

Hydrophobic Al₂O₃ Membrane for Sucrose Concentration via Vacuum Membrane Distillation System

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Hydrophobic Al₂O₃ membranes were prepared by grafting C₆F₁₃C₂H₄Si(OC₂H₅)₃ molecules, and then applied to a vacuum membrane distillation (VMD) system for concentration of sucrose solution as a model solution of fruit juice. The effects of sucrose concentration and solution temperature on the VMD performance were discussed. By exposing the surface side of the tube membrane to an aqueous solution of 10 wt% sucrose at 60°C and applying vacuum at the inner side of the Al₂O₃ tube to a pressure of 0.5 kPa, permeation flux of over 7 kg m⁻² h⁻¹ was attained through the hydrophobic Al₂O₃ membrane with asymmetric structure. A mathematical model based on Knudsen and Knudsen-viscous models revealed that the permeance of the asymmetric membrane depends on that of the substrate layer, due to its thickness of 1.47 mm.

Introduction

To reduce the storage and shipping costs, and to achieve longer storage, fruit juices are usually concentrated by multi-stage vacuum evaporation. This process results in a loss of fresh juice flavors, and color degradation due to the thermal effects. Since consumers generally prefer the flavor, aroma, appearance and mouth feel of freshly squeezed juices, great effort has been devoted to develop new techniques for retaining such characteristics of freshly squeezed juice in the concentrate, and ultimately in the reconstituted juice.

Membrane distillation (MD) is a relatively new process that is being investigated worldwide as a low-cost and energy-saving alternative to conventional separation processes such as conventional distillation and reverse osmosis (Lawson and Lloyd, 1997). The idea started in 1967 in the United States when Findley (1967) suggested a new separation method based on evaporation through microporous membranes. The MD system is a thermally driven process in which a microporous membrane acts as a physical support to separate a warm solution containing either a liquid or a gas mixture. Because of vapor pressure difference at both sides of the membrane, vapor molecules diffuse through a dry membrane. The MD system has advantages such as low operating temperature and pressure, less interaction between the membrane and the process solution and small space requirement for the vapor (Lawson and Lloyd, 1997). Vacuum membrane distillation (VMD) is one of the MD

system configurations in which vacuum is applied on the permeate side for the withdrawal of the vapor. Compared with the other MD configurations, VMD permits higher partial pressure gradients, and hence higher permeate flux can be achieved (Banat and Simandl, 1999; Mericq *et al.*, 2009). The VMD system has been used for many applications, such as desalination (Wirth and Cabassud, 2002; Fang *et al.*, 2012), removal of alcohols, volatile organic compounds and chloroform (Hoffmann *et al.*, 1987; Urtiag *et al.*, 2000; Suk *et al.*, 2010), and concentration of fruit juice, sucrose and ethylene glycol (Mohammadi and Akbarabadi, 2005; Al-Asheh *et al.*, 2006; Diban *et al.*, 2009).

The porous membranes used so far in the MD systems are prepared from different hydrophobic polymeric materials such as poly(propylene), poly(tetrafluoroethylene) or poly(vinylidene fluoride) (Lawson and Lloyd, 1997; Alklaibi and Lior, 2005; El-Bourawi *et al.*, 2006; Kang and Cao, 2014). On the other hand, ceramic membranes are known for their mechanical, thermal and chemical stability. The application of ceramic membranes offers the long operational life and robustness of the process. Commercial ceramic membranes are usually prepared from metal oxides like Al₂O₃, ZrO₂, and TiO₂. These materials ordinarily have a hydrophilic character due to the presence of the surface hydroxyl groups, which can very easily link water molecules. So far, chemical modifications of such membranes to obtain a higher hydrophobicity have been investigated. Surface-modified ceramic membranes have been applied in membrane distillation process for desalination (Hendren *et al.*, 2009; Lu *et al.*, 2009; Fang *et al.*, 2012; Kujawa *et al.*, 2014) and removal of alcohols (Suk *et al.*, 2010). However, hydrophobic ceramic membranes have not been applied for concentration processes.

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In this study, fluoroalkylsilane (FAS) was grafted on a microporous Al_2O_3 membrane with asymmetric structure, and the surface-modified Al_2O_3 membrane was used in a VMD system for the concentration of a sucrose solution as a model solution of fruit juice. The effects of sucrose concentration and sucrose solution temperature on the vapor permeation performance of the surface-modified Al_2O_3 membrane were investigated. A mathematical model for the membrane permeability was also developed.

1. Experimental

1.1 Membrane preparation

Three types of microporous Al_2O_3 membranes (outer diameter: 10 mm; inner diameter: 7 mm; and length: 30 mm, purchased from Noritake Co., Ltd.) were used in this study. The characteristics of each Al_2O_3 membrane are summarized in **Table 1**. The S1 and S2 membranes were symmetric porous tubes with average pore sizes of 0.15 and 0.7 μm , and porosity of 40 and 50%, respectively. The A1 membrane is an asymmetric porous tube consisting of the S1 and S2 membranes as dense and substrate layer, respectively. The thickness of dense layer is 30 μm .

The surface modification was conducted in reference to the procedures of Lu *et al.* (2009) with modifications. The Al_2O_3 membranes were first cleaned via ultrasonication in *n*-hexane (purchased from Wako Pure Chemical Industries, Ltd.) for 5 min, and then dried at 100°C for 24 h. The dried membranes were immersed into 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (FAS, purchased from Tokyo Chemical Industry) in *n*-hexane solution at 25°C for 6–24 h. The concentration of the FAS/*n*-hexane solution was 10 mmol/L. After the immersion, the filters were washed with *n*-hexane and dried at 100°C for 24 h.

1.2 Sucrose concentration via VMD

A schematic diagram of an apparatus for VMD experiments is shown in **Figure 1**. One end of the hydrophobic Al_2O_3 membrane was sealed using a solid glass plate. The other end was connected with a vacuum line, and then the membrane was immersed into a sucrose solution in a concentration of 0 to 50 wt%. The sucrose solution was strongly stirred to eliminate the concentration differences between membrane surface and the solution. The temperature of the sucrose solution was controlled at the range of 30–60°C by a water bath. The permeate water vapor was collected in an ethanol cold trap to determine the permeation flux J [$\text{kg m}^{-2} \text{h}^{-1}$]. At any time, the concentration of sucrose in the feed solution was determined using an Abbe refractometer.

2. Theory

For the VMD system, the mass transfer process consists of the convective transfer in the boundary layer and the vapor permeation through the membrane pores, and the mass transfer resistance in the vacuum side is ignored. Additionally, in this study, the sucrose solution was stirred strongly to eliminate the concentration differences between the membrane surface and the solution. Thus, the mass transfer resistance in the boundary layer at the feed side is also ignored. The mechanism of vapor diffusion across micropores can be classified according to the value of the Knudsen number ($Kn = \lambda/2r_p$) that applies, with λ being the mean free path that represents the average distance a gas molecule travels before it collides with another gas molecule and r_p is the membrane pore radius (Alkhudhin *et al.*, 2012). When Kn is >10 , the molecule-pore wall collisions control the vapor transport mechanism (Knudsen flow model) and the flux J can be obtained by the following equation.

$$J = \frac{2}{3RT} \left(\frac{8RT}{\pi M_{wi}} \right)^{0.5} \frac{\varepsilon r_p}{\delta \tau} (P_f - P_p) \quad (1)$$

Here, ε , δ and τ are the porosity, the thickness and the pore tortuosity of membrane, R is the universal gas constant, T is the temperature, M_{wi} is the molecular weight of species i , and P_f and P_p are the pressure of species i at the feed and permeate side, respectively.

If Kn is between 0.01 and 10, both molecular-molecular and molecular-wall collisions should be considered. The total mass transfer is described by the Knudsen-viscous model and can be represented by the following equation.

$$J = \frac{\varepsilon}{RT\delta\tau} \left[\frac{2}{3} \left(\frac{8RT}{\pi M_{wi}} \right)^{0.5} r_p + \frac{r_p^2}{8\mu_i} P_{\text{avg}} \right] (P_f - P_p) \quad (2)$$

Here, μ_i is the viscosity of species i , and P_{avg} is the average

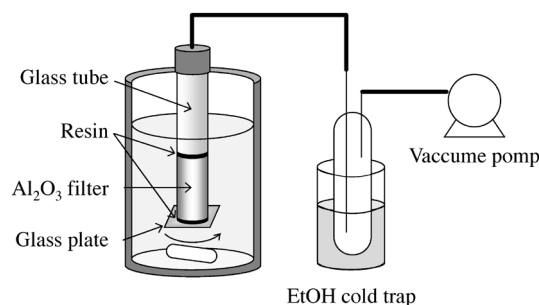


Fig. 1 Schematic diagram of the VMD experiment apparatus

Table 1 Characteristics of microporous Al_2O_3 membranes

Membrane	S1	S2	A1
Structure	Symmetric	Symmetric	Asymmetric
Pore size [μm]	0.15	0.70	0.15 (dense layer), 0.70 (substrate layer)
Thickness [mm]	1.5	1.5	0.03 (dense layer), 1.47 (substrate layer)
Porosity [%]	38	47	38 (dense layer), 47 (substrate layer)

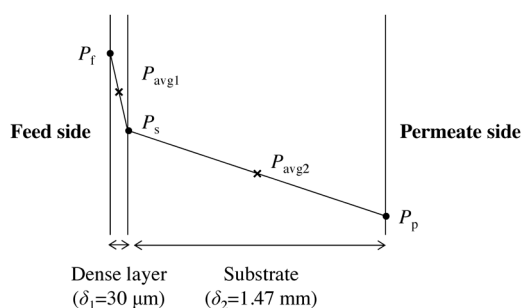


Fig. 2 Schematic representation of a cross section of the A1 membrane

pressure in the pore.

The value of P_f was calculated using the Antoine equation taking into account the vapor-pressure depression. Water activity in the aqueous solution of sucrose was estimated using Starzak's report (Starzak and Mathlouthi, 2006). The pressure at the permeate side (P_p) was 0.5 kPa, and P_{avg} was the mean value of P_f and P_p in this study. The viscosity of water vapor (μ) in the membranes was calculated using the Chapman–Enskog equation.

Figure 2 shows a schematic representation of the cross section of the A1 membrane. Permeation resistance in the A1 membrane is modeled as a series circuit in which the dense and substrate layers are serially connected. Boundary pressure P_s can be calculated from the ratio of permeation resistance of the dense and substrate layers. The pore tortuosity τ of both layers was estimated from the results of VMD experiments of pure water for the S1 and S2 membranes, and the obtained values were used for model calculation of the permeability through the A1 membranes.

3. Results and Discussion

3.1 Surface hydrophobicity of Al_2O_3 membrane and VMD performance for pure water

The amount of grafted FAS was not increased after 18 h. The amount of grafted FAS on the S1 and A1 membranes was about 9 mg/membrane. On the other hand, 3.5 mg of FAS was grafted on the S2 membrane. The membranes after surface modification for 18 h were used for further characterization and VMD experiments in this study. Figure 3 shows water contact angles of the A1 membrane before and after grafting with FAS. While water droplets were immediately absorbed into the Al_2O_3 membrane before grafting, the contact angle of the FAS-grafted membrane increased to 145° . The contact angle of the S1 and S2 membranes also increased $>140^\circ$ after the surface modification. These results indicate that the surface had been changed to hydrophobic.

Prior to the sucrose concentration experiments, the VMD experiments for pure water were performed to determine the water flux through the modified Al_2O_3 membranes and the pore tortuosity (τ) of the S1 and S2 membranes. The time courses of permeation flux are plotted in Figure 4. The permeation flux of the A1 and S1 membranes was stable over 9 h, indicating that the high hydrophobicity of the A1

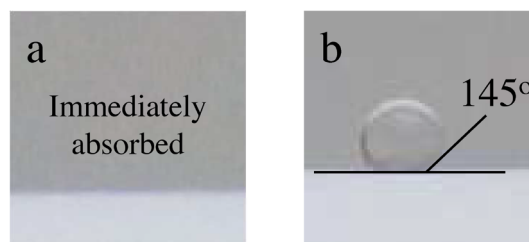


Fig. 3 Water contact angle of the A1 membrane (a) before and (b) after grafting with FAS

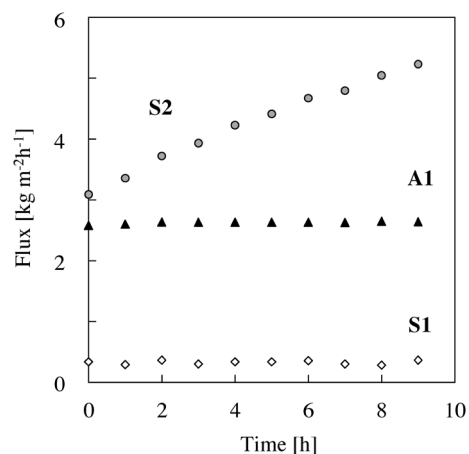


Fig. 4 Time courses of water flux through the hydrophobic Al_2O_3 membranes; feed temperature of 40°C

and S1 membranes could be stably ensured. The values of the permeation flux were 2.6 and $0.33 \text{ kg m}^{-2} \text{ h}^{-1}$, respectively. On the other hand, the permeation flux of the S2 membrane increased with time. The value of the permeation flux changed from 3.1 to $5.2 \text{ kg m}^{-2} \text{ h}^{-1}$. The S2 membrane could not prevent the permeation of water with the lapse of time. In the VMD system, the surface tension of membrane must be balanced with the pressure difference between the feed and permeate sides to prevent the permeation of liquid. Due to its large pore size and small amount of grafted FAS molecules, the hydrophobicity of the S2 membrane would not be enough for the experimental conditions. The VMD experiments for pure water indicate that the asymmetric structure of the A1 membrane is suitable to achieve both high permeation flux and stability of its hydrophobicity.

The pore tortuosity (τ) of the S1 and S2 membranes were estimated from Eqs. (1) or (2) using the results of VMD experiments for pure water. In the case of the S2 membrane, the initial permeation flux ($3.1 \text{ kg m}^{-2} \text{ h}^{-1}$) was used for the calculation. The calculated value of pore tortuosity of the S1 and S2 membranes was 4.2 and 2.8, respectively.

3.2 Effect of sucrose concentration and solution temperature on VMD performances

Figure 5 shows the effect of sucrose concentration on the permeation flux through the hydrophobic A1 membrane. The solution temperature was 40°C in these experiments. The model calculated permeation flux, P_f and P_s , are

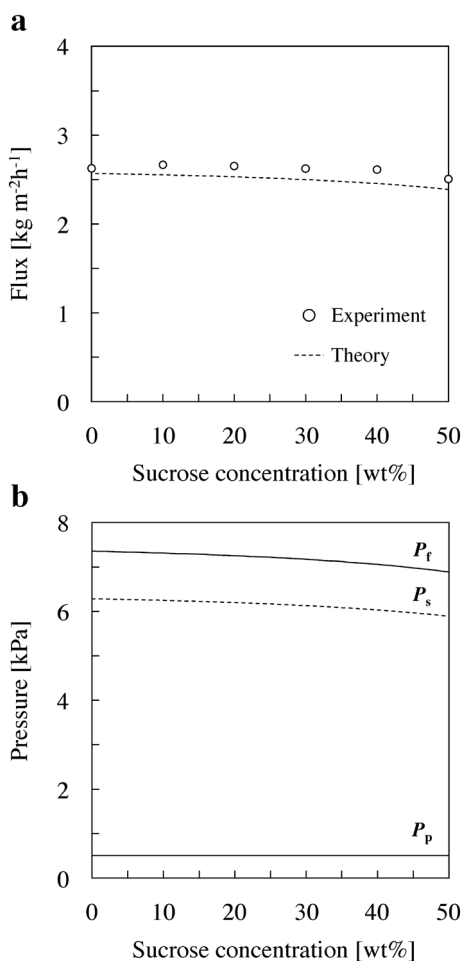


Fig. 5 Sucrose concentration dependence of (a) water flux and, (b) P_t , P_p and P_s through the hydrophobic A1 membrane; feed temperature of 40°C

also plotted as a function of sucrose concentration. The mass transfer through the dense and substrate layers were calculated by the Knudsen flow and the Knudsen-viscous model, respectively. The viscosity of water vapor is about $1.12 \times 10^{-5} \text{ kg m}^{-2} \text{ s}^{-1}$ in this experiment, and the contribution of the total viscous flow to the vapor permeance through the substrate layer was about 4%. The permeation flux was $2.6 \text{ kg m}^{-2} \text{ h}^{-1}$ when the sucrose concentration was 10 wt%. Deposition of sucrose on the permeate side was not observed. Thus, the sucrose rejection was 100% in this experiment. Al-Asheh *et al.* (2006) reported the concentration of sucrose solution using a polypropylene membrane in the VMD system and the permeation flux of $1.46 \text{ kg m}^{-2} \text{ h}^{-1}$ was obtained. The hydrophobic A1 membrane showed superior VMD performance compared to the polypropylene membrane. The vapor pressure at the feed side was decreased with increasing the sucrose concentration, due to the vapor-pressure depression (Figure 5(b)). Similar to P_p , the values of P_s were also decreased with increasing the sucrose concentration. As a result, the permeation flux was slightly decreased with increasing the sucrose concentration. The model calculated permeation flux was close to

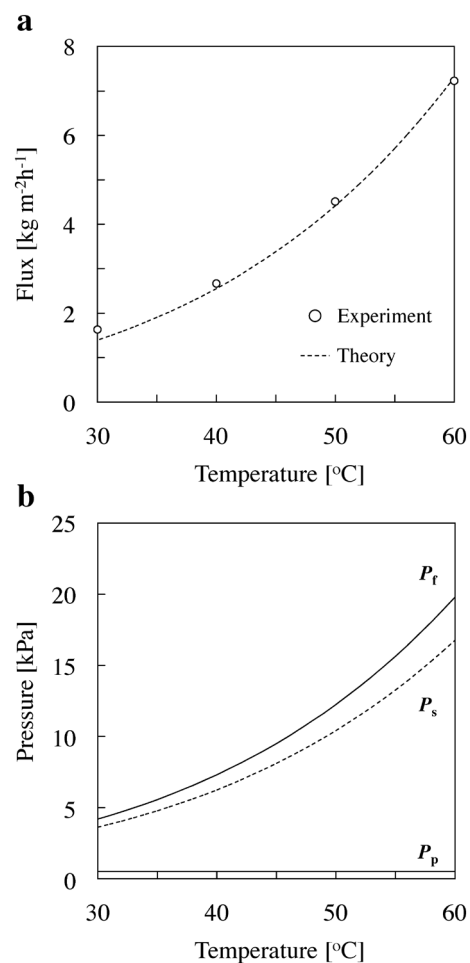


Fig. 6 Temperature dependence of (a) water flux and, (b) P_t , P_p and P_s through the hydrophobic A1 membrane; feed sucrose concentration of 10 wt%

the measured values, indicating that the permeation flux was successfully represented by the Knudsen and Knudsen-viscous models. Using the value of P_s , the permeances of S1 and S2 layer were estimated as about 3.7×10^{-5} and $6.8 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, respectively.

The effect of the solution temperature on the permeation flux through the hydrophobic A1 membrane, the model calculated permeation flux, P_t and P_s are summarized in **Figure 6**. The sucrose concentration was 10 wt% in these experiments. The mass transfer through the dense and substrate layers were calculated by the Knudsen flow and the Knudsen-viscous model, respectively. The viscosity of water vapor was about 1.12 – $1.20 \times 10^{-5} \text{ kg m}^{-2} \text{ s}^{-1}$ in this experiment, and the contribution of the total viscous flow to the vapor permeance through the substrate layer changed from 4 to 10% with increasing the solution temperature. A permeation flux of over $7 \text{ kg m}^{-2} \text{ h}^{-1}$ was obtained, when the solution temperature was 60°C. Deposition of sucrose on the permeate side was not observed in this experiment. The sucrose rejections were 100% for each solution temperature. Due to the vapor-pressure rising, the values of P_t were increased with increasing solution temperature (Figure 6(b)).

Similar to P_f , the boundary pressure P_s was also increased with solution temperature. As a result, the permeation flux was significantly increased with solution temperature. The permeances of S1 and S2 layers were estimated as about 3.7×10^{-5} and $6.9 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, respectively.

The theoretical analysis reveals that the permeance of the A1 membrane depends on that of the S2 layer, due to its large thickness. The obtained results show the possibility to use the hydrophobic Al_2O_3 membranes in VMD system for concentrations including sucrose. Moreover, asymmetric Al_2O_3 membranes offer advantages for both ease surface modification and superior permeance.

Conclusions

Hydrophobic Al_2O_3 membranes have been prepared by surface grafting with FAS. The sucrose concentration performances of the prepared Al_2O_3 membranes have been evaluated using the VMD system. By exposing the hydrophobic Al_2O_3 membrane with asymmetric structure to a sucrose solution of 10 wt% at 60°C , a water flux as high as $7.2 \text{ kg m}^{-2} \text{ h}^{-1}$ was attained. The theoretical analysis reveals that the permeance of the asymmetric membrane depends on that of its substrate layer, due to its large thickness. These results showed that hydrophobic ceramic membranes are one of the promising membranes in the VMD system for concentration processes. Especially, asymmetric Al_2O_3 membranes offer advantages for both ease surface modification and superior permeance.

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