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Pervaporation of aqueous dilute 1-butanol, 2-propanol, ethanol and acetone using a tubular silicalite membrane

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ABSTRACT

Pervaporation is a promising method to recover bio-alcohols from fermentation broths because of its high energy-saving potential. A silicalite membrane was prepared and applied to the pervaporation separation of 1-butanol, 2-propanol, ethanol and acetone from dilute aqueous solutions. In feed solvent concentrations in the range of 0.5−5.0 wt.%, the solvent flux of ethanol, 2-propanol and acetone increased with the increase of feed concentration, whereas 1-butanol flux was not greatly influenced by the feed concentration. In contrast to other solvents, the separation factor for 1-butanol solution decreased with the increase of feed 1-butanol concentration. This is because 1-butanol concentration in the permeate did not increase along with the increase of the feed 1-butanol concentration due to adsorption saturation. The solvent flux increased with the increase of separation temperature for all the solvents. The separation factor of 1-butanol and 2-propanol increased with the increase of separation temperature in the range of 30−60°C, while the separation factor of acetone and ethanol was not greatly influenced by the separation temperature. Silicalite membrane shows higher selectivity toward 1-butanol solutions than silicone membrane when the feed concentration is low and the temperature is high.

Keywords: Pervaporation; Silicalite membrane; Separation factor; Bio-butanol; Permeate flux; Silicone membrane

1. Introduction

Utilization of renewable and non-edible biomass resources greatly contributes to reducing dependence on fossil resources, and as a result will lead to the reduction of CO_2 emissions related to global warming. Of particular interest are bio-alcohols such as ethanol and butanol, which can be used both as liquid fuels and as feedstock [1]. Bio-ethanol is generally produced at a concentration of about 10 wt.% from fermentative sugars such as glucose and sucrose, while bio-butanol is generally produced at below 2 wt.% [2,3]. Butanol has some merits over ethanol, e.g., high energy density, miscibility with diesel fuel, and a low vapor pressure [4]. Moreover, butanol-producing bacteria can ferment pentoses such as xylose and arabinose, which originate from cellulosic biomass [2] and cannot be converted into ethanol by natural yeasts. Therefore, establishing an efficient methodology for producing bio-butanol has been a recent focus of research [5]. Low butanol concentration solutions are generally refined by distillation. However, distillation for this application is energy-ineffective. For example, the energy requirement for purification of butanol from 5 to 790–810 g/l was calculated to be 24.2 MJ/kg-butanol [6] when steam stripping distillation was used. This value corresponds to about 70% of the heat value of butanol.

In order to overcome this problem in the purification process, other separation methods, including adsorption and gas-stripping, have been applied and evaluated. Among the separation methods applied to

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butanol separation, pervaporation (PV) is one of the most promising methods to concentrate butanol with low energy requirements [7]. In typical PV of alcoholic solutions, hydrophobic organic/inorganic membranes are used. We have recently reported that it is possible to separate ethanol selectively from a yeast fermentation broth as well as from the binary mixtures of ethanol/water using silicone rubber-coated silicalite membranes [8].

In the present study, the potential of PV using a silicone rubber-coated silicalite membrane for producing highly concentrated 1-butanol solutions was investigated and compared to PV performance using a silicone rubber membrane, which is generally used for this purpose. The PV performance of the silicalite membrane was also measured for acetone, ethanol and 2-propanol solutions, which are the solvents produced by *Clostridium* strains as byproducts of ABE fermentation.

2. Experiments

2.1. Membranes and pervaporation measurements

A tubular silicalite membrane was prepared on a tubular porous sintered stainless-steel support (outside diameter: 10 mm, length: 100 mm, and pore size: 2 μm). At first, the outside surface of a tubular porous stainless-steel support was coated with the silicalite seed crystals by electrophoretic deposition (EPD). The silicalite membrane was prepared on the support surface after hydrothermal synthesis of the seeded support in an autoclave. The obtained membrane was calcined at 375°C. The details of the EPD and hydrothermal synthesis conditions have been previously described [9]. The prepared membrane was coated with two types of silicone rubber according to our previous report [10]. A commercially available silicone rubber sheet was also used in order to compare with the pervaporation performance exhibited by the silicalite membrane. Batch pervaporation experiments using the tubular silicalite membrane were carried out at 30–60°C with homogeneous agitation at 500 rpm in an apparatus described previously [10]. The inside of the tubular membrane was kept under vacuum, and the permeated vapor through the membranes was collected in a liquid nitrogen cold trap. The working volume of the vessel was 1400 cm^3, and the effective surface area of the silicalite membrane installed in the apparatus was 28.3 cm^2. Batch pervaporation experiments using a commercially available silicone flat membrane of 50 μm thickness and 14.5 cm^2 effective surface area were carried out in an apparatus described previously, using a vessel with a working volume of 400 cm^3 [11]. All experimental data were obtained at steady state.

2.2. Analysis

Concentrations of 1-butanol, ethanol, acetone and 2-propanol both in the feed and in the permeate were determined by a gas chromatograph equipped with a thermal conductivity detector and a 1 m packed column of Gaskuropack 56 (GL Sciences Inc., Tokyo, Japan). When the permeate separated into two phases, the condensate was diluted with water, generating a single phase, before analysis.

3. Results and discussion

3.1. PV with silicalite membrane

The effect of feed concentration on PV performance of a silicalite membrane was investigated for aqueous binary solutions of 1-butanol, 2-propanol, ethanol and acetone. Fig. 1 shows the solvent flux versus feed concentration at 30°C in the range of 0.5–5.0 wt.% of feed concentration. The flux of 2-propanol, ethanol and acetone increased with the feed concentration in the experimental range, while the 1-butanol flux remained at an approximately constant value in the feed concentration range of 0.5–4.0 wt.%. Fig. 2 shows the separation factor versus feed concentration for each of the four solvents at 30°C. The separation factor is an index of membrane selectivity and is defined by [($C_{solvent}/C_{water}$) in permeate]/[($C_{solvent}/C_{water}$) in feed], where C is the weight fraction of solvents or water. The separation factor of 2-propanol

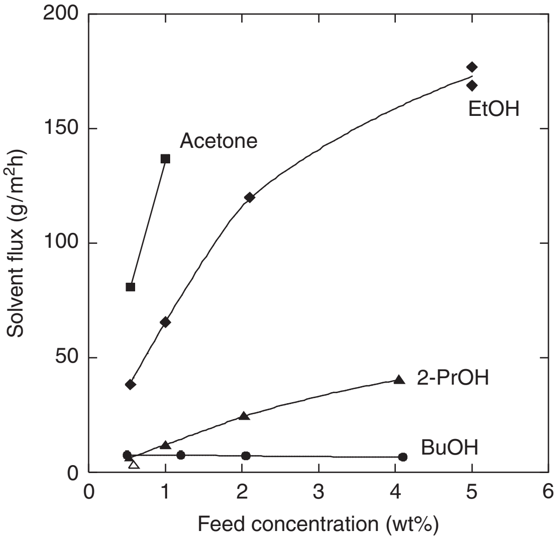

Fig. 1. Effect of feed concentration on solvent flux for the pervaporation of binary aqueous solutions of 1-butanol, 2-propanol, ethanol and acetone using a silicalite membrane at 30°C.

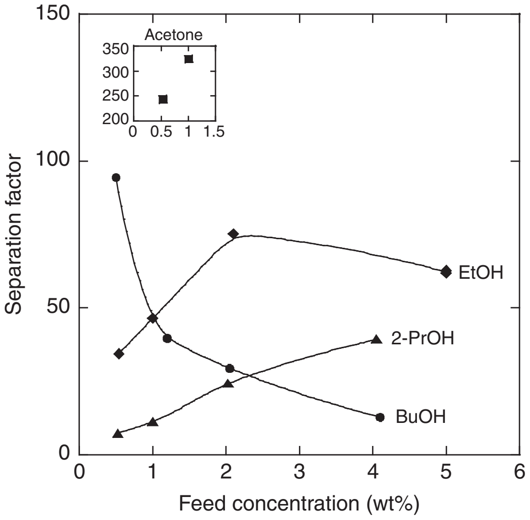

Fig. 2. Effect of feed concentration on separation factor for the pervaporation of binary aqueous solutions of 1-butanol, 2-propanol, ethanol and acetone using a silicalite membrane at 30°C.

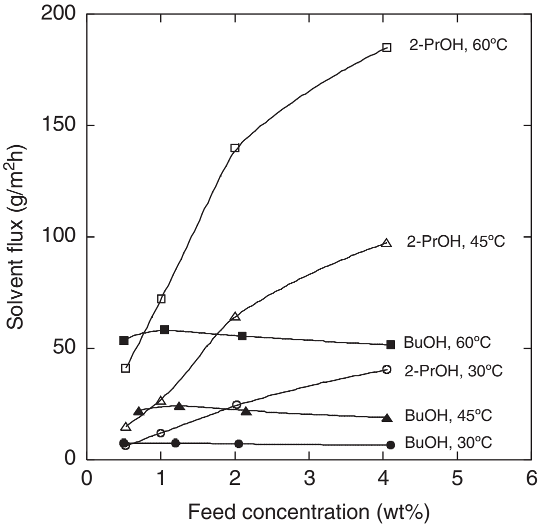

Fig. 3. Solvent flux versus feed concentration for the pervaporation of binary mixtures of 1-butanol/water and 2-propanol/water using a silicalite membrane at 30, 45 and 60°C.

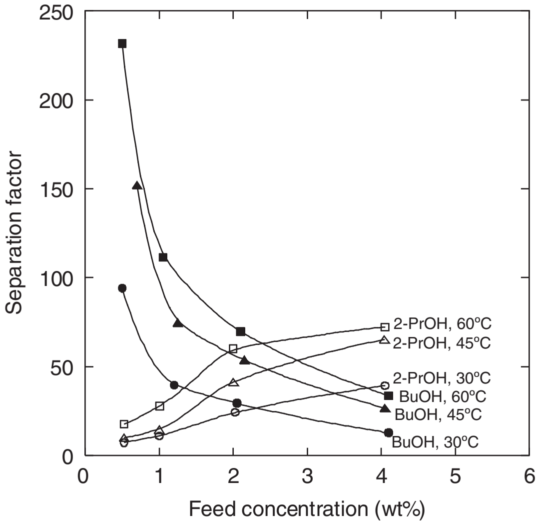

Fig. 4. Separation factor versus feed concentration for the pervaporation of binary mixtures of 1-butanol/water and 2-propanol/water using a silicalite membrane at 30, 45 and 60°C.

and acetone solutions increased with the feed concentration, while the separation factor of ethanol solution showed a maximum value around 2 wt.% of the feed concentration. On the other hand, the separation factor of 1-butanol solution decreased with the increase of feed concentration in the range of 0.5–4.0 wt.%. The decrease of separation factor for 1-butanol solutions is due to the low dependency of the permeate 1-butanol concentration with the feed 1-butanol concentration. Considering that the transportation mechanism in PV through membranes can be described by the sorption-diffusion model [12], this result suggests that 1-butanol adsorption on the silicalite membrane should be saturated even at 0.5 wt.% of butanol feed solution. This view is supported by the adsorption isotherm of 1-butanol on high-silica zeolites, which shows stronger affinity between high-silica zeolites and 1-butanol compared with the affinity between the zeolites and ethanol/acetone [13,14].

Fig. 3 shows the solvent flux versus feed concentration for the PV of binary mixtures of 1-butanol/water and 2-propanol/water using a silicalite membrane at 30, 45, and 60°C. The solvent flux through the silicalite membrane increased with the increase of separation temperature for all the solvents used. This is because the vapor pressure of each solvent, which is the driving force for transportation in PV, increased with the increase of temperature. Fig. 4 shows the separation factor versus feed concentration for the PV of 1-butanol/water and 2-propanol/water using a silicalite membrane at 30, 45, and 60°C. The separation factors for the PV of 1 wt.% acetone/water solution were 324, 321 and 271 at 30, 45 and 60°C, respectively. The separation factors for the PV of 5 wt.% ethanol/water solution were 62 and 63 at 30 and 60°C, respectively. The separation factor for the PV of both 1-butanol/water and 2-propanol/water increased with the separation temperature in the range of 30–60°C, while the separation factors for acetone/water and ethanol/water were not influenced greatly by the separation temperature. The increase of separation factor with the increase of temperature observed for the PV of 1-butanol/water and 2-propanol/water indicates that the flux of 1-butanol and 2-propanol through the silicalite membrane is more sensitive to the temperature than the water flux. The PV flux of 1-butanol at 0.5 wt.% of feed concentration changed from 7.4 g/m^2 h at 30°C to 53.6 g/m^2 h at 60°C, while water flux changed from 15.5 g/m^2 h at 30°C to 46 g/m^2 h at 60°C.

In the PV process, desorption of molecules from membrane to vapor occurs on the permeate side, and this step may affect the selectivity between 1-butanol and water. Desorption behavior on silicalite crystals was reported to be different between 1-butanol and water, where water is desorbed from silicalite at a lower temperature than 1-butanol [14]. This result shows that the PV separation using silicalite membranes at high temperature is preferable for 1-butanol recovery from dilute solutions [15].

3.2. PV separation with silicone membrane

Fig. 5 shows 1-butanol flux versus feed concentration for the PV using a silicone membrane at 30 and 60°C in the feed range of 0.5–6 wt.%. In contrast to the results with silicalite membrane, the 1-butanol flux through the silicone membrane increased with feed concentration in the experimental range. A higher separation temperature also led to higher 1-butanol flux. The silicone membrane also showed higher 1-butanol flux at the same temperature and feed concentration in the feed concentration range of more than 1.0 wt.%. Fig. 6 shows the separation factor versus feed concentration for the PV of 1-butanol/water using a silicone membrane at 30 and 60°C in the feed range of 0.5–6 wt.%. The separation factor was not influenced greatly by the separation temperature, differing from the silicalite membrane.

To compare the PV performance of a silicalite membrane with a silicone membrane, the relationship between permeate 1-butanol concentration and feed 1-butanol concentration for both membranes is shown in Fig. 7. This figure clearly shows that the silicalite membrane gives higher permeate 1-butanol concentration than the

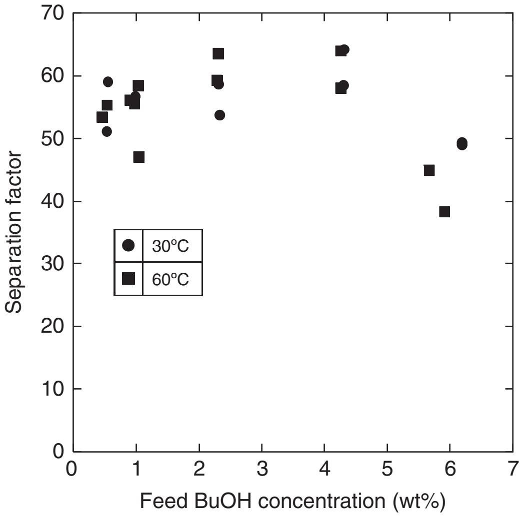

Fig. 6. Separation factor versus feed butanol concentration for the PV of 1-butanol/water using a silicone membrane at 30 and 60°C.

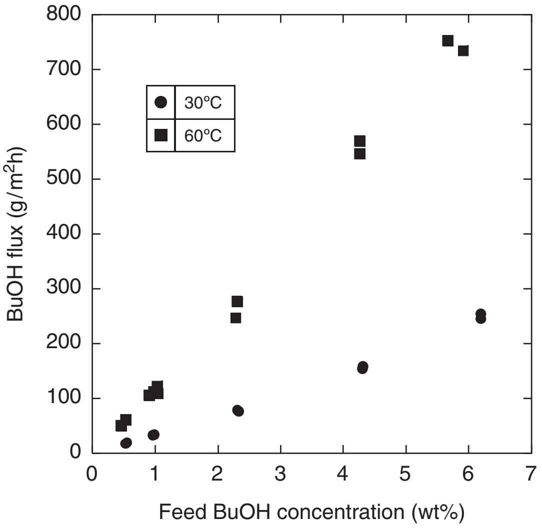

Fig. 5. Butanol flux versus feed butanol concentration for the PV of 1-butanol/water using a silicone membrane at 30 and 60°C.

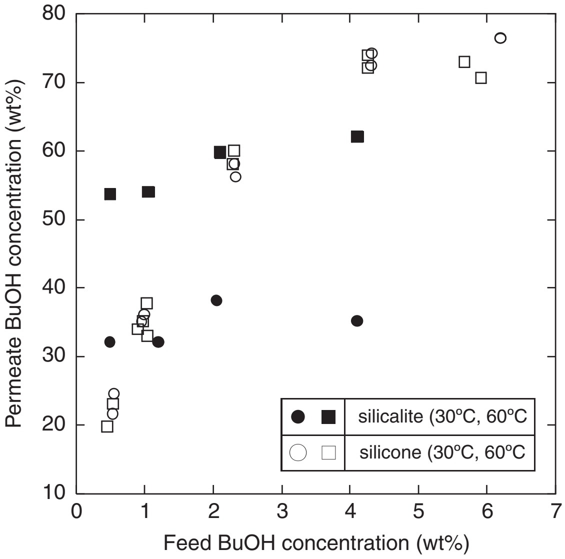

Fig. 7. Comparison between silicalite and silicone membranes for 1-butanol concentration from dilute solutions by pervaporation.

silicone membrane when the feed concentration is low and the temperature is high. Considering that 1-butanol concentration in typical ABE fermentation broths is usually below 1.5 wt.%, the silicalite membrane has greater potential to recover 1-butanol from the dilute solutions.

4. Conclusions

PV performance of a silicalite membrane was investigated for the separation of 1-butanol, 2-propanol, ethanol and acetone from dilute aqueous solutions. In the range of feed solvent concentration of 0.5–5.0 wt.%, the solvent flux of ethanol, 2-propanol and acetone increased with the increase of feed concentration, while 1-butanol flux was not greatly influenced by the feed concentration. This is because 1-butanol adsorption on the silicalite membrane should be saturated even at 0.5 wt.% of 1-butanol feed solution. Both flux and separation factor for the PV of 1-butanol/water increased with the increase of separation temperature in the range of 30–60°C. The increase of separation factor with the increase of temperature can contribute to the difference in desorption behavior with silicalite between 1-butanol and water. Silicalite membrane showed better PV performance than silicone membrane for the recovery of 1-butanol from aqueous solutions when the feed concentration was low and the temperature was high.

Acknowledgement

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