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Separation of ethyl tert-butyl ether–ethanol by combined pervaporation and distillation

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Abstract

A cellulose derivative membrane (30 wt.% cellulose acetate butyrate (CAB) combined with 70 wt.% cellulose acetate propionate (CAP)) was prepared, and its properties were evaluated by the pervaporation separation of mixtures of ethyl tert-butyl ether (ETBE) and ethanol. The experimental results showed that the selectivity and permeability of the membrane were dependent on the blend composition, the processed feed and the experimental temperature. With respect to the temperature, the fluxes obeyed the Arrhenius equation. On the basis of these results, a separation process for the production of ETBE was developed by combining pervaporation and distillation. The distillation column was designed with the software ASPEN PLUS, and the liquid–vapour equilibria were predicted by the UNIFAC method. The area of the membrane was calculated according to the production capacity. It may be concluded that the combined process for the separation of mixtures of ETBE and ethanol is simple with high recovery of the ETBE product.

Keywords: Distillation; ETBE; Ethanol; Pervaporation

1. Introduction

The demand for ethyl tert-butyl ether (ETBE), a very efficient octane value enhancer, has increased rapidly with the development of environmental concern in recent years [1]. Lead-free fuels with low aromatic contents are increasingly required. Ethanol can be produced from farm products and recycled. Therefore it is estimated that much more ETBE will be demanded in the future.

Fig. 1 shows an ether production process. ETBE is produced by reacting ethanol with isobutylene. An excess of ethanol is required to reach high degrees of conversion, and ethanol combined with ETBE can form an azeotropic mixture. Therefore, a very complex flow sheet with several distillation columns was designed. This is a high capital, energy intensive separation process. Pervaporation separation has been widely recognized as an alternative separation process for azeotropic mixtures, close boiling point mixtures and isomers, because of its special characteristics [2,3]. Mass transfer through a dense polymer membrane is rather slow, and therefore pervaporation is not a complete separation technique in itself, since a pervaporator cannot be assembled in a cascade, as with plates in a distillation column. Pervaporation is generally used to complement distillation when the latter process is inefficient, e.g. to pass over the azeotropic composition of a given binary liquid mixture. A hybrid distillation–pervaporation process for methyl tert-butyl ether (MTBE) production, developed by Air Products & Chemicals, has shown that significant cost and energy savings can be obtained [4,5]. Some results of the design methodology for a membrane–distillation column hybrid process have been reported [6–11]. Humphrey and Seibert [12] have reported that the distillation–pervaporation hybrid system is an energy efficient system. However, due to the shortage of high performance membranes and a lack of understanding of the per-

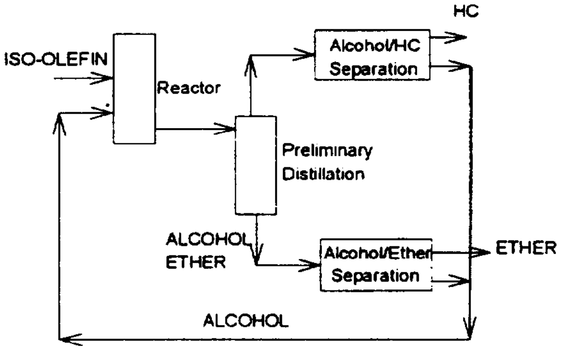

Fig. 1. Ether production process.

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vaporation process, difficulties have been encountered. A common method for all samples is still required.

In this work, a cellulose derivative membrane was prepared for the separation of ETBE–ethanol mixtures [13]. The properties of the membrane were evaluated by the pervaporation separation of ETBE–ethanol mixtures. On the basis of this work, a separation process for the production of ETBE was designed by combining pervaporation and distillation. Two combination methods were developed for different composition feeds, and the area of the membrane was calculated according to the production capacity.

2. Experimental details

Cellulose acetate butyrate (CAB) (52 wt.% butyryl content; average molecular weight, 30 000), cellulose acetate propionate (CAP) (46 wt.% propionyl content; average molecular weight, 75 000) and ethanol (EtOH) were purchased from Aldrich Chemical Company. ETBE was kindly supplied by the Institut Français du Pétrole (IFP). All chemical products were used directly without further purification.

CAB (30 wt.%) and CAP (70 wt.%) were dissolved in acetone to obtain the desired polymer solution at room temperature. Homogeneous membranes were prepared by casting the solution onto the plate surface of PVC films, followed by evaporation under no air flow conditions at room temperature. The average thickness of the membranes prepared by this method was around 50 μm.

The experimental apparatus used in this work is shown in Fig. 2. A dry membrane was installed in the pervaporation cell equipped with a heating jacket. The effective membrane area in the cell was 22.8 cm^2. Warm water was circulated to keep the experimental temperature at the desired value. The pervaporation experiments were carried out at 40, 50 and 60 °C. The feed solutions were mixtures of ETBE and EtOH (EtOH content, 3.1–30 wt.%). The pressure downstream was evacuated to less than 0.75 mmHg. The permeates were collected in cold traps cooled with liquid nitrogen. The compositions of the permeates were analysed with a VARIAN STAR 3400CX gas chromatograph. The fluxes of different membranes were normalized to a membrane thickness of 5 μm, assuming a proportionality between the fluxes and the membrane thickness. The distillation column was designed by the software ASPEN PLUS, and the vapour–liquid equilibria were predicted by the UNIFAC method.

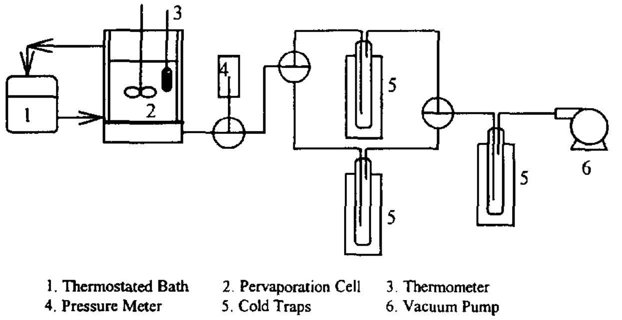

Fig. 2. Schematic diagram of experimental apparatus: 1, thermostatically controlled bath; 2, pervaporation cell; 3, thermometer; 4, pressure meter; 5, cold traps; 6, vacuum pump.

3. Results and discussion

3.1. Pervaporation characteristics of blended membrane of 30% CAB with 70% CAP

As shown in Fig. 3, with an increase in CAB (wt.%) in the blend, the total flux increases rapidly, EtOH (wt.%) in the permeate decreases slowly and the membrane becomes more fragile at 40 °C. With regard to the stability of the blended membrane, the fluxes and the purpose of passing the azeotropic point with high selectivity, a blended membrane of 30 wt.% CAB with 70 wt.% CAP was chosen in our experiments. Under the experimental conditions, this blended membrane is stable; no change in properties was observed.

The pervaporation characteristics of the membrane of 30% CAB with 70% CAP were studied systematically. The influences of the amount of EtOH (wt.%) in the feed and the experimental temperature were studied. As shown in Fig. 4, the total, EtOH and ETBE fluxes increase rapidly when the temperature and EtOH (wt.%) in the feed are increased. This is because the molecules of the mixture move more quickly when the temperature is increased, and the diffusion coefficients of EtOH and ETBE in the membrane increase. As EtOH (wt.%) in the feed increases, the swelling ratios of the membrane increase, causing the fluxes to increase. However, due to the strong interactions between the polymer and EtOH molecules, EtOH can pass through the membrane preferentially; therefore, the EtOH flux is much higher than that of ETBE.

From the curves in Fig. 5 and the diagram of ln J_{EtOH} vs. $(1/T-1/T_0)$ shown in Fig. 6, we can see that all of these curves pass through the origin and the slopes of the curves in Fig. 6 are almost the same. Therefore it can be estimated that, for the membrane, the EtOH flux obeys the following Arrhenius equation

$$J_{\mathrm{EtOH}}=(k_1X+k_2X^2)\,\mathrm{e}^{-[(E/R)(1/T-1/T_0)]} \quad (1)$$

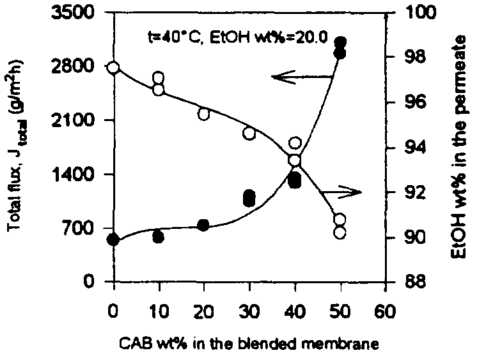

Fig. 3. Total flux and EtOH (wt.%) in the permeate as a function of the blend composition.

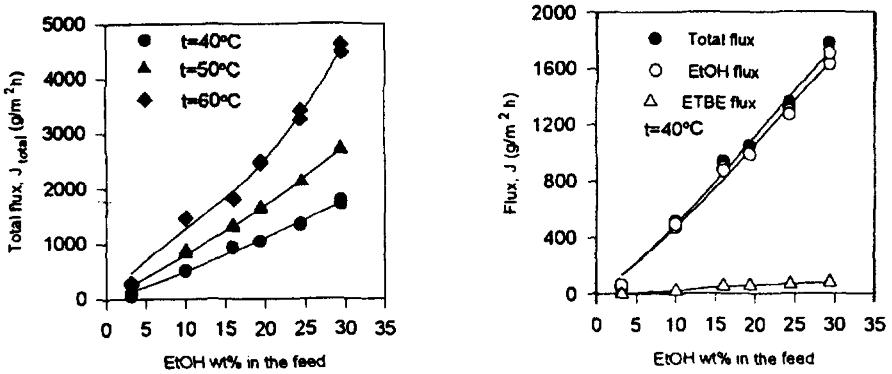

Fig. 4. Influence of EtOH (wt.%) in the feed and the experimental temperature on the fluxes.

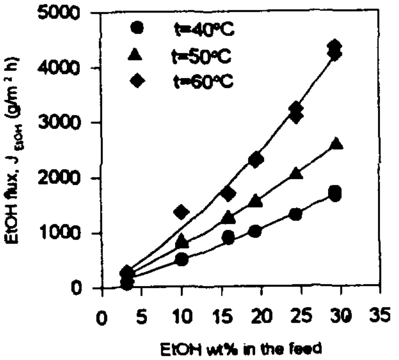

Fig. 5. Diagram of J_{EtOH} vs. EtOH (wt.%) in the feed.

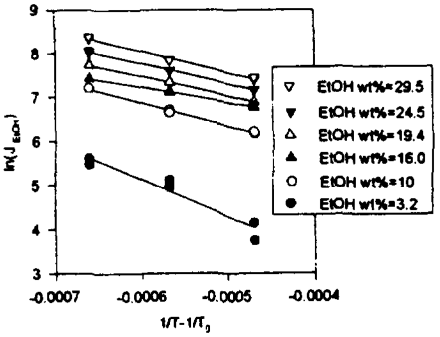

Fig. 6. Diagram of ln J_{EtOH} vs. $(1/T-1/T_0)$.

where J_{EtOH} is the EtOH flux ($g\ m^{-2}\ h^{-1}$), k_1 and k_2 are the constants of the equation ($g\ m^{-2}\ h^{-1}$), X is the EtOH (wt.%) in the feed, E is the so-called "activation energy" ($J\ mol^{-1}$), which is strongly dependent on the activation energy of permeation [14], T is the absolute temperature (K) and $T_0=273$ K. R is the gas constant ($J\ mol^{-1}\ K^{-1}$).

E, k_1 and k_2 were evaluated from the experimental data. $k_1=3.969\ g\ m^{-2}\ h^{-1}$, $k_2=0.072\ g\ m^{-2}\ h^{-1}$ and $E=3.944\times10^4\ J\ mol^{-1}$ were obtained. Therefore Eq. (1) for the membrane of 30% CAB with 70% CAP can be written as

$$J_{EtOH}=(3.969X+0.072X^2)\,e^{-[(3.944\times10^4/R)(1/T-1/T_0)]} \quad (2)$$

For the total flux, Eq. (3) can be obtained in the same way

$$J_{total}=(4.165X+0.068X^2)\,e^{-[(4.005\times10^4/R)(1/T-1/T_0)]} \quad (3)$$

As shown in Fig. 7 and Fig. 8, the calculated values and experimental data fit very well.

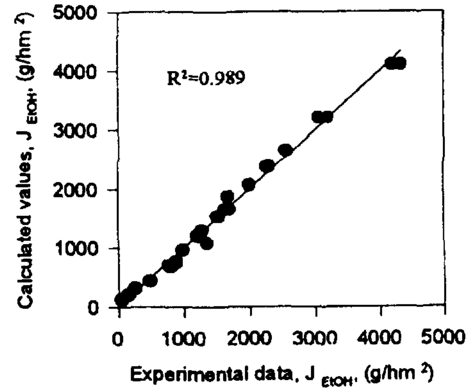

Fig. 7. Comparison of experimental data with calculated values (EtOH).

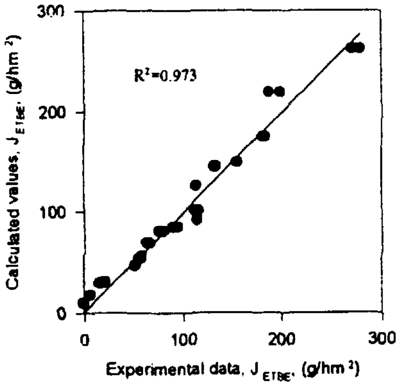

Fig. 8. Comparison of experimental data with calculated values (ETBE).

3.2. *Equations for the simulation of the continuous flow pervaporation separation of ETBE–EtOH mixtures*

The basic equations governing the pervaporation process are the three differential equations which formulate mass and heat transfer balances. For simplification of the equations, only the mass transfer balance for the binary mixture is presented here, as shown in Fig. 9.

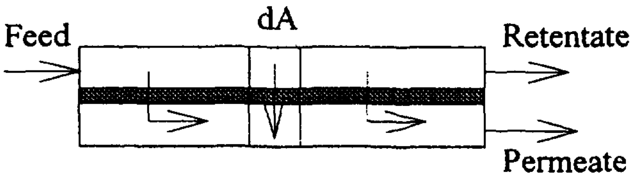

Fig. 9. Continuous flow pervaporation separation process.

The main assumptions in this model are:

1. constant temperature in the membrane module;
2. plug flow along the feed side of the membrane;
3. cross-flow along the permeate side of the membrane.

For one element dA, the overall mass balance is

$$dG = -J_{\text{total}}\, dA \tag{4}$$

where G is the retentate flow rate through the cross-section dA. The mass balance relative to the faster permeate, EtOH, is

$$d(GX) = -J_{\text{EtOH}}\, dA \tag{5}$$

where X is the concentration of EtOH. Eq. (5) can be rewritten as

$$d(X) = -\frac{XJ_{\text{total}} - J_{\text{EtOH}}}{G}\, dA \tag{6}$$

Eq. (4) and Eq. (6) can be numerically integrated by the usual Runge–Kutta method after defining the boundary conditions.

Because the azeotropic point of the mixture is at about 21 wt.% EtOH content under 1 atm, the feed containing 20 wt.% EtOH was considered. According to the requirement of the EtOH content in the retentate, the membrane areas for 2000 kg h^{-1} processed ability at 40, 50 and 60 °C were calculated by combining Eqs. (2)–(6). As shown in Fig. 10, the areas increase when the EtOH content in the retentate is required to be low and the temperature decreases. This is because the fluxes of the membrane decrease when the temperature and EtOH (wt.%) in the feed decrease.

3.3. Separation process of ETBE–EtOH by combined distillation and pervaporation

As reported by Matoqu et al. [15], the reaction mixture is a multicomponent solution. The feed to the distillation column usually ranges from 10 to 30 wt.% in ethanol content. For simplification of the simulation conditions, the feed was assumed to be a binary mixture containing only ethanol and ETBE. Therefore two combination methods shown in Fig. 11 were designed for 10 wt.% EtOH and 30 wt.% EtOH in the feed. For the feed containing 10 wt.% EtOH, distillation was performed first. ETBE was obtained at the bottom of the column. The azeotropic mixture from the top of the column was separated by the pervaporator. The permeate was recycled to the reactor. The retentate as a feed was passed to the distillation column. For the feed containing 30 wt.% EtOH, separation was performed first with the pervaporator to give the permeate and retentate. The permeate was recycled to the reactor, and the retentate containing 10 wt.% EtOH was passed to the distillation column. The bottom product was ETBE, and the top product was the azeotropic mixture which was passed to the pervaporator.

Because the permeate is returned to the reactor, the ETBE content is required to be low. For the membrane, the stability and selectivity are much better at low temperature than at

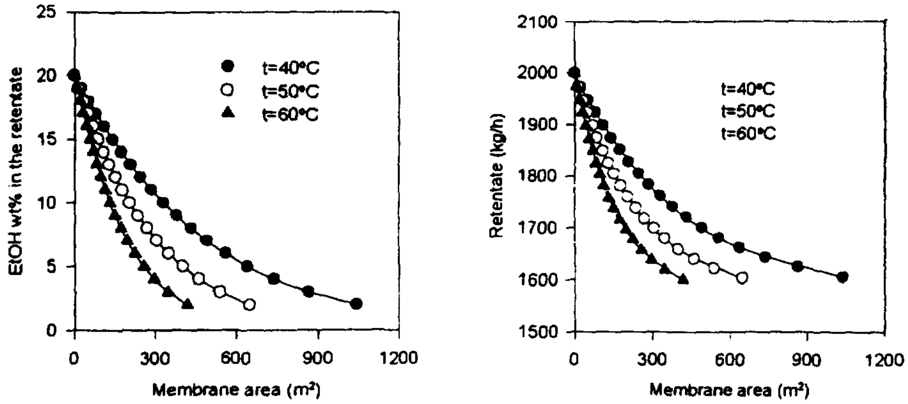

Fig. 10. Membrane area for continuous pervaporation process.

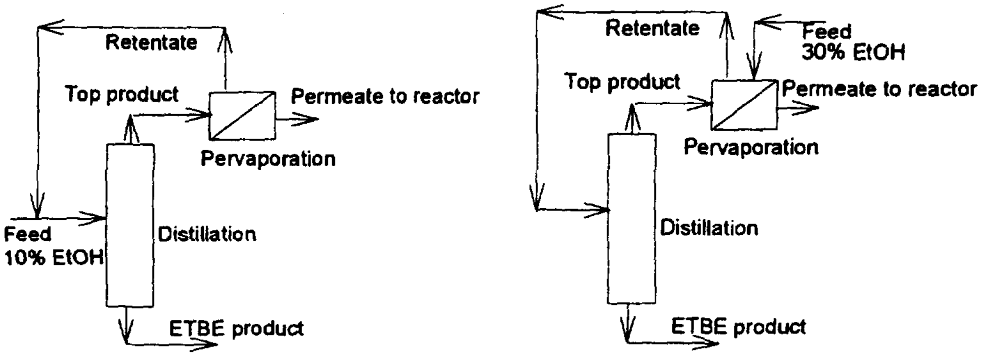

Fig. 11. Separation processes by combined distillation and pervaporation.

Table 1
Calculation results of the two processes

	10 wt.% EtOH in the feed			30 wt.% EtOH in the feed		
	Flux (kg h^{-1})	EtOH (wt.%)	ETBE (wt.%)	Flux (kg h^{-1})	EtOH (wt.%)	ETBE (wt.%)
Feed	2000	10	90	2000	30	70
Bottom product	1799	0.6	99.4	1370	0.6	99.4
Top product	1799	19.4	80.6	1370	19.4	80.6
Permeate	201	94.0	6.0	630	94.0	6.0
Retentate	1598	10.0	90.0	2740	10.0	90.0

high temperature, although the flux at low temperature is not as high. With all these considerations, 40 °C was chosen as the pervaporation temperature. For the two processes, the operation of the distillation column is the same. The reflux ratio is 2.5, the number of plates is 10, the feed position is at the fourth plate, and the pressure at the top of the column is 1 atm. For the feed of 10 wt.% EtOH to the pervaporator, the membrane area is 286 m^2. For the second condition, an area of 722 m^2 is required. The calculated results are listed in Table 1. From these two processes, we can see that this is a simple method of separation of azeotropic mixtures. If optimum processes are used in practical production, a higher efficiency and a lower consumption of energy will be achieved.

For the same feed and separation requirements in the same distillation column, if the distillation unit alone is used, the recovery of ETBE will be only 55.2% for the feed of 10 wt.% EtOH. Compared with the combined process, the recovery of ETBE by the distillation unit alone is much lower.

4. Conclusions

The mass fluxes through the blended membrane of 70% CAP with 30% CAB can be described by Arrhenius equation. The fluxes increase when the temperature and EtOH concentration in the feed are increased.

The required membrane areas in the continuous flow pervaporation process increase when the temperature and EtOH concentration (wt.%) in the retentate decrease. The calculation results show that combined distillation and pervaporation is a simple process for the separation of the mixtures of ETBE and EtOH with high recovery of the ETBE product.

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