AJChE 2005, Vol. 5, No. 1, 16–21

Simulation of Ethyl *Tert*-Butyl Ether Production from *Tert*-Butyl Alcohol and Ethanol in Reactive Distillation

Suttichai Assabumrungrat
Varong Pavarajarn
Darin Wongwattanasate
Piyasan Praserthdam
Center of Excellence in Catalysis and Catalytic Reaction Engineering
Department of Chemical Engineering, Faculty of Engineering
Chulalongkorn University
Bangkok 10330 Thailand
Email: Suttichai.A@eng.chula.ac.th

Shigeo Goto
Department of Chemical Engineering
Nagoya University
Chikusa, Nagoya 464-8603 Japan

Reactive distillation was applied for the synthesis of ethyl *tert*-butyl ether (ETBE) from a liquid-phase reaction between *tert*-butyl alcohol (TBA) and ethanol (EtOH) catalyzed by commercial β-zeolite catalyst with Si/Al ratio of 55. The major side reaction of this system was the dehydration of TBA to isobutene (IB). From the present researchers' previous work, it was found that β-zeolite was superior to commercial Amberlyst–15 catalyst in reaction selectivity. The kinetic parameters for the reactions, which were determined using a semibatch reactor operated at various temperatures, were used for simulation in Aspen Plus™ program. Various operating parameters, such as heat duty, molar ratio of H_2O: EtOH, and reflux ratio, were investigated for their effects on reactive distillation performance.

Keywords: *β*-zeolite, ethyl *tert*-butyl ether (ETBE) synthesis, *and* reactive distillation.

INTRODUCTION

Currently, there is a pending legislation on the use of methyl *tert*-butyl ether (MTBE) in a number of U.S. states because it was found that MTBE has a tendency to pollute underground water. Ethyl *tert*-butyl ether (ETBE) can be a potential alternative as it has been found to outperform MTBE.

ETBE has lower bRvp (4 psi) than MTBE (8–10 psi), which allows ETBE to be used successfully in obtaining gasoline with less bRvp than 7.8 psi as required in some hot places during summer (Cunill et al. 1993). From the environmental viewpoint, ETBE is derived from ethanol (EtOH) which can be obtained from renewable resources such as biomass.

Reactive distillation, as a promising process for equilibrium-limited reactions, has been applied to various esterification reactions such as MTBE, ETBE, and *tert*-amyl methyl ether (TAME) productions. Although there are a number of researchers considering the synthesis of ETBE in reactive distillation, most of them have focused on the use of EtOH and isobutene (IB) as reactants (Sneesby et al. 1999, Bisowarno and Tade 2000, Tade and Tian 2000). *Tert*-butyl alcohol (TBA), a major byproduct of propylene oxide production in the ARCO process, can be an alternative reactant (Norris and Rigby 1932).

There are two routes to produce ETBE from TBA, the indirect and direct methods. In the *indirect method,* TBA is dehydrated in a first reactor producing IB which reacts with EtOH to produce ETBE in a second reactor. In the direct method, TBA and EtOH react directly to form ETBE in one reactor.

Various catalysts have been tested for the direct route. These include Amberlyst–15 (Quitain et al. 1999a), heteropoly acid (Yin et al. 1995), potassium hydrogen sulphate (Matouq et al. 1996), S–54 and D–72 (Yang et al. 2000), and β-zeolite (Assabumrungrat et al. 2002). However, only a few studies have applied the concept of reactive distillation to the direct synthesis route (Yang and Goto 1997, Quitain et al. 1999a,b).

This paper studied reactive distillation for the direct synthesis of ETBE from EtOH and TBA using β-zeolite catalyst which Assabumrungrat et al. (2002) found to offer high selectivity. A set of experiments in a semibatch reactor was performed to find the reaction rate expressions. Simulation studies were carried out using the Aspen Plus™ program to investigate the effects of various operating parameters such as heat duty, molar ratio of H_2O: EtOH, and reflux ratio.

EXPERIMENTAL

Catalyst

Supported β-zeolite was prepared by cutting Cordierite monolith (400 cell/in^2) into small cubes (0.5x0.5x0.5 cm^3). They were weighed, soaked in 2.5 wt% acetic acid solution for 2 min, washed with distilled water several times, and then dried in an oven at 383 K overnight. β-zeolite powder (Si/Al=55) supplied by Tosoh Co. was added into 2.5 wt% acetic acid solution to give 30–50 %wt/volume washcoat. The monolith supports were dipped into the prepared washcoat for 15 min, followed by drying at 383 K overnight in the oven. The supports were repeatedly dipped in the washcoat 2–3 times and calcined at 773 K for 3.5 h in air atmosphere.

Kinetic study

In the kinetic study, supported β-zeolite was packed in a specially designed basket-type reactor as shown in Figure 1a. A condenser was used to condense all liquid vapors back to the reaction mixture. A frame of four catalyst baskets was equipped with a rotating shaft driven by a motor via an inverter controller to determine the accurate startup time in a semibatch reactor. The cylindrical baskets were made of stainless steel tubes with a wall made of stainless steel mesh. The frame was held above the liquid level by upper hooks as shown in Figure 1b. After the temperature was maintained at a desired value, the reaction was started by inverting the direction of agitation so that the frame of baskets dropped into the liquid mixture. The lower hooks were securely connected with slots on the disk turbine and the frame was rotated without slip. A liquid sample (1 cm^3) was taken every hour to analyze its composition using a TCD gas chromatograph with a Gaskuropack 54 packed column.

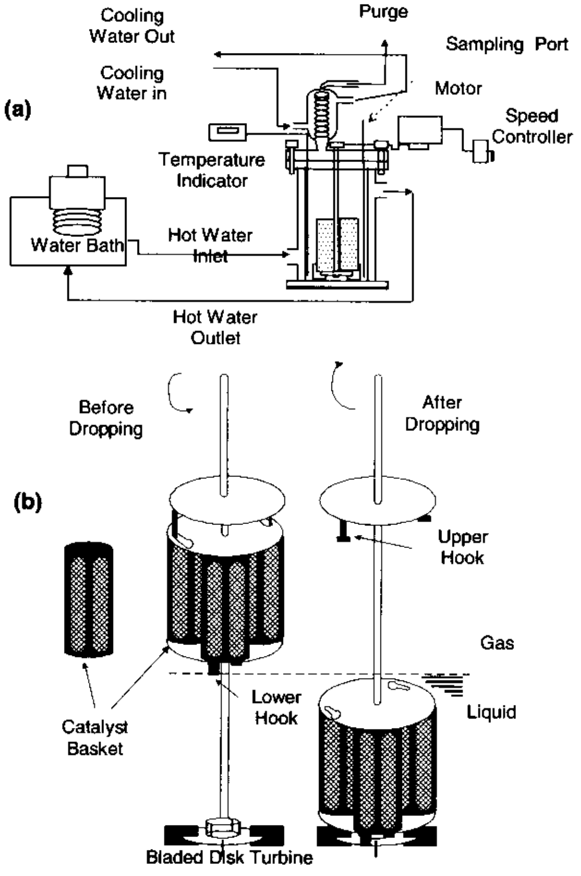

Figure 1. Experimental Setup for Kinetic Study

SIMULATION

Simulation studies were carried out using Aspen Plus™, a sequential modular simulation software package for various chemical engineering applications. The RADFRAC module, a rigorous model for simulating all types of multistage vapor-liquid fractionation operations, was selected to simulate the reactive distillation column.

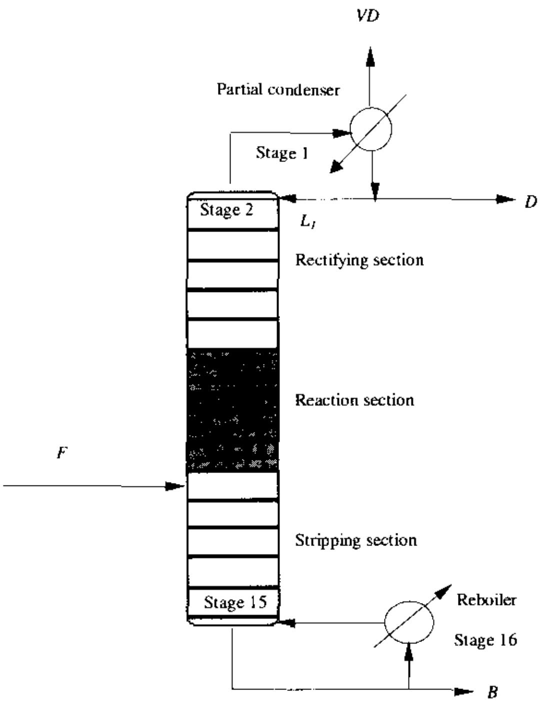

Figure 2. Column Configuration for Simulation of Reactive Distillation

The column configuration (shown in Fig. 2) and operating conditions (shown in Table 1) were adopted from Quitain, Itoh, and Goto (1999a) as the standard conditions.

However, instead of defining the ratio of distillate to feed (*D/F*) at 0.033 and the ratio of vapor to distillate (*VD/D*) at 0.52, the condenser temperature and reboiler heat duty were set at 318.5 K and 52.2 kW, respectively. A property option set PSRK based on the predictive Soave–Redlich–Kwong equation of state was used to estimate thermodynamic properties. This method has been widely used for prediction of enthalpy and other properties (Sneesby et al. 1997).

RESULTS AND DISCUSSION

Reaction rate expression

The reactions taking place in the reactor can be summarized as follows

$$\mathrm{TBA}_{(l)} + \mathrm{EtOH}_{(l)} \rightleftharpoons \mathrm{ETBE}_{(l)} + \mathrm{H_2O}_{(l)} \qquad (1)$$

$$\mathrm{TBA}_{(l)} \rightleftharpoons \mathrm{IB}_{(g)} + \mathrm{H_2O}_{(l)} \qquad (2)$$

$$\mathrm{IB}_{(g)} + \mathrm{EtOH}_{(l)} \rightleftharpoons \mathrm{ETBE}_{(l)} \qquad (3)$$

The reverse reaction in Eq. (2) and the reaction in Eq. (3) were neglected since the operating pressure in this study was at atmospheric pressure and, consequently, only a small amount of IB can be dissolved in the liquid. As a result, the rate laws of reactions (1) and (2) can be expressed in terms of concentration as:

$$r_1 = k_1 C_{TBA} \cdot C_{EtOH} \qquad (4)$$

$$r_{-1} = k_{-1} C_{ETBE} \cdot C_{H2O} \qquad (5)$$

$$r_2 = k_2 C_{TBA} \qquad (6)$$

where k_j is the reaction rate constant of reaction j (j=1,2) and c_i is a concentration of species i. Experimental results at T=323, 333, and 343 K

Table 1. Standard Operating Conditions

Feed conditions		**Column specifications**	
Temperature [*K*]	298	Rectification stages (including the condenser)	6
Total Molar Feed Flowrate (*F*) [*mol/s*]	4.14	Stripping stages (including the reboiler)	6
Composition [*mol%*]		Reaction stages (stages 7 to 10)	4
ETBE	0.0	Total stages	16
TBA	2.5	Catalyst weight per stage [*kg*]	25
EtOH	2.5	Reflux ratio (L_l/D) [-]	3.37
H_2O	95	Heat duty (*Q*) [*kW*]	52.2
Pressure [*kPa*]	101.3	Condenser temperature [*K*]	318.5

were fitted with the mathematical model as illustrated in Quitain et al. (1999a) and the following kinetic parameters for β-zeolite were obtained.

$$k_1 = \exp(7.286\text{-}10{,}785/T)\ [\text{m}^6/(\text{kg.s.mol})] \quad (7)$$

$$k_{-1} = \exp(8.517\text{-}11{,}729/T)\ [\text{m}^6/(\text{kg.s.mol})] \quad (8)$$

$$k_2 = \exp(19.227\text{-}12{,}196T)\ [\text{m}^3/(\text{kg.s.})] \quad (9)$$

Reactive distillation study

Standard condition

The reaction rate expressions discussed in the prior section were then applied in the simulation of the reactive distillation column. Figure 3 shows the concentration profile of liquid along the reactive distillation column under the standard condition. Water was the only main component of the bottom product, whereas the distillate contained 39.2 mol% ETBE, 32.2 mol% EtOH, and 8.5 mol% TBA.

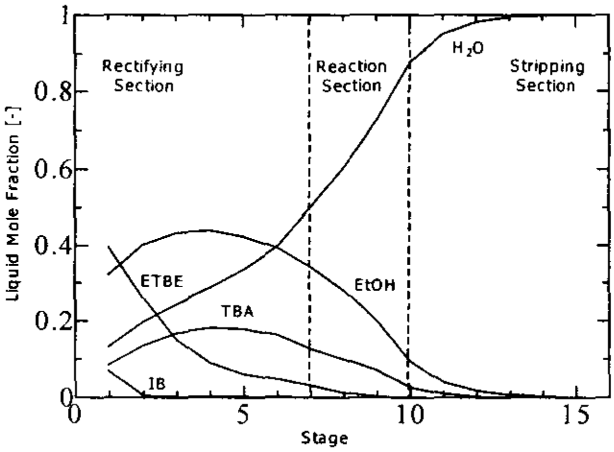

Figure 3. Mole Fraction Profiles of Liquid Distillate on Stage

The performance of the reactive distillation can be represented by conversion (X_{TBA}) and selectivity (S_{ETBE}) defined as follows:

$$X_{TBA} = \frac{\text{Molar flow rate of TBA reacted}}{\text{Feed molar flow rate of TBA}} \times 100\% \quad (10)$$

$$S_{ETBE} = \frac{\text{Molar flow rate of ETBE in the liquid distillate}}{\text{Molar flow rate of TBA reacted}} \times 100\% \quad (11)$$

The corresponding conversion and selectivity at the standard condition, using β-zeolite as catalyst, are 88.9% and 53.7%, respectively; whereas, those values from the simulation of reactive distillation with Amberlyst–15 catalyst performed by Quitain et al. (1999a) were 91.2% and 38.3%, respectively.

It is obvious that the reactive distillation with β-zeolite catalyst offered higher performance than that with Amberlyst–15. Therefore, β-zeolite catalyst is a promising catalyst for this reaction system.

Effect of heat duty at reboiler

The effect of heat duty was investigated by varying the values Q=52.2, 55, 60, 65, and 70 kW. As shown in Figure 4, the conversion of TBA decreased with increasing heat duty while the selectivity of ETBE remained almost constant. It was obvious that increasing the heat duty resulted in increased vapor load in the column. As the feed flow rate remained unchanged, the amount of TBA remaining in liquid phase decreased. Moreover, due to the fixed reflux ratio, higher unconverted reactant appeared in the distillate. Consequently, the conversion decreased. It was noted that there was minimum heat duty sufficient to vaporize the reactant and to keep the column temperature at a high value.

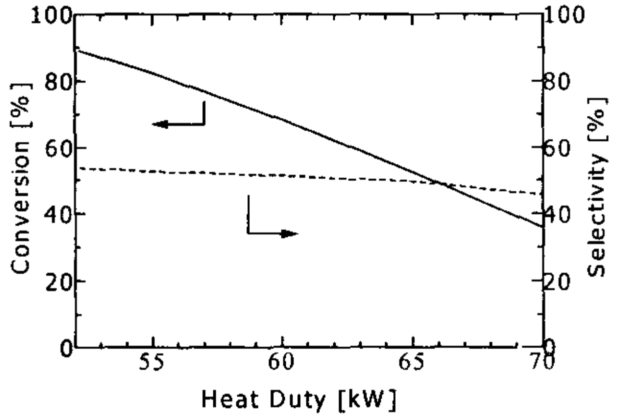

Figure 4. Effect of Heat Duty at Reboiler on Conversion of TBA and Selectivity of ETBE

Effect of H_2O composition in feed

EtOH derived from fermentation usually contains significant amounts of H_2O. Figure 5 shows the effect of H_2O concentration in feed

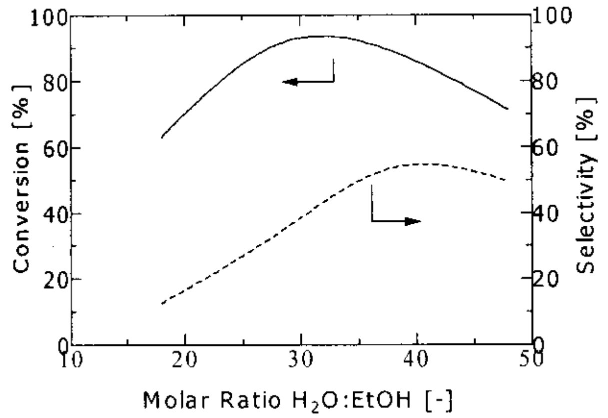

Figure 5. Effect of Molar Ratio of H_2O:EtOH in Feed on Conversion of TBA and Selectivity of ETBE

expressed as the molar ratio of H_2O to EtOH. Four values of 18:1, 28:1, 38:1, and 48:1 were simulated. The molar ratio of TBA to EtOH was set to 1. It was found that the selectivity increased with increasing molar ratio; however, the conversion increased initially and then dropped at high H_2O to EtOH ratio.

Since the boiling point of water was significantly higher than those of the other components, an increase in H_2O fraction in feed while heat duty was kept unchanged would result in lower column temperature, especially in the rectifying section. Therefore, more ETBE could be collected in the distillate.

Moreover, the side reaction took place at a less significant rate when the column temperature was lowered. Consequently, the selectivity of ETBE was improved with the increase in the molar ratio of H_2O to EtOH. Because the reactant concentrations and reactant feed flowrate decreased with increasing molar ratio, the former decreased the rate of reaction while the latter improved the extent of reaction. Hence, these competing effects resulted in the observed conversion results.

Effect of reflux ratio

In Aspen Plus™, *reflux ratio* is defined as the reflux liquid flow from the condenser (stage 1, L_1) divided by the total distillate flow (D). Figure 6 shows the conversion of TBA and the selectivity of ETBE as a function of the reflux ratio. Increasing the reflux ratio did not only increase the residence time of the reactants but also improved the separation performance. As a result, the conversion increased with increasing reflux ratio. Selectivity, on the contrary, did not increase with the increase in reflux ratio.

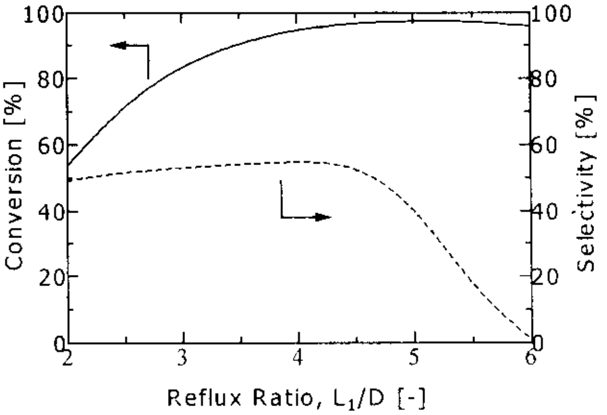

Figure 6. Effect of Reflux Ratio on Conversion of TBA and Selectivity of ETBE

It was found that the selectivity at a reflux ratio below 4.5 remained roughly constant. However, at a reflux ratio higher than 4.5, the selectivity decreased dramatically. This was because the H_2O concentration of the liquid in the column went higher with increasing reflux ratio.

The higher the concentration of H_2O, the more difficult reaction (1) could proceed in a forward direction. On the one hand, the backward reaction of reaction (1) became significant. On the other hand, reaction (2) was unaffected by the amount of H_2O in the system, since IB did not remain in the liquid phase. Therefore, at very high reflux ratios, the system indeed produced IB instead of ETBE; hence, the selectivity of ETBE was decreased.

CONCLUSIONS

Synthesis of ethyl *tert*-butyl ether (ETBE) from the liquid phase reaction between ethanol (EtOH) and *tert*-butyl alcohol (TBA) was investigated using an Aspen Plus™ simulator.

The results at standard condition revealed that the reactive distillation column with β-zeolite was superior to that with Amberlyst–15. Other operating parameters such as heat duty, molar ratio of H_2O:EtOH, and reflux ratio were investigated for their effects on the reactive distillation performance.

ACKNOWLEDGMENT

Support from the Thailand Research Fund and the Thailand-Japan Technology Transfer Project–Japan Bank for International Cooperation (TJTTP–JBIC) are gratefully acknowledged.

NOMENCLATURE

c_i	concentration of component *i*, *mol/m*^{3}
F	total molar feed flowrate, *mol/s*
Q	heat duty at the reboiler, *W*
S_{ETBE}	selectivity of ETBE, %
W	mole ratio of water in feed mixture, -
X_{TBA}	conversion of TBA, %

REFERENCES

Assabumrungrat, S., Kiatkittipong, W., Srivitoon, N., Praserthdam, P., Phatanasri, S., and Goto, S. (2002). "Kinetics of liquid-phase synthesis of ethyl *tert*-butyl ether from *tert*-butyl alcohol and ethanol catalyzed by supported β-zeolite," *Int. J. Chem. Kinetics, 34,* 292–299.

Bisowarno, B. H., and Tade, M. O. (2000). "Dynamic simulation of startup in ethyl *tert*-butyl ether reactive distillation with input multiplicity," *Ind. Eng. Chem. Res., 39,* 1950–1954.

Cunill, F., Vila, M., Izquierdo, J. F., Iborra, M., and Tejero, J. (1993). "Effect of water-presence on methyl *tert*-butyl ether and ethyl *tert*-butyl ether liquid-phase syntheses," *Ind. Eng. Chem. Res., 32,* 564–569.

Matouq, M., Quitain, A., Takahashi, K., and Goto, S. (1996). "Reactive distillation for synthesizing ethyl *tert*-butyl ether from low-grade alcohol catalyzed by potassium hydrogen sulfate," *Ind. Eng. Chem. Res., 35,* 982–984.

Norris, J. F., and Rigby, G. W. (1953). "The reactivity of atoms and groups in organic compounds," *J. Am. Chem. Soc., 54,* 2088–2100.

Quitain, A., Itoh, H., and Goto, S. (1999a). "Reactive distillation for synthesizing ethyl *tert*-butyl ether from bioethanol," *J. Chem. Eng. Japan, 32,* 280–287.

Quitain, A., Itoh, H., and Goto, S. (1999b). "Industrial-scale simulation of proposed process for synthesizing ethyl *tert*-butyl ether from bioethanol," *J. Chem. Eng. Japan, 32,* 539–543.

Sneesby, M. G., Tade, M. O., and Smith, T. N. (1997). "ETBE synthesis via reactive distillation—1. Steady-stage simulation and design aspects," *Ind. Eng. Chem. Res., 36,* 1855–1869.

Sneesby, M. G., Tade, M. O., and Smith, T. N. (1999). "Two-point control of a reactive distillation column for composition and conversion," *J. of Process Contr., 9,* 19–31.

Tade, M. O., and Tian, Y. C. (2000). "Conversion inference for ETBE reactive distillation," *Sep. Puri. Tech., 19,* 85–91.

Yang, B., and Goto, S. (1997). "Pervaporation with reactive distillation for the production of ethyl *tert*-butyl ether," *Sep. Sci. Tech., 32,* 971–981.

Yang, B., Yang, S., and Yao, R. (2000). "Synthesis of ethyl *tert*-butyl ether from *tert*-butyl alcohol and ethanol on strong acid cation-exchange resins," *React. Funct. Polym., 44,* 167–175.

Yin, X., Yang, B., and Goto, S. (1995). "Kinetics of liquid-phase synthesis of ethyl *tert*-butyl ether from *tert*-butyl alcohol and ethanol catalyzed by ion-exchange resin and heteropoly acid," *Int. J. Chem. Kinetics, 27,* 1065–1074.