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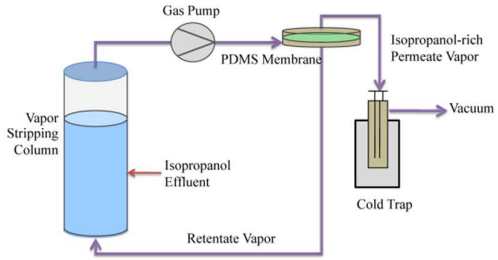
The novel process, integrated gas stripping and vapor permeation, is environmental, energy-efficient and high selective for isopropanol recovery.



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Paper

Separating isopropanol from its diluted solutions via a process of integrating gas stripping and vapor permeation

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Considering environmental pollution, disposal costs, high-value of isopropanol (IPA) and other factors, recovering isopropanol from the industrial effluent is considered to be attractive, practical and cost-effective. However, the separation techniques including gas stripping, distillation, and pervaporation often yield low selectivity and high energy consumption. In this paper, a process of integrating gas stripping and vapor permeation was conducted for separating isopropanol from dilute solutions. A PDMS (polydimethylsiloxane) membrane was prepared by using green method. The effects of gas flow rate, membrane model temperature, feed solution temperature, and feed solution concentration on the performance of the separation system were investigated. The results in this study showed that the optimized separation performance (isopropanol flux 437.8 g/m^{2}h, separation factor 125.8) was obtained for separating 3 wt. % isopropanol solution at 75 °C, which were 1.48 times and 7.4 times of those obtained in the PV process, respectively. The energy consumption of evaporation was only 1.28 MJ/kg; this was 26 % and 30 % of the evaporation energy needed for the PV process and the distillation process at the same conditions, respectively. Additionally, a comparison of separation performance with other separation techniques was also conducted in the study.

Introduction

Isopropanol (2-propanol, IPA) is an important solvent and is widely used as a cleaning agent in industries, particularly in semiconductor, liquid crystal display, and pharmaceutical industries[1, 2]. In these plants, large quantities of waste water containing low concentration of isopropanol are produced every day. However, due to the biotoxicity of isopropanol, it is difficult to treat these effluents by microbial methods[3]. Thus, considering environmental pollution, disposal costs, high-value of isopropanol and other factors, recovering isopropanol from the industrial effluent is considered to be attractive, practical, and cost-effective [4].

A lot of separation techniques, such as distillation, gas stripping and pervaporation, have been applied for IPA separation. Since isopropanol can form an azeotrope with 14.7 wt. % water, distillation was considered to be uneconomical for the recovery of isopropanol[1]. Gas stripping was also not useful due to its low selectivity and high energy cost for the subsequent separation process[5]. Recently, pervaporation (PV) has been regarded as a promising alternative separation technique for the separation of IPA/water system. It's separation mechanism is based on the different solubility and mass transfer resistance of feed components through the membrane[6]. Hence, it can overcome azeotropic compositions while minimizing the energy demand[7]. Recent studies focused on the feasibility of pervaporation for dehydration of IPA[8-10], however, only a limited studies focus on the recovery of IPA from water, especially from low concentration solutions. Mulder *et al.*[11] employed PDMS membrane for recovering 5 wt. % IPA, the separation factor was only 9.5. Similar selectivity was also reported in Kittur's study with the total flux of 121-137 g/m^{2}h[4]. Although a relatively high separation factor of 29 was achieved by using Ge-ZSM-5 membrane in Li's report[12], its performance was still unsatisfactory in industrial application. Another problem is that membrane fouling caused by the effluents in pervaporation process is serious. Overall, there is no economically feasible separation technique currently available for separating IPA from dilute solutions.

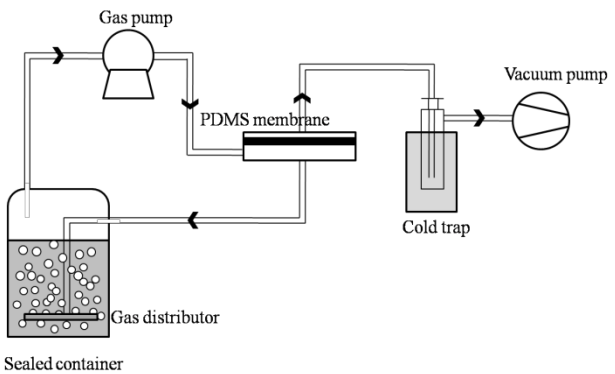

Fig 1. Schematic diagram of the process of integrating gas stripping and vapor permeation.

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In this work, we integrated gas stripping and vapor permeation (GSVP) to treat the industrial effluent containing low concentrations of IPA. The separation mechanism of vapor permeation is similar to pervaporation. The difference between the two separation processes is that liquid is fed to membrane module in pervaporation while vapor is fed to membrane module in vapor permeation. As illustrated in Fig. 1, gas (air in the sealed container) was bubbled into the separation system, capturing the volatile component (product-isopropanol). The gas containing the product was introduced into a membrane module equipped with a PDMS membrane, and subsequently the product in the gas permeated through the membrane and was condensed, while the other components were rejected and returned to the container. This approach avoided the membrane fouling observed in PV process and the need of an entrainer to break the azeotrope. In addition, it also displayed a promising potential to combine separation with the IPA fermentation, which can eliminate the toxic effects of IPA, thus bringing forth higher productivity. To study the GSVP process, the effect of temperature, IPA concentration, and gas flow rate were investigated, and the performance of GSVP was also compared with results from other separation techniques reported in the literature.

Results and discussion

Effects of gas flow rate on GSVP performance

As gas was used as the feed, the gas flow rate in the GSVP process was important to the performance of the system. The corresponding experiments were conducted and the results are shown in Fig. 2. In the experiments, the IPA/water solution with the IPA concentration of 2.5 wt % in feed tank was maintained at 65 °C. With the gas flow rate ranging from 2 L/min to 10 L/min, the total flux increased from 420 g/m^{2}h to 607 g/m^{2}h, but the separation factor decreased from 92.9 to 27.4. As can be seen from Fig. 2, the increase in total flux was primarily due to the rise of water flux, which also resulted in a huge reduction in the separation factor. This phenomenon can be interpreted as follows: because of the circulation of gas mixtures, the cycle times in unit time increased as the gas flow rate increase, thereby yielding an increase of contact time between gas mixture and IPA/water solution. Furthermore, IPA is easily volatilized

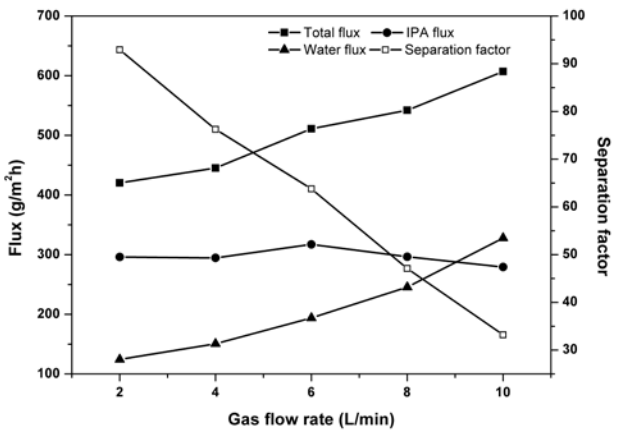

Fig 2. GSVP performance as a function of s gas flow rates with 2.5 wt. % feed solution and 65 °C feed solution temperature.

compared with water due to its higher saturated vapor pressure. Thus, with the residence time enhancing, the water content in gas phase increased significantly, while the IPA concentration in gas phase was saturated and maintained at a constant value. As a result, a significant increase in water flux and a minor fluctuation in IPA flux were observed, respectively. In summary, a low gas flow rate is conducive to the high separation performance and low energy consumption.

Effects of temperature on the performance of the GSVP process

Because of the very low thermal conductivity of gases, there was a large difference between the membrane temperature and the feed solution temperature. Therefore, the effects of feed solution temperature and membrane temperature on the GSVP performance were separately evaluated.

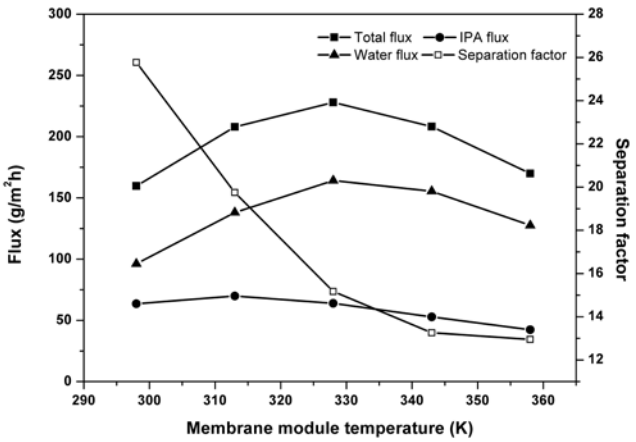

Fig 3. Fluxes and separation factor as a function of membrane module temperature with 2.5 wt. % feed solution and 37 °C feed solution temperature.

To investigate the former, the membrane module was placed in a thermostatic container with temperature ranging from 25 °C to 85 °C, while the feed solution temperature was maintained at 37 °C. The results are shown in Fig. 3. With membrane module temperature increasing, the total flux and water flux initially enhanced and then subsequently decreased. Furthermore, the separation factor declined with the increase of membrane module temperature. These phenomena were caused by the two conflicting influences: one is the increase in free volume of the membrane; the other one is the decrease in the concentration of IPA and water in the vapor phase. The free volume of the membrane increased as the membrane temperature increased, along with reduction of the mass transfer resistance[13], which led to the increase in fluxes and decrease in the separation factor. On the other hand, the partial pressures of IPA and water in the vapor phase increased with the increase of the temperature of the membrane module. For this reason, the vapor pressure differences of IPA and water between feed solution and gas mixture decreased, thus led to the reduction of their concentrations in the gas phase (giving rise to the decline in fluxes) until the system reached a new equilibrium. So overall, the initial increase in fluxes and the reduction in separation factor were mainly due to the increase in free volume of the membrane, and the subsequent decline in fluxes was mainly due to the reduction of the

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concentration of IPA and water in the vapor phase. Furthermore, the results also indicated that a single process of vapor permeation (VP) was not suitable for separating IPA/water solutions, because the membrane temperature is approximately equal to the feed solution temperature in the VP process, and the high temperature of membrane module is not beneficial to the separation performance.

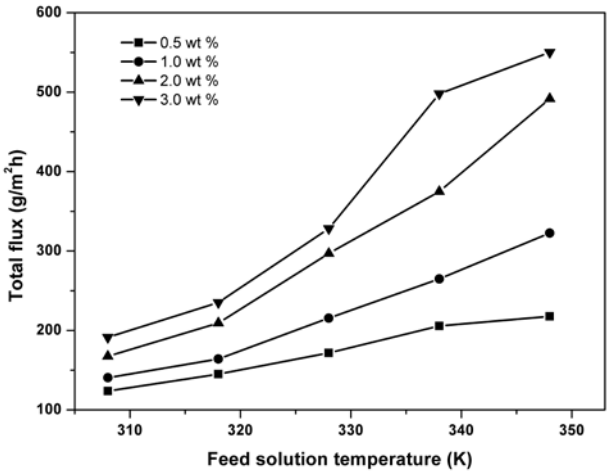

Fig 4. Effect of feed solution temperature on total flux. Gas flow rate was 2 L/min.

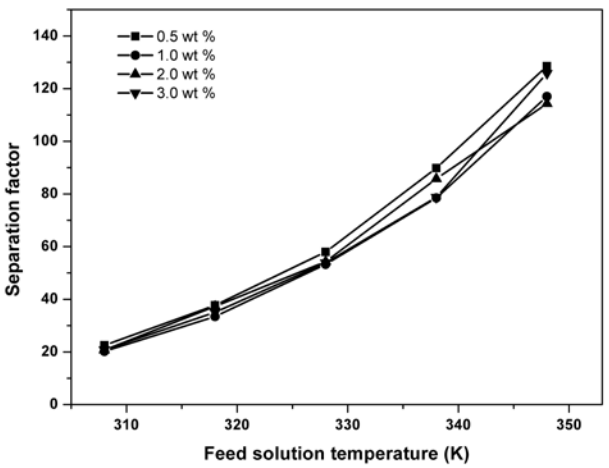

Fig 5. Effect of feed solution temperature on separation factor. Gas flow rate was 2 L/min.

To investigate the influence of feed solution temperature, the membrane module was placed at room temperature, and the gas flow rate was maintained at 2 L/min. The results showed that the total flux and the separation factor reached 550.2 g/m^{2}h and 125.8, respectively, when separating 3 wt. % isopropanol aqueous solution at 75 °C. As shown in Fig. 4 and Fig. 5, with feed solution temperature rising, a rapid increscent of the total flux and the separation factor was obtained. The results didn't follow the "trade-off effect" that exists between the flux and the separation factor. This may be caused by the fact that the temperature fluctuation of the PDMS membrane was not obvious because of very low thermal conductivity of gases. Therefore, the effect of free volume of PDMS on the membrane performance, caused by membrane temperature, was negligible. Moreover, the mass transfer coefficient of the liquid phase to the gas phase apparently increased with the increase of the feed solution temperature[14]. For this reason, the isopropanol concentration in the gas phase was improved, which resulted in the increase of the total flux and the separation factor. As summary, it can be seen from the results that the reduction of separation factor caused by the increase of feed solution temperature[1,4] was weaken in the GSVP process, which is a great advantage relative to PV process.

Effects of feed solution concentration on the performance of the GSVP process

In the process of recovering IPA from dilute solutions, the IPA concentration varies due to its different sources[15-17], e.g. effluents from various industries, fermentation broths depending on different raw materials or strains. It is, therefore, necessary to study the GSVP performances at different IPA concentrations in the feed, especially at low IPA concentration (literature reports are very few). IPA/water model solutions with the IPA concentration ranging from 0.5 wt. % to 3 wt. % were used as feed solutions to examine the performances of GSVP at different temperatures. The gas flow rate was maintained at 2 L/min. Total flux, permeate concentration, and separation factor are plotted in Fig. 6-8 as a function of feed solution concentration at different temperatures.

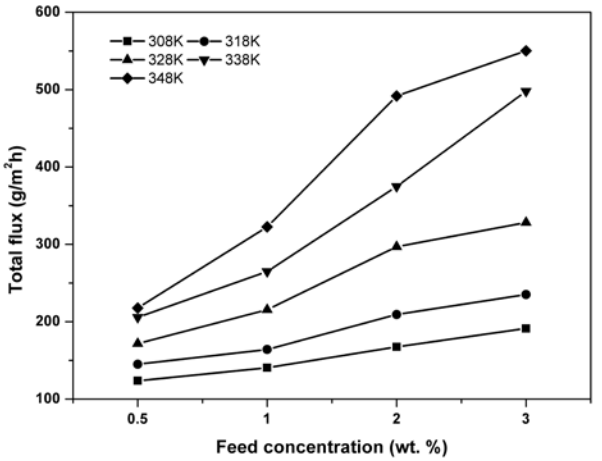

Fig 6. Total Flux as a function of feed solution concentration for various feed solution temperatures with 2 L/min gas flow rate.

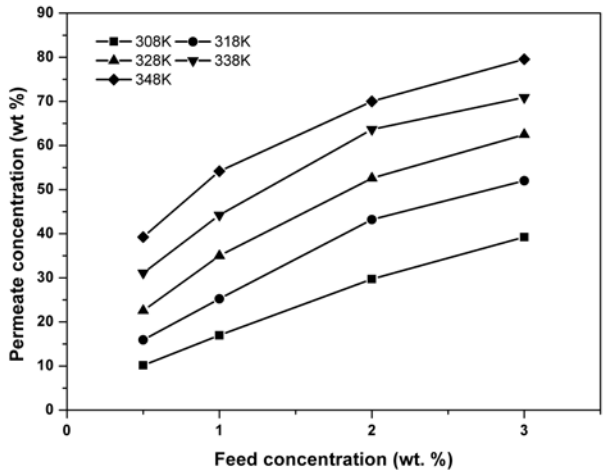

Fig 7. Permeate concentration as a function of feed solution concentration for various feed solution temperatures with 2 L/min gas flow rate.

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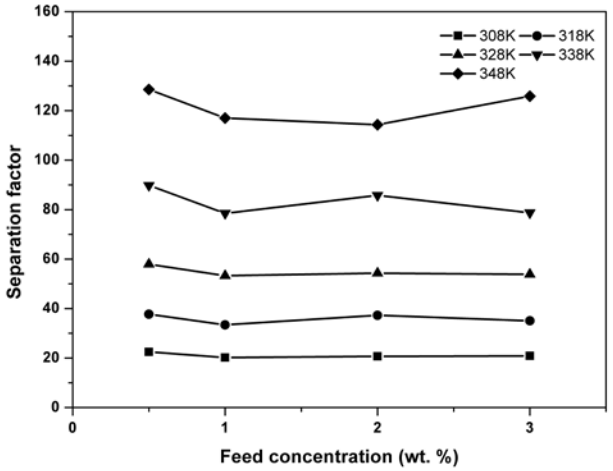

Fig 8. Separation factor as a function of feed solution concentration for various feed solution temperatures with 2 L/min gas flow rate.

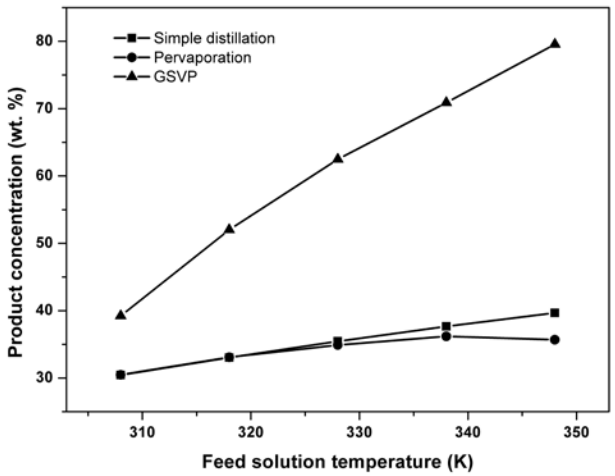

Fig 9. Comparison of product concentration of different process at various temperatures at 3 wt. % feed solution concentration.

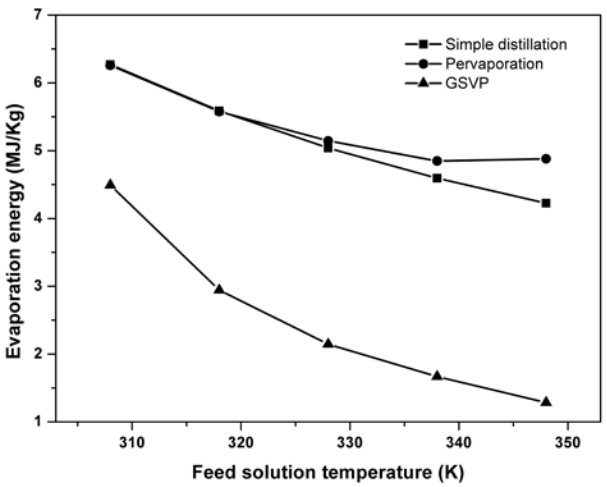

Fig 10. Evaporation energies of different process required for separating 3 wt. % IPA solutions.

As illustrated in Fig. 7, when separating 3 wt. % isopropanol aqueous solutions at 75 °C, the permeate concentration of IPA reached 79.6 wt. %. At such a high concentration, a dehydration process, such as pervaporation with hydrophilic membranes or adsorption or extraction[18, 19], can be directly used as the subsequent separation step so as to get pure isopropanol (≥99.5 wt. %). In addition, with the feed solution concentration ranging from 0.5 wt. % to 3.0 wt. %, the total flux (Fig. 6) increased significantly, especially at high temperatures. The concentration of permeate (Fig. 7) has also been improved, while the separation factor (Fig. 8) fluctuated in a narrow range. It can be explained as follows: the IPA concentration in the gas phase improved with the increase of feed solution concentration; this increased the driving force of IPA through the membrane. Thus, the IPA flux enhanced significantly, which was the main reason that caused the rise in the total flux and the permeate concentration. Additionally, the slight variation of the separation factor also indicated that the effect of membrane swelling on the GSVP process for the recovery of isopropanol was small.

Comparison with other separation techniques

A comparison between GSVP and pervaporation as well as simple distillation showing IPA concentration of products and evaporation energy, is given in Fig. 9 and Fig. 10. The data of permeate concentration in the pervaporation process was obtained by using the same membrane as that used in the GSVP process, and the data for the simple distillation (VLE dates) was obtained by using the Aspen Plus 8.0 software based on the NRTL model. The evaporation energy needed for each process was obtained according to Eq. (1)[20, 21]; physical parameters of components were taken from Aspen Plus 8.0.

$$Q_{norm}^{evap} = \Delta H_{IPA}^{evap} + \Delta H_{H_2O}^{evap}\left(\frac{1-\chi_{IPA}}{\beta * \chi_{IPA}}\right) = \Delta H_{IPA}^{evap} + \Delta H_{H_2O}^{evap}\left(\frac{1}{y_{IPA}} - 1\right) \quad (1)$$

Where Q_{norm}^{evap} is the evaporation energy needed in the process of recovering a mass unit of isopropanol, MJ/kg; ΔH_{IPA}^{evap} and $\Delta H_{H_2O}^{evap}$ represent the evaporation heat of isopropanol and water in MJ/kg, respectively. β is the separation factor of the process; χ_{IPA} and y_{IPA} are the mass fractions of isopropanol in the feed solution and the product, respectively.

As illustrated in Fig. 9, the product concentration during the GSVP process was considerably higher than that in the PV process or the simple distillation process, while IPA concentration showed in PV process was similar to the product concentration in the simple distillation process, even lower than that at high temperatures. These results indicated that the GSVP process was much more selective for isopropanol than the PV and the simple distillation process. With respect to the energy consumption (Fig. 10), evaporation energies for the GSVP process were also below those of the PV or the distillation processes. It is noted that the advantage of energy efficiency in the GSVP process was more significant at high temperatures. The evaporation energy needed for the GSVP process to separate 3 wt. % isopropanol solution at 75 °C was only 1.28 MJ/kg, which was 26 % and 30 % of the evaporation energy needed for the PV process and the simple distillation at the same conditions, respectively. Although many factors including the energy consumption for condensation, maintaining vacuum, and heating of the feed solution were not taken into account in this comparison; however, the evaporation energy was considered to

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Table 1. A comparison of separation performance with other separation techniques

Separation techniques	Medium	Conditions	IPA concentration in feed solution (wt. %)	IPA concentration in product (wt. %)	IPA flux (g/m^2h)	Separation factor	Ref.
Salting-out extraction	30 wt. % K_2CO_3/hexane	Room temperature	51	91		9.7	[25]
Supercritical Fluid Extraction	Isobutane	380K, 40 bar, solvent: feed, mass basis=1.74	10	92.7		114.3	[26]
Gas stripping	air	30 °C, 25 mL/min	~1.97	~14		8.1	[27]
Distillation		75 °C	0.5	10.4		23.1	Aspen 8.0
Distillation		75 °C	3	39.68		21.26	Aspen 8.0
Pervaporation	Silicone rubber membrane	25 °C	9	68.4	30	22	[19]
Pervaporation	PDMS/PS membrane	50 °C	8	48.11	422	10.1	[28]
Pervaporation	30% ZSM-5 loading PDMS membrane	50 °C	10	76.2	104.8	11.22	[4]
Pervaporation	SY-2 loading PDMS membrane	50 °C	4.84	40.88	51.9	13.6	[29]
Pervaporation	3 wt. % TMSH-silica incorporated PDMS	50 °C	4	56.9	230.4	31.7	[30]
Pervaporation	PDMS membrane	65 °C	0.53	8.7	42.1	17.8	This study
Pervaporation	PDMS membrane	35 °C	3	30.4	62.6	13.7	This study
Pervaporation	PDMS membrane	75 °C	3	34.5	296	17.1	This study
GSVP	**PDMS membrane**	**75 °C**	**0.5**	**39.2**	**80.7**	**128.5**	**This study**
GSVP	**PDMS membrane**	**75 °C**	**3**	**79.6**	**437.8**	**125.8**	**This study**

be the main energy sink according to many researchers' reports[22-24]. Thus it is clear that the GSVP process displayed higher energy efficiency than the distillation and PV processes.

In addition, a comparison of the separation performance with other separation techniques and the PV process with different membranes is shown in Table 1. In our work, the IPA flux and separation factor observed in the GSVP process were 1.48 and 7.4 times higher than those observed in the PV process, when recovering IPA from 3 wt % dilute solution at 75 °C via the same PDMS membrane. Moreover, the performance observed in the GSVP process was superior to that of other traditional separation processes, e.g. salting-out extraction, gas stripping, distillation, and pervaporation; only the performance of supercritical fluid extraction was comparable to the GSVP process. However, for feed solution concentrations of isopropanol below 15 wt. %, the energy consumption of supercritical fluid extraction is not competitive with that of the conventional distillation [26]. Since the GSVP process is more energy efficient than the distillation, the GSVP process can be viewed to be superior to supercritical fluid extraction for recovering isopropanol at low concentrations. Besides, due to the use of gas as the feed in the GSVP process, the membrane fouling caused by the residues in effluent or the components in fermentation broth was virtually non-existent. Thus, GSVP may be considered as the "best separation" technique for the recovery of isopropanol from a dilute solution.

Conclusions

There is a need of economically feasible, environmentally friendly and energy-efficient separation technique for separating IPA from dilute solutions, a process of integrating gas stripping and vapor permeation (GSVP) was introduced in this paper to solve these problems. A PDMS membrane, prepared by a green method with employing water as the solvent in the presence of DBSA, was used. Low gas flow rate, low membrane temperature and high feed solution temperature were found to be conducive to superior performance of the GSVP process. The best separation performance (IPA flux 437.8 g/m^2h, separation factor 125.8) was found for separating 3 wt. % isopropanol solutions at 75 °C, which were 1.48 and 7.4 times higher than those observed in the PV process, respectively. Meanwhile, its energy consumption for evaporation was found to be 1.28 MJ/kg, and it consumed only 26 % and 30 % of the evaporation energy needed for the PV and the simple distillation processes at the same conditions, respectively. Additionally, the membrane fouling caused by the residues in effluents or the components in fermentation broth was virtually non-existent. Finally, the comparison with other traditional separation techniques, including salting-out extraction, gas stripping, distillation, and pervaporation with different membranes, also indicated that the GSVP may be considered as a superior separation technique for isopropanol recovery from dilute solutions.

Experiment

Materials

Isopropanol was purchased from Beijing Chemical Works (Beijing, China). Deionized water was obtained by a water purification system (ROP15, Heal Force Bio-Meditech Holdings Limited) and used in all experiments.

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Membrane preparation

The PDMS membrane was prepared by a green method with employing water as solvent in the presence of DBSA (dodecyl benzene sulphonic acid). The PDMS polymer, cross-linking agent TEOS and catalyst dibutyltin dilaurate (DBTDL) were dissolved in water in the presence of surfactant, dodecyl benzene sulfonic acid (DBSA). And then, the mixture solution was vigorously stirred for 2 h at room temperature in order to get homogeneous solution. Finally, the mixture was coated on a PVDF membrane by employing an automatic coating machine, and subsequently the composite membrane (membrane dimensions: 15cm*25cm) was dried at 80 °C for 24 h. More details can be seen in our previous work[31, 32].

Separation experiments

The performance of PV and GSVP were evaluated by employing the same PDMS membrane and tested on a lab-scale apparatus. The schematic diagram of the pervaporation apparatus was given in detail in our previous work[32], and the diagram of GSVP apparatus is shown in Fig. 1. In the experiments, in order to diminish vapor condensation, the tubing and membrane module were wrapped by rubber insulation board and the length of tubing was shortened as much as possible.The separation systems used in the tests were isopropanol/water binary solutions. In the PV test, the binary solution was circulated between the feed tank and the membrane module at the rate of 350 ml/min by a liquid pump (WKY600, Chengdu Qihai E&M Manufacturing Co., Ltd, China). In the GSVP test, the air in the sealed container was circulated between the container and the membrane module by a mini gas pump (PCF5015N, Chengdu Qihai E&M Manufacturing Co., Ltd, China); the tubing was wrapped by the insulation material in order to avoid the condensation of vapors. The gas flow rate was controlled in the range of 2 L/min to 10 L/min by a precision flow control valve. The effective area of the membrane was 30.2 cm^2 and the pressure in the permeate side was maintained below 200 Pa. To guarantee the experimental accuracy, the permeate was collected in cold trap cooled by liquid nitrogen and subsequently weighed per hour (repeat two times) after 1 hour of stable operating. The concentration of the feed and the permeate were determined by GC-14C gas chromatograph equipped with a Porapak-Q packed column. The temperatures for the injector, the column, and the detector were 150 °C, 160 °C and 160 °C, respectively.

The separation performance was evaluated by total flux (J), isopropanol flux (J_{IPA}), separation factor (β), which can be calculated according to the following equations:

$$J = \frac{m}{A * t} \quad (2)$$

$$J_{IPA} = J * y_{IPA} \quad (3)$$

$$\beta = \frac{y_{IPA}/(1 - y_{IPA})}{x_{IPA}/(1 - x_{IPA})} \quad (4)$$

Where m, A and t are the weight of permeate collected in cold trap, the active area of membrane and the collected time, respectively. y_{IPA} represents the mass fraction of IPA in the permeate, and x_{IPA} refers to the mass fraction of IPA in the liquid phase of the feed tank.

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Notes and references

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