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โครงการ การผลิต Ethyl-tert-Butyl Ether ด้วยหอกลั่นแบบมีปฏิกิริยา
(Production of Ethyl-tert-Butyl Ether Using Reactive Distillation)

โดย ผู้ช่วยศาสตราจารย์ ดร. สุทธิชัย อัสสะบำรุงรัตน์ และคณะ

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Abstract

Project Code: PDF/19/2543

Project Title: Production of Ethyl-tert-Butyl Ether Using Reactive Distillation

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This research investigated the synthesis of ethyl *tert*-butyl ether (ETBE) from the liquid phase reaction between ethanol (EtOH) and *tert*-butyl alcohol (TBA) in reactive distillation. Performances of β-zeolite and commercially available Amberlyst-15 were compared by performing the reaction in a semi-batch reactor. Synthesized β-zeolite was confirmed by an XRD measurement and its composition was analyzed by an XRF measurement. It was found that even though the catalytic activity of β-zeolite was lower than that of Amberlyst-15, the selectivity of ETBE was much higher than Amberlyst-15, resulting in almost the same level of ETBE yield. The dehydration of TBA to isobutene (IB) was the major side reaction. In, the kinetic study of the reaction catalyzed by β-zeolite supported on monolith in the semi-batch reactor, the effect of external mass transfer was investigated by varying stirring speeds. The activity-based rate expressions were developed taking into account of water inhibition. Three temperature levels of 323, 333 and 343 K were performed in the study to obtain the parameters in the Arrhenius's equation and the Van't Hoff equation. The reactive distillation was employed to continuously synthesize ETBE from TBA and bioethanol using β-zeolite as the catalyst. Results at the standard operating condition indicated that ETBE at 57 mol% could be obtained in the top product while almost pure water in the residue. Other operating parameters such as heat duty, feed flowrate, reflux ratio and feed molar flow rate of water were investigated to find effects on the reactive distillation performance.

Keywords: Reactive Distillation, ETBE production, β-Zeolite

บทคัดย่อ

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ชื่อนักวิจัย: ผู้ช่วยศาสตราจารย์ ดร. สุทธิชัย อัสสะบำรุงรัตน์
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งานวิจัยนี้เป็นการศึกษาการสังเคราะห์เอทิล เทอร์เชียรี บิวทิล อีเทอร์ จากเอทานอลและเทอร์เชียรี บิวทิล อัลกอฮอล์ ในหอกลั่นแบบมีปฏิกิริยา ตัวเร่งปฏิกิริยาที่ใช้ในการทดสอบสมรรถนะในงานวิจัยนี้คือตัวเร่งปฏิกิริยาแอมเบอลิส 15 ซึ่งเป็นตัวเร่งปฏิกิริยาที่ใช้ในเชิงการค้าและตัวเร่งปฏิกิริยาซีโอไลท์เบตาที่สังเคราะห์ขึ้นมา ตัวเร่งปฏิกิริยาซีโอไลท์เบตาที่ได้ถูกตรวจสอบโครงสร้างโดยใช้เทคนิค XRD และองค์ประกอบโดยเทคนิค XRF การเปรียบเทียบสมรรถนะพบว่าตัวเร่งปฏิกิริยาซีโอไลท์เบตานั้นมีค่าความว่องไวต่ำกว่าตัวเร่งปฏิกิริยาแอมเบอลิส 15 แต่ค่าการเลือกเกิดมีค่าสูงกว่า ส่งผลให้ค่าผลได้ใกล้เคียงกัน ปฏิกิริยาข้างเคียงในระบบนี้คือปฏิกิริยาดีไฮเดรชั่นของเทอร์เชียรี บิวทิล อัลกอฮอล์ไปเป็นแก๊สไอโซบิวทีน การศึกษานี้ได้ทำการทดลองเพื่อหาสมการแสดงอัตราการเกิดปฏิกิริยาเคมีของตัวเร่งปฏิกิริยาซีโอไลท์เบตา การทดลองได้พิจารณาผลของการถ่ายโอนมวลสารภายนอกของตัวเร่งปฏิกิริยาโดยการเปลี่ยนอัตราการหมุนของใบพัดในเครื่องปฏิกรณ์ สมการอัตราการเกิดปฏิกิริยาแสดงอยู่ในเทอมของค่าแอกติวิตี้โดยพิจารณาผลของการยับยั้งของน้ำต่ออัตราการเกิดปฏิกิริยาด้วย การทดลองทำขึ้นที่อุณหภูมิเท่ากัน 323, 333 และ 343 เคลวิน เพื่อหาค่าพารามิเตอร์จากสมการของ Arrhenius และสมการของ Van't Hoff หอกลั่นแบบมีปฏิกิริยาได้ถูกใช้ในการศึกษาการสังเคราะห์เอทิล เทอร์เชียรี บิวทิล อีเทอร์ จากเอทานอลและเทอร์เชียรี บิวทิล อัลกอฮอล์ ที่ดำเนินการอย่างต่อเนื่อง ผลของการดำเนินงานที่สภาวะมาตรฐานพบว่าผลิตภัณฑ์ยอดหอมีเอทิล เทอร์เชียรี บิวทิล อีเทอร์ เป็นองค์ประกอบเท่ากับ 57% โดยโมล และผลิตภัณฑ์ก้นหอมีน้ำเป็นองค์ประกอบหลัก การศึกษายังได้พิจารณาถึงผลของสภาวะการดำเนินงานอื่นๆ เช่น ภาระทางความร้อน อัตราการไหลของสายป้อน สัดส่วนการป้อนกลับ และความเข้มข้นของน้ำในสายป้อน เพื่อดูผลของสภาวะดังกล่าวต่อสมรรถนะของหอกลั่นแบบมีปฏิกิริยา

คำหลัก: หอกลั่นแบบมีปฏิกิริยา การผลิตสาร ETBE และตัวเร่งปฏิกิริยาซีโอไลท์เบตา

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Abstract

บทคัดย่อ

APPENDIX

1. INTRODUCTION

Although methyl *tert*-butyl ether (MTBE) commercially produced from the reaction of isobutene (IB) and methanol currently predominates in the world industries, a recent investigation revealed that it has tendency to pollute underground water due to its high solubility in water. As a result, there is a pending legislation in a number of states in the US [1]. A review on oxygenate fuels-market expansion and catalytic aspect of synthesis was given by Ancilloti and Fattoro [2].

Similar to MTBE, ethyl *tert*-butyl ether (ETBE) showed a considerable reduction in CO, a small reduction in unburned hydrocarbon, and a non-significant effect on NOx [3-4]. It may be a good alternative compared to lighter alcohols because of its lower bRvp, lower vaporization latent heat, very low solubility in water and so on which account for its full fungibility in the petroleum refining and distribution system [5], and compared to other *tert* ethers such as TAME and TAEE because of their high cost. From the viewpoint of environment, ETBE is also attractive as it is derived from ethanol (EtOH) which can be obtained from renewable resources like biomass [6,7]. It was expected in France that 5% of fuel used in transportation should be produced from renewable energy by 2005 [8]. ETBE outranks MTBE as an octane enhancer and is more attractive than MTBE for low bRvp blends less than 8 psi as required in some hot places during summer or in tropical countries because ETBE has lower bRvp (4 psi) than MTBE (8-10 psi) [5]. In addition, since the water solubility of MTBE (43 kg/m^3) was about 4 times higher than that of ETBE (12 kg/m^3), the use of ETBE reduces the risk of water contamination.

Generally, ETBE can be produced by an exothermic reversible reaction between ethanol (EtOH) and IB. However, the supply of IB is mainly limited from refinery catalytic cracking and steam cracking fractions. Hence, alternative routes for the synthesis of ETBE were currently explored [9]. *tert*-Butyl alcohol (TBA), a major byproduct of propylene oxide production from IB and propylene in the ARCO process, can be employed instead of IB as a reactant [10]. TBA was firstly investigated in laboratory study for the ETBE synthesis over 60 years ago [11]. There are two routes to produce ETBE from TBA; namely direct and indirect methods. In the indirect method, TBA is dehydrated to IB in a first reactor and then the produced IB is reacted with EtOH to produce ETBE in a second reactor. In the direct method which is the reaction route of our interest, ETBE is produced directly from TBA and EtOH in one reactor. It is favorable because it shortens the process itself [12]. However, selection of proper catalysts with high activity and selectivity is a major concern for the success of this process.

Considering the ETBE synthesis by the direct method, a number of researches have been carried out on catalyst screening. Various catalysts such as Amberlyst-15, heteropoly acid (HPA), $KHSO_4$, $NaHSO_4$ and H_2SO_4 were tested. Yin and coworkers [12] compared the performance of Amberlyst-15 and heteropoly acid by performing the reactions in a semi-batch reactor. The conversion and selectivity of Amberlyst-15 at 338 K and 8 h reaction time of 62% and 43%, respectively, were reported. Heteropoly acid was found to yield superior selectivity (79%); however, it was less attractive because it was significantly inhibited by the presence of water. Matouq and coworkers [13] employed $KHSO_4$, $NaHSO_4$, H_2SO_4 and Amberlyst-15 as catalysts for the direct ETBE synthesis from TBA and EtOH in reactive distillation columns. $NaHSO_4$ failed to synthesize ETBE. The homogeneous catalyst $KHSO_4$ was found to be superior to H_2SO_4 and Amberlyst-15 which produced IB as a main product; however, a subsequent catalyst separation unit was required. Recent research compared three cation-exchange resins of S-54, D-72 and Amberlyst-15 [14]. It was observed at T = 338 K that S-54 showed the improvements of activity and selectivity of 6 and 5%, respectively, compared to those of Amberlyst-15 while the improvements were 10 and 1%, respectively, for D-72.

Apart from the catalyst screening, process design is another key issue that has drawn great attentions from a number of researchers worldwide. A production process is usually based on reactive distillation, which has been a promising process for carrying out esterification reactions since the beginning of 19th century, when the first proposal for the use of distillation as a reactor was considered. Reactive distillation is more attractive than other conventional processes whenever conversions are limited by unfavorable reaction equilibrium and when selectivity can be increased by allowing simultaneous reaction and separation in the same processing unit [15]. Many oxygenate fuels such as MTBE, ETBE and TAME have been successfully produced using reactive distillation. A number of reviews on this topic were published recently [16-17].

The synthesis of ETBE in reactive distillation has attracted some researchers [18-21]; however, most of them considered the system with IB and EtOH as the reactants. In the direct synthesis method from TBA and EtOH, the reactive distillation does not only shift the equilibrium conversion by simultaneous removal of H_2O produced from the reaction but it also reduce demand to the purity of EtOH as the reaction produces water and the water inhibition effect on many catalysts can be suppressed. Only limited number of works focused on the direct synthesis of ETBE from EtOH and TBA in reactive distillation column [6,7,10].

The purpose of this investigation was to compare the performance of β-zeolite catalyst with the commercial Amberlyst-15, which is usually used for *tert*-ethers synthesis, for the production of ETBE via the direct route from TBA and EtOH. A zeolitic catalyst was chosen as it showed promising properties on high thermal stability and no acid fume emission against conventional resin-based catalysts [22]. In the study, the kinetic parameters based on an activity model of β-zeolite catalyst were determined and the performance of the reactive distillation packed with β-zeolite catalyst under various operating parameters such as heat duty, feed flowrate, reflux ratio and feed molar flow rate of water were investigated.

2. EXPERIMENTAL

2.1 Catalyst preparation

Synthesis of β-zeolite powder was carried out in an autoclave at 408 K and 300 kPa. Colloid of SiO_2 and $NaAlO_2$, which were the main reagents employed in the zeolite synthesis, were used to obtain a Si/Al ratio of 42. A compound of tetraethylammonium hydroxide was used as a template for crystals. Sodium and potassium ions, contained in NaCl, NaOH and KCl were used as seeds for the crystals, as well as to balance the ionic charges in the crystals. All these components when mixed together formed a gel. In order to avoid quick solidification of the gel, HCl was added to keep pH at low level. The gel was stirred thoroughly at a room temperature before transferring to the autoclave. Then, the mixture was stirred and heated for 40 h. In order to remove the template from the catalyst precursor, the catalyst was calcined at 813 K for 3.5 h. After this, the catalyst in the Na^+ form was ion exchanged twice with solution of 2M NH_4NO_3 at 353 K for 1 h. Then, the ion-exchanged crystals were dried in an oven at 383 K for at least 3 h. The resulting crystals were in NH_4^+ form. Finally, calcination of the catalyst at 773 K for 2 h was necessary to dissociate the ammonium ion, NH_4^+ into NH_3 and protonated form of hydrogen, H^+. NH_3 escaped to the atmosphere while the H^+ stayed onto the catalyst to balance the ionic charge. The catalyst was characterized by an X-ray diffraction (XRD-SIEMENS D5000) and its composition was measured using an X-ray fluorescence spectrometer (XRF-model Fision).

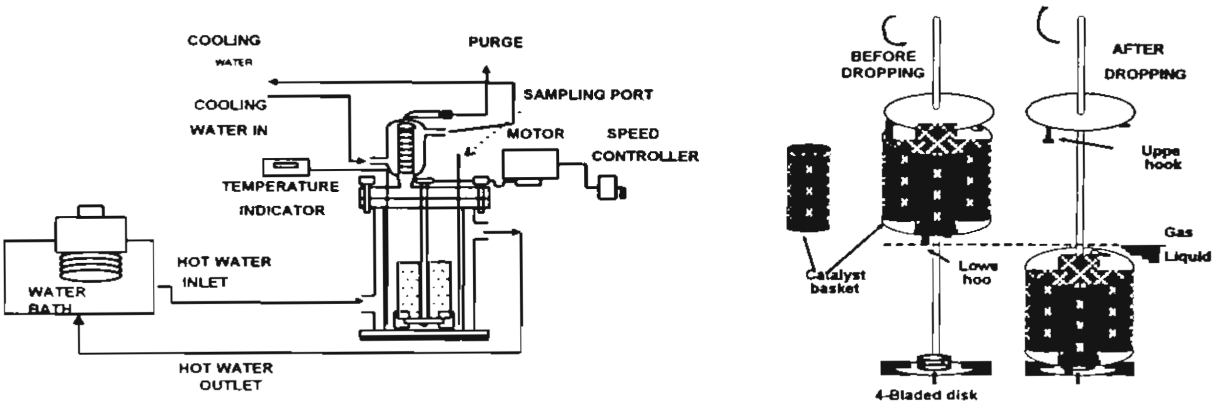
2.2 Preparation of supported β-zeolite

Supported β-zeolite was prepared by coating the obtained powder catalysts on a cordierite monolith support (400 cell/in^2) which was cut into small cubes of 0.5x0.5x0.5 cm^3. The supports were weighted and soaked in 2.5wt% acetic acid solution for 2 min. After that, they were washed by distilled water several times to remove residual acid solution, and then dried in an oven at 383 K until the weight became constant. β-Zeolite powder was added into 2.5wt% acetic acid solution to give 30-50%wt/volume washcoat. The obtained slurry was stirred for 10 min. Then, 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 the increased weight of the monolith. The uniformity of the catalyst distribution was examined by measuring distribution of Al using a scanning electron microscope – energy dispersive x-ray spectrometer (SEM-EDX). It was shown that the catalyst was well dispersed on the monolith surface

2.3 Kinetic study

The powder β-zeolite was used in a preliminary study to compare the catalyst performance between β-zeolite and Amberlyst-15 (obtained from Fluka). The latter is a sulfonated styrene divinyl benzene copolymer with a macroreticular structure. The mesh size was in the range of 20-50 and the ion exchange capacity was 4.96 mol-H$^+$/kg-dry resin. A certain amount of catalyst was weighted and pretreated by leaving it 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 slurry reactor consisting of 250 cm^3 three-necked flask fitted with a condenser in the central opening. The mixture was stirred and heated up to 338 K by circulating hot water through the jacket. The reaction was started by adding the catalyst into the reaction mixture. Liquid samples of 1 cm^3 were taken to measure concentrations of H_2O, EtOH, TBA, IB and ETBE at different reaction times. They were analyzed by a TCD gas chromatography with a column packed with Gaskuropack 54.

In the kinetic study, β-zeolite supported on monolith was packed in a special-design basket-type reactor as shown in **Fig. 1(a)**.



(a) (b)

Fig. 1 Schematic diagrams: (a) experimental setup, (b) catalyst basket.

A frame of four catalyst baskets was equipped with a rotating shaft which was driven by a motor via an inverter controller to determine the accurate start-up time in a semi-batch reactor [15]. 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 **Fig. 1(b)**. When 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. Three temperature levels, T = 323, 333 and 343 K were performed under atmospheric pressure. It is noted that the liquid samples taken from the reactor were small compared to the total liquid volume.

2.4 Preparation of packing material for reactive distillation

Stainless-steel sieves (30 mesh) with 0.7x0.7 cm^2 size in saddle-like shape were used as packing materials in distillation sections in the reactive distillation column. Before they are 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.

2.5 Reactive distillation study

Fig. 2 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 0.7x0.7 cm^2 of stainless-steel packing materials. The middle section of the column was filled with the supported catalyst bed. Like the upper section, the lower section of the column was packed with the same packing materials. The heights of the sections were 0.1, 0.5, 0.1 m, respectively. The temperature profile in the reactive distillation column was determined by using thermocouples with a temperature indicator.

The top of the column was connected using a condenser with ice water as a coolant to condense vapor from the reactive distillation column. Then, the condensate was passed into a solenoid valve. A multi-timer was used as a reflux ratio controller. The bottom of the column was connected to a reboiler which was filled with the reactant mixture of approximately $4.2\text{x}10^{-4}$ m^3. The level of bottom product in the reboiler was controlled by a Masterflex pump. Heat supply to the reboiler was controlled by a variac. Current and voltage were measure to calculate heat duty. 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 which took around 3 h. Top and bottom products were sampled and their flow rate was measured every 0.5 h. For batch operation, no feed stream was introduced to the system. The reactant was initially filled in the reboiler. The top products were measured at different reaction time. **Table 1** provides the operating conditions of the reactive distillation study.

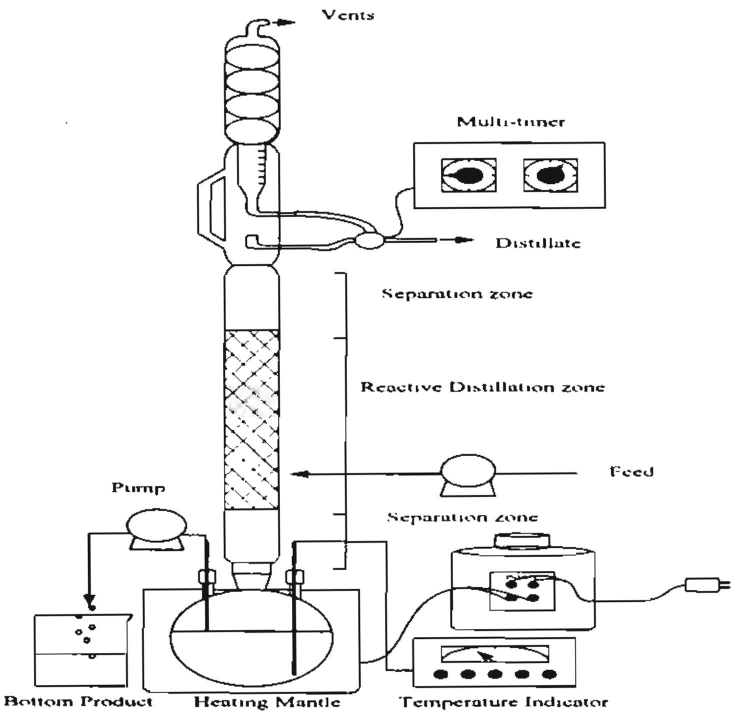


Fig. 2 Schematic diagram of the reactive distillation system.

Table 1 Lists of the experimental conditions.

No.	Heat duty (kW)	Feed			Operation
		Flow rate (m^3/s)	TBA:EtOH:H_2O	Reflux ratio	
1	0.057	-	1:1:38	5	Batch
2	0.048	-	1:1:38	5	Batch
3	0.040	-	1:1:38	5	Batch
4	0.040	-	1:1:38	Total	Batch
5	0.048	1.67×10^{-8}	1:1:38	1	Continuous
6	0.073	1.67×10^{-8}	1:1:38	1	Continuous
7	0.105	1.67×10^{-8}	1:1:38	1	Continuous
8	0.073	3.33×10^{-8}	1:1:38	1	Continuous
9	0.073	6.67×10^{-8}	1:1:38	1	Continuous
10	0.073	1.67×10^{-8}	1:1:38	3	Continuous
11	0.073	1.67×10^{-8}	1:1:38	5	Continuous
12	0.073	1.67×10^{-8}	1:1:20	1	Continuous
13	0.073	1.67×10^{-8}	1:1:10	1	Continuous

3. RESULTS AND DISCUSSION

3.1 Catalyst Screening and Kinetics Study

3.1.1 Catalyst Characterization

Synthesized β-zeolite was analyzed by an X-ray diffraction measurement to identify crystal structure. **Fig. 3** showed an X-ray diffraction pattern which agreed well with those reported in a literature [23].

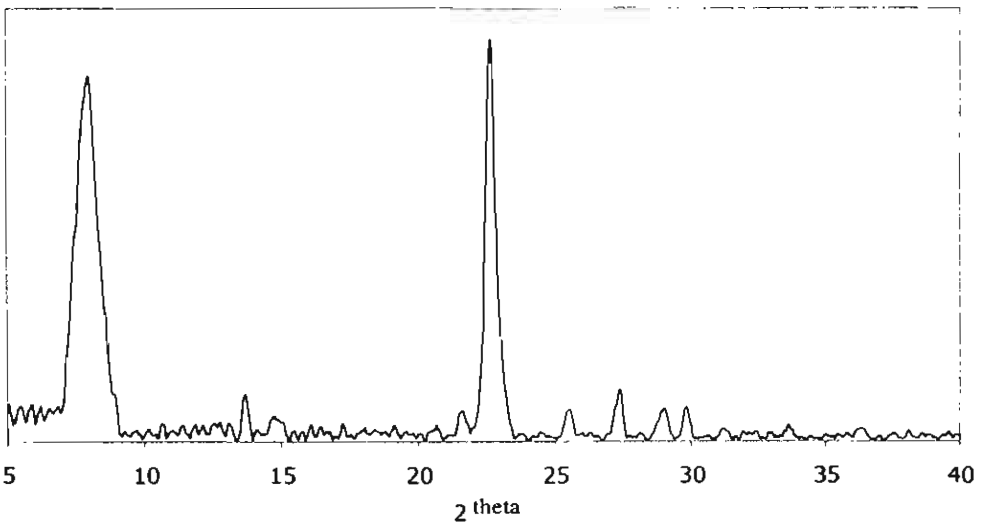


Fig. 3 X-ray diffraction pattern of β-zeolite (Si/Al = 42).

This indicated that the synthesized catalysts had the same structure as β-zeolite. The particle size of the obtained β-zeolite powder was approximately 0.5 μm. The Si, Al and Na contents of β-zeolite measured by X-ray fluorescence spectrometer (XRF-model Fision) were 96.97, 2.30 and 0.21wt%, respectively, thus yielding the Si/Al ratio of 42.

3.1.2 Comparison between catalyst performances

Two types of catalysts; i.e. commercial Amberlyst-15 and powder β-zeolite were tested in a slurry reactor to compare the performance on the synthesis of ETBE from EtOH and TBA. The experiments were carried out at the following condition; i.e. catalyst weight = 4 g, T = 338 K, stirring speed = 660 rpm and the initial amount of ethanol and TBA = 0.5 and 0.5 mol, respectively. The reactions taking place in the reactor can be summarized as follows

$$\text{TBA} + \text{EtOH} \Leftrightarrow \text{ETBE} + H_2O \quad (1)$$

$$\text{TBA} \Leftrightarrow \text{IB} + H_2O \quad (2)$$

$$\text{IB} + \text{EtOH} \Leftrightarrow \text{ETBE} \quad (3)$$

Fig. 4 shows the number of moles of TBA, EtOH, ETBE and H_2O in liquid mixtures at different reaction time of both catalysts. Filled and empty symbols represent results of Amberlyst-15 and β-zeolite, respectively.

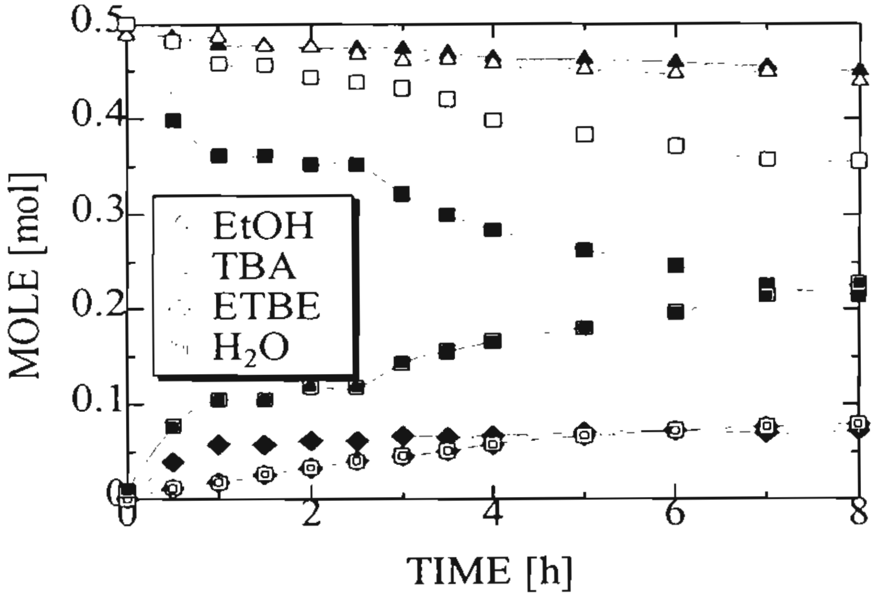


Fig. 4 Comparison between different catalysts: filled symbol = Amberlyst-15, empty symbols = β-zeolite (Catalyst weight = 4.0 g, $m_{TBA,o}$ 0.5 mol, $m_{EtOH,o}$ = 0.5 mol, T = 338 K and reactor type = slurry reactor).

It should be noted that the side product, IB was mainly present in the gas phase. Considering the disappearance of TBA, it was found that β-zeolite was less active than Amberlyst-15. However, when considering the formation of ETBE, it is obvious that the ETBE yields of both catalysts were almost the same. By defining selectivity as the ratio of the produced amount of ETBE to the produced amount of water, it was investigated that the selectivities of β-zeolite and Amberlyst-15 were 70% and 34% respectively. It can be concluded that β-zeolite was much more attractive than Amberlyst-15 and, consequently, the following studies would consider only β-zeolite catalyst.

3.1.3 Kinetic study

Effect of external mass transfer

The kinetic study was investigated in the basket-type reactor using β-zeolite supported on monolith. The effect of external mass transfer of catalyst was studied by varying stirring speeds. **Fig. 5** shows the relationship between the conversion of TBA at 7 h and the stirring speed.

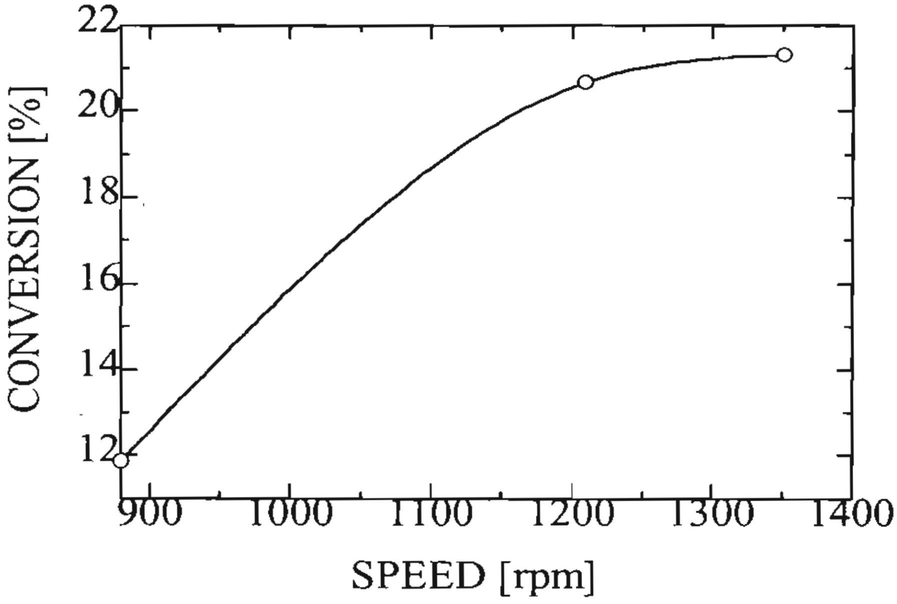


Fig. 5 The effect of speed level on the conversion (Catalyst = β-zeolite, catalyst weight = 15 g, $m_{TBA,o}$=2 mol, $m_{EtOH,o}$= 2 mol, T = 333 K, time = 7 h and reactor type = basket reactor).

It was found that the conversion increased with increasing speed level and, finally, it leveled off at the speed level of 1210 rpm. This can be concluded that the effect of external mass transfer can be neglected when the speed level is higher than 1210 rpm. In the subsequent studies, the speed of 1210 rpm was used to ensure negligible external mass transfer resistance.

Development of mathematical models

Mathematical models were developed by following our previous study [6]. 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 small amount of IB can be dissolved in the liquid. It was also confirmed by our experimental results that the concentration of IB was very small in liquid mixture. As a result, the rate laws of the reactions (1) and (2) can be expressed in terms of activities as

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

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

where k_j is the reaction rate constant of reaction j (j = 1, 2). a_i is an activity of species i. K_W is the water inhibition parameter.

The expression of K_1 is given as follow [24].

$$K_1 = \exp(1140.0 - 14580/T + 232.9 \ln T + 1.087T - 1.114x10^{-3}T^2 + 5.538x10^{-7}T^3) \tag{6}$$

It should be noted that the resistance of pore diffusion should play an important role on the reaction rate due to very fine pore size of β-zeolite. However, it was assumed that this effect was included into the kinetic parameters obtained from the data fitting.

By performing the 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 is noted that the number of moles in the liquid phase at any time is constant because IB can only slightly dissolved in the liquid phase. In addition, every one mole of

TBA consumption produces one mole of water, and every one mole of EtOH consumption produces one mole of ETBE. The activity can be calculated from the following relation.

$$a_i = \gamma_i x_i \qquad (9)$$

where x_i is mole fraction of species i in the liquid mixture and γ_i is the activity coefficient. The activity coefficients can be calculated using the UNIFAC method [25].

Kinetic parameter determination

A set of experiments was carried out at three temperature levels of 323, 333 and 343 K to investigate the kinetic parameters. **Fig. 6** shows typical results of mole changes with time at T = 343 K. The initial moles of each species were given in the figure caption. It should be noted that the experimental results showed very good material balance since the disappearance of ethanol and the formation of ETBE were very close. This was also true for the case of TBA disappearance and water formation. The experimental results showed that the production of ETBE became higher with the increase of temperature as expected in the Arrhenius's equation.

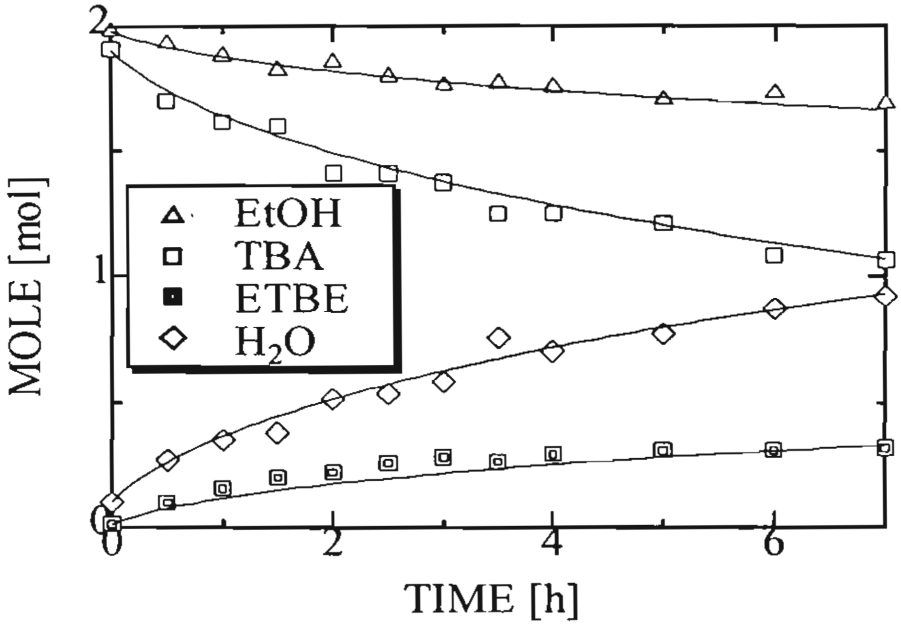


Fig. 6 Mole changes with time (Catalyst = β-zeolite, catalyst weight = 15.0 g, $m_{TBA,o}$ = 1.91 mol, $m_{EtOH,o}$ = 1.98 mol, $m_{ETBE,o}$ = 0.01 mol, $m_{H_2O,o}$ = 0.10 mol, T = 343 K and reactor type = basket reactor).

A curve fitting method was employed to find the kinetic parameters, k_1, k_2 and K_w at each temperature. Initial guess values of the parameters, k_1 and k_2 were obtained by using an initial rate method. The continuous lines in the figure represent the simulation results. It was found that within the ranges of the study the model fit the experimental results well with the sum square of the residual at T = 343, 333 and 323 K of 0.061, 0.099 and 0.002, respectively.

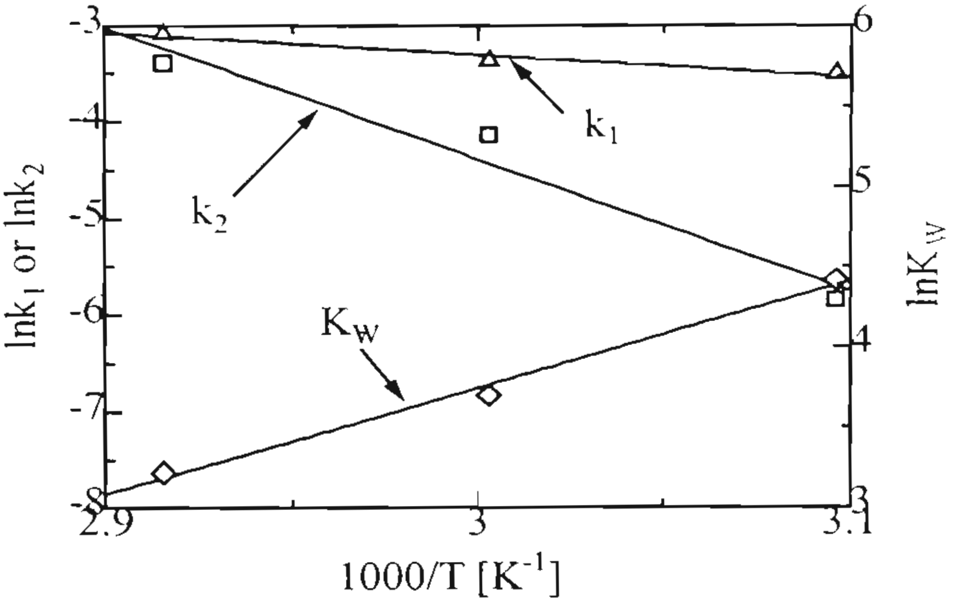


Fig. 7 Arrhenius and van't Hoff plots.

Fig. 7 shows the Arrhenius's plot of the reaction rate constants and the van't Hoff's plot of the adsorption parameters using the obtained results from the 3 temperature levels. The following equations were determined from the plots.

$$k_1 = \exp(3.55 - 2286/T) \tag{10}$$

$$k_2 = \exp(36.57 - 13653/T) \tag{11}$$

$$K_W = \exp(-16.16 + 6636/T) \tag{12}$$

Table 2 compares the values of the activation energy of the reactions (1) and (2) and the heat of adsorption of water with those values of different catalysts. It was observed that the heat of adsorption of water of β-zeolite catalyst was quite close to the values of other catalysts except that of HPA which showed significant water-inhibition effect. The activation energy of the dehydration reaction of β-zeolite was within the range reported in the other catalysts. This indicates that the production of the undesired product, IB was greatly enhanced with increasing temperature. However, the activation energy of the etherification reaction (1) of β-zeolite was much lower than those of the other catalysts. This may indicate the pore-diffusion limitation arisen from the transport of large molecule ETBE from the pore of β-zeolite.

Table 2 Comparison of activation energy and heat of adsorption of water among different catalysts

Catalysts	Activation energy of reaction (1) (kJ/mol)	Activation energy of reaction (2) (kJ/mol)	Heat of adsorption of water (kJ/mol)	Reference
β-zeolite	19	114	55	This work
Amberlyst-15	57	85	63	[12]
HPA	95	108	20	[12]
S-54	48	74	67	[14]
D-72	43	30	63	[14]
Amberlyst-15	-	142	55	[26]

The obtained rate expressions can be used for modeling of production processes such as a reactive distillation column with and without a pervaporation unit and a pervaporative membrane reactor; however, it should be noted that it is desirable to operate the reactor at low operating temperature. This is because the activation energy of the dehydration reaction (2) is higher than the main reaction (1) and, consequently the selectivity to ETBE decreases with increasing temperature.

3.2 Reactive distillation study

3.2.1 Standard condition

Fig. 8 shows the performance of the reactive distillation at the standard condition; i.e. continuous operation, β-zeolite weight=50 g, feed molar ratio TBA:EtOH:H_2O=1:1:38, F=1.67x10^{-8} m^3/s, Q=0.073 kW and reflux ratio=1. The temperature profile inside the column shown in Fig. 8(a) decreases from the bottom (374 K) to the top (368 K). However, the temperature was almost constant at T=371 K in the reactive distillation zone. **Fig. 8(b)**

shows the mole fraction profiles of the distillate and bottom products represented by empty and filled symbols, respectively.

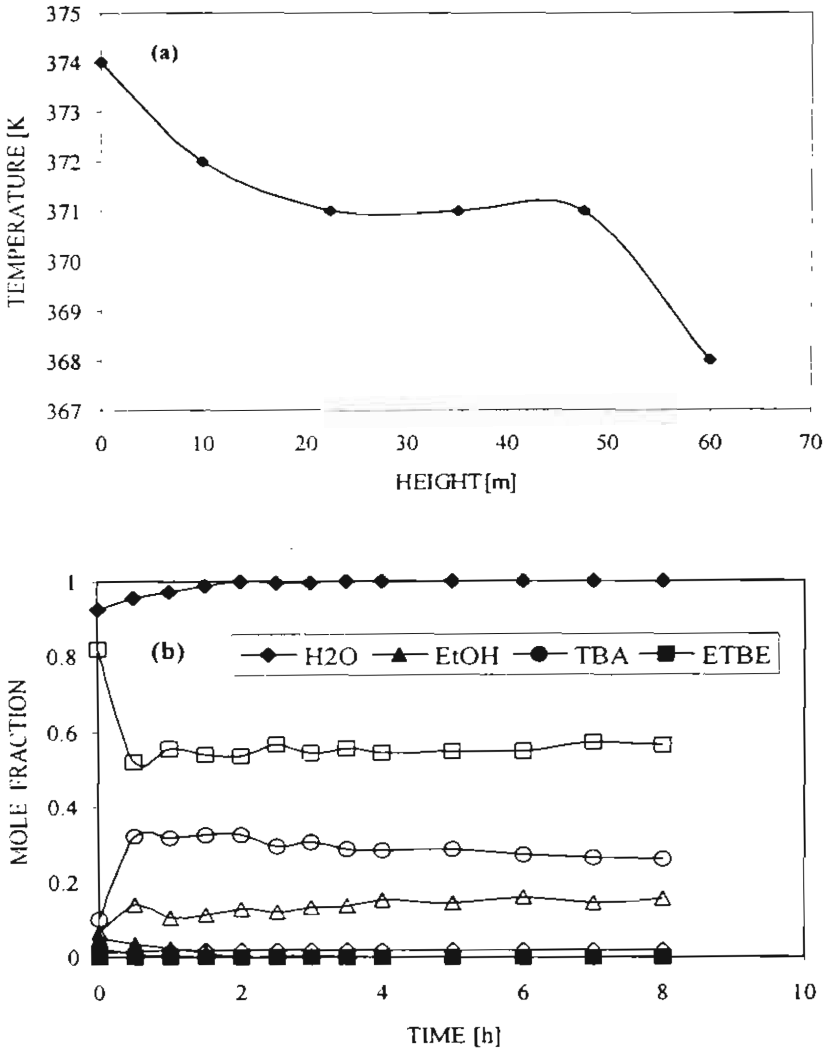


Fig. 8 Performance of reactive distillation at the standard condition (a) The temperature profile of a reactive distillation column, (b) the concentration profile of the distillate and the residue, O: distillate , ● bottom (molar ratio of TBA:EtOH:H_2O=1:1:38, F=1.67x10^{-8} m^3/s, Q=0.073 kW, reflux ratio=1).

It was found that the steady state was attained after approximately 3 h. At steady state, the mole fraction of distillate was about 57 mol% ETBE, while the residue consisted of mostly water and slight amount of ethanol. Both the mole fractions of ethanol and TBA in the distillate were about 20mol%, while water was negligible.

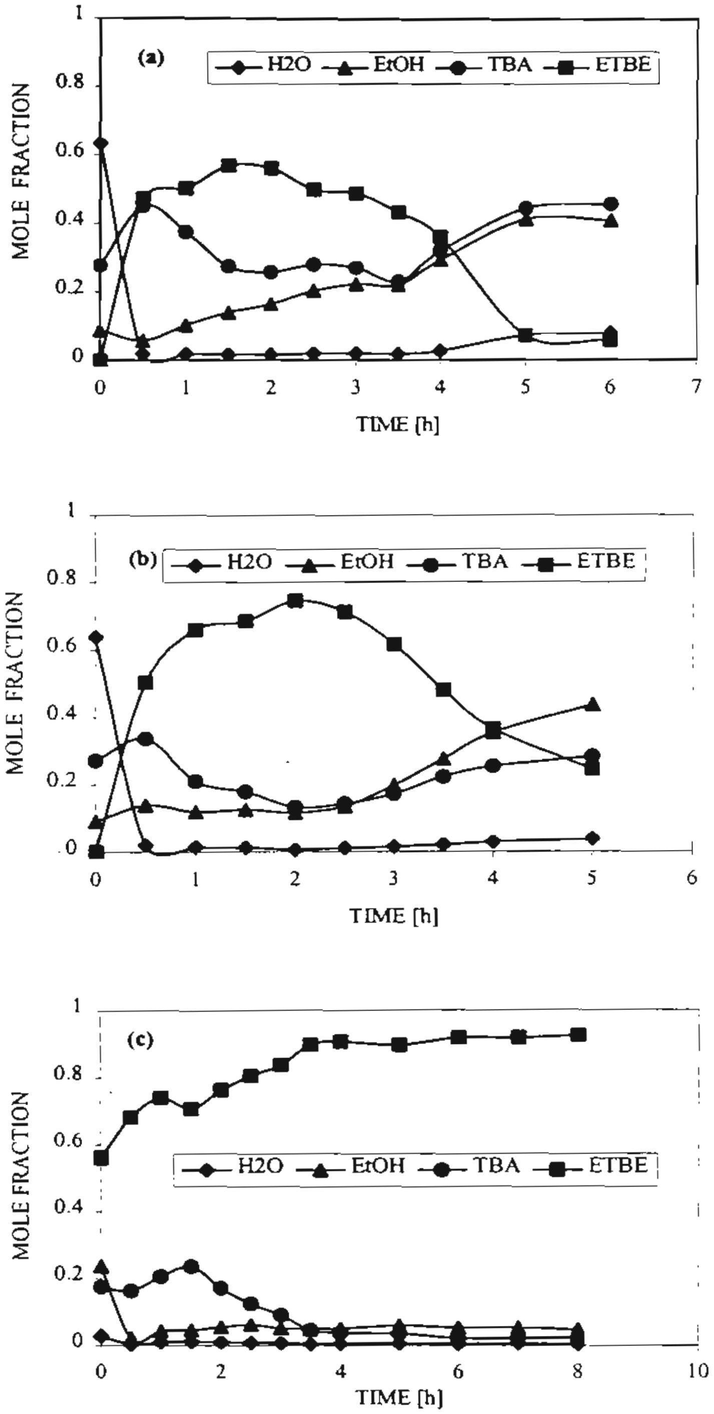


Fig. 9 The concentration profiles of distillated for (a) Q =0.057 kW, (b) Q =0.048 kW, and (c) Q =0.040 kW (molar ratio of TBA:EtOH:H_2O=1:1:38, reflux ratio=5, F=0 m^3/s).

The performance of the reactive distillation can be represented as conversion and selectivity. The conversion and selectivity in the study were defined as follows:

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

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

The corresponding conversion and selectivity at the standard condition are 61% and almost 100%, respectively. Previous study by Quitain *et al.* [6] reported the selectivity of 35.9 % for the same reaction with Ambelyst-15 catalyst.

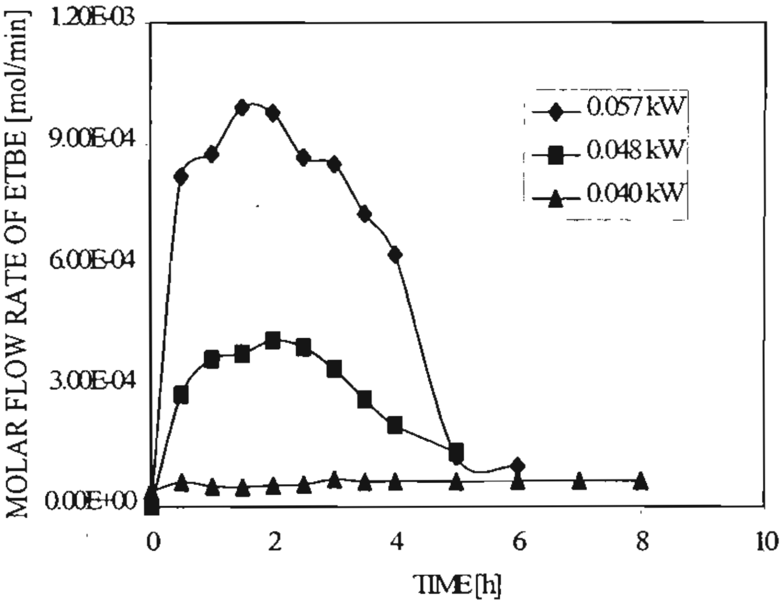


Fig. 10 Effect of heat duty on the molar flow rate of ETBE in distillate (molar ratio of TBA:EtOH:H_2O=1:1:38, reflux ratio=1, F =0 m^3/s).

3.2.2 Effect of heat duty

The effects of heat duty for both batch and continuous reactive distillation operations were investigated. For the batch reactive distillation, three experiments were carried out at the condition summarized as Runs 1, 2 and 3 in **Table 1**. The mole fraction profiles of distillates are shown in **Fig. 9**. It was found that the mole fraction of ETBE decreased with increasing heat duty, while the mole fractions of unconverted ethanol and TBA increased with increasing heat duty. However, when considering the molar flow rate of ETBE and EtOH shown in **Figs. 10 and 11**, respectively, it was noticed that even though the mole fraction of ETBE was high at the lowest heat duty (Q) of 0.040 kW rate was extremely low. Increasing the heat duty resulted in higher amount of reactant vaporization and the ETBE production. It should be noted that for the batch operation, the production rate of ETBE decreased with time due to the reduced amount of reactants in the system.

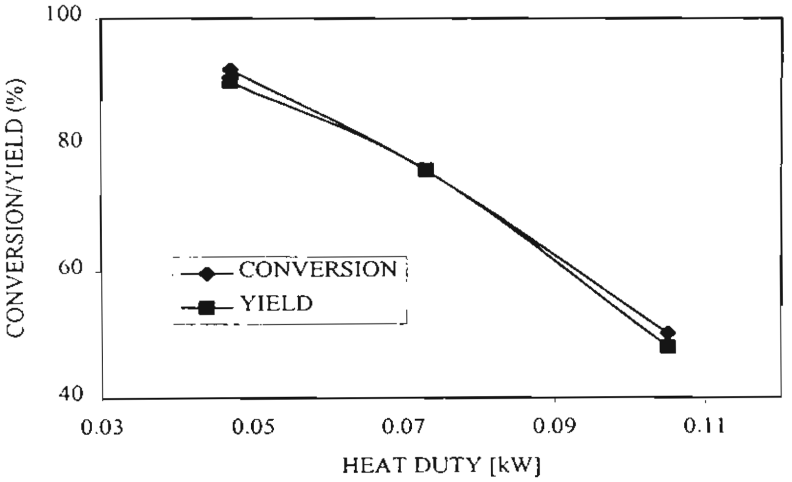


Fig. 11 Effect of heat duty on the molar flow rate of EtOH in distillate (molar ratio of TBA:EtOH:H_2O=1:1:38, reflux ratio=1, *F* =0 m^3/s).

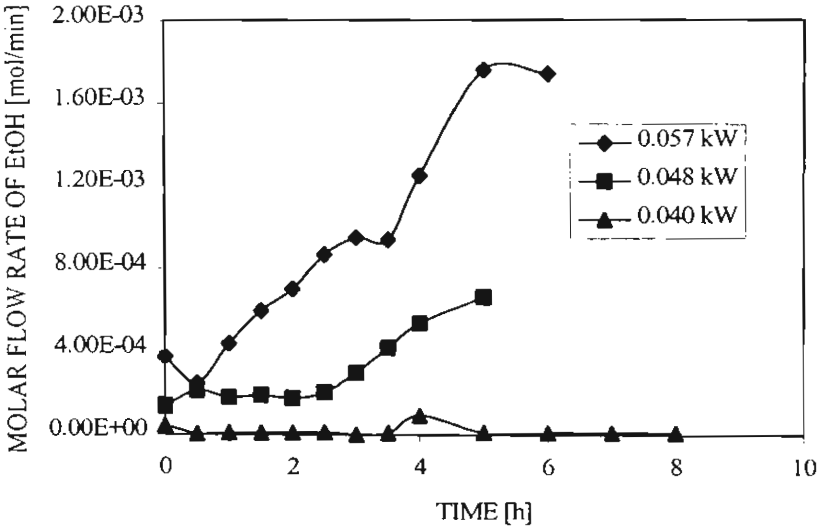


Fig. 12 Effect of heat duty on the conversion and yield of reactive distillation (molar ratio of TBA:EtOH:H_2O=1:1:38, reflux ratio=1, *F* = 1.67x10^{-8} m^3/s).

For the continuous reactive distillation, **Fig. 12** shows the effect of heat duty on conversion and selectivity. It was found that the yield and the conversion were very close to each other. This emphasized that β-zeolite was suitable for this system. In addition, it was found in the range of this study that the conversion and the yield increased with decreasing heat duty. The maximum conversion of 92% was obtained at the heat duty of 0.048 kW. This result can be explained by considering the flow rates of the distillate which were 4.17×10^{-9}, 6.67×10^{-9} and 1.42×10^{-8} m^3/s for the heat duty of 0.048, 0.073 and 0.105 kW, respectively. It was obvious that increasing the heat duty resulted in the increased vapor load in the column and, consequently, the flow rate of the distillate. Due to the limited amount of catalyst bed in the column, more unconverted reactants should be present in the distillate and, as a result, the conversion decreased. However, it should be noted that at very low heat duty the conversion and the yield should be small due to the insufficient heat to vaporize the reactants and to keep the column temperature at high value. As a result, there should be an optimum heat duty for the system although it was not indicated in the study.

3.2.3 Effect of feed flow rate

Fig. 13 shows the effect of feed flow rate on the conversion of ethanol and the yield of ETBE at three different feed flow rates of 1.67×10^{-8}, 3.33×10^{-8} and 6.67×10^{-8} m^3/s. It was found that the highest conversion of ethanol and the yield were obtained at the optimum feed flow rate of 3.33×10^{-8} m^3/s. Considering this case that the heat duty and the amount of catalyst remained constant, increasing the feed flow rate obviously reduces the column temperature and the conversion, resulting in the decline of the conversion. However, it was noticed that from the optimum feed flow rate, decreasing the fed flow rate lowered the conversion and the yield. This can be explained by considering the vaporization of the reactants, at low feed flow rate the reactants can be easily vaporized and present in the distillate as unconverted reactants. Consequently, the conversion was decreased.

3.2.4 Effect of reflux ratio

Fig. 14 shows the effect of reflux ratio on the conversion of ethanol and the yield of ETBE. It was found that the conversion and the yield increased with increasing reflux ratio. Because the unconverted reactants were refluxed into the column, more reaction can take place in the reaction zone. In addition, at high reflux ratio the separation of ETBE in the distillation part became more efficient. It should be noted that increasing the reflux ratio can be considered as increasing the residence time of the reactants in the reactants and the catalysts are efficiently utilized.

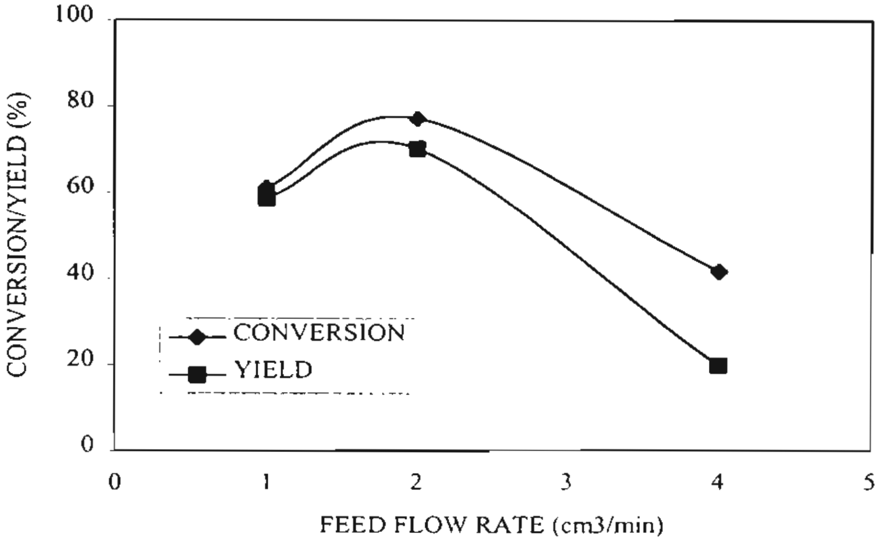


Fig. 13 Effect of feed flow rate on the conversion and yield of reactive distillation (reflux ratio=1, molar ratio of TBA:EtOH:H_2O=1:1:38, *Q* =0.073 kW).

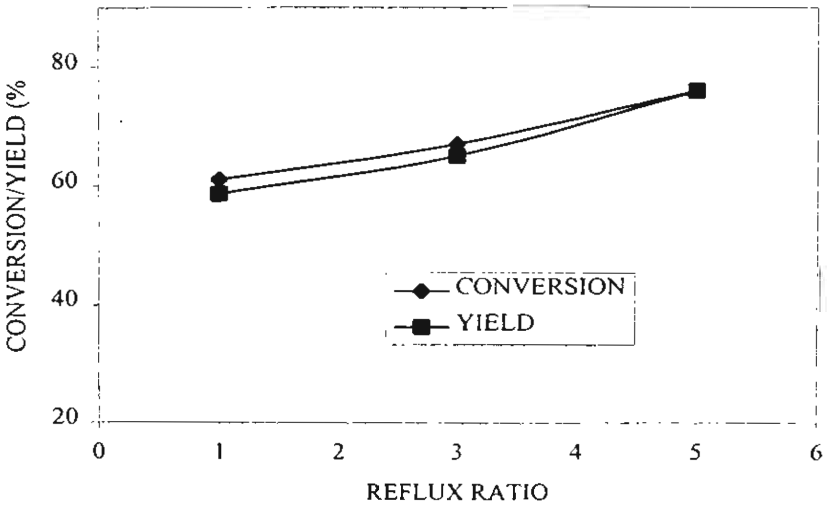


Fig. 14 Effect of reflux ratio on the conversion and yield of reactive distillation (molar ratio of TBA:EtOH:H_2O=1:1:38, *Q* =0.073 kW, *F* =1.67×10^{-8} m^3/s).

3.2.5 Effect of feed molar ratio of water

Fig. 15 shows the effect of the feed molar ratio of water. The feed molar ratio of TBA:EtOH:H_2O was 1:1:x where x is the ratio of water. Three values of x of 10, 20 and 38 were investigated. It was found that at the constant feed flow rate and heat duty, there was an optimum feed composition providing the maximum conversion. At high amount of water in the feed heat was mainly utilized to raise the water temperature, resulting in the lower column temperature and the reaction rate. Thus, the conversion and the yield dropped. However, at the optimum composition when the extent of water decreased, the conversion and the yield again decreased. This may be because more reactants were vaporized and present in the distillate as unconverted reactants. This may be similar to the case of the decreasing of flow rate.

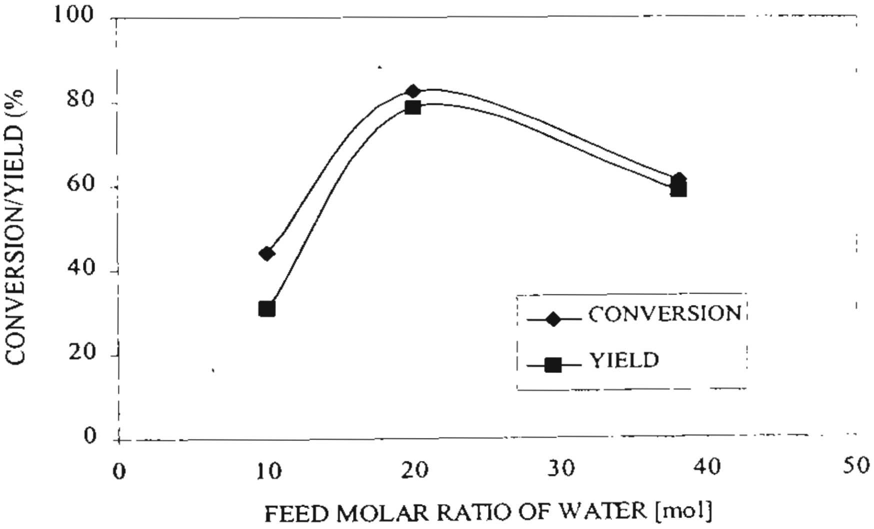


Fig. 15 Effect of feed molar ratio of water on the conversion and yield of reactive distillation (Q=0.073 kW, reflux ratio=1, F =1.67x10^{-8} m^3/s).

4. CONCLUSION

It was found that β-zeolite showed superior performance over the commercial Amberlyst-15 for the direct production of ETBE from TBA and EtOH. Even though the activity was moderate, the selectivity was much higher. The kinetic study of the reaction catalyzed by β-zeolite supported on monolith was carried out using a semi-batch reactor. The effect of external mass transfer was negligible at the stirring speed higher than 1210 rpm. The activity-based model taking into account of the effect of water inhibition was developed. Three temperature levels of 323, 333 and 343 K were used in the study to obtain the parameters in the Arrhenius's equation of the reaction rate constants and the van't Hoff equation of the water inhibition coefficient.

Reactive distillation was employed to continuously synthesize ETBE from TBA and bioethanol using β-zeolite as the catalyst. Results at the standard operating condition indicated that ETBE at 57mol% could be obtained in the top product while almost pure water in the residue. Other operating parameters such as heat duty, feed flowrate, reflux ratio and feed molar flow rate of water were investigated to find effects on the reactive distillation performance.

5. NOMENCLATURE

a_i	Activity of species i [-]
F	feed flowrate [m^3/s]
k_1	Reaction rate constant of reaction (1) in the activity-based model [$mol.kg^{-1}.s^{-1}$]
k_2	Reaction rate constant of reaction (2) in the activity-based model [$mol.kg^{-1}.s^{-1}$]
K_1	Equilibrium constant of reaction (1) in the activity-based model [-]
K_W	Water inhibition parameter in the activity-based model [-]
r_j	Reaction rate of reaction j [$mol.kg^{-1}.s^{-1}$]
m_i	Number of mole of species i [mol]
Q	heat duty at the reboiler [kW]
S_{ETBE}	selectivity of ETBE [%]
t	Reaction time [s]
T	Temperature
W	Catalyst weight [kg]
x_i	Mole fraction of species i in liquid mixture [-]
X_{EtOH}	conversion [%]

Greek

γ_i	Activity coefficient of species i [-]

Subscripts

ETBE	Ethyl *tert*-butyl ether, 2-ethoxy 2-methyl propane (IUPAC)
EtOH	Ethanol
H_2O	Water

TBA *tert*-Butyl alcohol, 2-methyl 2-propanol (IUPAC)

o Initial value a *t* = 0

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7. OUTPUT

7.1 International Publication

1) S. ASSABUMRUNGRAT, W. KIATKITTIPONG, N. SEVITOON, P. PRASERTHDAM and S. GOTO "Kinetics of Liquid Phase Synthesis of Ethyl tert-Butyl Ether from tert-Butyl Alcohol and Ethanol Catalyzed by -Zeolite Supported on Monolith" International Journal of Chemical Kinetics 34: (5) 292-299 MAY 2002 (Appendix A)
2) Suttichai ASSABUMRUNGRAT, Darin WONGWATTANASATE, Worapon KIATKITTIPONG, Piyasan PRASERTHDAM and Shigeo GOTO "Reactive Distillation for the Production of Ethyl tert-Butyl Ether from tert-Butyl Alcohol and Ethanol Catalyzed by b-Zeolite" to be submitted to Journal of Chemical Engineering of Japan (under preparation)

7.2 International Conference

1) S. Assabumrungrat, N. Srivitoon, V. Kiatkittipong, P. Praserthdam, S. Phatanasri, S. Goto and A. Quitain "Kinetics of the Liquid Phase Synthesis of Ethyl *tert*-Butyl Ether from *tert*-Butyl Alcohol and Ethanol Catalyzed by β-Zeolite", The Regional Symposium on Chemical Engineering 2000, Singapore, December, 2000 (oral presentation) (Appexdix B)
2) Suttichai ASSABUMRUNGRAT, Darin WONGWATTANASATE, Worapon KIATKITTIPONG, Piyasan PRASERTHDAM and Shigeo GOTO "Reactive Distillation for the Production of Ethyl tert-Butyl Ether from tert-Butyl Alcohol and Ethanol Catalyzed by b-Zeolite" 4th International Symposium on Catalysis in Multiphase Reactors, to be held from September 22-25th, 2002 in Lausanne, Switzerland (Poster presentation) (Appendix C)
3) Darin WONGWATTANASATE, Suttichai ASSABUMRUNGRAT, Piyasan PRASERTHDAM and Shigeo GOTO Simulation of Ethyl tert-Butyl Ether Production from tert-Butyl Alcohol and Ethanol in Reactive Distillation Regional Symposium on Chemical Engineering (RSCE) 2002 In conjunction with 16th Symposium of Malaysian

Chemical Engineers (SOMChE) Kuala Lumpur, MALAYSIA 28-30th October 2002 (Poster presentation) (Appendix D)

7.3 National Conference

1) สุทธิชัย อัสสะบำรุงรัตน์, นิสากร ศรีวิฑูรย์, ปิยะสาร ประเสริฐธรรม, ดาริน วงศ์วัฒนะเศรษฐ์ และ Shigeo Goto การกลั่นที่มีปฏิกิริยาสำหรับการสังเคราะห์เอทิล เทอร์เชียรี-บิวทิล อีเทอร์จากเอทานอลและเทอร์เชียรี บิวทานอล โดยใช้ตัวเร่งปฏิกิริยาซีโอไลต์เบตา การประชุมวิชาการวิศวกรรมเคมีและเคมีประยุกต์แห่งประเทศไทยครั้งที่ 11 มหาวิทยาลัยเทคโนโลยีสุรนารี 9-10 พย. 44 (นำเสนอแบบปากเปล่า) (Appendix E)