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EVALUATION OF DIFFERENT POLYMERIC MEMBRANE SUPPORT FOR ACETIC ACID REMOVAL BY SUPPORTED LIQUID MEMBRANE PROCESS

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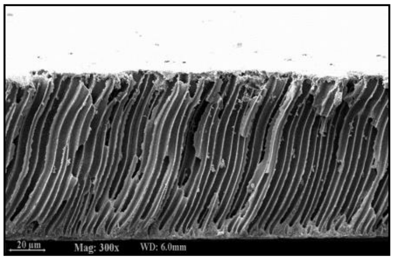
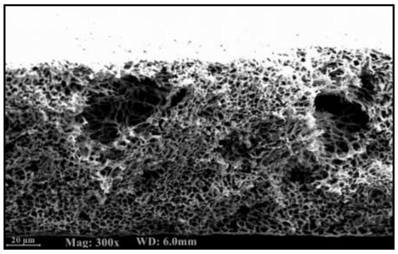
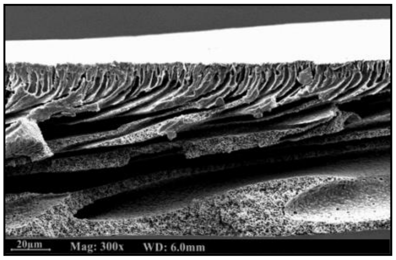
Graphical abstract







Abstract

In this study, the removal of acetic acid from aqueous solution through supported liquid membrane (SLM) process by using tri-n-octylamine (TOA) as a carrier and sodium hydroxide as a stripping agent was conducted. Acetic acid can inhibit the microbial activity during fermentation process of biomass hydrolysate, thus decreasing the bioethanol production. It is crucial to remove acetic acid prior to fermentation process in order to increase the yield of bioethanol from biomass resources. In this study, the removal of acetic acid was conducted using different types of polymeric membrane in supported liquid membrane process. Three types of polymeric membranes support which are polyethersulfone (PES), polysulfone (PSF) and polyvinylflouride (PVDF) prepared by vapour induced phase separation (VIPS) were used as a support material. The types of polymer give a significant effect on membrane morphology and its physical characteristics. PES exhibited a porous membrane support with a symmetric structure and high contact angle. Almost 86% of 10 g/l of acetic acid was successfully removed by using PES as a support membrane, compared to the 6% and 38% removal using PSF and PVDF membrane, respectively.

Keywords: Supported liquid membrane, vapor induced phase separation, acetic acid, biomass hydrolysate, polymeric membrane

Abstrak

Dalam kajian ini, penyingkiran asid asetik dari larutan akueus melalui proses membran cecair bersokongan (SLM) dengan menggunakan tri-n-octylamin (TOA) sebagai pembawa dan natrium hidroksida sebagai agen pelucutan telah dijalankan. Asid asetik boleh menghalang aktiviti mikrob semasa proses penapaian biojisim hidrolisat, dengan itu mengurangkan penghasilan bioetanol. Adalah penting untuk menyingkiran asid asetik sebelumproses penapaian bagi meningkatkan penghasilan bioetanol dari sumber biojisim. Dengan menggunakan kaedah fasa pemisah didorong wap bukan pelarut (VIPS), tiga jenis membran penyokong dihasilkan dari polyethersulfone (PES), polysulfone (PSF), dan polyvinylflouride (PVDF). Jenis polimer memberi kesan yang ketara pada morfologi dan sifat fizikal. Membran PES menghasilkan membran berliang dengan struktur simetri dan sudut sentuhan yang tinggi. Hampir 86% dari 10 g/l asid asetik telah berjaya disingkirkan menggunakan PES sebagai membran sokongan dibandingkan dengan 6% dan 38% penyingkiran menggunakan membrane PSF dan

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PVDF masing-masing.

Kata kunci: Membran cecair bersokongan, fasa pemisah didorong wap, asid asetik, biojisim hidrolisat, membran polimer

1.0 INTRODUCTION

Nowadays, the shortage of fossil fuels source, increasing oil price and global warming lead to high concerns on the use lignocelluloses biomass for the second generation of bioethanol. The lignocelluloses biomass can be converted to biofuels and fine chemicals by biochemical conversion. Efficient utilization of hemicelluloses and cellulose in lignocelluloses biomass can improve the production of bioethanol thus reduced the cost of production. However, lignocelluloses biomass is highly recalcitrant towards degradation due to high crystallinity of cellulose and its high molecular weight [1]. Therefore, the lignocelluloses biomass must be pretreated and hydrolyzed to make the carbohydrate accessible for further processing. Dilute acid treatment is commonly used because it is simple and effective in producing xylose-rich hemicelluloses hydrolysate [2]. Acetic acid is the major inhibitor released during the hydrolysis and presented in large amount in lignocellulosic biomass hydrolysate [3]. The presence of acetic acid cause inhibitory effect on yeast activities, thus decreasing the ethanol production rate [4, 5]. Therefore, it is crucial to remove acetic acid to the low concentration level to avoid these inhibition problems to microorganisms prior to fermentation [6, 7].

There are various separation methods have been employed to remove acetic acid from hydrolysate involving biological, chemical, physical and combine treatments method. The effectiveness of detoxification method is depends on type of biomass hydrolysate and the species of microorganisms used during the fermentation [7]. The detoxification method should be low cost, easy to integrate into the process and able to remove inhibitors selectively. Mussato *et al*. [7] and Huang *et al*. [8] had reviewed several existing methods for detoxification such as microbiology approach, vacuum evaporation, extraction, overliming, activated charcoal adsorption, and ion exchange. However, all these method were not suitable in industrial application due to high operation cost, generate additional waste, hard to integrate in the process and extensive lost of sugars.

Supported liquid membrane (SLM) is a new membrane based technology that uses for removal of desired solute from an aqueous solution. SLM system shows a great potential for acetic acid removal since it combines extraction and stripping process in one single step unit operation. Single step process provides the maximum driving force for separation which leads to an excellent removal process [9]. In SLM system, membrane support plays an important role in the stability of the system. Instability phenomenon commonly occurs when the liquid membrane fails to retain in pore of membrane, thus affects the transportation and separation efficiency. Microporous polymeric membrane with high hydrophobicity, high porosity, small pore size and high tortuosity are required as a support in SLM process [10]. In this study, three types of polymer which are polyethersulfone (PES), polysulfone (PSF) and polivinylidenefluoride (PVDF) were fabricated by using vapor induced phase separation (VIPS) technique and tested for the support in the SLM system for acetic acid removal. Different types of polymer have different crystallinity degree which can affect the morphology and physical characteristic of membrane support.

2.0 METHODOLOGY

Three types of polymer were used to fabricate the membrane support. PES and PSF were supplied by Amoco Chemicals and PVDF was purchased from Sigma Aldrich. The polymer was dried for 24 hours at 60°C. Dimethylacetamide (DMac) and polyethylene glycol (PEG 200) were purchased from Sigma Aldrich, were used as solvent and additive, respectively. Distilled water was used as a coagulation medium. The properties of PES, PSF and PVDF, are tabulated in Table 1.

In liquid membrane formulation, tri-n-octylamine (TOA) was used as a carrier and 2-ethyl-1-hexanol was used as a diluent. Both chemicals were supplied by Sigma Aldrich. Sodium hydroxide was used as a stripping agent and obtained by Merck

Table 1 Properties of polyethersulfone (PES), polysulfone (PSF) and polyvinylidenefluoride (PVDF)

Properties	**PES**	**PSF**	**PVDF**
Physical appearance	yellowish pellet	White pellet	Semi transparent pellet
Melting point (°C)	176	180-190	177
Boiling point (°C)	-		166

2.1 Membrane Fabrication

The polymeric membrane support was fabricated by using VIPS technique. 15 wt% of polymer was dissolved in solvent and additive at room temperature for 48 hours as shown detail in Table 2. The additive, PEG 200 was used as a pore forming agent. The amount of PEG 200 added to the solution depend on the thermodynamic stability of the system. Therefore, it is not possible to fix the same amount of PEG 200 in all dope polymer formulation. Instant gelation occurred once PEG 200 was added to the PVDF dope solution, which indicate that the thermodynamic system become unstable. The homogenous dope polymer solution was degassed at room temperature for 24 hours. Using semi automatic casting machine, the polymer solution was casted onto glass plate and exposed to air environment at 86% relative humidity for 30 second. The cast film was then immersed into water coagulation bath at temperature of 40°C to induce complete solidification process. Thirty minutes later, the solidified film was transferred to another water coagulation bath for 1 day and dried at room temperature for 48 hours.

Table 2 Dope polymer composition

Membrane	Composition
PES	15% PES, 42.5% PEG 200, 42.5% DMaC,
PSF	15% PSF, 18% PEG 200, 67% DMaC
PVDF	15% PVDF, 85% DMaC

2.2 Supported Liquid Membrane System

Polymeric membrane support was incubated with 0.5 M TOA in 2-ethyl-1-hexanol organic liquid membrane solution for almost 24 hours. Filter paper was used to remove the excess liquid on the membrane surface. The supported membrane with size dimension of 10.5 cm × 4 cm was placed in membrane cell and attached to the SLM system as shown in Figure 1. The membrane cell was made of two Teflon compartment of equal size with the dimension of 16.5 cm × 10 cm. 10 g/L acetic acid solution and 0.5M NaOH solution were used as the feed and stripping solution, respectively. The solutions were circulated into the membrane cell by two channels peristaltic pump. The concentration acetic acid was detected by Synergy Hydro C18 HPLC column (150 mm x 4.6 mm x 4 μm) connected to Waters Acquity UPLC system. 0.02M potassium dihydrogen phosphate was used as mobile phase and acetic acid was detected by UV detector at 221nm wavelength.

2.3 Acetic Acid Removal Percentage

Equation 1 was used to calculate the percentage of acetic acid removal during the SLM process

$$\text{Removal (\%)}=\frac{[AA]_{fi}-[AA]_{fo}}{[AA\ ]_{fi}}\ x100\% \qquad (1)$$

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 feed phase.

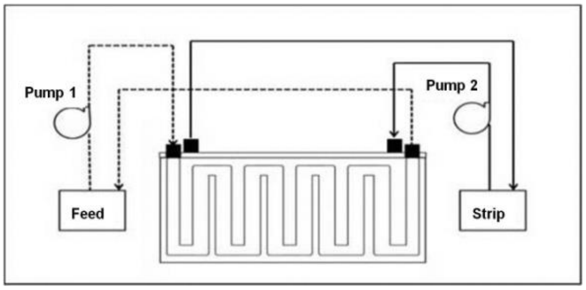


Figure 1 Schematic diagram of supported liquid membrane system

2.4 Scanning Electron Microscope (SEM)

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.

2.5 Porosity Measurement

The porosity of membrane was determined by Equation 2.

$$\varepsilon=\frac{W_1\text{-}W_2}{[Al\rho]_{fi}}\ x100\% \qquad (2)$$

Where W_1 is the weight of the wet membrane (kg), W_2 is the weight of the dry membrane (kg), A is the membrane effective area (m^2); l is the membrane thickness (m) and ρ is the density of olive oil (800 kg m^{-3}). The membrane was dried in an oven at 80 °C for 24 hours to ensure there is no water presence on the pores of the membrane. The dried membrane was weighted as W_2. After that, the membrane was immersed in oil for 24 hours. The wet surface of the membrane was wiped with filter paper and weighted it as W_1.

2.6 Contact Angle

Optical contact angle measurement system (CAM 101 optical Contact Angle Meter, KSV Instruments) was used to determine the surface hydrophilicity of the membranes. A water was dropped on the membrane surface by using a microsyringe with stainless steel needle at room temperature. At least three measurements were performed at different membrane locations to obtain the average contact angle for one membrane sample.

3.0 RESULTS AND DISCUSSION

3.1 Morphology of Membrane Support

Two important factors that influence SLM performance are physical stability of the membrane and rate of mass transfer of solute through membrane. Therefore, the choice of polymer gives significant effect in SLM stability, lifetime and separation performance [10]. Types of polymer affect the resulted membrane in terms of morphology, hydrophobicity and pores structure. A best polymeric support for SLM process should displayed high hydrophobicity, small pore size, right tortuosity and high porosity [10]. Figure 2 shows the cross section of polymeric membrane support prepared from different types of polymer. It can be seen that both PES and PSF membrane showed a symmetrical structure. A symmetric membrane is suitable for the SLM process because it has higher stability compared to that of an asymmetric membrane [12]. According to Lv *et al*. [13], forces exerted on both sides of the symmetric membranes are likely to be almost the same thus there is possibility of improving the SLM process. As shown in Figure 2 (a), PES membrane consist of cylindrical microvoids structure that uniformly distributed throughout the cross section of membrane. PSF membrane had a microporous sponge like pore structure with some large disruptive void fractions in the middle of the membrane cross section. PVDF membrane had an asymmetric structure consisting thin fine porous structure on the top upper side, followed by finger like pore structure and finally macrovoid pores at the bottom part of the membrane.

Figure 3 shows the top surface of PES, PSF and PVDF membrane support. As shown in Figure 3 (b), the PSF membrane exhibits a porous top surface compare to PES and PVDF membrane. No obvious pores were seen on the top surface of PES and PVDF membrane. However, PES membrane had smoother surface compared with PVDF membrane. In SLM process, instability phenomenon can be occurred when the liquid membrane fails to retain inside the membrane pore during SLM process [10]. The surface structure of PSF membrane is found not suitable to be used as a support since the liquid membrane had a tendency to leach out during the SLM process.

3.2 Contact Angle and Porosity of the Membrane

Hydrophobicity of supports is one of the major factors influence the performance of SLM process. Support material must be hydrophobic in nature so that it can retain the organic liquid membrane within the membrane pores by capillary force [14]. Figure 4 shows the dispersion of one drop of water on the membrane support. The corresponding contact angle value was calculated and shown in Table 3. PES membrane shows higher contact angle compared to others polymer. PES is well known hydrophobic material, which had been applied successfully as the support in the SLM system [15,16]. The typical contact angle of pure PES membrane is around 50-70°, but it is depends on the fabrication methods and membrane composition [17,18]. In this study, PES membrane prepared by VIPS method showed a high contact angle of 92.6 ° which make it more suitable to be a support for SLM process. There are lot of studies using PVDF as a support [19,20] in the SLM process due to it well known hydrophobic character. However, the casting condition can turn the PVDF to become more hydrophilic as shown in Table 3. Therefore, PVDF membrane is not suitable to be used as a support since it can promotes instability problem.

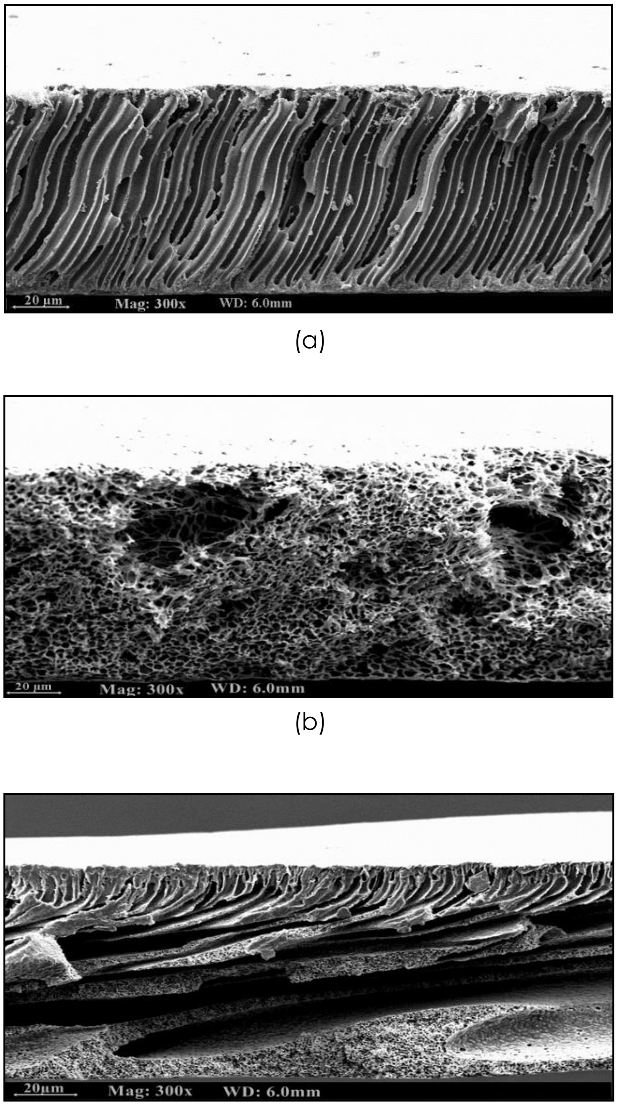
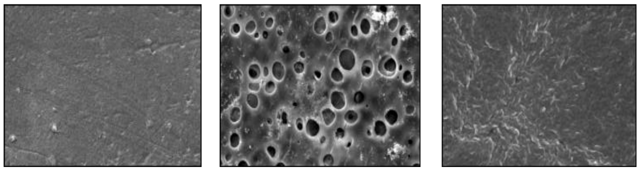


Figure 2 Cross section of membrane support, Mag: 300K x a) PES, b) PSF c) PVDF



(a) (b) (c)

Figure 3 Surface of membrane support, Mag: 300K x a) PES, b) PSF c) PVDF

(a) (b) (c)

Figure 4 Contact angle, Mag: 300K x a) PES b) PSF, c) PVDF

Table 3 Contact angle and porosity of membrane support, Mag: 300K x a) PES, b) PSF and c) PVDF

Polymeric Membrane Material	Contact Angle (°)	Porosity (%)
PES	92.6	48.9
PSF	77	27.5
PVDF	48	23.6

Table 3 also shows the porosity of the membrane support. The porosity of PES membrane almost double compared to PSF and PVDF. This result can be related to dope polymer composition where the PES polymer solution contain high amount pore forming agent, PEG 200. Addition of large amount of PEG 200 induce the voids formation in membrane [21]. An attempt to add PEG 200 to the PDVF solution and to increase the amount of PEG 200 in PSF polymer solution led to the instability of dope solution and the solution become cloudy and too viscous.

3.3 Performance of Different Membrane Support on Removal of Acetic Acid from an Aqueous Solution

Figure 5 exhibits the removal percentage of acetic acid from the aqueous phase using different type of membrane support. Fabricated PES membrane shows an excellent performance with 86% of acetic acid removal. The PES membrane remains stable within 8 hours of SLM process. This performance is related to the suitable morphology of PES membrane in term of high hydrophobicity, good porosity and symmetric structure as discussed previously. Although PSF membrane has a symmetric structure with high hydrophobicity compare to PVDF membrane, it able to remove 6% of acetic acid. This might be due to the porous top surface of PSF membrane that can cause the instability and leaches out of organic liquid membrane from the support. The acetic acid removal percentage for PVDF membrane (38%) is almost half from PES support which is in line with the value of contact angle and porosity as shown previously in Table 3.

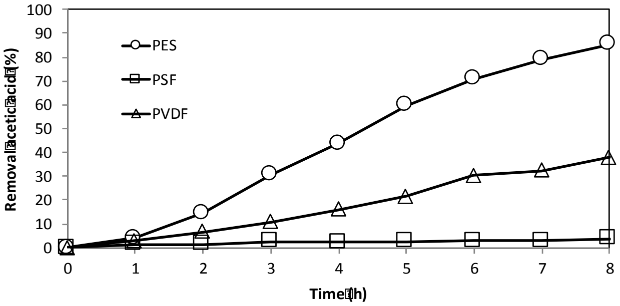


Figure 5 Removal of acetic acid from the aqueous solution using different type of membrane support in SLM process

4.0 CONCLUSION

Three types of polymeric membrane were successfully fabricated by VIPS method. The best membrane support for the removal of acetic acid from an aqueous solution using SLM process was fabricated from 15% PES, 42.5% DMaC and 42.5% PEG 200. Under favorable condition, almost 86% of acetic acid was successfully removed from an aqueous phase within 8 hours of extraction using PES membrane support. Meanwhile, PSF and PVDF only able to remove 6% and 38% of acetic acid respectively due to low hydrophobicity and porosity of the support.

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