Pervaporation of Ethanol/Water Mixtures using Bacterial Cellulose-Poly(Vinyl Alcohol) Membrane

Supaporn Jewprasat, Theerawat Suratago, and Muenduen Phisalaphong*

***Abstract*—**The composite membranes composed of bacterial cellulose (BC) and poly(vinyl alcohol) (PVA) were developed for dehydration of ethanol by pervaporation. BC film was modified by immersing BC in 10% (w/v) PVA solution followed by cross-linking with glutaraldehyde. The degree of swelling of the composite membrane in water was significantly higher than that in ethanol, which was due to the presence of the hydrophilic BC and PVA. The permeate flux and selectivity were studied as a function of temperature. When temperature was increased, the total permeation flux increased, while the selectivity decreased. The selectivity toward water and permeate flux at feed solution of 95 wt% ethanol aqueous solution of 30 °C were 125 and 73 g/m^2h, respectively.

***Keywords*—**Membrane, Pervapoarion, Bacterial Cellulose, Poly(vinyl alcohol).

I. Introduction

THE productions of ethanol from fermentation processes have a low ethanol concentration (9-12% v/v). Distillation is used to increase ethanol concentration from fermentation broth. However the problem in distillation of ethanol-water mixtures is ethanol and water form a homogeneous minimum-boiling azeotrope of 95.6 wt% alcohol and cannot be further purified by distillation.

Pervaporation is a membrane separation technology with high selectivity, efficiency and low energy consumption which can be used to separate azeotropic and close-boiling temperature mixtures or dehydrate temperature-sensitive products [1]. Pervaporation is a separation process involving the partial vaporization of a liquid mixture through a dense membrane whose downstream side is usually kept under vacuum.

There are three kinds of pervaporation membranes: (a) hydrophilic membranes, (b) hydrophobic membranes and (c) organophilic membranes. Hydrophilic membranes can be used for the dehydration of ethanol/water mixtures. The membranes are made of many kinds of hydrophilic polymers [2]. Cellulose nanocomposites have been successfully employed as pervaporation membranes. Recently, cellulose nanofibrous membranes synthesized by bacteria, namely bacterial cellulose (BC) has been studied for use in pervaporation. BC produced by Acetobacter species, displays unique properties, including high water absorption capacity, high mechanical strength, high crystallinity and an ultra-fine and highly pure fibre network structure [3].

BC membrane has been examined for the pervaporation of binary ethanol-water mixtures. It was found that for ethanol/water binary system, the permeate flux was high but the selectivity was fairly low [1]. Poly(vinyl alcohol) (PVA) is one of the important membrane pervaporation materials for the dehydration of organic mixtures owing to its good chemical stability, film-forming ability and high hydrophilicity, especially high water permselectivity in pervaporation separation of aqueous ethanol solutions[4]. However, PVA easily swells in aqueous solutions, and this usually results in a decrease in the water permselectivity of PVA membranes [5]. To improve the membrane stability and permeation properties, the PVA membranes were cross-linked with an organic chemicalsuch as glutaraldehyde, polyacrylic acid and tetraethoxysilane. Glutaraldehyde is frequently used to crosslink PVA membranes to enhance water permselectivity [6].

To improve the pervaporative performance of BC membrane, in this study, BC membrane was modified by immersing BC in PVA solution followed by cross-linking with glutaraldehyde solution.

II. Materials and methods

A. Microbial strains

Acetobacterxylinum, AGR60, was isolated from nata de coco. The stock culture was kindly supplied by PramoteTammarat, the Institute of Food Research and Product Development, Kasetsart University, Bangkok, Thailand.

B. Preparation of culture media and membranes

The medium for the inoculum was coconut-water supplemented with 5.0%sucrose, 0.5% ammonium sulfate and 1.0% acetic acid. The medium was sterilized at 110°C for 5 mins. Precultures were prepared by a transfer of 50 ml stock

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culture to 1000 ml in 1500 ml bottle and incubated statically at 30 °C for 7 days. After the surface pellicle was removed, a 5% (v/v) preculture broth was added to sterile medium and statically incubated at 30°C for 7 days in a Preti-dish.

All sample membranes were first purified by washing with deionized water and then was treated with sodium hydroxide at room temperature to remove bacterial cells followed by a rinse with 1% (w/v) acetic acid and deionized water and until pH came to 7. The BC hydrogel was then immersed in 10% (w/v) PVA solution. After approximately 7 days, the BC hydrogel was saturated with PVA solution. Saturated BC was washed with deionized water and air dried at room temperature. Afterthat, the membrane was cross-linked with 0.1% (w/w) glutaraldehyde follow by washed with deionized water. Next, the BC-PVA membrane was air-dried at 30 °C and stored in plastic film at room temperature.

C. Pervaporation experiment

A schematic diagram of pervaporation experiments is shown in Fig. 1. It consisted of a stirred batch reactor where the feed solution was contained in it. The upper part of the reactor holds the feed solution at atmospheric pressure, and the lower part holds the membrane. The feed solution was kept vigorously stirred during the pervaporation by a magnetic stirrer. The reactor was provided with an inlet port for temperature measurement.

The permeate was condensed and collected in a liquid nitrogen trap.The permeate pressure was kept below 10 mmHg. The concentration of ethanol in the feed solution was 95 %wt. The studyfor the effects of temperature was performed in the range of 30, 40 and 50 °Cand the permeation rate was determined from the weight of the collected samples. The permeation flux(g/m²h) was calculated by

$$J = \frac{Q}{A \cdot t} \qquad (1)$$

where, Q (g) is the total mass permeated in time t (hour) and A (m²) is the effective membrane area. Selectivity is calculated as the ratio of the permeable component in the permeate divided by the respective ratio in the feed. The selectivity is calculated using the following equation:

$$\alpha = \frac{(Y_W / Y_E)_{permeate}}{(X_W / X_E)_{feed}} \qquad (2)$$

where, Y_W, Y_E, X_W and X_E are the weight fractions of water and ethanol in the permeate and feedsolutions, respectively. The higher value of α is the greater degree of separationtoward water offered by the membrane. As $\alpha \to \infty$, the membrane tends towards being super selective [7].

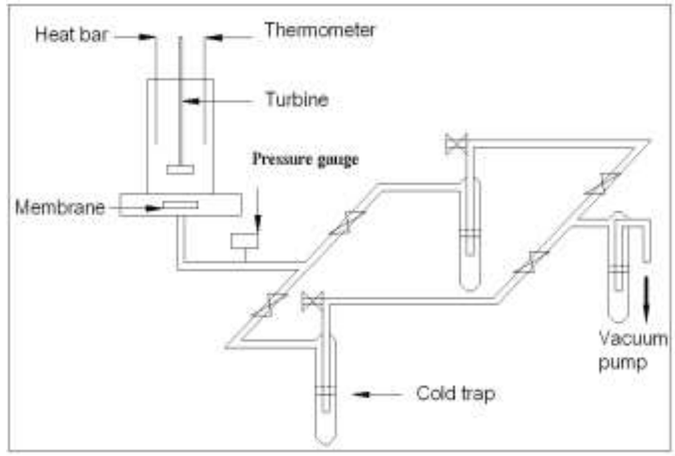

Fig. 1 Schematic diagram of the pervaporation system [8]

D. Characterization of membranes

The degree of swelling of membranes was determined by immersing the dried membrane in distilled water and in absolute ethanol solution (≥99.5% (v/v)) at room temperature until equilibration. The membrane was then removed from the water and ethanol solution. After that, the surface of the membrane was blotted out with tissue paper, the weight of the swollen membrane was measured and the procedure was repeated until there was no further weight change. The degree of swelling was calculated using the following formula:

$$Swelling\,(\%) = \frac{W_w - W_d}{W_w} \times 100 \quad (3)$$

where, W_w and W_d are the weights of wet and dry membranes, respectively.

III. RESULTS AND DISCUSSION

A. The degree of swelling

The swelling behaviors of the membranes can infer the ability of a membrane to specifically absorb the liquid. The swelling degrees of the BC-PVA membranes in both pure water and absolute ethanol are shown in Fig. 2 and Fig. 3 respectively. From Fig. 2, it is observed that the degree of swelling of the BC-PVA membranes in pure water remarkably increases during 1-3 hours and slightly increased during 3-6 hours. The results from Fig. 3 showed that the degree of swelling of the BC-PVA membranes in ethanol gradually increased during 1- 4 hours and the equilibrium was reached after 4 hours. Under equilibrium conditions, the degree of swelling of the membrane in ethanol and in water were approximately 16% and 290%, respectively.

The results from Fig. 2 and Fig. 3 showed that the degree of swelling of membrane in water was considerably higher than that in ethanol. This indicates that the membranes have more affinity to water, which is due to the presence of the hydrophilic BC and PVA in the composite film.

Previoulsy, it has been reported that the degrees of swelling of both BC and PVA membranes increase with increasing water content because both BC and PVA membranes are hydrophilic in nature and sorb more water than ethanol [1,15].

Likewise, the BC-PVA membrane is hydrophilic. It has greater affinity towards water than ethanol. The BC-PVA membrane also showed good stability in water and ethanol, therefore, it has the potential to be applied as a membrane for the pervaporation dehydration of ethanol–water.

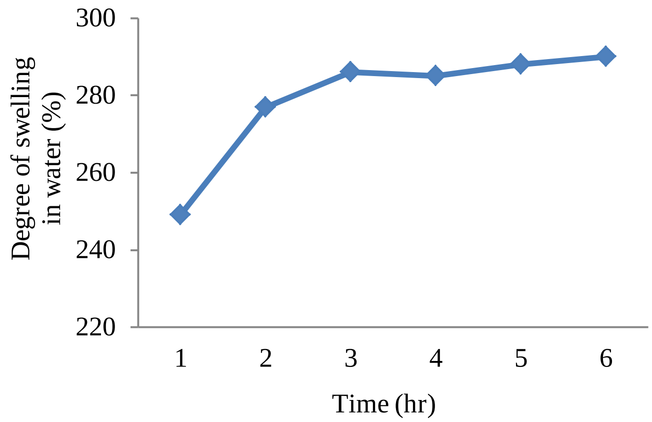

Fig. 2 The degree of swelling in water of the BC-PVA membranes as a function of time

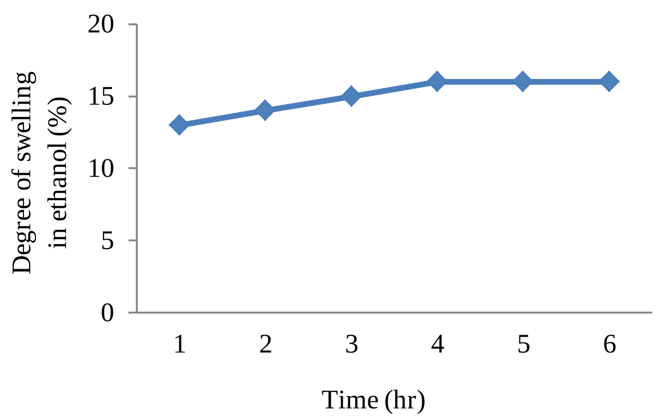

Fig. 3 The degree of swelling in absolute ethanol of the BC-PVA membranes as a function of time

B. The effect of temperature on permeate flux and selectivity

The pervaporation process is known to be temperature dependent as both flux and selectivity are influenced by the change in temperature [9-12]. The influences of feed temperature on pervaporation performances of the crosslinked BC-PVA composite membrane for the dehydration of an ethanol-water (95/5 weight) are shown in Fig.4.

As expected, when temperature was increased, the total permeation flux increased, while the selectivity decreased. From Fig. 4, it was observed that the total permeate flux increased from 73 g/m^{2}h at 30 ◦C to 130g/m^{2}h at 50 ◦C and the selectivity simultaneous decreased from 125 to 31. This phenomenon occurred because the temperature affected the transport of components in the liquid feed and in the membrane. Both mass transfer coefficient of components in the liquid and sorption of components into the membrane increase with increasing feed temperature [13]. In addition, the polymer chains were more flexible at higher temperature and caused larger available free volume of polymer matrix for diffusion [9,10]. The latter effect also causes the decrease in selectivity as the diffusivity of both the permeants is enhanced [14]. Therefore, the selectivity decreased with increasing temperature. The similar results were previously reported in the pervaporationstudy by BC membranes [9,10].

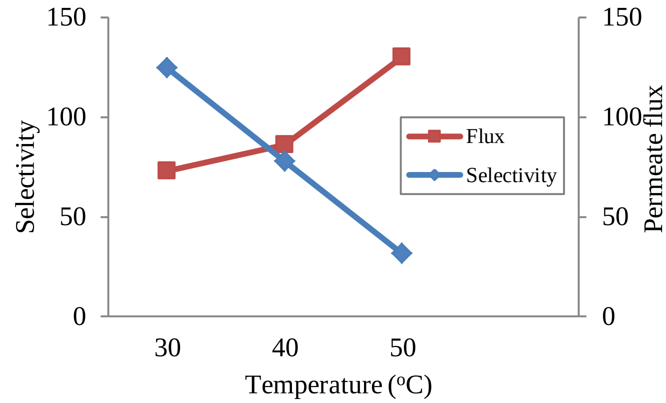

Fig. 4 The effect of temperature on total permeate flux and selectivity

IV. Conclusion

The BC-PVA composite membrane was prepared for the dehydration of ethanol–water solutions by the pervaporation process. The swelling degree of the composite membrane in water and ethanol and the effect of temperature on total flux and selectivity were discussed.

Based on the experimental results, the degree of swelling of the BC-PVA membranes in water and ethanol increases over time for about 4-6 hours. The degree of swelling of the membrane in water was considerably higher than that in ethanol. Under equilibrium conditions, the degree of swelling of the membrane in water was about 18 times of that in ethanol. From the study of the influences of feed temperature on pervaporation performances of the membrane for the dehydration of 95% ethanol, with an increase of the feed temperature from 30 ◦C to 50 ◦C, the permeation flux of the BC-PVA composite membrane increased but the selectivity decreased. The selectivity toward water and permeate flux at feed solution of 95% ethanol at 30 °C were 125 and 73 g/m^{2}h, respectively.

The developed BC-PVA composite membrane isexpected to have potential applications in membraneseparation processes.

V. Recommendations

Based on this study, further studies for the improvement of BC film for pervaporation are recommended.

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