Supported liquid membrane for acetic acid extraction: Screening of membrane support preparation factors

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Abstract. It is essential to remove acetic acid from the biomass hydrolysate during the biorefinery process. The product yield can be effected by the acetic acid due to it inhibition to the microorganism used during the fermentation. Supported liquid membrane (SLM) can be used to remove the acetic acid. The membrane support plays important role in the SLM process. However, due to the use of the commercial membrane support, lack of studied was conducted on the fabrication of custom made membrane support for the SLM process. In the current study, two level full factorial design was employed to screen three fabrication factors during preparation of polyethersulfone-graphene membrane support via vapor induced phase separation technique. The factors screened were temperature of water bath (A) (30-60 °C), exposure time (B) (10-60 s) and air humidity (C) (70-90 RH%). The response was evaluated based on the extraction percentage of the acetic acid from 10 g/L aqueous acetic acid feed solution. All three main factors were significant to the SLM performance. Air humidity factor (C) gave the highest contribution of 28.96% among the main factors. In term of the interaction between factors, water bath temperature (A) and exposure time (B) give the most significant effect with 45.01% percentage of contribution. The highest extraction percentage of the acetic acid using SLM system was 75.95% using the membrane prepare at 30 °C water bath temperature, 10 s exposure time and 70% air humidity.

1. Introduction
Energy consumption and demand in the world constantly increased every year due to the continuous development of many countries worldwide and increased growth of the human population. Majority of energy currently used globally is derived from non-renewable sources [1] and almost 80% is provided from the fossil fuel. The main sector that used energy is transportation industry which accounts more than 58% of the total amount of energy produced [2]. However, the supplies of the fossil fuels are limited and will be depleted one day. In addition, some hazard gases were release with the use of fossil fuels, thus give harmful impact to the environment [3]. These concerns have led to increased global attention in supporting the development of alternative energy based on renewable sources.

Recently, production of biofuels especially bioethanol using lignocellulose biomass has gained a lot of attention to overcome the problems of the nonrenewable energy resources. The main component of the lignocellulose biomass which are cellulose, hemicelluloses and lignin can be broke down into sugar component and later can be converted into bioethanol. Hydrolysis is used to release these sugars from the
biomass matrix. However, some inhibitors byproduct also formed along with the sugars during the hydrolysis process. These compounds are considered to be toxic to the fermenting organism used during the bioethanol fermentation process. These inhibitor compounds are mainly grouped into three classes which are furan, phenolic derivatives and weak acids such as formic and acetic acid [4]. Among them, acetic acid was found in significant amount in the biomass hydrolysate [5]. Therefore, it is critical to reduce the level of acetic acid concentration in the biomass hydrolysate to the acceptable level which is less than 5 g/L [6].

Different methods were used to remove acetic acid from biomass hydrolysates in the previous study. Acetic acid can be removed by ion exchange resins, but the resins have limitations in which the pore diffusion is often slow that leads to long processing time [7]. Membrane process such as nanofiltration and reverse osmosis have been investigated to separate acetic acid from hydrolysate under severe operating condition. Although the retentions of glucose obtained is high, but negative retention were observed with acetic acid, thus making it as inefficient method [8,9]. Liquid membrane is a promising technology for the recovery of various carboxylic acids [10]. Supported liquid membrane (SLM) represents one of the feasible types of liquid membrane. It uses a porous membrane support impregnated with complexing carriers to interact specifically with the targeted solute. It use of relatively small volume of organic liquid membrane phase but lead to high separation factor and low energy process [11].

The liquid membrane formulation and the properties of the membrane support are the important aspect of the SLM process. The composition of the liquid membrane phase should be formulated based on the specific interaction between the carrier and the targeted solute. Meanwhile the membrane support should have adequate porosity and hydrophobic to retain the organic liquid membrane within the membrane pore. In addition, the support should be chemically and thermally stable on exposure to the feed, stripping and organic liquid membrane phases. Most of the previous SLM processes are using commercial membrane as their support. Therefore, limited study has been conducted on the fabrication of the custom made membrane support for the SLM process. In this study, vapour induced phase separation (VIPS) method was used to fabricate polyethersulfone (PES) flat sheet membrane support for the SLM process. Small amount of graphene was added into the PES matrix to improve the hydrophobicity, porosity and mechanical properties of the membrane. The morphology and structure of the membrane is heavily dependent on the fabrication process parameters. During VIPS process, the dope polymer solution is transformed from the liquid phase to the solid membrane phase by exchanging the solvent from the control environment to the dope solution. The rate of this phase inversion process will determined the structure of the membrane formed. Therefore, three important VIPS fabrication parameters which are exposure time to non-solvent water vapors, relative humidity and coagulation bath temperature [12] were screen using two-level full factorial design to determine the significant factor toward producing good membrane support for SLM process for acetic acid removal.

2. Material and methods

2.1. Chemicals
The membrane dope solution was made from the mixture of PES (Radel A300, Amoco Chemicals), polyethylene glycol 200 (PEG 200, Sigma Aldrich, St. Louis, MO), dimethyl acetamide (DMAc, Sigma Aldrich), and graphene (Low Dimensional Material Research Centre, Universiti Malaya). The chemical used in liquid membrane formulation were tri-n-octylamine (TOA, Sigma Aldrich) and 2-ethyl-1-hexanol (Sigma Aldrich). Acetic acid (Sigma-Aldrich) and sodium hydroxide (Merck, Darmstadt, Germany) were used as feed and stripping phase, respectively.

2.2. Preparation of dope polymer solution
The base polymer solution of 15 wt.% PES, 42.5 % DMAc, 42.5 % PEG 200 was used. The amount of graphene added to the base polymer solution was 0.1 wt.% relative to the PES content in the dope solution. All the components were mixed continuously at room temperature using motorized stirrer (IKA C-MAG
HS 7) until homogenous dope solution was formed. The air bubbles trapped in the dope solution was removed by degassing the dope in ultrasonic machine for 24 hours.

2.3. Flat sheet membrane casting and factorial screening

Semi-automatic casting machine was used to produce the flat sheet PESgraphene membrane through VIPS process. The casting machine was placed in the closed box equipped with Deerma F430 air humidifier to control the air relative humidity. The dope solution was casted on the glass plate with a casting gap of 380 µm. The casted film was exposed to the humid air at room temperature at specified exposure time and air relative humidity. Then, the cast film was immersed into water coagulation bath at specific temperature to induce solidification process. During solidification process, the casted film changed their color from transparent to white immediately after the immersion into the coagulation bath and detached out from the glass plate after some time. The solidified film was transferred to another water coagulation bath for 24 hours to remove residual solvent and was dried at room temperature for 48 hours [13].

The screening of parameters involved during membrane support preparation was performed using 2³ Full Factorial Design in Design-Expert software (Version 7.1.6, 2008; Stat-Ease, Minneapolis, MN, USA) was used to screen the VIPS fabrication parameters. There parameters was selected as the factor which are temperature of water coagulation bath, exposure time and air humidity. The extraction percentage of acetic acid was set as a response. The screening was based on 2³ Full Factorial Design as shown in table 1. The number of experiment generated for the screening experiment was 14.

| Table 1. Experimental ranges and levels of the factors used in the factorial design |
|-----------------------------------|---------|------|
| Independent variables | Coded symbol | −1 | 0 | +1 |
| Temperature of water coagulation bath (°C) | A | 30 | 45 | 60 |
| Air exposure time (sec) | B | 10 | 35 | 60 |
| Air humidity (%) | C | 70 | 80 | 90 |

2.4. Supported liquid membrane system

The membrane support was impregnated with organic liquid membrane phase for 24 hours. The organic liquid membrane phase was formulated from 0.5 M tri-n-octylamine (TOA) carrier dissolved in 2-ethyl-1-hexanol solvents. SLM system consist of membrane cell made up of two Teflon blocks, two channel peristaltic pump Masterflex L/S, feed channel and strip channel as shown in figure 1. Supported membrane impregnated with the liquid membrane was placed in between these two blocks membrane cell. The feed and stripping phase used in the SLM were 10 g/L of acetic acid and 0.5 M sodium hydroxide, respectively. The flow rate of the feed and stripping phase was set at 75 ml/min and 50 ml/min, respectively at countercurrent flow direction within the system. SLM was operated for 8 h and the concentration of the acetic acid in the feed phase was analyzed using High Performance Liquid Chromatography (HPLC) column.

2.5. High performance liquid chromatography

The concentration of acetic acid in the feed phase samples after the SLM experiments was analyzed to calculate the acetic acid extraction percentage as the response in the screening experiment. Synergy 4µ Hydro-RP 80 (Phenomenex) HPLC column was connected to the Water Acquity UPLC System. The mobile phase and UV detection wavelength were 0.02M potassium dihydrogen phosphate and 221nm, respectively. The percentage of acetic acid extraction was calculated using equation (1).
Acetic Acid Extraction (%) = \frac{c_0 - c_f}{c_0} \times 100\% \quad (1)

Where \(c_0\) and \(c_f\) are the initial and final concentration of acetic acid in the feed phase, respectively.

Figure 1. SLM system

3. Result and discussion

3.1. Design of experiment (DOE) and data analysis

Table 2 shows the response obtained from the SLM experiment. Based on these results, the following mathematical model was derived by the software:

\[
Y = 128.12 - 0.256A - 0.862B - 0.5348C + 2.35 \times 10^{-3}AB - 1.9533 \times 10^{-3}AC + 3.98 \times 10^{-3}BC + 1.0367 \times 10^{-4}ABC
\]

Where \(Y\) is the extraction percentage of acetic acid and the letters A, B, C represent individual factors of temperature of water coagulation bath, air exposure time, and air humidity, respectively.

The relationships between variables were elicited using Pareto chart as shown in figure 2. The significance of the factors and their interactions was obtained by employing “Bonferroni limit” and “t-value limit” test. The effects above the “Bonferroni limit” were almost certainly significant, while effects above the “t-value limit” were possibly significant [14]. The main factors (A, B and C) and interaction of factor AB and BC showed t-value of effect beyond the “Bonferroni limit”. They are the most significant factor and have a positive effect. Interaction of factor ABC sit on the “Bonferroni limit” are considered probably significant. Meanwhile, the factor of AC is considered insignificant as it locates slightly above the “t-value limit”. This factor could be ignored as its contribution effect including small “t-value” will not affect the result of the experiment.
Table 2. Experimental design of removal of acetic acid using $2^3$ full factorial designs

| Run | Values of independent variables | Y (Extraction % of acetic acid) |
|-----|---------------------------------|---------------------------------|
|     | A ($^\circ$C) | B (s) | C (%RH) |                        |
| 1   | 60       | 60    | 90      | 65.90                 |
| 2   | 30       | 60    | 70      | 61.19                 |
| 3   | 30       | 10    | 90      | 65.50                 |
| 4   | 60       | 60    | 70      | 66.70                 |
| 5   | 45       | 35    | 80      | 62.68                 |
| 6   | 45       | 35    | 80      | 62.61                 |
| 7   | 30       | 10    | 70      | 75.95                 |
| 8   | 60       | 10    | 90      | 56.05                 |
| 9   | 45       | 35    | 80      | 63.20                 |
| 10  | 45       | 35    | 80      | 62.45                 |
| 11  | 60       | 10    | 70      | 67.05                 |
| 12  | 30       | 60    | 90      | 57.83                 |
| 13  | 45       | 35    | 80      | 62.76                 |
| 14  | 45       | 35    | 80      | 62.91                 |

Analysis of variance (ANOVA) was conducted to examine the reliability of the model. Based on table 3, the regression model had a high coefficient of determination ($R^2 = 0.9988$), implying that 99.88% of the variations in acetic acid extraction can be explained by the model and the model does not explain only 0.12% of the variations. The model F-value which is 570.80 implies the model is significant and there is only 0.01% chance that model F-value this large could occur due to noise. Besides, values of p-value less than 0.05 indicate model terms are significant. In this case, all of the factors are significant in the model term. The adequate precision for the ANOVA was obtained to be 95.084, which is favorable. The preferred
value for adequate precision is >4 [15]. The lower coefficient of variation (CV % = 0.41) which is less than 10% clearly demonstrated that the deviations between actual and predicted values were low and affirmed the precision and reliability of conducted experiments.

Table 3. Analysis of variance model

| Factor | Degrees of freedom | Sum of squares | Mean of squares | F value | p value |
|--------|--------------------|----------------|----------------|---------|---------|
| Model  | 7                  | 272.25         | 38.89          | 570.80  | < 0.0001|
| A      | 1                  | 2.84           | 2.84           | 41.74   | 0.0013  |
| B      | 1                  | 20.90          | 20.90          | 306.71  | < 0.0001|
| C      | 1                  | 81.98          | 81.98          | 1203.23 | < 0.0001|
| AB     | 1                  | 127.44         | 127.44         | 1870.37 | < 0.0001|
| AC     | 1                  | 0.51           | 0.51           | 7.41    | 0.0417  |
| BC     | 1                  | 37.37          | 37.37          | 548.43  | < 0.0001|
| ABC    | 1                  | 1.21           | 1.21           | 17.74   | 0.0084  |

3.2. Main effect analysis

Table 4 shows the percentage contribution of main factor and their interaction with other factors during preparation of membrane support for the extraction of acetic acid via SLM process. As shown in Table 4, air humidity factor (C) gave the highest contribution of 28.96% among the main factor. In VIPS, the relative humidity is a very important parameter that influence the structure of the membrane formed. The vapor humidity greatly influenced the hydrophobicity of the membrane surface in the VIPS process, thus affecting the SLM process [16]. Low relative humidity will form dense skin on the membrane surface resulting in low pure water permeation flux. In contrast, high relative humidity will result in cellular structure that has high pure water permeation flux [16].

Table 4. Percentage contribution of each factor and their interaction

| Factor         | Contribution (%) |
|----------------|------------------|
| A Water bath temperature | 1.00             |
| B Air exposure time     | 7.38             |
| C Air humidity          | 28.96            |
| AB                  | 45.01            |
| AC                  | 0.18             |
| BC                  | 13.20            |

*AB: Water bath temperature and air exposure time
*AC: Water bath temperature and air humidity

The second highest contribution for the main factor was air exposure time with 7.38% contribution. Dense film will be formed at long exposure time [17]. Low exposure time will form cellular opening structure, hence membrane with low pure water permeation flux and rejection capabilities will be produced. The last factor with 1.00% contribution was water bath temperature. Although the percentage of contribution is low, Xu et al. [18] reported that the increase in the coagulation water bath temperature resulted in great formation of macrovoids. This produces more porous structure in accommodate more organic liquid phase, thus can increase the extraction percentage in the SLM process.
3.3. Interaction between factors

The interaction between factors of water bath temperature (A) and air exposure time (B) contributed to the 45.01% of the proposed model. The interaction graph between factors AB was illustrated in Figure 3. At high water bath temperature of 60 °C, the extraction of acetic acid increased from 62% to 66% when the exposure time increased from 10 s to 60 s. Factor A and B were interact at water bath temperature of 50 °C. High water bath temperature results in greater formation of the macrovoids and more porous structure was formed [18]. In addition, complete vapor-induced phase separation occurred at high air exposure time that increased the pore formation [17]. High porosity membrane support can accommodate more liquid membrane organic phase, thus increases the percentage removal of acetic acid.

The second highest interaction effect with 13.20% contribution was the interaction between air exposure time (B) and air humidity (C). The interaction between these factors was illustrated in Figure 4. High percentage of extraction of acetic acid (72%) was obtained from the membrane prepared at 10 s exposure time and 70% relative humidity. As the relative humidity was decreased, membrane with dense skin was formed and hydrophobicity of the membrane was improved. This will lower the pure water permeation flux, thus increase the extraction of acetic acid [16].

As shown in Pareto chart previously, the interaction effect of factor water coagulation bath (A) and air humidity (C) is insignificant. The interaction of these factors to the acetic acid extraction was shown in Figure 5. The line for both factors are parallel and were not intercept with each other even at wide range of factor. An increment for both factors will result in low extraction of acetic acid, thus proving that both factors are insignificant.

![Interaction graph between water bath temperature (A) and exposure time (B).](image)
4. Conclusion

FFD was successfully applied for screening of the important factors involved during VIPS process for the preparation of PES graphene membrane support in SLM system. All the main factors played important role on the membrane formation. The air humidity factor (C) gave the highest contribution of 28.96% among the main factor. The interaction effects of the water bath temperature with exposure time (AB) were the most significant with 45.01% contribution. Meanwhile, the interaction effect of water bath temperature (A) and air humidity (C) is insignificant as extraction of acetic acid decrease as both factors were increased. The highest extraction percentage for the acetic acid using SLM system was 75.95% which is using the membrane prepare at 30°C water bath temperature, 10 s exposure time and 70% air humidity.
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