

COMBINED PROCESS FOR PRODUCTION OF METHYL *tert*-BUTYL ETHER FROM *tert*-BUTYL ALCOHOL AND METHANOL

MOHAMMED MATOUQ, TOMOHIKO TAGAWA
AND SHIGEO GOTO*

Department of Chemical Engineering, Nagoya University,
Nagoya 464-01

Key Words: Reactive Distillation, Pervaporation, Methyl *tert*-Butyl Ether, Heteropoly Acid, Ion Exchange Resin, *tert*-Butyl Alcohol, Membrane Reactor.

Reactive distillation for the production of methyl *tert*-butyl ether (MTBE) from methanol (MeOH) and *tert*-butyl alcohol (TBA) using two types of catalysts, ion exchange resin and heteropoly acid (HPA), has been studied. The reaction was performed in the liquid phase and at the boiling point of the reactant mixture under atmospheric pressure. The reactive distillation was examined with and without pervaporation. An azeotropic mixture of MTBE and MeOH was obtained as a top product. HPA showed higher selectivity than did ion exchange resin. It was found that the pervaporation might be effective in removing water.

Introduction

Methyl *tert*-butylether (abbreviated as MTBE) has gained great attention as a gasoline additive to replace lead oxides. MTBE is preferable from the environmental point of view because of its non-toxic and non-pollutant properties²⁾.

MTBE is usually produced from the reaction between isobutene (IB) and methanol (MeOH) in the presence of a strong acid catalyst. The production of MTBE on a commercial scale using sulphonated ion-exchange resin is well established¹⁾.

Butylene sources are limited to natural gas, crude oil and catalytic cracking, which cannot meet the increasing demand for MTBE. Thus, *tert*-butyl alcohol (TBA) becomes an alternative route for the synthesis of MTBE.

In previous papers^{3,4)}, the kinetics of the synthesis of MTBE from TBA and MeOH were investigated using two types of catalysts: ion exchange resin and heteropoly acid (abbreviated as HPA). The water produced during the reaction should be separated so as to enhance the purity of the MTBE. Reactive distillation may be suitable for separating MTBE from water and other reaction mixtures.

A schematic diagram of a reactive distillation for the synthesis of MTBE from TBA and MeOH using ion-exchange resin is shown in Fig. 1-a. MeOH and TBA are fed continuously to the catalytic packed column. The MTBE produced can be separated as a top product. The water produced can be obtained as a bottom product.

This separation is based on the physical properties of the reactants and products which are indicated in Table 1.

Although the insoluble HPA (cesium ion salt) has much higher selectivity of MTBE than does the ion exchange resin (commercially known as Amberlyst 15), the particle size is too fine to separate from the liquid phase³⁾. To overcome this drawback, pervaporation can be combined with reactive distillation. The water produced can be continuously permeated from the bottom product through a highly selective membrane by the pervaporation technique.

Figure 1-b shows this concept. The apparatus consists simply of a lower and an upper part. The lower section is a reactor with a pervaporation cell to remove water. The upper part is a conventional packed distillation column. TBA and MeOH are fed continuously to the reactor. The produced MTBE, which has the lower boiling point, is fractionated in a packed distillation column and obtained as a top product.

The objective of this study is to introduce new routes for the efficient production of MTBE from TBA and MeOH by using reactive distillation.

1. Experimental

1.1 Catalysts

1) Ion exchange resin particles The ion exchange resin Amberlyst 15 (H⁺ form), 0.75-0.92 mm in size, was used to compare it with other catalysts.

2) Ion exchange pellets Amberlyst 15 was commercially available as particles of less than 1 mm diameter. The pressure drop was too high to propel the liquid phase downward in the distillation column. Therefore, cylindrical pellets were made by mixing Amberlyst 15 particles with polyethylene powders (15 wt%) in a mold of 8 mm diameter and heated to 413 K for one hour to bind

* Received November 29, 1993. Correspondence concerning this article should be addressed to S. Goto.

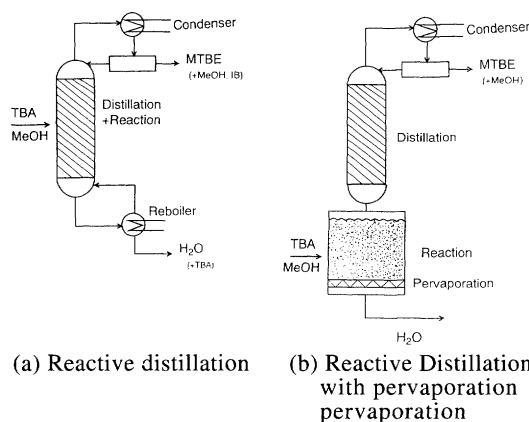


Fig. 1 Combined process to produce MTBE from TBA and MeOH

Table 1. Physical properties

Component	Molecular weight	Boiling point [K]
Isobutene (IB)	56.12	267
Methyl <i>tert</i> -butyl ether (MTBE)	88.15	328
Methanol (MeOH)	32.04	338
<i>tert</i> -Butyl alcohol (TBA)	74.12	355
Water (H ₂ O)	18.00	373
Azeotropic mixture (MeOH-MTBE)		
Azeotropic temperature		325
Azeotrope composition		
	(mol)	(vol)
MTBE	69 %	87 %
MeOH	31 %	13 %

particles. The ion exchange capacity was 3.98 mol/(kg-dry pellet), which was smaller than that of the particles (4.90 mol/(kg-dry particle)). This might be due to the addition of binders to the pellets.

3) HPA In the previous work³⁾, several kinds of HPA for the synthesis of MTBE were investigated. Among tested catalysts, cesium ion-exchanged tungstosilicic acid (H_{0.5}Cs_{3.5}SiW₁₂O₄₀) showed the highest selectivity. In this study, that catalyst was chosen to examine reactive distillation with pervaporation. The catalyst properties and the preparation method were described elsewhere³⁾.

1.2 Membrane

Polyvinyl alcohol (PVA) membrane was used in this work (PVA-1001 made by Mitsui Engineering and Shipbuilding Co. Ltd.). PVA membrane was treated in a solution of ethanol-water (95 vol% ethanol) for 8 hours before performing the experiment. The membrane was kept in an equimolar mixture of TBA and MeOH after the experiment.

1.3 Apparatus

1) Reactive distillation without pervaporation A schematic diagram for the details of the reactive distillation column without pervaporation is shown in **Fig. 2**. A vacuum-insulated column with 2.0 cm inside diameter and 1.0 m length was used to study the synthesis of MTBE. Ion exchange resin pellets were packed in the column up to a height of 30 cm in the lower part of the

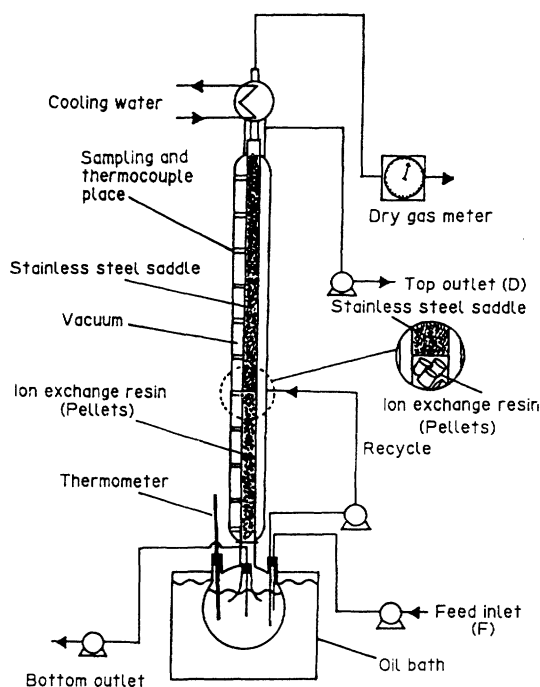


Fig. 2 Experimental setup for reactive distillation without pervaporation

column (reaction zone). The upper part of the column (separation zone) was packed with stainless steel saddles to provide a proper separation of MTBE in the upper zone of the column. Eleven holes were made to measure the temperature and concentration profiles inside the reactive distillation column. A thermochart recorder was connected to record the temperature. A four-neck round-bottom flask (reboiler) was connected to the column through the central opening. The feed and output pumps were connected through the other two openings. A thermocouple was placed in the fourth opening. An oil bath was used to heat the reactant mixture to its boiling point. Cooling water above the column was used as a condenser. A dry gas meter was connected to the condenser to measure IB production in the gas phase.

2) Reactive distillation with pervaporation The apparatus consisted of two parts. The lower part was a reactor (1.2 × 10⁻⁴ m³) with a pervaporation cell unit. The upper part is a distillation column (15 cm) packed with stainless steel saddles. Details are shown in the schematic diagram in **Fig. 3**. To suspend the catalyst, a magnetic stirrer was used. To maintain the reaction temperature at the boiling point, hot water at 355 K was circulated in the jacket.

The membrane was placed in the bottom of the lower part of the apparatus. A glass filter was used to support the membrane. An aspirator was used to reduce the pressure to 2.67 kPa. The permeated water was collected in a cold trap. A condenser was placed at the top of the column. A dry-gas meter was connected after the condenser to measure the IB produced in the gas phase.

1.4 Analysis

In the case of HPA, it is difficult to remove catalyst

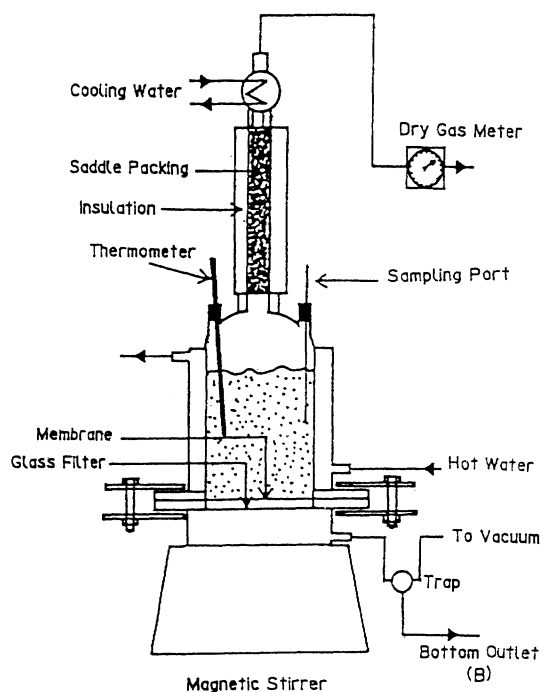


Fig. 3 Experimental setup for reactive distillation with pervaporation

from the reaction mixture by a simple filtration since the catalyst is finely suspended in the liquid. Therefore, the analysis of the bottom product was performed as follows. The sample from the slurry solution was centrifuged for 10 minutes. The clear layer was removed and recentrifuged again for 10 minutes. Then the sample was injected into a gas chromatograph with a 2.5 m column of Gaskuropack 54 at 463 K. In other cases, sample was injected directly into the gas chromatograph.

All components (TBA, MeOH, IB, MTBE and H₂O) could be well separated.

1.5 Procedure

1) Reactive distillation without pervaporation An equimolar ratio of TBA and MeOH ($2.76 \times 10^{-4} \text{ m}^3$) was placed in the bottom and heated to the boiling point of the mixture. Simultaneously, the recycle pump withdrew a portion of the reacted solution from the bottom to the top of the reaction zone. The speed of the recycle pump was controlled so as to keep the level of the liquid at the top of the packed catalyst bed section. By this method, the reaction was performed in the liquid phase. This procedure was adopted for about 2 hours from the startup as a batch process. When the temperatures across the column and the liquid level in the bottom became constant, a continuous process was started up by feeding an equimolar mixture of TBA and MeOH at the bottom and switching on the bottom and top pumps. By controlling the volumetric flow rate of the top pump, the reflux ratio was adjusted.

2) Reactive distillation with pervaporation An equimolar mixture of MeOH and TBA ($7 \times 10^{-7} \text{ m}^3$) was placed in the reactor and heated to the boiling point. When the boiling point was reached, a measured amount of catalyst

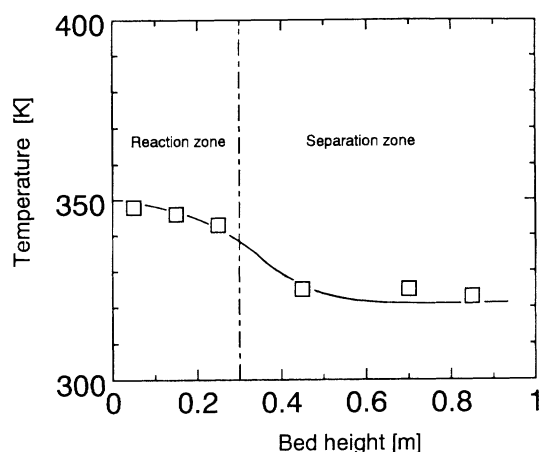


Fig. 4-a Temperature profile inside the reactive distillation column without pervaporation

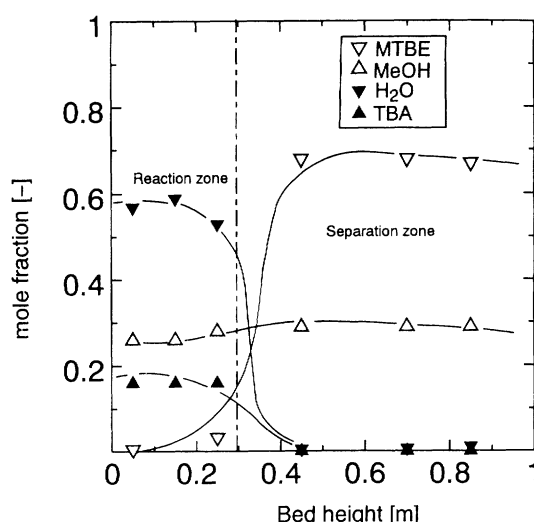


Fig. 4-b Concentration profiles inside the reactive distillation column without pervaporation

was added and the reaction was begun. Simultaneously, the vacuum pump was started to permeate water. Samples were taken every hour from top and bottom products.

2. Results and Discussion

2.1 Reactive distillation without pervaporation

The temperature and liquid-phase concentration profiles at the standard condition (6.5 reflux ratio, 30 g catalyst and $1.33 \times 10^{-8} \text{ m}^3/\text{s}$ feed flow rate) are shown in Figs. 4-a and 4-b, respectively. The temperature in the bottom was about 350 K. It rapidly changes around the interface of the reaction and separation zones. The temperature in the separation zone was about 325 K, which was the azeotropic temperature.

Water and TBA, with higher boiling points, existed in the reaction zone. MTBE, with a lower boiling point, existed in the separation zone. However, MeOH with its middle boiling point existed in both reaction and separation zones. The mixture of MTBE and MeOH in the

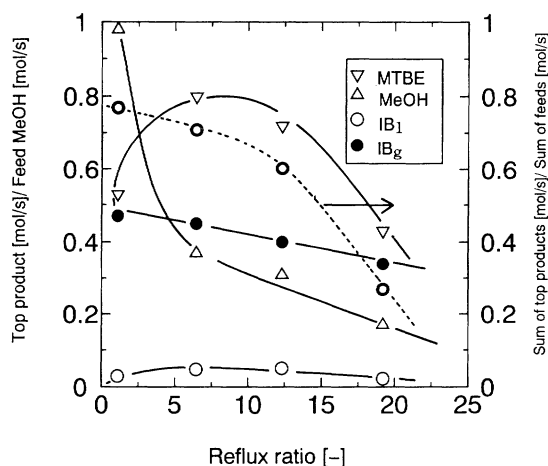


Fig. 5-a Effect of reflux ratio on top products for reactive distillation column without pervaporation

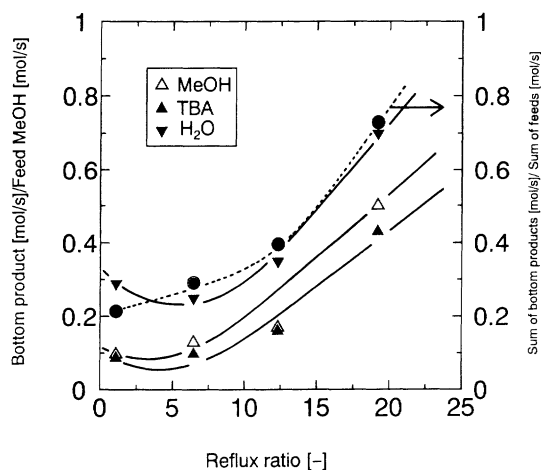


Fig. 5-b Effect of reflux ratio on bottom products for reactive distillation column without pervaporation

upper part of separation zone and condenser was azeotropic. Thus, complete separation of MTBE and MeOH could not be accomplished even if the separation zone was longer.

The effects of reflux ratio ($R = L/D$) on the yield for both top and bottom products have been studied. Other operating variables were kept at the standard condition. **Figure 5-a** shows the relations of the ratio of the distillate molar rate to the feed molar rate of MeOH versus the reflux ratio, R , together with the ratio of the summation of top products to the summation of feeds, S_t , versus R .

As the value of R increases, S_t is decreased. This tendency can be explained by lower distillate flow rate, D , at higher reflux ratio. Therefore, all components have the same tendencies except for MTBE at low reflux ratio.

When the reflux ratio is low, the retention time in the reaction zone is short. Therefore, most of MeOH may flow out without under going the main reaction to synthesize MTBE. This is the reason why MTBE has its maximum at about 6.5 of R .

IB in the liquid phase is low, while it is significant

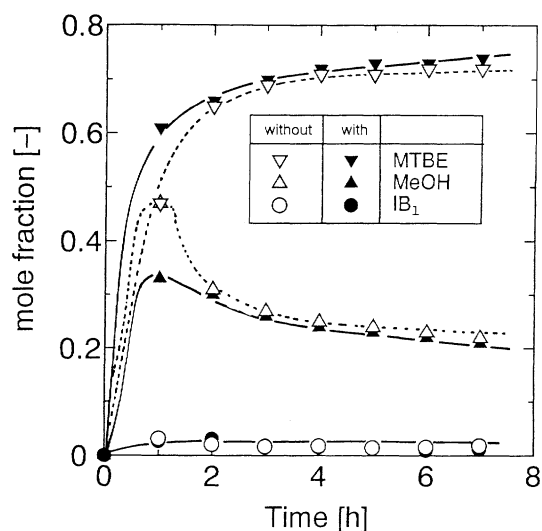


Fig. 6-a Comparison between top products with and without pervaporation

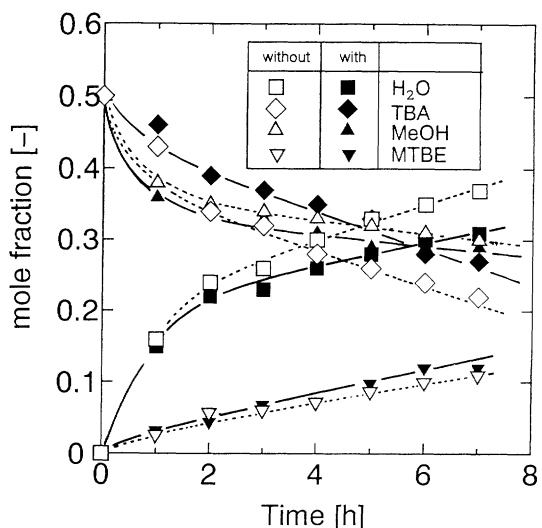


Fig. 6-b Comparison between bottom products with and without pervaporation

in the gas phase. Therefore, the dehydration of TBA cannot be neglected.

Figure 5-b shows the relation of the ratio of the residual molar rate to the feed molar rate of MeOH versus R together with the ratio of summation of bottom products to the summation of feeds, S_b , versus R . As the value of R increases, S_b ($\approx 1 - S_t$) is increased. Therefore, all components have the same tendencies except for H_2O at low reflux ratio.

When the reflux ratio is low, the dehydration of TBA to produce IB and H_2O is significant, because the retention time in the bottom flask is long. This is the reason why H_2O has the minimum at about 6.5 of R .

2.2 Reactive distillation with pervaporation

The surface area of the membrane ($3.85 \times 10^{-3} \text{ m}^2$) was limited to the reactor's inside diameter, which implied a low permeation flux rate. Then, semibatch mode operation was done by permeating the produced water continuously from the bottom products during the

Table 2. Experimental results for reactive distillation with pervaporation

Cat.	Cat. wt. [g]	IB _g [-]	H ₂ O (b) [-]	H ₂ O (p) [-]	PV rate kg/(s·m ²)
A15*	1.89	0.064	0.37	0.53	5.2×10^{-5}
HPA	34.5	0.016	0.31	0.43	4.2×10^{-5}
HPA	17.0	-	0.29	0.32	3.2×10^{-5}
HPA	8.5	-	0.25	0.27	2.6×10^{-5}

1) IB_g: accumulated IB in the gas phase after 7 hours per initial mole of MeOH

2) H₂O (b): water mole fraction in the bottom at 7 hours

3) H₂O (p): accumulated permeated water after 7 hours per initial mole of MeOH

*) Amberlyst 15

reaction, keeping the top products at total reflux.

Typical concentration profiles at 34.5 g HPA for the top products with and without pervaporation are shown in **Fig. 6-a**. The top products were mainly MTBE, MeOH and dissolved IB. There is little difference between the two profiles after four hours in top products with or without pervaporation. This is due to the azeotropic mixture of MeOH and MTBE.

The bottom concentration profiles with and without pervaporation are shown in **Fig. 6-b**. The water mole fraction in the bottom was lowered significantly when pervaporation was conducted. MeOH mole fraction in the bottom was lower when pervaporation was performed. Since water could be removed from the mixtures, the MTBE production rate was higher in the case of pervaporation. Therefore, the reaction was shifted toward forming more MTBE and then consuming more MeOH.

Table 2 shows the experimental results for reactive distillation with pervaporation for two kinds of catalysts (Amberlyst 15 particles and HPA). The 1.89 g of Amberlyst 15 was used to adjust to the same catalytic activity as 34.5 g HPA³⁾.

In the case of Amberlyst 15, the dehydration of TBA into water and IB was significant. The IB produced in the gas phase after 7 hours with pervaporation (0.064 mol IB in gas/mol-MeOH) was about 4 times (0.016 mol IB in gas/mol-MeOH) that for HPA.

In the case of HPA, as the catalyst weight decreased from 34.5 to 8.5 g the water mole fraction in the bottom, H₂O (b), the permeated water mole ratio,

H₂O (p), and the average pervaporation rate were decreased from 0.31 to 0.25, from 0.43 to 0.27, and from 4.2×10^{-5} to 2.6×10^{-5} kg/(s·m²), respectively. These behaviors could be explained by the decrease in the reaction rate to produce water.

Comparing the two catalysts the amount of permeated water, H₂O (p), and the pervaporation rate, PV in the case of Amberlyst 15 were higher than those for HPA. This may be attributed to a higher mole fraction of water, H₂O (b), due to the dehydration of TBA when Amberlyst 15 was used.

If the pervaporation flux can be much higher than in this work, the water mole fraction in the bottom, H₂O (b), may be negligible. The continuous operation as given in **Fig. 1-b** will be realized.

Conclusions

The reactive distillation column with and without pervaporation has been studied to produce MTBE. Two types of catalysts (ion-exchange resin and heteropoly acid) have been investigated. HPA showed higher selectivity than did ion exchange resin. The purity of MTBE as a top product was 85 vol% azeotropic mixture in all cases. Isobutene production rate in the gas phase could not be neglected due to the dehydration of TBA when the ion-exchange resin was used.

Nomenclature

<i>D</i>	=	distillate volumetric flow rate	[m ³ /s]
<i>L</i>	=	liquid volumetric flow rate	[m ³ /s]
<i>R</i>	=	reflux ratio (<i>L/D</i>)	[-]
<i>S_b</i>	=	molar ratio of the summation of bottom products to the summation of feeds	[-]
<i>S_t</i>	=	molar ratio of the summation of top products to the summation of feeds	[-]

Acknowledgments

The authors are deeply indebted to Mr. H. Itoh and Mr. T. Imura for skilled technical help in the reactor design. We thank the Mitsui Engineering and Shipbuilding Co. Ltd. for supplying the membrane.

Literature Cited

- 1) Hutchings, G., C. Nicolaides and M. Scurrall: *Catalysis Today*, **15**, 23-49 (1992)
- 2) Lee A.K.K. and A. Al-Jarallah: *Chem. Econm. Eng. Rev.*, **18**, 25-34 (1990)
- 3) Matouq, M., T. Tagawa and S. Goto: *J. Chem. Eng. Japan*, **26**, 254-258 (1993)
- 4) Matouq, M. and S. Goto: *Int. J. Chem. Kinet.*, **25**, 825-831 (1993)