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Extraction of Glucose by Supported Liquid Membrane using Polyethersulfone Flat Sheet Membrane Support

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ABSTRACT

Sugar is released during biomass hydrolysis together with unwanted inhibitory compounds such as acetic acid, furfural and hydromethylfurfural. The extraction of particular sugar prior to fermentation process is needed in order to increase the yield of biofuel generated from biomass resources. In the current study, glucose was extracted from the aqueous solution using supported liquid membrane (SLM) system. Polyethersulfone (PES) flat sheet membrane support was fabricated using 15 wt.% PES, 42.5 wt.% DMAc and 42.5 wt.% PEG 200. Liquid membrane was formulated using 2-ethyl hexanol and methyl cholate as solvent and carrier, respectively. The effect of several parameters involved in SLM system such as type of diluent and flowrate of feed and stripping phase on the extraction performance of glucose were studied. About 52.77% of glucose was successfully extracted from aqueous solution using SLM system with 0.01M of methyl cholate in 2-ethyl hexanol. Using simulated biomass hydrolysate solution, almost 54.55% of glucose and 51.08% of xylose were successfully extracted using the SLM system.

Keywords: Biomass hydrolysate, supported liquid membrane, glucose extraction

1.0 INTRODUCTION

Lignocellulosic biomass is abundant organic material that can be used for sustainable production of biofuels, bioenergy and value added chemicals [1, 2]. Lignocelluloses are a polymer matrix composed of hemicellulose, cellulose and lignin. Hydrolysis is required in order to release the sugar compounds from the lignocellulose biomass for further conversion through fermentation process. Some inhibitory components also produced during the hydrolysis which hinder the subsequent bioconversion of the solubilized sugars into the desired products. Depending on the types of hydrolysis process selected, the common inhibitory compounds are acetic acid, furfural and hydroxymethylfurfural [3, 4]. The extraction of particular sugar prior to fermentation process is needed in order to remove the inhibitor and to increase the yield of biofuel or chemicals generated from biomass resources.

Various methods have been proposed for separating sugars and inhibitors in biomass hydrolysates such as nanofiltration, reverse osmosis, adsorption and chromatography and reactive extraction. Each of these methods has their own restrictions such as high operating pressure, membrane fouling, low selectivity and high energy consumption [5]. Liquid membrane process has gained much interest and had potential for biomass hydrolysate separation. Liquid membrane consists of organic liquid phase dissolved with suitable carrier, that placed between aqueous feed phase and aqueous stripping phase. The carrier forms a complex with the targeted solute from

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the feed and then facilitated the transport of this complex to the stripping phase. In the stripping phase, targeted solute will be released from the complex and can be recovered. The advantages of liquid membrane process over conventional solvent extraction process are highly selective separation, simplicity of the process, low separation cost, and small amount of organic phase and carrier used in liquid membrane formulation [6].

Two steps emulsion liquid membrane (ELM) process was used by Lee [6, 7] to enrich the xylose in simulated hemicellulosic hydrolysate consist of 100 mmol/dm^3 xylose, 50 mmol/dm^3 acetic acid and 50 mmol/dm^3 sulfuric acid. In the first ELM [6], the acetic acid was removed using an organic liquid membrane consisted of C9232 nonionic polyamine (Infineum UK Ltd.), Span 85 (sorbitan trioleate) and kerosene. The aqueous stripping solution used was NaOH solution. Extraction degree for acetic acid higher than 99% was reported in the first ELM process while xylose and sulfuric acid were retained in the feed phase. Second ELM system was targeting to remove sulfuric acid [7] by using an organic membrane solution of C9232 and Span 85 dissolved in kerosene with Amberlite LA-2 secondary amine (Merck) as an extractant. An aqueous stripping phase for second ELM system was Na_2CO_3 solution. Sulfuric acid was extracted to the stripping phase and the final feed phase become concentrated in the xylose that is suitable for further fermentation to convert to the ethanol. Almost 90% of xylose has been successfully purified by ELM [7]. However, ELM process had a limitation especially with regard to its stability and leakage of the organic phase [8,9].

Supported liquid membrane (SLM) is prefers configuration with regards to the liquid membrane stability and industrial applicability [9]. An organic liquid membrane is imbedded within the porous structure of polymeric membrane support in the SLM system. Different types of carrier were incorporated into the organic liquid phase for selectively transport the targeted sugar through the membrane support. The most common carrier used for sugar extraction are boronic acid derivatives [10, 11] and methyl cholate [12–16]. In order to achieved high carrier concentration in the liquid membrane, typical solvent such as toluene, benzene and xylene were used as the diluent [14]. However, these solvents should be avoided due to their carcinogenic effect. Therefore, methyl cholate carrier was dissolved in a polar and non-carcinogenic organic solvent of 2-ethyl-1-hexanol as an organic liquid membrane in this study. Polyethersulfone (PES) flat sheet membrane was fabricated using phase inversion process and used as the support in the SLM system. The membrane conditioning step before incubating the liquid membrane phase into the membrane support was not required in this study compare to the 44 hours conditioning time practices by Hassoune *et al*. [13]. The membrane can be directly incubated with liquid membrane, thus shortens the preparation of the SLM. The SLM were tested for glucose extraction from aqueous glucose solution and simulated biomass hydrolysate solution.

2.0 METHODS

2.1 Materials

For the preparation of membrane casting solution, PES (RADEL A-300A, Solvay Advanced Polymers, Alpharetta, GA, USA) was used as the base polymer, dimethyl acetamide (DMAc), supplied by Sigma Aldrich (St. Louis, USA), was used as the solvent and polyethylene glycol with average molecular 200 Da

(PEG 200, Merck, Darmstadt, Germany) was used as a nonsolvent pore forming additive.

In organic liquid membrane formulation, methyl cholate (Sigma Aldrich) carrier was dissolved in various solvents. The tested solvents were cyclohexane, cyclohexene, toluene and 2-ethy-1-hexanol. All the solvents were purchased from Sigma-Aldrich. Glucose was purchased from Fluka. Xylose and acetic acid were purchased from Sigma-Aldrich.

2.2 Preparation of Flat Sheet Membrane

Flat sheet membrane support was prepared based on dope composition of 15 weight % PES, 42.5% PEG 200 and 42.5% DMAc. All the components were stirred continuously using overhead stirrer at room temperature until a homogenous polymer solution was formed. The polymer solution was spread over a smooth glass plate with 200 μm gap between the casting knife and glass plate using semi automatic casting machine. The casted gel film was left for air evaporation about 30 seconds before being immersed into warm water of 40°C for about 30 minutes [17]. The hardened membrane were further transferred to another water bath to complete phase separation for 48 hours and then air dried in room temperature.

2.3 Formulation of Liquid Membrane

An organic liquid membrane phase was formulated by dissolving 0.01 M methyl cholate in different tested solvents which are cyclohexane, cyclohexene, toluene, and 2-ethyl-hexanol. PES membrane support was directly impregnated into liquid membrane phase for overnight. Before conducting the SLM run, the membrane was conditioned in pure water bath for 48 hours [15].

2.4 Supported Liquid Membrane System

The schematic diagram for SLM system is shown in Figure 1. Membrane cell was made of two Teflon compartment of equal size with the dimension of 16.5 cm × 10 cm. The supported PES membrane (10.5 cm × 4 cm) was placed between these two compartments. 10 g/L glucose solution and pure water were used as the feed and stripping solution, respectively. The solutions were circulated into the membrane cell by two channel peristaltic pump. The flow rate of the feed and stripping phase was kept identical. The effect of feed and strip phase flowrate was studied at 1.35, 2.07 and 2.79 L/h based on speed of the pump at 25 rpm, 40 rpm and 55rpm, respectively. The SLM was run for 7 hours with 1 ml sample was taken from each phase every hour for analysis. The degree of solute extraction and recovery were calculated using Equation 1 and Equation 2, respectively.

$$\text{Degree of Extraction (\%)} = \frac{C_{fi} - C_{f0}}{C_{fi}} \quad (1)$$

$$\text{Degree of Recovery (\%)} = \frac{C_s}{C_{fi}} \quad (2)$$

where C_{fi} is the initial concentration of solute in feed phase (g/L), C_{f0} is the concentration of solute in feed phase at any time (g/L), C_s is the concentration of solute in stripping phase at any time (g/L). The concentration of single glucose was measured using digital refractometer (Hanna Instruments, Model HI 96803).

The SLM system was also run using simulated biomass hydrolysate containing 4.14 g/L acetic acid, 4.64 g/L glucose and 18.8 g/L xylose. Liquid membrane was formulated from 0.01M

methyl cholate dissolved in 2-ethyl-1-hexanol. The flow rate for both feed and stripping streams was set at 2.79 L/h. The concentration glucose and xylose from the biomass hydrolysate were quantified using Waters carbohydrate column (300 mm ×3.9 mm) connected to Waters Acquity UPLC system with refractive index detector. 5 μL sample was injected to the column and run for 10 min using 75:25 acetonitrile-water as the mobile phase at flow rate 1 mL/min.

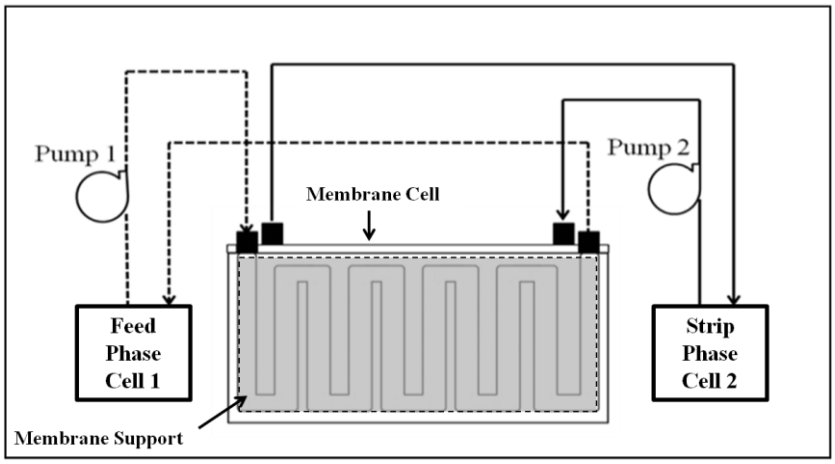


Figure 1 Membrane cell for SLM system with feed phase and stripping stream

2.5 Membrane Characterization

The cross section of the membrane was analysed using ZEISS SEM EVO-50 scanning electron microscopy. The hydrophobicity of the membrane was measured using optical contact angle equipment (CAM 101 optical Contact Angle Meter, KSV Instruments).

3.0 RESULTS AND DISCUSSION

3.1 PES Membrane Support

The separation performance of SLM process is highly depends on the morphological features of the membrane support such as membrane structure, pore size and chemical nature of the polymeric membrane [18]. The good criteria of the membrane support used in SLM process must have several characteristics such as high hydrophobicity, high porosity, acceptable pore size and proper tortuosity [19]. These physical characteristics have greatly influenced the physical stability of membrane support, rate of the mass transfer through the liquid membrane and performance of the separation process. Therefore, phase inversion process by using immersion precipitation technique was chosen in this study in order to produce support membrane with porous structure. PES was chosen as the membrane material due to its advantageous in term of high hydrophobicity and high chemical and thermal stabilities [20].

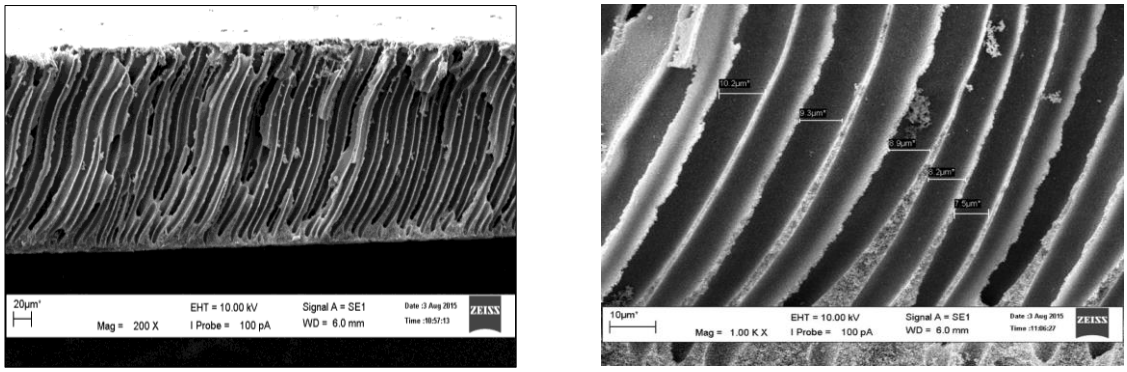
Figure 2 shows the morphology of the PES membrane support visualized by SEM. The support membrane had a porous structure with cylindrical flow through pores that distribute uniformly throughout the membrane (Figure 2 (a)). The diameter of this cylindrical pore was in the micron size as shown by Figure 2(b). Low molecular weight PEG

200 in dope polymer solution was acted as pore forming agent. Large diffusion velocity and high collision frequency of PEG 200 during the phase inversion process resulting large pore size of the membrane [21, 22]. Phase inversion operating conditions such as temperature of coagulation bath and exposure time will also affect the final membrane morphology [23, 24]. High coagulation bath temperature promotes large pores formation [17]. When the coagulation bath temperature increases, the cooling rate decrease and the crystal get enough time to completely grow during the phase inversion (Akbari and Yegani, 2012). In addition, exposure of the casted membrane film to humid air around 30 sec prior to immersion into coagulation bath leads to low transfer rate of water vapor from the humid air into the polymer solution which can reduce the phase separation process, thus enhance the pore formation [23].

Contact angle of the membrane support plays an important role in the stability of SLM system. The membrane support must be hydrophobic in order to prevent any leakage of organic liquid membrane phase that contained inside the membrane support. Hydrophilic membrane support is usually not suitable in SLM system and can lead to organic liquid membrane washed out from the pores and being replace with an aqueous feed or stripping phase [8]. The average contact angle value of the PES membrane support prepared during this study is 92.78°±3.19 based on five samples measurement. This value is considered as normal hydrophobic membrane. The addition of PEG 200 in dope formulation could reduce the PES membrane hydrophobicity by altering the surface morphology of the membrane during phase inversion process [22].

3.2 Effect of Flow Rate on Glucose Extraction

A preliminary experiment was conducted to choose a suitable solvent for dissolving methyl cholate carrier in the organic liquid membrane formulation. The solvents tested were cyclohexane, cyclohexene, toluene and 2-ethyl-1-hexanol. Methyl cholate was not able to dissolve completely in non-polar organic solvent of cyclohexane and cyclohexene and formed a precipitate. Polar solvent of toluene and 2-ethyl-1-hexanol can dissolved the methyl cholate. However, when organic liquid membrane based on toluene was incubated into the PES membrane support, the physical properties of the membrane support was changed. The PES membrane support shrunk, becoming fragile, and easily broken. In addition, toluene is a strong and carcinogenic solvent that can causes adverse health effect and the usage of it should be avoid. Therefore, a polar and non-carcinogenic solvent of 2- ethyl-1-hexanol was selected for the formulation of organic liquid membrane phase for glucose extraction in this study.



(a) (b)

Figure 2 SEM image of PES membrane support under (a) 200× magnification and (b) 1000x magnification

The mass transfer rate of the solute in the SLM process was effected by the flow rate of the feed and strip phase [25]. The degree of glucose extraction at three different feed flow rates was shown in Figure 3. The lowest glucose extraction was observed at the lowest flow rate of 1.35 L/h with 32.5% degree of glucose extraction. Glucose extraction was increased with the increment of the flow rate. During SLM process, a boundary layer was formed near the feed side and membrane interface. The thickness of this layer will be increase if the system was operated under insufficient flow rate. Hence, the solute will have more resistance to transfer from the feed solution into the organic liquid membrane phase at relatively low flow rate. Highest flow rate of 2.79 L/h used was able to improve the degree of glucose extraction significantly to the value of 47.22%. At high flow rate, the boundary layer thickness between the feed and membrane can be reduced and hence promote better mass transfer [26, 27].

3.3 SLM Extraction of Simulated Biomass Hydrolysate

The performance of SLM system was tested using simulated biomass hydrolysate feed solution containing 4.14 g/L acetic acid, 4.64 g/L glucose and 18.8 g/L xylose (Rafiqul *et al*., 2015). Table 1 showed that the degree of glucose extraction from the simulated biomass hydrolysate solution was almost similar with the aqueous glucose feed solution. However, methyl cholate was able to extract glucose and xylose simultaneously from the biomass hydrolysate solution. Although, this SLM system was not able to fractionate glucose-xylose into individual component but it still will be useful to extract sugars component from acetic acid inhibitor that typically found in the biomass hydrolysate. Both glucose and xylose can be recovered back in the stripping phase as shown by the value in Table 1. Ideally, the recovery percentage should be as same as the extraction percentage for good SLM system.

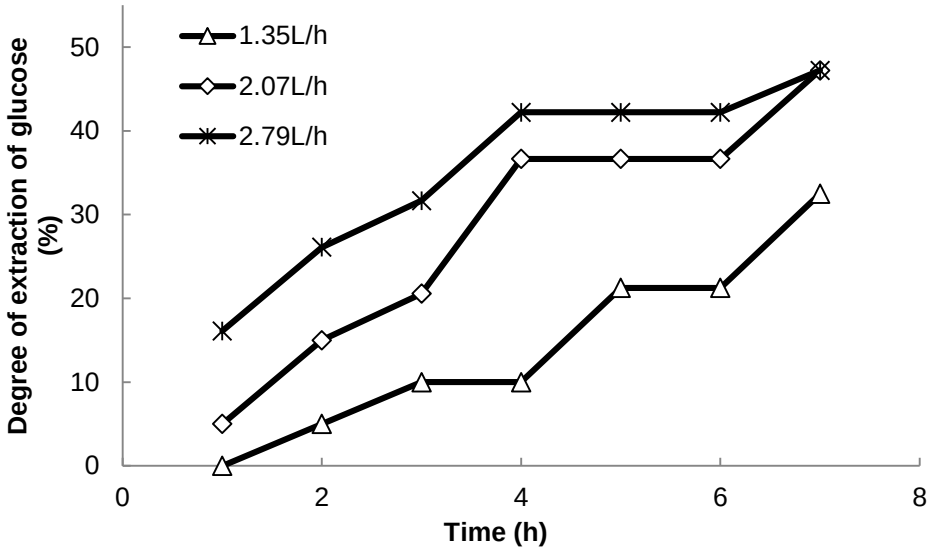


Figure 3 Effect of the feed and stripping flow rates on the degree of glucose extraction

Table 1 Extraction of simulated biomass hydrolysate using SLM system

Time	Glucose		Xylose	
	Feed Phase Extraction (%)	Strip Phase Recovery (%)	Feed Phase Extraction (%)	Strip Phase Recovery (%)
1	10.13	11.71	8.29	7.41
2	17.70	18.43	21.50	19.50
3	32.23	23.24	30.69	25.76
4	39.21	30.77	37.34	32.43
5	47.17	31.02	44.60	35.99
6	48.11	39.65	47.89	40.79
7	54.55	42.16	51.08	42.68

4.0 CONCLUSION

PES flat sheet membrane was fabricated through phase inversion process using 15 wt. % PES, 42.5 % DMAc and 42.5%PEG 200. The membrane was successfully used as the support in the SLM process for extraction of glucose. 0.01 M Methyl cholate dissolved in non-carcinogenic solvent of 2-ethyl-1-hexanol was used as an organic liquid membrane phase in the SLM process. The degree of glucose extraction from aqueous solution and simulated hydrolysate solution were 52.77% and 54.55%, respectively. However, xylose was simultaneously extracted with glucose when simulated hydrolysate was used. Nevertheless, this SLM system can be useful for recovery of sugars component from acetic acid inhibitor in the biomass hydrolysate.

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