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Pervaporation with Reactive Distillation for the Production of Ethyl *tert*-Butyl Ether

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ABSTRACT

The combined process of pervaporation with reactive distillation was studied for the production of ethyl *tert*-butyl ether (ETBE) from ethanol (EtOH) and *tert*-butyl alcohol (TBA) on an ion-exchange catalyst. An apparatus consisting of a stirred batch reactor, a distillation column, and a pervaporation membrane was used to test this technique. The permeation flux and selectivity of water in the membrane were investigated in water–alcohols system. The etherification was performed in the liquid phase by using a batch reactor. The reactive distillation was examined with and without pervaporation at the boiling point of the reactant mixture under atmospheric pressure. When pervaporation was not conducted, two layers formed in the top products because of a higher concentration of water. However, these phenomena were not observed when pervaporation was added. It was revealed that pervapovation might be effective for removing water from the bottom and that a higher fraction of ETBE could be obtained as a top product.

INTRODUCTION

Recently, the combined processes of separation with chemical reaction have attracted much attention. A typical example is the reactive distillation process that has been used to produce tertiary ethers on a large scale. The use of membranes in chemical reactions has also aroused interest because it leads to a less energy-intensive process. Okamoto et al. (1) reported the result of pervaporation-aided esterification of oleic acid with

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ethanol through asymmetric polyimide membranes in the presence of *p*-toluenesulfonic acid. They presented a model in which the kinetic equation was combined with the permeation flux equation.

Keurentjes et al. (2) also investigated the esterification of tartaric acid with ethanol. The calculated results showed that the pervaporation could remove the water produced in this reaction. The equilibrium composition could be shifted significantly toward the formation of the final product, diethyltartrate.

In this paper a process of reactive distillation combined with pervaporation is proposed to produce ethyl *tert*-butyl ether [$(CH_3)_3(COC_2H_5)$, ETBE], one kind of nontoxic and nonpollutant gasoline additive.

Generally, ETBE can be produced by an exothermic reversible reaction between ethanol (CH_3CH_2OH, EtOH) and isobutene [$(CH_3)_2C{=}CH_2$, IB] using acidic catalysts. However, IB sources are limited to catalytic cracking and steam cracking fractions. Thus, *tert*-butyl alcohol [$(CH_3)_3COH$, TBA], as a coproduct of propylene oxide synthesis from isobutane and propylene, can be used as an alternative route to produce ETBE.

Studies using TBA and EtOH to synthesize ETBE can be traced back to 60 years ago by the research of Norris and Rigby (3) and of Evans and Edlund (4). Nevertheless, little attention has been given to this process. Research on the homogeneous catalysis of ETBE formation from TBA in hot compressed liquid ethanol with sulfuric acid catalyst was reported recently by Habenicht et al. (5). They proposed a kinetic model that would embody the detailed mechanism of ETBE production.

In our previous paper (6) the following three reversible reactions were suggested for the synthesis of ETBE from TBA and EtOH by using heterogeneous catalysts, an ion-exchange resin, and a heteropoly acid.

$$\mathrm{EtOH} + \mathrm{TBA} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \mathrm{ETBE} + \mathrm{H_2O} \tag{1}$$

$$\mathrm{TBA} \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} \mathrm{IB} + \mathrm{H_2O} \tag{2}$$

$$\mathrm{EtOH} + \mathrm{IB} \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} \mathrm{ETBE} \tag{3}$$

Since ETBE has a lower boiling point than EtOH or TBA, a reactive distillation process may be suitable. If the pervaporation technique is introduced by using a selective membrane, the water produced, which has the highest boiling point, can be continuously permeated from the bottom.

The concentration of ETBE in the bottom will thereby be increased, and its purity in the top product can be enhanced.

This process has been successfully used in the synthesis of MTBE in our earlier work (7). In this case, two types of catalysts, an ion-exchange resin and a heteropoly acid, were used. Reactive distillation was examined with and without pervaporation. When pervaporation was introduced, the water mole fraction in the bottom was lowered. The purity of MTBE as a top product was an 85 vol% azeotropic mixture in all the cases. However, since the flat membrane was placed in the bottom of the reactor, the surface area of the membrane was limited to the reactor's inside diameter, which implied a low permeation flux.

One of objectives in this work is to evaluate new routes for the efficient production of ETBE from TBA and EtOH by using a more efficient membrane module.

EXPERIMENT

Membrane

A microporous hollow fiber membrane module (made by Daicel Chemical Industry Co., Japan) was used in this work. The membrane was composed of polyacrylonitrile (support layer) and a poly-ion complex (permselective layer). The membrane module system consisted of 220 hollow fibers with an ID/OD of 500/800 μm and a length of 0.37 m. The total membrane area was 0.13 m^2.

Catalysts

The strong cation-exchange resin Amberlyst 15 in the H^+ form (abbreviated as A15) was used as a catalyst. This resin is a sulfonated styrene divinyl benzene copolymer with a macroreticular structure. The mesh size was in the 20–24 range, and the particle average diameter was 0.78 mm. The ion-exchange capacity, Q, was 4.96 [mol H^+/(kg dry resin)].

The catalyst was treated with ethanol and kept at 368 K in a vacuum oven overnight to remove any moisture before use.

Apparatus

A schematic diagram of the apparatus is shown as Fig. 1. The lower section was a glass reactor (7×10^{-4} m^3). The four catalyst baskets made of stainless steel screen with openings of 0.16 mm, they were attached on baffles at the reactor wall. A magnetic stirrer was used to mix the reactants. Hot water at 355 K was circulated in the reactor jacket to maintain the reaction temperature at the boiling point. The upper part was a distillation column (15 cm) packed with stainless steel saddles. A condenser was placed in the top of the column, and cooling water at 278 K was circulated within it. A trap was connected through the condenser to collect the IB gas produced during the reaction. The membrane module was connected with a vacuum pump to keep the permeation pressure within 5–10 torr.

Analysis

Analysis was carried out by gas chromatography with a 2.5-m column of Gaskuropack-54 (60/80 mesh) as the packing material. The column temperature was set at 443 K, and the carrier gas was helium at 0.12 MPa. Good separation was achieved for all components.

Procedure

The standard conditions for reactive distillation with pervaporation were as follows. Catalyst baskets packed with 13 g catalyst were attached on baffles. EtOH (4 mol) was poured into the reactor. When the reactor was heated up to 323 K, EtOH was supplied to the membrane module and returned continuously to the reactor from the top of the membrane module. When the EtOH was heated to 343 K (reaction temperature), 2 mol of TBA was added and the reaction was started. This procedure was adopted for about 1 hour from start-up as a batch process. When the liquid level in the bottom of condenser was high enough, the continuous process was started up by switching on the feed and output pumps. The feed was a mixture with a TBA/EtOH molar ratio of 2. The reflux ratio was adjusted by controlling the volumetric flow rate of the output pump. Two traps were connected with a vacuum pump and alternately used during the reaction to recover the water. The total quantity of water was weighed and analyzed after the reaction was stopped. Samples (1.0×10^{-6} m^3) were taken at a 1-hour intervals from the both the output and bottom to measure the concentrations of H_2O, EtOH, TBA, IB, and ETBE. The IB liquefied in a trap was also weighed after the reaction.

RESULTS AND DISCUSSION

Permeation Rate of Water by Pervaporation

Pervaporation experiments were carried out at 345 K with EtOH–H_2O two-component and EtOH–TBA–H_2O three-component systems, respectively, in a batch mode by using the stirred vessel (the reactor for reactive distillation apparatus in Fig. 1) with a condenser and membrane module. As shown in Fig. 2, the permeation rate is proportional to the water con-

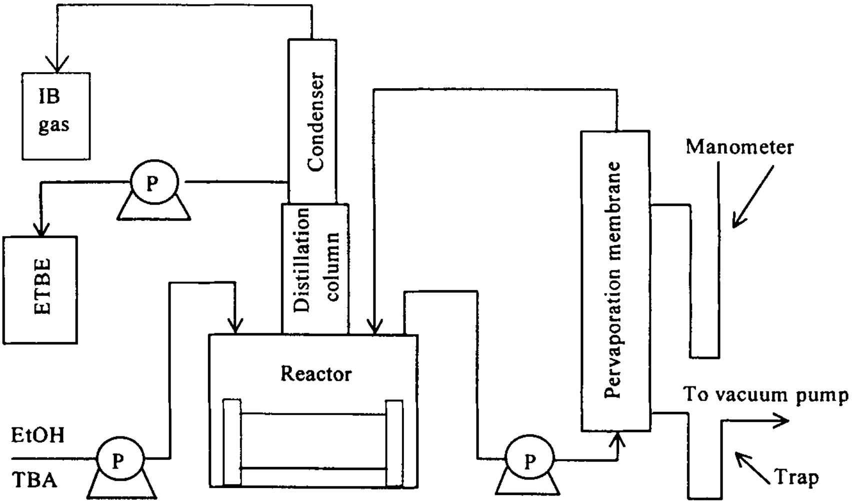

FIG. 1 Schematic diagram of the apparatus.

centration at low water content up to a 15% molar fraction) and can be expressed as

$$q = 0.022X_{H_2O}\ [\text{mol}/(\text{m}^2\cdot\text{s})] \tag{4}$$

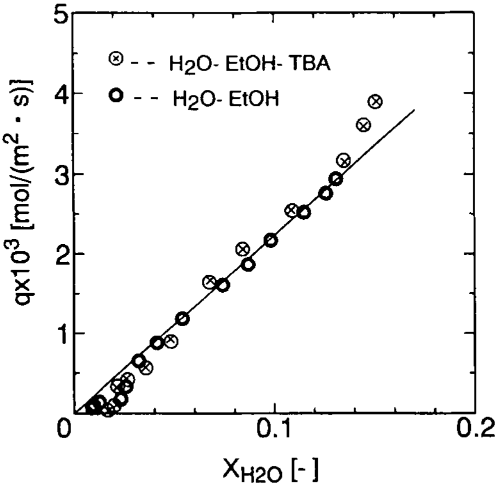

FIG. 2 Permeation rate vs water concentration.

The permeation flux rate of water in this membrane was about 2.8 times more than that in earlier work (7), and the membrane surface area was 34 times larger. As a result, the permeation flux was about 95 times greater. The selectivity of the membrane, α, is defined as the permeation ratio of water to alcohol. The value of α was 138 for a binary mixture and 101 for a ternary mixture. The pervaporation experiment results show that the membrane module possesses higher water transport selectivity relative to alcohol. Therefore, it can be effective for removing water from reactant mixtures.

Etherification in the Batch Reactor With and Without Pervaporation

The experiment of etherification with pervaporation was carried out at 340 K below the boiling point of the reactant mixtures by using the same apparatus as for the pervaporation experimental system. The molar ratio of EtOH/TBA was 2 in order to decrease the hydrolyzation of TBA. The same feed composition and reaction temperature were also adopted for the cases of reaction without pervaporation. The stirred vessel with a condenser was used as a batch reactor without pervaporation.

The time courses of etherification for both cases are given in Figs. 3 and 4, respectively. The solid lines in both figures are the results calculated by using the kinetics parameters developed in our previous work (6). The

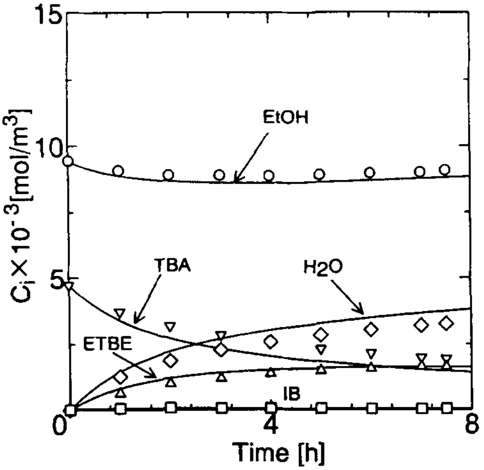

FIG. 3 Time course of etherification without pervaporation (A15 = 12 g, 340 K, $EtOH_0$ = 4 mol, TBA_0 = 2 mol).

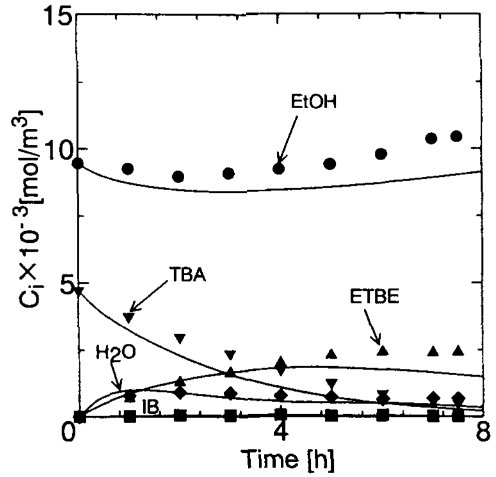

FIG. 4 Time course of etherification with pervaporation (A15 = 12 g, 340 K, $EtOH_0$ = 4 mol, TBA_0 = 2 mol).

symbols represent experimental results. Since water was removed from reactant mixtures by introducing pervaporation, the quantity of water after 7 hours in the reactor was just 0.15 times that found without pervaporation. The quantity of ETBE was 1.25 times larger.

Reactive Distillation With and Without Pervaporation

Experiments of reactive distillation with and without pervaporation were carried out at the boiling point of reactant mixtures (343 K for those with pervaporation and 345 K for those without pervaporation). Typical concentration profiles of bottom products for both cases are shown in Fig. 5. When pervaporation was conducted, the water fraction was lowered significantly and the concentration of ETBE was higher. The reason may be considered as follows: Since water could be removed from the mixture, the reaction was shifted toward the formation of more ETBE when pervaporation was performed. Steady-state was not attained after 7 hours, especially in the case without pervaporation, because the residence time was longer than 5 hours.

Figure 6 shows the concentration profiles of top products for cases with and without pervaporation. The desired product, ETBE, could not be obtained with high purity.

Since the mixtures were highly nonideal, azeotropic mixtures of ETBE–ETOH, ETBE–H_2O and EtOH–H_2O were formed. The concen-

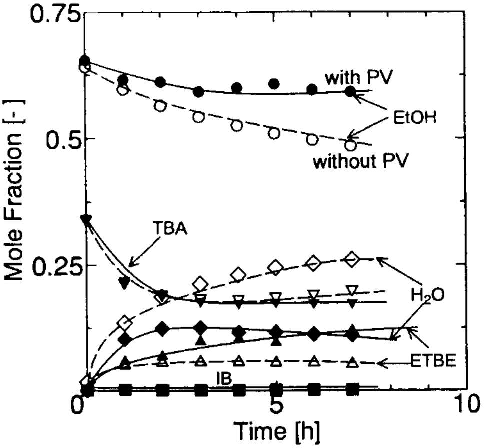

FIG. 5 Comparison between bottom products with and without pervaporation (A15 = 13 g, $V_F = 1.1 \times 10^{-8} m^3/s$, $V_P = 5 \times 10^{-9} m^3/s$, $R = 6$).

tration of ETBE in the top products cannot exceed the limit of the azeotropic mixtures. When pervaporation was not conducted, two layers were formed in the top products because of a higher concentration of water. This behavior was observed in our other work, which used low-grade

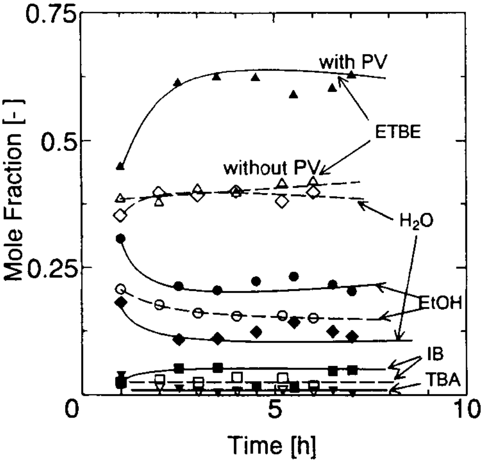

FIG. 6 Comparison between top products with and without pervaporation (A15 = 13 g, $V_F = 1.1 \times 10^{-8} m^3/s$, $V_P = 5 \times 10^{-9} m^3/s$, $R = 6$).

alcohol (mixture of 80 mol% water) as a feed material (8). The compositions in the upper layer were similar to those in a single layer with pervaporation. On the other hand, the lower layer contains about 90 mol% water and 10 mol% ethanol. Since ethanol is substantially more polar than ethers, it can easily combine with water to form a new layer.

The open symbols and broken lines (without pervaporation) in Fig. 6 indicate mole fractions as averaged from moles in the upper and lower layers. They are very different from the filled symbols and solid lines (with pervaporation). The effect of pervaporation is revealed by this difference.

CONCLUDING REMARKS

Reactive distillation to produce ETBE with and without pervaporation has been studied. Pervaporation can be an effective way to remove water from the bottom product and to enhance the concentration of ETBE in the top product. The method should apply to commercial processes for the production of other fuel ethers and esters.

To obtain richer ethers by etherification of two kinds of alcohol, the following steps should be considered for improving the present process.

1. Return gaseous products to the reactor. In our work, the dehydration of TBA, Eq. (2), is significant at the boiling point conditions. The conversion of TBA to the gaseous product, IB, was about 25% as determined from the volume of liquefied IB in the trap. Therefore, the desired products, fuel ethers, can be produced in greater quantity by recycling the gaseous components.

2. Use two kinds of membranes. As shown in Fig. 7, a new concept of using two kinds of membranes may be considered. One is the membrane used to remove water by pervaporation in this work. The other is the membrane used to remove the ether. If high selectivities are realized with these membranes the desired product, ether, can be produced by etherification from two kinds of alcohol. Jonquieres et al. (9) studied the pervaporation of ETBE–EtOH mixtures through a polyurethaneimide film. The pervaporation selectivity of EtOH was higher than that of ETBE. However, if the polymer structure is changed, the selectivity may be inverted.

3. Add an inert component. Azeotropic mixtures can be separated with the help of an inert component. This component does not affect the chemical reaction but may have a significant influence on the characteristics of the separation. This procedure was reported by Ung and Doherty (10). In their research, *n*-butane was added to the MTBE–MeOH–IB reactive distillation system, and high purity MTBE was obtained as the bottom

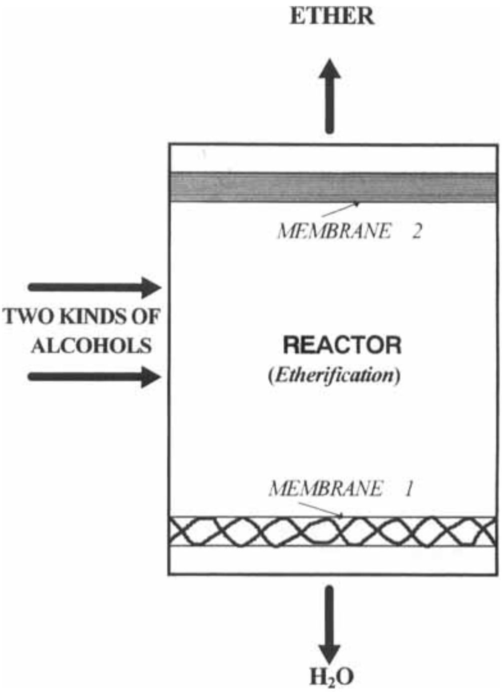

FIG. 7 Ideal process with two kinds of membranes.

product. The same procedure can also be applied to our system by choosing a suitable inert component.

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SYMBOLS

C_i	concentration of composition (mol/m^3)
q	permeation flux rate of water [(mol/(m^2·s)]
V_F	flow rate of feed (m^3/s)
V_P	flow rate of product (m^3/s)

R	reflux ratio (—)
X_{H_2O}	molar fraction of water (—)
α	selectivity of membrane (—)

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