Production of Ethyl *tert*-Butyl Ether from *tert*-Butyl Alcohol and Ethanol Catalyzed by *β*-Zeolite in Reactive Distillation

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(*Received 22 June 2004 • accepted 11 October 2004*)

Abstract−The synthesis of ethyl *tert*-butyl ether (ETBE) from a liquid phase reaction between *tert*-butyl alcohol (TBA) and ethanol (EtOH) in reactive distillation has been studied. *β*-Zeolite catalysts with three compositions (Si/Al ratio=13, 36 and 55) were compared by testing the reaction in a semi-batch reactor. Although they showed almost the same performance, the one with Si/Al ratio of 55 was selected for the kinetic and reactive distillation studies because it is commercially available and present in a ready-to-use form. The kinetic parameters of the reaction determined by fitting parameters with the experimental results at temperature in the range of 343-363 K were used in an ASPEN PLUS simulator. Experimental results of the reactive distillation at a standard condition were used to validate a rigorous reactive distillation model of the ASPEN PLUS used in a simulation study. The effects of various operating parameters such as condenser temperature, feed molar flow rate, reflux ratio, heat duty and mole ratio of $H_2O : EtOH$ on the reactive distillation performance were then investigated via simulation using the ASPEN PLUS program. The results were compared between two reactive distillation columns: one packed with *β*-zeolite and the other with conventional Amberlyst-15. It was found that the effect of various operating parameters for both types of catalysts follows the same trend; however, the column packed with *β*-zeolite outperforms that with Amberlyst-15 catalyst due to the higher selectivity of the catalyst.

Key words: Reactive Distillation, ETBE Synthesis, *β*-Zeolite, ASPEN PLUS

INTRODUCTION

Currently, there are pending legislations on the use of methyl *tert*-butyl ether (MTBE) in a number of states in the US because MTBE has a tendency to pollute underground water. Ethyl *tert*-butyl ether (ETBE) can be a potential alternative since it has been found to outperform MTBE. ETBE has lower blend Reid Vapor Pressure (4 psi) than MTBE (8-10 psi), which allows ETBE to be used successfully in obtaining gasoline with less blend Reid Vapor Pressure 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 like biomass [Chang et al., 1998].

Reactive distillation, a promising process for equilibrium-limited reactions, has been applied to many esterification reactions such as the production of MTBE, ETBE and TAME [Seo et al., 1999]. Although there are a number of researchers considering the synthesis of ETBE in reactive distillation, most of them focus on the use of EtOH and isobutylene (IB) as the 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]. ETBE can be produced from TBA either by direct or indirect methods. In the indirect method, TBA is dehydrated to IB in a first

reactor and then 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. They are, for example, 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].

There are a limited number of works focusing on the direct synthesis of ETBE from EtOH and TBA in reactive distillation. Yang and Goto [1997] considered batch reactive distillation using Amberlyst-15 as a catalyst with and without pervaporation. The use of pervaporation helped to remove water from the residue, and a higher fraction of ETBE was obtained as a top product. Quitain et al. [1999a] used Amberlyst-15 as a catalyst in a reactive distillation column with continuous operation. The conversion of TBA and the selectivity of ETBE were 99.9 and 35.9%, respectively. The distillate was further purified by a solvent extraction with the bottom product, resulting in the product with 95 mol% ETBE. Later, the same authors proposed a process for industrial production of ETBE by using ASPEN PLUS program [Quitain et al., 1999b]. Another reactive distillation column with high pressure was introduced to convert the by-product IB to ETBE. Yang et al. [2001] developed a mathematical model of the continuous reactive distillation and compared their simulation results with those of Quitain et al. [1999a].

The aim of this paper is to study the reactive distillation for the direct synthesis of ETBE from EtOH and TBA using *β*-zeolite catalyst, which was found in our previous work to offer high selectiv-

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ity [Assabumrungrat et al., 2002]. Experiments in a semi-batch reactor are performed to find a suitable composition of β-zeolite and the reaction rate parameters for simulation studies in ASPEN PLUS program. A rigorous distillation model (RADFRAC module) which is verified by the reactive distillation experiment at standard condition, are chosen for the prediction of the reactive distillation behavior. The effects of various operating parameters such as heat duty, molar ratio of H_2O : EtOH and reflux ratio, on the reactive distillation performance are further studied using the ASPEN PLUS simulator. The simulation results are compared between two reactive distillation columns: one packed with β-zeolite and the other with commercial Amberlyst-15.

EXPERIMENTAL

1. Preparation of Supported Catalyst

Supported β-zeolite was prepared by cutting Cordierite monolith (400 cell/in²) into small cubes (0.5×0.5×0.5 cm³). They were weighted, soaked in 2.5 wt% acetic acid solution for 2 min, washed by distilled water several times and then dried in an oven at 383 K overnight. β-Zeolites with three compositions (Si/Al=13.5, 36 and 55) were used in the study. The zeolites with Si/Al=13.5 and 55 were supplied by Tosoh Company, Japan, whereas the other was synthesized by the method described in our previous work [Assabumrungrat et al., 2002]. To prepare the supported catalyst, zeolite powder 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 and 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. The amount of catalyst was calculated from the increased weight of the monolith.

2. Preparation of Packing Material for Reactive Distillation

Stainless-steel sieves (30 meshes) with 0.7×0.7 cm² size in saddle-like shape were used as packing materials in distillation sections in the reactive distillation column. Before they were packed in the column, they were washed with boiled toluene twice to remove residuals. Then they were dried in the oven at 383 K overnight.

3. Catalyst Selection Study

Catalyst performance was studied in a semi-batch reactor. Powder catalyst was weighted and left in an oven at 363 K overnight to remove moisture from the catalyst. A desired amount of ethanol and TBA was mixed and placed into a 2.5×10⁻⁴ m³ three-necked flask. The mixture containing 1 mol of TBA and 1 mol of EtOH was stirred and heated to a desired temperature (T=333 K) by circulating hot water through the jacket. The reaction was started by adding 10 g of catalyst into the reaction mixture. Liquid samples of 1.0 cm³ were taken to measure concentrations of H_2O, EtOH, TBA, IB and ETBE at different reaction times for 7 h. They were analyzed by TCD gas chromatography with a column packed with Gaskuropack 54.

4. Kinetic Study

In the kinetic study, the supported β-zeolite was packed in a special-design basket-type reactor as described in our previous work [Assabumrungrat et al., 2002]. A frame of four catalyst baskets was mounted to a rotating shaft driven by a motor via an inverter controller to determine the accurate start-up time in a semi-batch reac-

tor. 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. When the temperature was maintained at a desired value, the reaction was started by changing 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 cm³) was taken every hour to analyze its composition by using TCD gas chromatography with a Gaskuropack 54 packed column.

5. Reactive Distillation Study

Fig. 1 shows the schematic diagram of the reactive distillation experimental set-up. The height and diameter of the column are 0.7 m and 0.035 m, respectively. The upper section of the column was filled with 0.7×0.7 cm² of stainless-steel packing materials. The middle section of the column was filled with the supported catalyst (45 g of β-zeolite). Like the upper section, the lower section of the column was packed with the same packing materials. The heights of the sections were 0.21, 0.18, 0.21 m, respectively.

The top of the column was connected with a condenser where a coolant (T=288 K) was circulated to condense vapor from the reactive distillation column. The condensate was passed into a solenoid
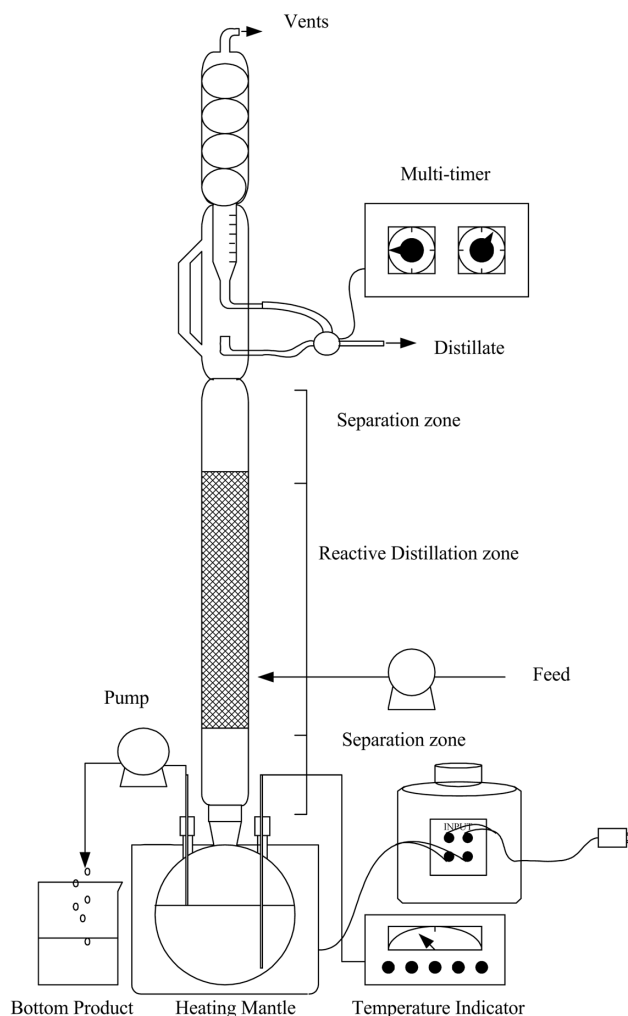

Fig. 1. Schematic diagram of the reactive distillation system.

valve. A multi-timer was used as a reflux ratio controller. The bottom of the column was connected to a reboiler filled with the reactant mixture of approximately $4.2 \times 10^{-4}\,m^3$. The bottom product level in the reboiler was controlled by a Masterflex pump. Heat supply required for the reboiler was regulated by a variable transformer (also known as a variac) via adjustable voltage. In continuous operation, feed was introduced to the column at the lower part of the catalyst bed. The reaction was carried out until reaching steady state. Top and bottom products were sampled and their flow rates were measured every 0.5 h.

SIMULATION

Simulation studies were carried out by using the ASPEN PLUS program, 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 for simulation of the reactive distillation column. A property option set PSRK based on the predictive Soave-Redlich-Kwong equation of state was selected for the prediction of thermodynamic properties of this system [Sneeby et al., 1997].

Fig. 2 shows the column configuration used in the simulation. It consists of 16 stages, including a partial reboiler (stage 16) and a partial condenser (stage 1). The reaction section in the middle of the column is represented by six reactive stages (stage 6-11). According to our previous work and results from the preliminary runs for this work, this column configuration has proven to be a good representative for the column used for actual experiments. The reaction is assumed to take place in the liquid phase. The feed is introduced at the stage 10. The simulation inputs to the program are mainly based on experimental operating conditions. However, the reflux ratio defined in the ASPEN PLUS is the reflux liquid flow (L1) from the condenser (stage 1) divided by the total distillate flow (D= LD+VD), L1/D. This definition is different from the experimental reflux ratio (L1/LD) because the liquid flow from the condenser is distributed into L1 and LD with a multitimer.

The RADFRAC simulation requires two more input parameters which can be chosen from the following four parameters: heat duty at reboiler (Q), condenser temperature (T_c), ratio of total distillate flow to feed (D/F) and ratio of vapor distillate to total distillate (VD/D). It should be noted that the two parameters, the condenser temperature and heat duty, are chosen in this work because it is difficult to control the values of D/F and VD/D in practical operation.

RESULTS AND DISCUSSION

1. Catalyst Characterization

Various techniques were employed to characterize β-zeolite catalysts: X-Ray Diffraction (XRD), X-Ray Fluorescence spectrometer (XRF), Scanning Electron Microscope (SEM), BET surface area measurement via nitrogen adsorption and Temperature Programmed Desorption (TPD). To confirm the structure of β-zeolite, the XRD pattern of the synthesized catalyst (shown in Fig. 3) was compared with that of a standard β-zeolite published in the literature [Borade and Clearfield, 1992]. The same diffraction patterns are observed and, hence, it is confirmed that the synthesized catalyst was a β-zeolite. The compositions of the zeolite were measured with an X-ray fluorescence spectrometer (XRF-model Fision) which shows Si/Al=36 for the synthesized zeolite and Si/Al=13.5 and 54.9 for the commercial zeolites. They are in good agreement with their specifications. Uniformity of the catalyst distribution on monolith support was examined by measuring distribution of Al using a scanning electron microscope-energy dispersive X-ray spectrometer (SEM-
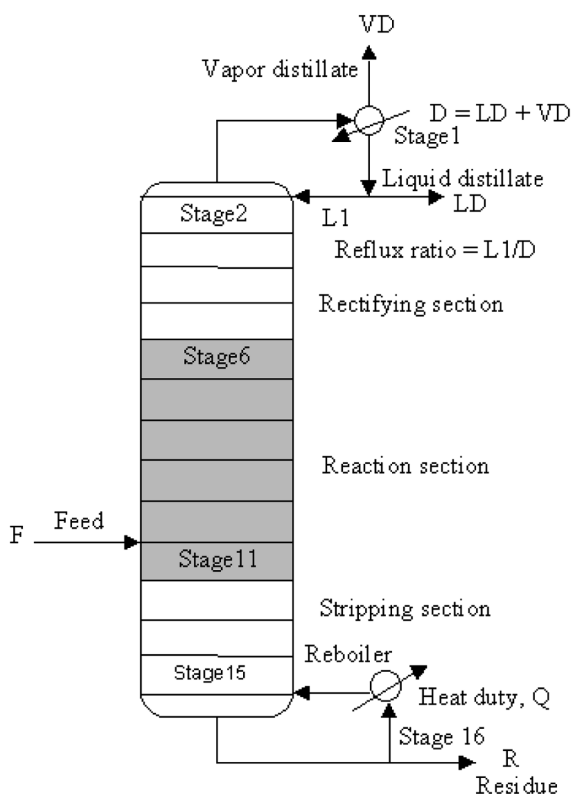

Fig. 2. Column configuration for simulation of reactive distillation.
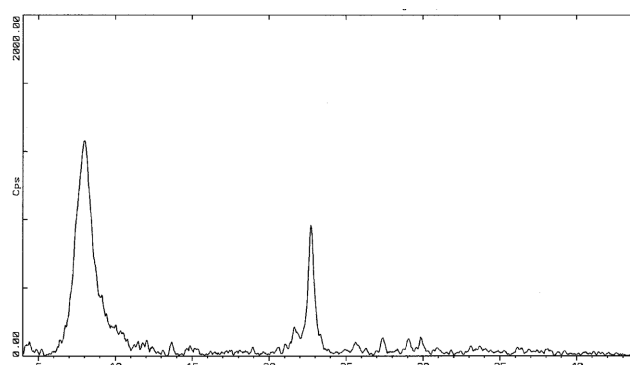

Fig. 3. X-ray diffraction pattern of synthesized catalyst (Si/Al=36).

Table 1. BET surface areas of β-zeolite

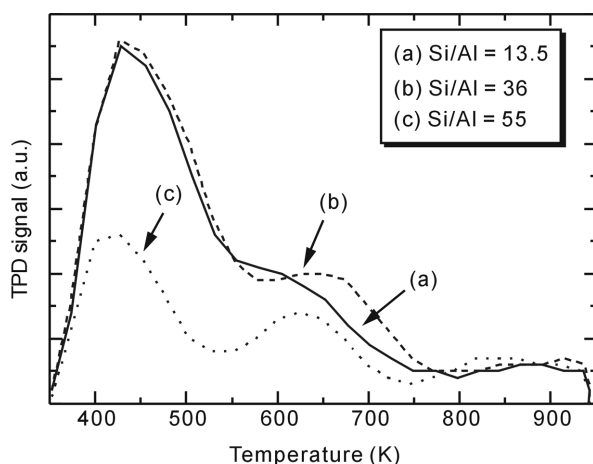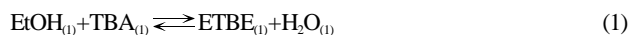| β-zeolite	BET surface area (m^2/kg of β-zeolite)
H-Beta (Si/Al=13.5)	6.35×10^5
H-Beta (Si/Al=36)	6.18×10^5
H-Beta (Si/Al=55)	6.28×10^5

Fig. 4. TPD profile showing acidity and acid strength of β-zeolite with different Si/Al ratio (a) Si/Al=13.5 (b) Si/Al=36 and (c) Si/Al=55.

EDX). It was found that the catalyst was well dispersed on the monolith surface.

Table 1 shows BET surface area of the β-zeolites. They are almost the same regardless of the different values of the Si/Al ratio. The temperature programmed desorption technique (TPD) was employed to characterize the acid properties of the catalyst. The results shown in Fig. 4 reveal that the higher the Si/Al ratio, the lower the acid strength and the acidity. These properties are observed from the peak height and the area of peak, respectively.

2. Catalyst Selection

The performance of β-zeolite with three Si/Al ratios was investigated in the semi-batch reactor. The reaction-taking place in the reactor can be summarized as follows:

$$EtOH_{(l)} + TBA_{(l)} \rightleftharpoons ETBE_{(l)} + H_2O_{(l)} \tag{1}$$

$$TBA_{(l)} \rightleftharpoons IB_{(g)} + H_2O_{(l)} \tag{2}$$

$$EtOH_{(l)} + IB_{(g)} \rightleftharpoons ETBE_{(l)} \tag{3}$$

Under the operating pressure in this study (101.3 kPa), the majority of IB is in the gas phase, while other species are in the liquid phase. Reactions involving IB are then limited by the liquid-gas contact. Hence, by comparing with the main reaction in Eq. (1),
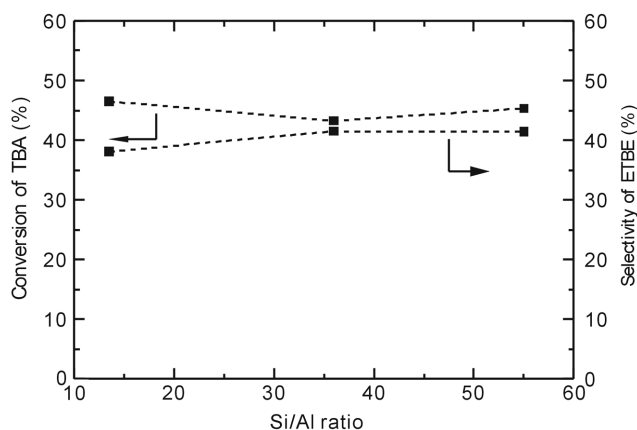

Fig. 5. The performance of β-zeolite with difference Si/Al ratio.

the reverse reaction in Eq. (2) and the reaction in Eq. (3) are considered as minor side reactions and neglected in this work. Only the forward reaction of Eq. (2) is considered as a side reaction of this reaction system.

Fig. 5 shows the effect of Si/Al ratio on the reaction conversion and selectivity of ETBE, displayed as dashed lines. It was observed that both of them are not significantly affected by the change in the Si/Al ratio. Although the acid properties and the surface area of catalyst are reported as main parameters affecting the reaction performance [Matouq et al., 1996], the range of the acid properties in this study does not significantly influence the catalyst performance. Therefore, the β-zeolite with the Si/Al ratio of 55 was used in all subsequent studies, as it is commercially available and present in a ready-to-use form unlike those with other ratios which require a second calcination to convert the NH_3-form to the H^+-form.

3. Kinetic Study

Mathematical descriptions were developed for concentration-based model to follow the requirement of the ASPEN PLUS program. Since the solubility of IB in the liquid mixture is low under atmospheric condition, the reaction of IB with EtOH or H_2O is negligible. As a result, the rate laws of the reactions (1) and (2) can be expressed in terms of concentrations as

$$r_1 = k_1 \frac{(c_{TBA}c_{EtOH} - c_{ETBE}c_{H_2O}/K_1)}{1 + K_W c_{H_2O}} \tag{4}$$

$$r_2 = k_2 \frac{c_{TBA}}{1 + K_W c_{H_2O}} \tag{5}$$

where k_j, c_i, K_1 and K_W are the reaction rate constants of reaction j (j=1, 2), the concentration of species i, the equilibrium constant and the water inhibition parameter, respectively. The expression of K_1 can be expressed as follows [Quitain et al., 1999b]

$$K_1 = \exp(-1.23 + 944/T) \tag{6}$$

By performing a material balance for a semi-batch reactor, the following expressions are obtained.

$$-\frac{dm_{TBA}}{dt} = \frac{dm_{H_2O}}{dt} = W(r_1 + r_2) \tag{7}$$

$$-\frac{dm_{EtOH}}{dt} = \frac{dm_{ETBE}}{dt} = Wr_1 \tag{8}$$

where m_i and W represent the number of mole of species i and the catalyst weight, respectively. It should be noted that the number of moles in the liquid phase at any time is constant because IB can only slightly dissolve in the liquid phase. In addition, the summation of stoichiometric coefficients for both sides of the reaction is equivalent in all reactions.

A set of experiments was carried out at three temperatures: 323, 333 and 343 K. Arrhenius and Van't Hoff plots were then obtained, as shown in Fig. 6. By using the method described in our previous work [Assabumrungrat et al., 2002], the following expressions are consequently obtained.

$$k_1 = \exp(7.286 - 10785/T) \tag{9}$$

$$k_2 = \exp(19.227 - 12196/T) \tag{10}$$
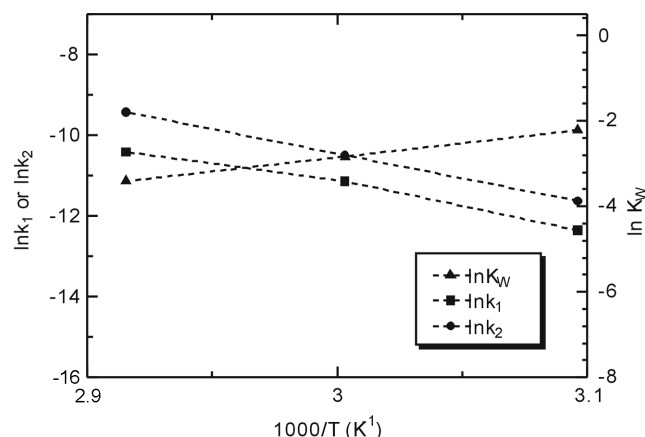
$$K_W = \exp(-45.37 + 7003/T) \tag{11}$$

Fig. 6. Arrhenius and Van't Hoff plots.

Fig. 7. Concentration profiles of distillate and residue at standard operating condition (Catalyst=*β*-zeolite with Si/Al=55, catalyst weight=0.040 kg, feed flow rate=2.7×10^{-3} mol/s, reflux ratio=1.5 : 1, and molar ratio of TBA : EtOH : H_2O=1 : 1 : 38).

4. Reactive Distillation Study

4-1. Performance of Reactive Distillation at Standard Condition

An experiment was carried out at the standard condition as given in Table 2. The mole fraction profiles for both the residue and the distillate are shown in Fig. 7. Solid markers represent distillate, while empty markers represent residue. After approximately 4 hours of operation, the column reached a steady state condition. It was found that water was the main component of the bottom product, whereas the distillate contained 18.2 mol% ETBE, 32.4 mol% TBA, 19.4 mol% EtOH and 28.3 mol% H_2O.

The terms "conversion of TBA (X_{TBA})" and "selectivity of ETBE (S_{ETBE})" defined by the following expressions are used to represent the performance of the reactive distillation.

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

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

The corresponding conversion and selectivity obtained experimentally from the standard condition are 60.5% and 27.7%, respectively.

The ASPEN PLUS program using a rigorous distillation model (RADFRAC module) was used to simulate the reactive distillation. The reliability of the model prediction was verified by comparing its result with that obtained from the experiment, as shown in Fig. 7. It was found that the simulation results (shown by the dashed lines) agreed well with the experimental results. Due to the limitation of
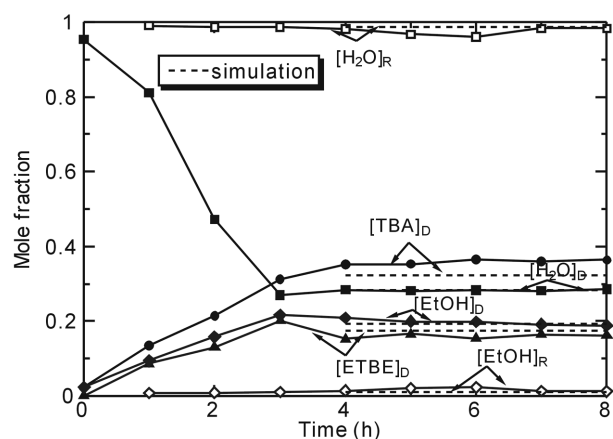
the equipment, only the simulations using ASPEN PLUS were further studied in the following section in order to investigate the effects of various operating parameters such as condenser temperature, feed flow rate, reflux ratio, heat duty and molar ratio of H_2O : EtOH in feed on the performance of the reactive distillation column. These provide useful information for improving an operation and designing of the reactive distillation. Furthermore, the results from the column packed with *β*-zeolite were also compared to ones from the column packed with the commercial Amberlyst-15 catalyst. It is noted that the kinetic parameters of the commercial Amberlyst-15 are obtained from Quitain et al. [1999a].

4-2. Effects of Operating Parameters

4-2-1. Effect of the Condenser Temperature

The effect of the condenser temperature (T_c) was investigated in the range of 303 to 333 K. Fig. 8 shows that the condenser temperature affects only the selectivity of ETBE, while it has no effect on the conversion of TBA. The selectivity obtained from the experiment in the previous section (27.7%) can be improved to 43.1% by reducing the condenser temperature from 333 to 303 K. The improved selectivity is due to the increased condensation of ETBE from vapor distillate at lower condenser temperature. On the other hand, no significant effect of the condenser temperature on the conversion of TBA is found because the majority of the reactions take

Table 2. Standard operating condition

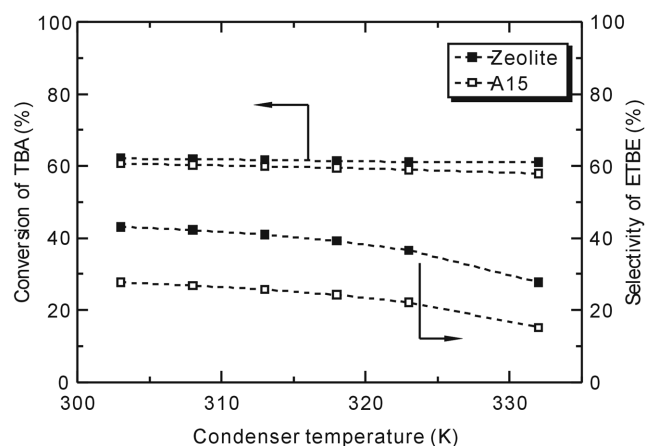| Feed condition		Column specification	
Temperature [K]	298	Rectification stages	5
Flow rate$\times 10^3$ [mol/s]	2.71	Reaction stages	6
Molar ratio (TBA : EtOH : H_2O)	1 : 1 : 38	Stripping stages	5
Composition [% mol]		Total stages	16
EtOH	2.5	Catalyst weight per stage [kg]	0.065
TBA	2.5	Pressure [kPa]	101.3
H_2O	95	Reflux ratio [*L1/D*]	1.5
Pressure [kPa]	101.3	Condenser temperature [K]	333
		Heat duty [W]	26.3

Fig. 8. Simulation results for the effect of the condenser temperature on conversion of TBA and selectivity of ETBE.
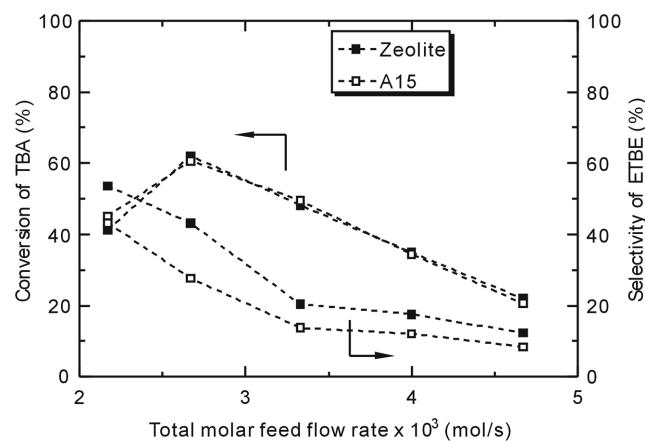

Fig. 9. Simulation results for the effect of feed flow rate on conversion of TBA and selectivity of ETBE.

place in the reaction stages in the column, which are not considerably affected by the condenser temperature. It is noted that the condenser temperature is a key parameter controlling the performance of the reactive distillation. However, due to the limitation of the equipment, we could not perform actual experiments at the favorable condition. The value of T_c at 303 K will be used throughout the rest of the simulations in the following studies.

4-2-2. Effect of Feed Flow Rate

Fig. 9 shows the effect of feed flow rate on the conversion of TBA and the selectivity of ETBE. It can be seen that there is an optimum total feed molar flow rate that offers the maximum conversion. From the optimum value, increasing feed flow rate decreases the conversion as well as the selectivity. As the amount of catalyst, reflux ratio and heat duty are fixed, an increase of the feed flow rate results in a decrease in the residence time and column temperature, thus reducing the conversion. According to the rate parameters shown in Eqs. (9) to (11), the decrease in the column temperature should affect the side reaction, Eq. (2), more intensively than the main reaction, Eq. (1). Thus, the higher selectivity of ETBE should be expected. Nevertheless, the opposite trend is observed, which is in agreement with an observation reported by Quitain et al. [1999b]. This behav-

ior can be explained by the fact that the evaporation of ETBE is decreased by the decrease in column temperature. On the other hand, although the evaporation of TBA is also affected by the decrease in the column temperature, the effect is not as strong as ETBE, since TBA is more volatile than ETBE. The more ETBE presented in liquid phase, the less the main reaction, Eq. (1), can proceed, which results in lower selectivity of ETBE. It is noted that decreasing the feed flow rate from the optimum value decreases the conversion because the reactants could be easily vaporized and present in the distillate as the unconverted reactants.

4-2-3. Effect of Reflux Ratio

Fig. 10 shows the conversion and selectivity as a function of the reflux ratio. Increasing the reflux ratio from 1.0 to 3.0 increases the conversion but decreases the selectivity. It is obvious that the residence time of the reactants is increased with high reflux ratio. Consequently, the conversion becomes higher. It should be noted that an operation at high reflux ratio is economically unattractive due to the high energy consumption. It was also found in this system that increasing the reflux ratio causes the lower selectivity of ETBE. This can be explained by the higher H_2O concentration in liquid phase in the column when the reflux ratio is increased. Since H_2O is the
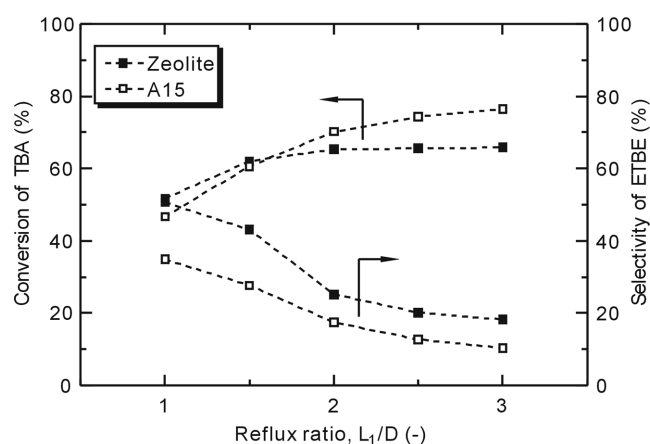

Fig. 10. Simulation results for the effect of reflux ratio on conversion of TBA and selectivity of ETBE.
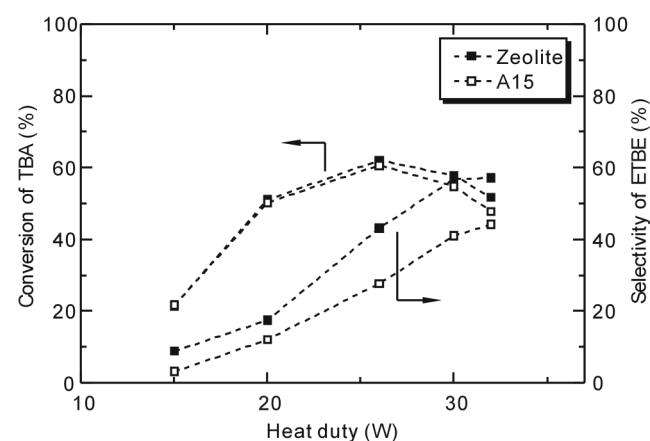

Fig. 11. Simulation results for the effect of heat duty on conversion of TBA and selectivity of ETBE.
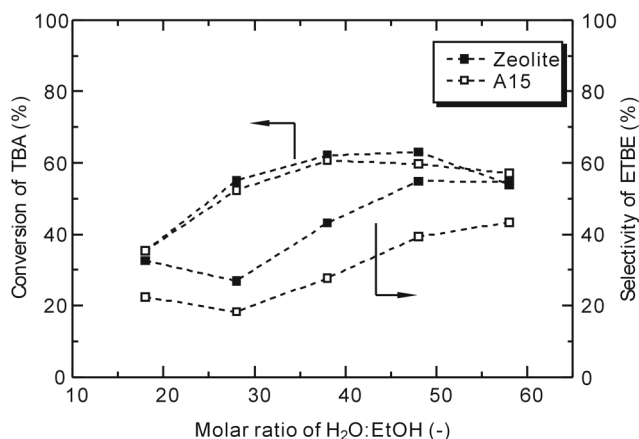
Fig. 12. Simulation results for the effect of molar ratio of H$_2$O : EtOH on conversion of selectivity of ETBE.

least volatile species in the system, the backward reaction of the main reaction (Eq. (1)) becomes significant compared to that of the side reaction (Eq. (2)), resulting in the decrease of the selectivity.

4-2-4. Effect of Heat Duty

Fig. 11 shows the effect of heat duty on the performance of the reactive distillation. An optimum heat duty, which provides the maximum conversion, was observed. Increasing the heat duty increases the column temperature and, also, the extent of the reaction. However, at high heat duty, significant vapor load can appear in the column and the effect of reactant loss becomes important. Consequently, the decrease in conversion is noticed. It is interesting that the increasing selectivity is found although the increasing column temperature should decrease the value. This is just the opposite from the case when the column temperature is decreased by increasing the feed flow rate.

4-2-5. Effect of Molar Ratio of H$_2$O : EtOH

EtOH derived from fermentation usually contains a significant amount of H$_2$O. Fig. 12 shows the effect of H$_2$O concentration in feed expressed as the molar ratio of H$_2$O to EtOH. Five different values of 18 : 1, 28 : 1 38 : 1, 48 : 1 and 58 : 1 were investigated. The molar ratio of TBA : EtOH was always kept at 1. It was found that when the molar ratio of H$_2$O to EtOH was increased, the conversion increased initially and then dropped, whereas the selectivity slightly decreased initially and then increased. Since the reactant concentrations and reactant feed flow rate decrease with the increasing molar ratio, the former tends to decrease the rate of reaction, while the latter tends to improve the reaction extent. Thus, these completing effects lead to the observed conversion results. The improved selectivity is because the column temperature is lowered at higher molar ratio of H$_2$O : EtOH.

4-2-6. Effect of Type of Catalysts

The results shown in Figs. 8-12 also compare the performance of the reactive distillation columns with different types of catalysts. It was found that although the effects of various operating parameters for both catalysts follow the same trend, the reactive distillation column packed with β-zeolite shows better performance than that packed with the commercial Amberlyst-15. It is obviously due to the better performance of β-zeolite as reported by our previous work [Assabumrungrat et al., 2002].

CONCLUSION

The synthesis of ethyl *tert*-butyl ether (ETBE) from the liquid phase reaction between ethanol (EtOH) and *tert*-butyl alcohol (TBA) was investigated in this work. The performance of three β-zeolites with different Si/Al ratio was compared. No significant change of the catalyst performance was observed. However, the one with Si/Al ratio of 55 was selected for further study due to the availability in the commercial market and the presence in the ready-to-use form. The ASPEN PLUS simulation results using a RADFRAC reactive distillation model was in good agreement with the experimental results at a standard condition. The ASPEN PLUS program was then employed to investigate the effects of various operating parameters on the performance of two reactive distillation columns: one packed with commercial Amberlyst-15 and the other with β-zeolite. It was revealed that the performance of the reactive distillation column with β-zeolite was superior to that with Amberlyst-15.

NOMENCLATURE

c_i : concentration of species i [mol/m^3]
D : total distillate flow [mol/s]
F : feed flow rate [mol/s]
k_1 : reaction rate constant of reaction in Eq. (1) [m^6/(mol·kg·s)]
k_2 : reaction rate constant of reaction in Eq. (2) [m^3/(kg·s)]
K_1 : equilibrium constant of reaction in Eq. (1) [-]
K_W : water inhibition parameter [m^3/mol]
L1 : reflux liquid flow rate [mol/s]
LD : liquid distillate flow rate [mol/s]
m_i : number of mole of species i [mol]
Q : reboiler heat duty [kW]
r_j : reaction rate of reaction j [mol/(kg·s)]
R : residue flow rate [mol/s]
S_{ETBE} : selectivity of ETBE [-]
t : time [s]
T : temperature [K]
T_c : condenser temperature [K]
V : dvapour distillate flow rate [mol/s]
W : catalyst weight [kg]
x_i : mole fraction of species i in liquid mixture [-]
X_{TBA} : conversion of TBA [-]

Abbreviations
EtOH : ethanol
ETBE : ethyl *tert*-butyl ether
H$_2$O : water
MTBE : methyl *tert*-butyl ether
IB : isobutylene
TAME : *tert*-amyl methyl ether
TBA : *tert*-butyl alcohol

Subscript

o   : initial value at t=0

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