causes instability of SLM process. Low feed flow rate of 50 mL/min was insufficient for minimising the thickness of aqueous boundary layer near the feed membrane and produced low acetic acid removal percentage.

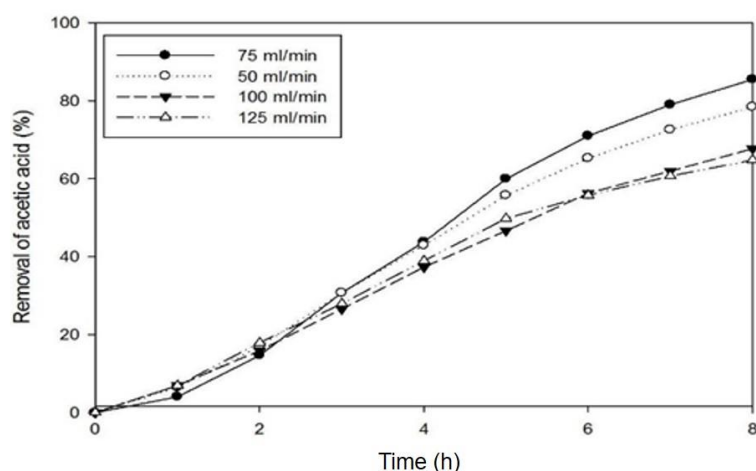


Figure 5: Effect of flow rate of feed phase on removal of acetic acid

## 4. Conclusions

In this study, acetic acid was removed from aqueous solution by using TOA as carrier and sodium hydroxide as a stripping agent using SLM process. Three parameters of SLM process, which were thickness of membrane support, type of diluents, and flow rate of feed phase, were tested. The highest removal of acetic acid of around 86 % was achieved by using membrane support with 380  $\mu\text{m}$  thickness, 2-ethyl-1-hexanol as diluents for TOA carrier and 75 mL/min of feed phase flow rate.

## Acknowledgments

The authors were grateful for the research financial support by the Ministry of Higher Education Malaysia under the Fundamental Research Grant Scheme (FRGS RDU140144), Long Term Research Grant Scheme (LRGS- UKM on Future Biorefineries), and Universiti Malaysia Pahang under Research University Grant Scheme (RDU140337). Author, Norlisa Harruddin thanked the sponsorship given by Ministry of Higher Education under MyBrain15 (MyPhD) scheme and Universiti Malaysia Pahang under Graduate Research Scheme (GRS 150303) for her PhD study.

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