Recovery of n-butanol from aqueous solution by hydrophobic silica-filled PDMS membrane by pervaporation

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Introduction

Pervaporation is an attractive separation process, which has been successfully utilized in separating azeotropic mixtures since it can overcome the limit of liquid - vapor equilibrium. With this particular characteristic, pervaporation has been proven as a highly efficient separation process for separation of heat-sensitive products and even the most challenging isomeric mixtures [1 - 3].

Butanol is a pure alcohol with energy content similar to that of gasoline. It does not have to be stored in high pressure vessels like natural gas, and can be but does not have to be blended (10 to 100 percent) with any fossil fuel. Butanol can also be transported through existing pipelines for distribution. Nowadays with increasing prices and taxes for fossil fuels, and the desire for cleaner-burning sources of energy, butanol gain a growing consumer acceptance and name recognition.

In this study, poly(dimethylsiloxane) (PDMS), which is the current benchmark hydrophobic pervaporation membrane material , was studied for the recovery of n-butanol from aqueous solution. The PDMS-based membranes were fabricated by incorporating two kinds of commercial hydrophobic silica TS530 and TS720 obtained from CAB-O-SIL® Corporation. The effects of feed temperature, feed concentration, membrane thickness, silica content on membrane performances were studied.

Theory

The permeate was weighed Flux and separation factor were calculated.

$$\text{Flux}=W/(At) \qquad g/m^2h$$

$$\text{Separation factor}=[y/(1-y)]/[x/(1-x)]$$

W, A and t are the weight of permeate collected, the effective membrane area and the time interval (8h) respectively. x and y are the weight fraction of component in the feed and permeate, respectively.

Experimental

Materials

n-butanol(99%extra pure) were obtained from Sigma-Aldrich Corp. PDMS(Polydimethylsiloxane) kit (Sylgard 184Abase and DC-184B curing agent) used for membrane preparation was purchased from Dow Corning Corp. Fumed silica TS530, and TS720 were supplied by CAB-O-SIL® Corp.

Methods

Sorption of n-butanol by two commercial fumed silica were investigated at 30℃ for 24h, the fumed silica were treated at 100℃ under vacuum before measuring the sorption. The initial concentration of the n-butanol aqueous solution is 5wt%, after adding the fillers (0.05g), centrifuge for 40min, the concentration of initial and after were examined by HP Agilent 6890 GC-FID equipped with HP 7863 autosampler.

Fumed silica filled PDMS flat membrane was prepared from Sylgard 184A and DC-184B, after adding the fumed silica, stirring for 2h and under sonication for another 1 h to make sure the fumed silica disperse well. The homogeneous solution was poured onto a teflon plate and spread mechanically to form a thin liquid layer. The plate was held at 20℃ in an oven for 24 h to dry and 100 ℃ curing the membrane. After the membrane was cured it was peeled off. The plate and cut to the size of the pervaporation plate (diameter 50mm).The thickness of the membrane was measured by micrometer.

2L of n-butanol aqueous solution(concentration ranging from 2wt% to 5wt%) was circulated at 200cc/min through the pipeline, stainless steel shell and a temperature-controlled instrument were used to heat the retentate to the desired temperature. The pressure on the permeate side of the membrane ranged from 2 to 5Torr. After steady state was reached, which usually required 0.5±1 h.

Results and Discussion

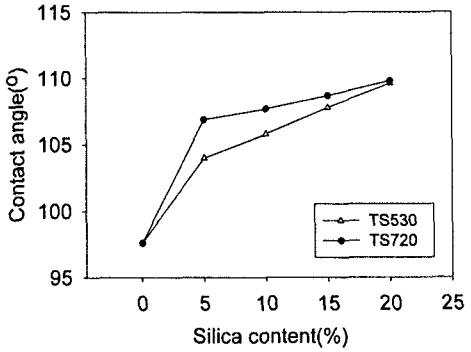

Fig.1 The contact angle of different silica contents of filled PDMS membrane

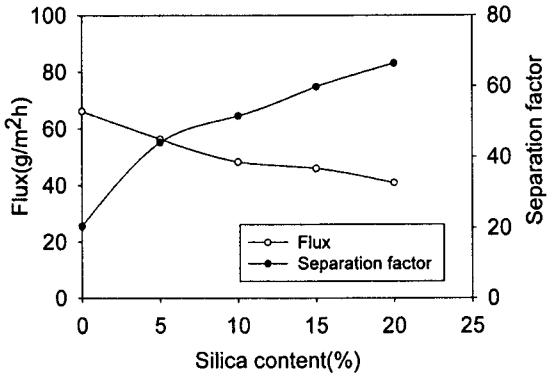

Fig.2 The effects of different silica content on flux and separation factor on TS530 filled PDMS membrane

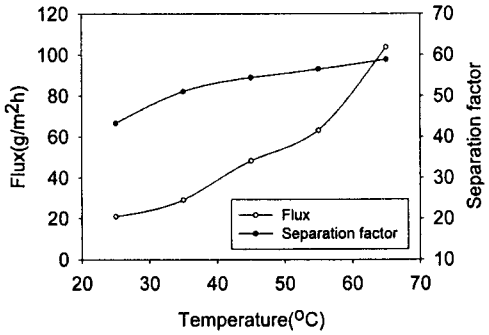

Fig.3 The effects of temperature on flux and separation factor on TS530 filled PDMS membrane

Table1. The sorption results of Fumed silica TS530 and TS 720

	TS530	TS720
B.E.T. Surface Area	205–245 m^2/g	105–130 m^2/g
Particle size(nm)	11.1-13.3	25.6- 31.7
Adsorption capacity(g/g)	0.3587	0.2878

As silica loading increased from 0 to 20wt%, separation factor increased from 20.5 to 66.5(Fig. 2). The increase in selectivity with increasing silica loading is caused by the selective sorption and permeation of n-butanol through the silica. The blockage of the silica to water causes

the water molecules to follow a more tortuous path around the silica particle to the permeate side resulting in a lower water flux and at the same time increase the separation factor.

The temperature effect on the flux and separation factor of n-butanol aqueous solution was determined using a 5wt% silica TS530 filled PDMS membrane with a thickness of 210μm. Flux and separation factor were evaluated at 25,35,45,55 and 65℃ with a 2wt% n-butanol feed solution (Fig.3).Both he flux and separation factor increased with the temperature increases, following the same trend of pure PDMS membrane.

When the feed temperature was increased from 25 to 65℃, the total flux increased from 20.95 to 103.72 $gm^{-2}h^{-1}$ and the separation factor of the membrane increased from 34.39to 48.21, respectively. This may be probably due to the more flexibility of polymer chains occurred at higher temperature and caused larger available free volume of polymer matrix for diffusion of solvent as well as water.

Conclusion

Based on the contact angle results, it was found that all the PDMS mixed matrix membranes showed more hydrophobic properties. Enhanced separation factor for n-butanol by TS530 loading was observed, this behavior could be attributed to higher sorption capacity of TS530 for n-butanol than that of TS720. TS530 Silica addition increased the separation factor of PDMS membrane for n-butanol from 20.5 to 66.5 at 2 wt% of butanol concentration. However, the total flux decreased from 66.1 to 40.9 g/m^2h. The n-butanol separation factor ranged from 20.5to 66.5 depending on different silica content.

Acknowledgement

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