CHAPTER V

RESULTS AND DISCUSSION

In this chapter, the results and discussion are divided to three sections; i.e. characterization of Beta zeolites, catalyst selection, kinetic study and reactive distillation study. Details are as follows.

5.1 Catalyst Characterization

5.1.1 X-ray Diffraction (XRD)

Synthesized Beta zeolite was analyzed by X-ray diffraction for identifying crystal structure. The X-ray diffraction pattern of H form of Beta zeolite (Si/Al = 30) is illustrated in Figure 5.1. The pattern was corresponding well with those reported by Ramesh *et al.* (1992). This indicated that the synthesized catalysts had the same structure as Beta zeolite.

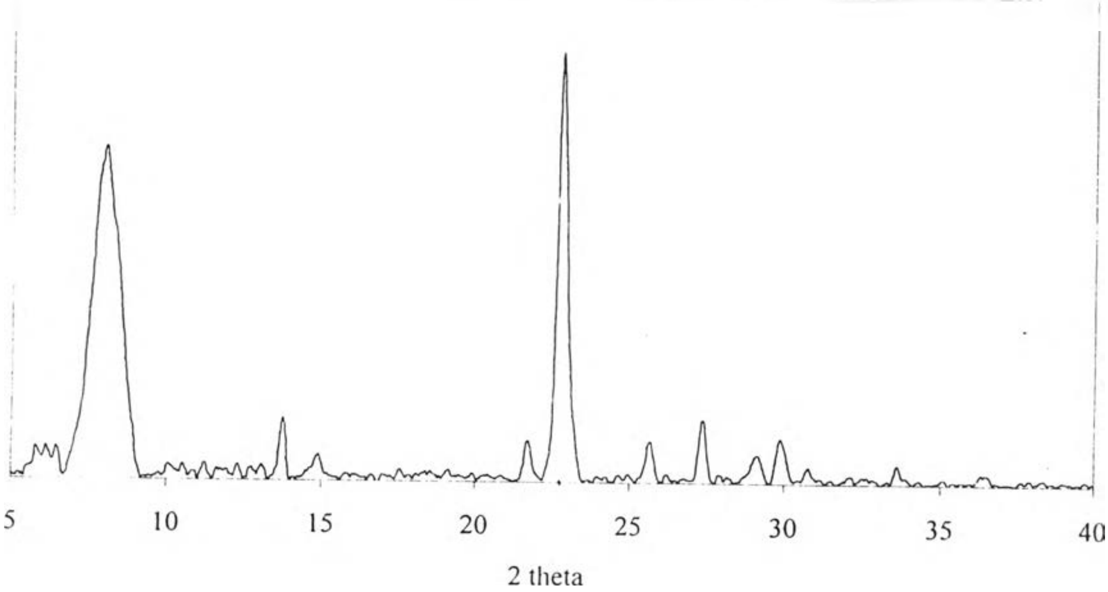


Figure 5.1 X-ray diffraction pattern of H-Beta zeolite (Si/Al = 30)

5.2 Catalyst selection and kinetic study

5.2.1 Comparison between catalysts

Two types of catalysts; i.e. commercial Amberlyst-15 and Beta zeolite were tested to compare the performance on the synthesis of ETBE from EtOH and TBA. The experiments were carried out at the following condition; i.e. 4 grams of Amberlyst-15 or Beta zeolite were used as catalyst at 338 K and the initial molar concentration of ethanol and TBA was 0.5 and 0.5 mol, respectively. The reactions taking place in the reactor can be summarized as follows

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

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

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

Figure 5.2 shows the number of moles of TBA, EtOH, ETBE and H_2O at different time on stream for Ambrlyst-15 and Beta zeolite. It should be noted that the side-product, IB was mainly present in the gas phase. The results show that the disappearance of TBA for Amberlyst-15 was greater than that of Beta zeolite. However, when considering the formation of ETBE, it is obvious that the yields to ETBE of Beta zeolite and Amberlyst-15 were almost the same. Previous investigation by Yin *et al.* (1995) compared the performance between Amberlyst-15 and Heteropoly acid (HPA). It was found that eventhough HPA yielded superior activity, it was significantly inhibited by the presence of water, compared with Amberlyst-15. It can be concluded that Beta zeolite is much more attractive, consequently, the following studies will focus on the use of Beta zeolite.

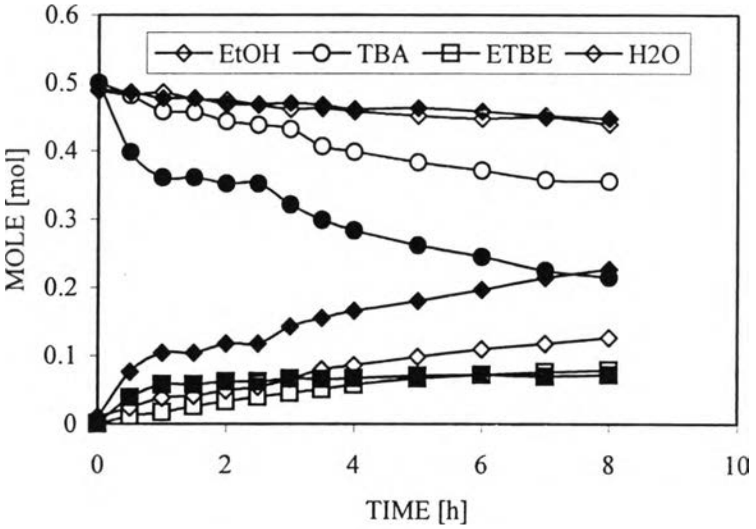


Figure 5.2 Comparison between different catalysts O:Amberlyst-15, O:Beta zeolite (Catalyst weight = 4.0 g, TBA_o= 0.5 mol, $EtOH_o$ = 0.5 mol and T = 338 K)

5.2.2 The effect of external mass transfer

The effect of external mass transfer of catalyst was studied by varying speed levels of the magnetic stirrer. Figure 5.3 shows the relationship between conversion of ethanol at 8 hours and the speed level. It was found that the conversion increased with increasing speed level and, finally, it leveled off at the speed level of 540 rpm. This can be concluded that the effect of external mass transfer can be neglected when the speed level is higher than 540 rpm. In the subsequent studies the maximum speed of 660 rpm will be used to ensure negligible external mass transfer resistance.

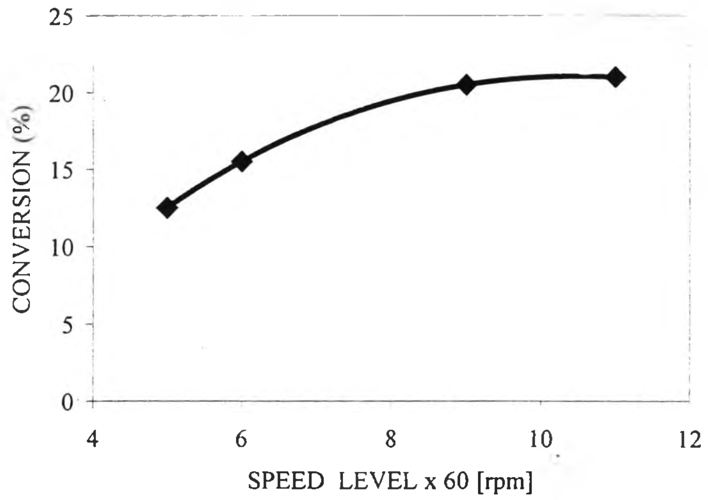


Figure 5.3 The effect of speed level on the conversion (Catalyst =Beta zeolite, catalyst weight = 5.0 g, TBA_0=0.5 mol, $EtOH_0$=0.5 mol, T=333 K and time= 8 hours)

5.2.3 Development of mathematical model

Since the operating pressure in this study was at atmospheric pressure, only small amount of IB can be dissolved in the liquid. This was also confirmed by our experimental results. Consequently, the reverse reaction in Eq. (2) and the reaction in Eq. (3) are small. Therefore, they were not considered in this study. The expressions of the rate of reactions in Eqs. (1) and (2) can be expressed as shown in Eq. (4) – (5), respectively (Yin *et al.*, 1995).

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

$$r_2 = k_2 a_{TBA} \tag{5}$$

where k_1 and k_2 are reaction rate constants, a_i is activity of species i and K is the equilibrium constant. The expression of K_1 is given as follow (Jensen and Datta, 1995).

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

The rate constant can be written by taking into account the effect of water inhibition, as

$$k_j = \frac{k_{jo}}{1 + K_W a_{H_2O}} \qquad \text{j = 1 or 2} \tag{7}$$

By performing the terial balance for the batch reactor, the following expressions are obtained.

$$-\frac{dm_{TBA}}{dt} = \frac{dm_{H_2O}}{dt} = W(k_1(a_{TBA}.a_{EtOH} - a_{ETBE}.a_{H_2O}/K_1) + k_2 a_{TBA}) \tag{8}$$

$$-\frac{dm_{EtOH}}{dt} = \frac{dm_{ETBE}}{dt} = Wk_1(a_{TBA}.a_{EtOH} - a_{ETBE}.a_{H_2O}/K_1) \tag{9}$$

Activity coefficients can be calculated using the UNIFAC method (Gmehling *et al.*, 1982).

A set of experiments was carried out at three temperature levels to investigate the reaction kinetics. The results of T = 323, 333 and 338 K are shown in Figures 5.4, 5.5 and 5.6, respectively. It can be seen that the production of ETBE becomes less with the decrease of temperature as expected in the Arrhenius's equation.

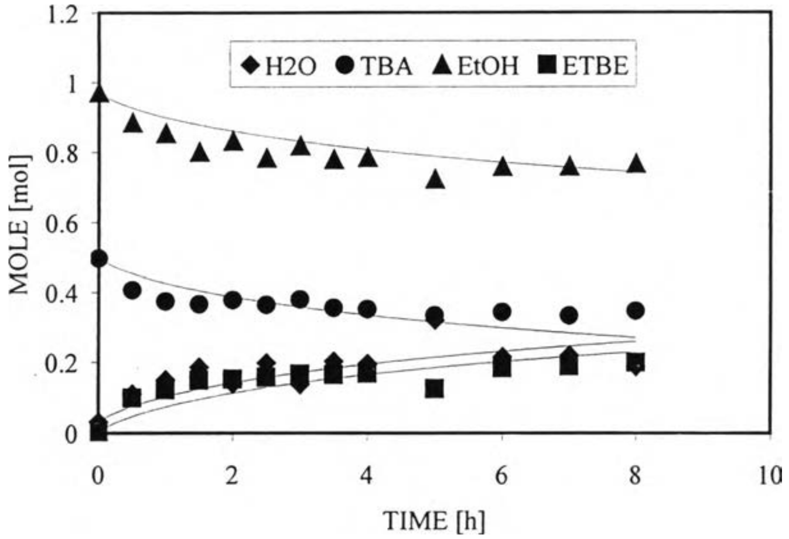


Figure 5.4 Mole changes with time (Catalyst=Beta zeolite, catalyst weight=30.0 g, TBA_o=0.97 mol, $EtOH_o$ = 0.50 mol, T = 323 K)

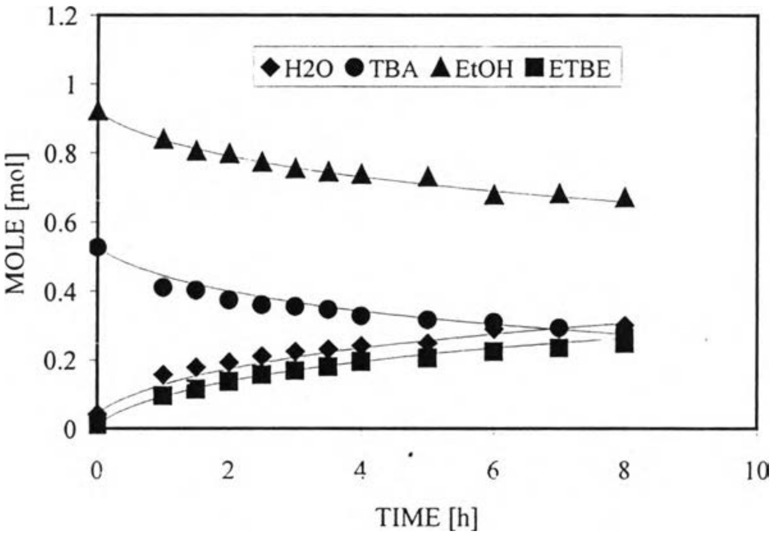


Figure 5.5 Mole changes with time (Catalyst=Beta zeolite, catalyst weight=30.0 g, TBA_o=0.92 mol, $EtOH_o$=0.52 mol, T = 333 K)

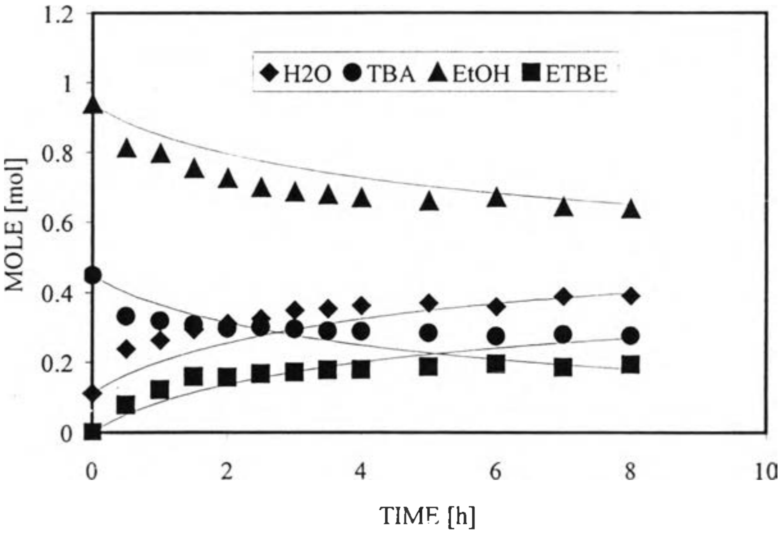


Figure 5.6 Mole changes with time (Catalyst=Beta zeolite, catalyst weight=30.0 g, TBA_o=0.92 mol, $EtOH_o$=0.52 mol, T = 338 K)

A curve fitting method was employed to find the kinetic parameters, k_{1o}, k_{2o} and K_w for the results shown in Figures 5.4, 5.5 and 5.6. However, the initial guess values of the parameters k_{1o} and k_{2o} were obtained by using the initial rate method (Fogler, 1992) in which the initial reaction rates were measured at different initial concentrations. The solid lines in the figures represent the simulation results using the corresponding parameters. Figures 5.7 and 5.8 show the Arrhenius plots of k_{1o} and k_{20} and the van't Hoff plot of K_w, respectively.

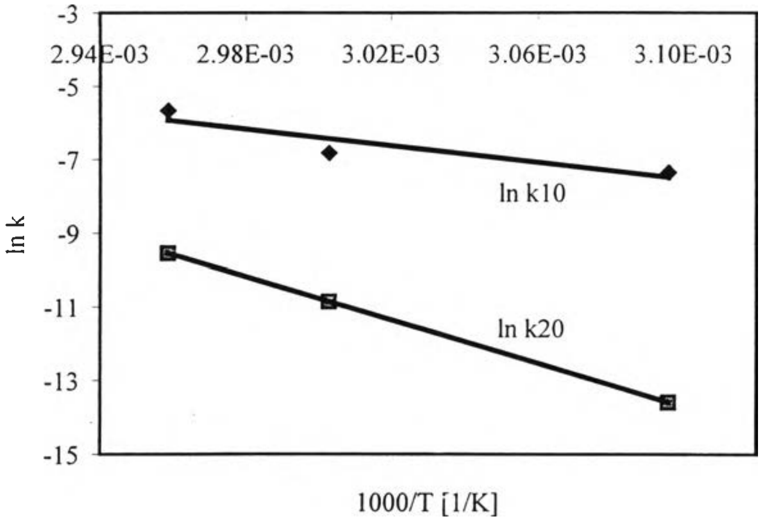


Figure 5.7 Arrhenius plot

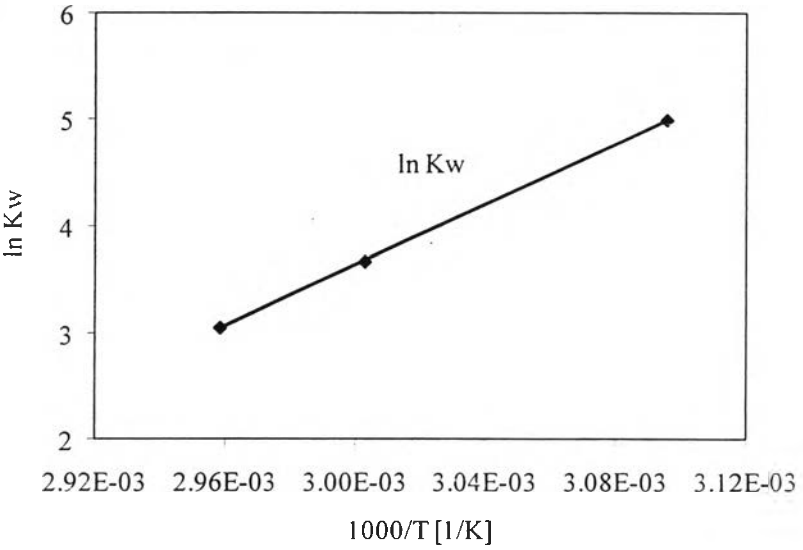


Figure 5.8 Van't Hoff plot

The following equations were determined for the plots

$$k_{1o} \quad \exp(27.297 - 11233/T) \tag{11}$$

$$k_{2o} = \exp(77.486 - 29451/T) \tag{12}$$

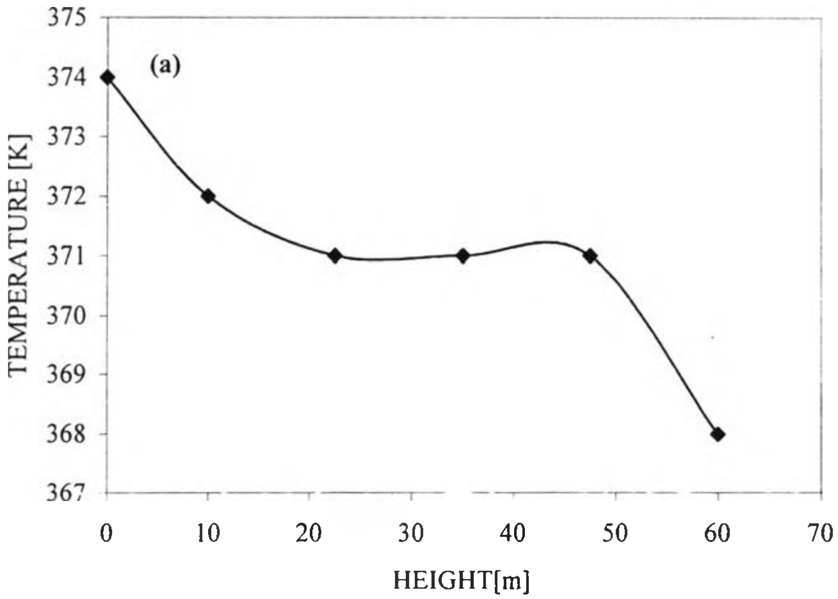
$$K_W = \exp(-38.756 + 14127/T) \tag{13}$$

where the values of the activation energy of the reactions in Eq. (1) and Eq. (2) are 93 and 244 kJ/mol, respectively.

5.3 Reactive Distillation Study

5.3.1 Standard condition

Figure 5.9 shows the performance of the reactive distillation at the standard condition; i.e. continuous operation, Beta zeolite weight=50 g, feed molar ratio TBA:EtOH:H_2O=1:1:38, feed flow rate=1 cm^3/min, heat duty=0.073 kW and reflux ratio=1. The temperature profile inside the column shown in figure 5.9(a) decreases from the bottom (374 K) to the top (368 K). However, the temperature was almost constant at 371 K in the reactive distillation zone. This behavior was indicated earlier in Chapter III. Figure 5.9(b) shows the mole fraction profiles of the distillate and bottom products represented by empty and filled symbols, respectively. It was found that the steady state can be attained after approximately 3 hours. 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 fraction of ethanol and TBA in the distillate were about 20 mol %, while water was negligible.



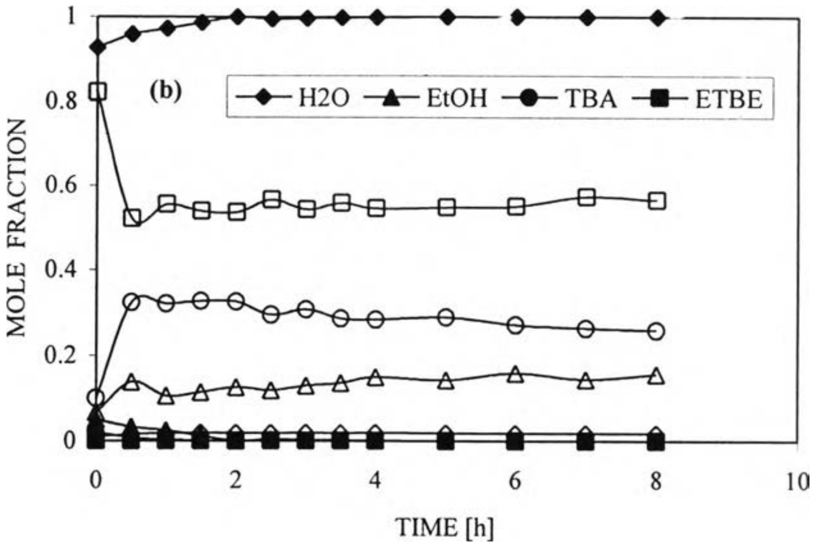


Figure 5.9 Performance of reactive distillation at the standard condition (a) The temperature profile of a reactive distillation column, (b) the concentration profile of the distillate and the residue, ○ :distillate , ● :bottom. (Catalyst=Beta zeolite, catalyst weight=50 g, molar ratio of TBA:EtOH:H2O=1:1:38, feed flow rate=1 cm^3/min, heat duty=0.073 kW, reflux ratio=1)

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

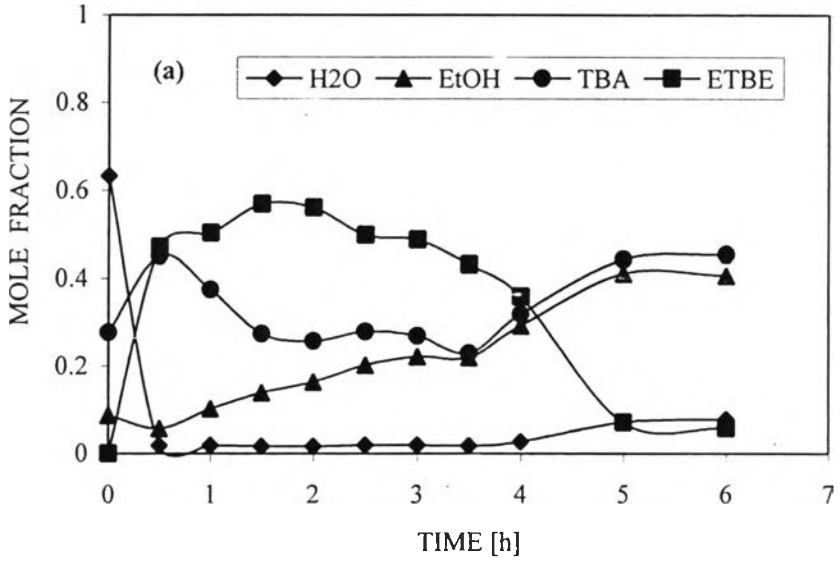
$$\text{Conversion of ethanol} = \frac{\text{Molar flow rate of EtOH reacted}}{\text{Feed molar flow rate of EtOH}} \times 100\ \%$$

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

The corresponding conversion and selectivity at the standard condition are 61 % and almost 100 %, respectively. It is noted that the high selectivity is due to use of the highly selective Beta zeolite. Previous study by Quitain *et al.* (1999) reported the selectivity of 35.9 % for the same reaction with Ambelyst-15 catalyst.

5.3.2 The 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 4.4. The mole fraction profiles of distillates are shown in Figure 5.10. It was found that the mole fraction of ETBE decreases 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 Figures 5.11 and 5.12, respectively, it was noticed that eventhough the mole fraction of ETBE was high at the lowest heat duty 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.



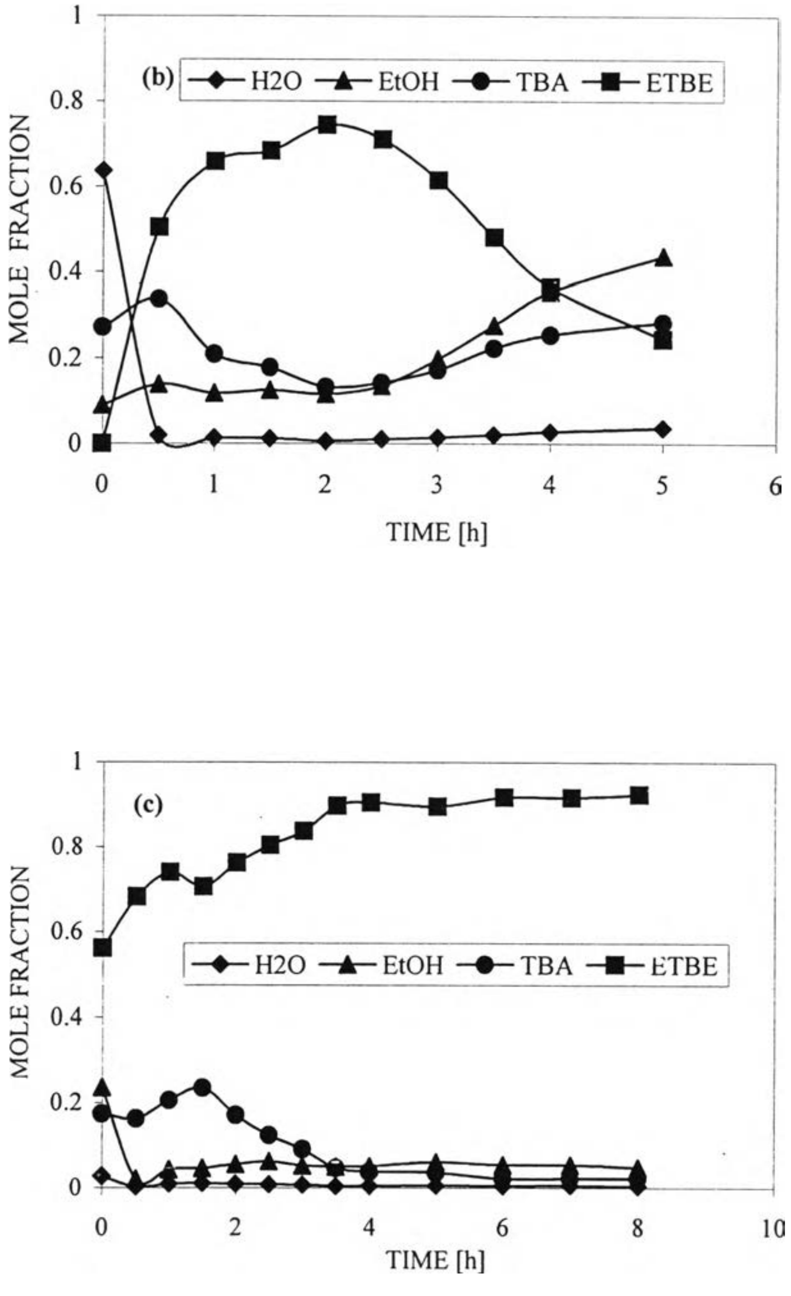


Figure 5.10 The concentration profiles of distillated for (a) heat duty=0.057 kW, (b) heat duty=0.048 kW, and (c) heat duty=0.040 kW. (Catalyst=Beta zeolite, catalyst weight=50 g, molar ratio of TBA:EtOH:H_2O=1:1:38, reflux ratio=5, feed flow rate=0 cm^3/min)

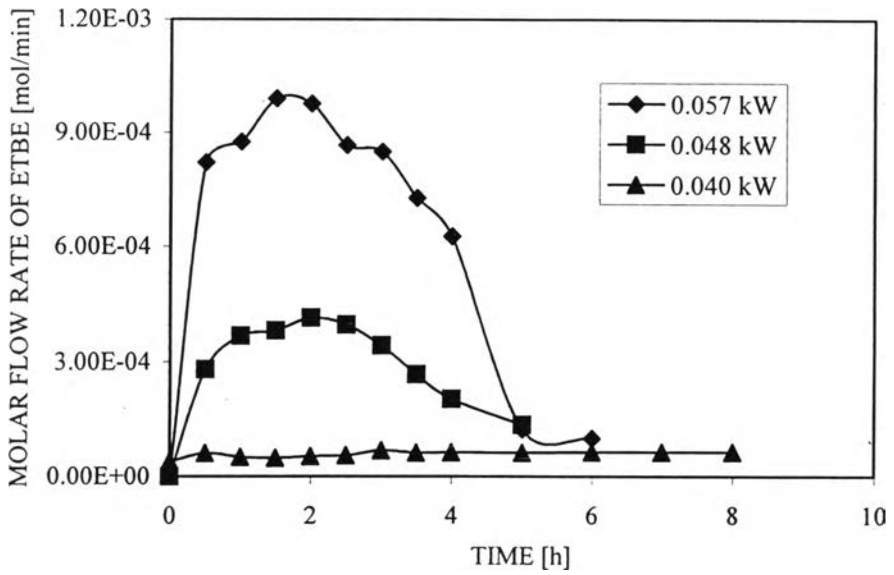


Figure 5.11 Effect of heat duty on the molar flow rate of ETBE in distillate. (Catalyst=Beta zeolite, catalyst weight=50 g, molar ratio of TBA:EtOH:H_2O=1:1:38, reflux ratio=1, feed flow rate=1 cm^3/min)

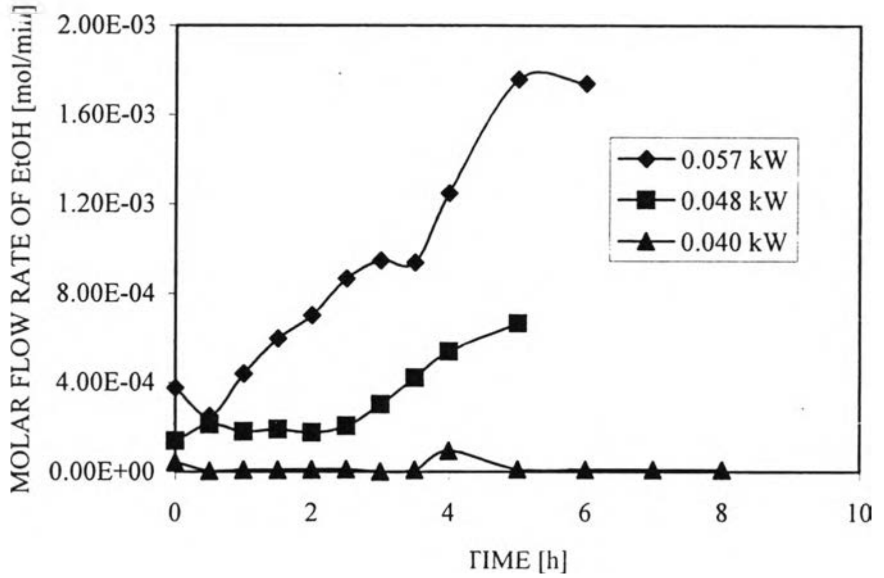


Figure 5.12 Effect of heat duty on the molar flow rate of EtOH in distillate. (Catalyst=Beta zeolite, catalyst weight=50 g, molar ratio of TBA:EtOH:H_2O=1:1:38, reflux ratio=1, feed flow rate=1 cm^3/min)

For the continuous reactive distillation, Figure 5.13 shows the effect of heat duty on conversion and yield. It was found that the yield and the conversion were very close to each other. This emphasized that Beta 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 0.25, 0.40 and 0.85 cm^3/min. 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.

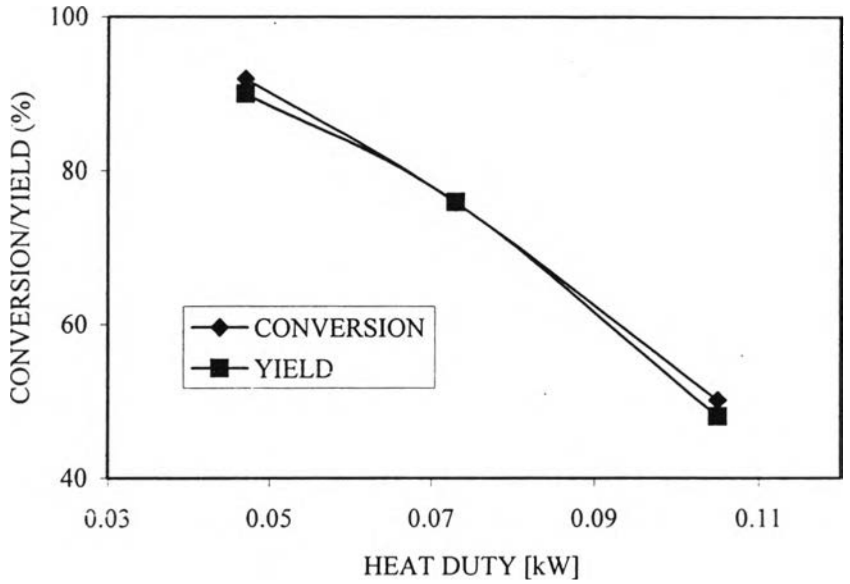


Figure 5.13 Effect of heat duty on the conversion and yield of reactive distillation. (Catalyst=Beta zeolite, catalyst weight=50 g, molar ratio of TBA:EtOH:H_2O=1:1:38, reflux ratio=1, feed flow rate=1 cm^3/min)

5.3.3 The effect of feed flow rate

Figure 5.14 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, 2 and 4 cm^3/min. It was found that the highest conversion of ethanol and the yield were obtained at the optimum feed flow rate of 2 cm^3/min. 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.

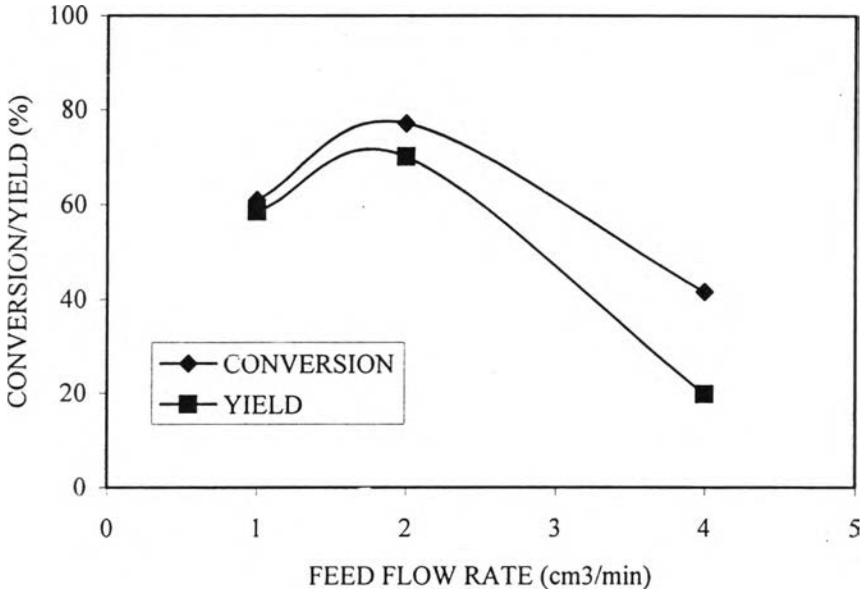


Figure 5.14 Effect of feed flow rate on the conversion and yield of reactive distillation. (Catalyst=Beta zeolite, catalyst weight=50 g, reflux ratio=1, molar ratio of TBA:EtOH:H_2O=1:1:38, heat duty=0.073 kW)

5.3.4 The effect of reflux ratio

Figure 5.15 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.

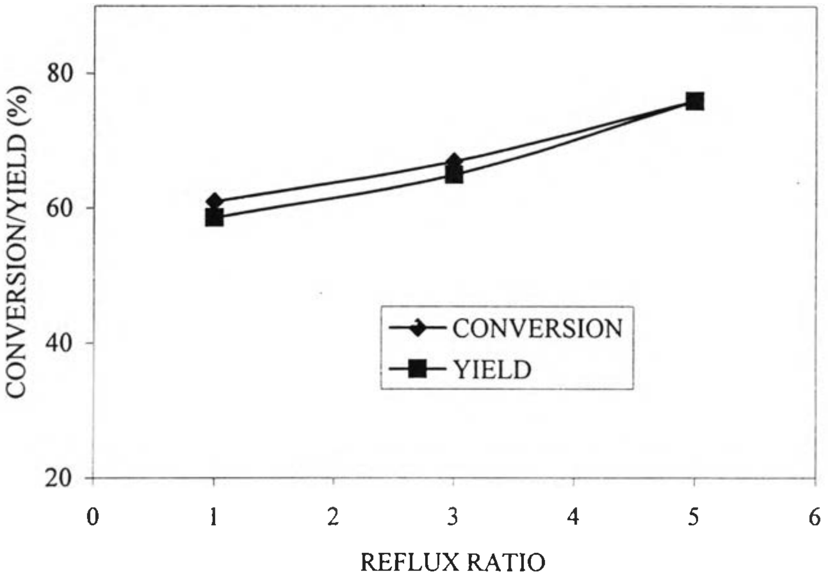


Figure 5.15 Effect of reflux ratio on the conversion and yield of reactive distillation. (Catalyst=Beta zeolite, catalyst weight=50 g, molar ratio of TBA:EtOH:H_2O=1:1:38, heat duty=0.073 kW, feed flow rate=1 cm^3/min)

5.3.5 The effect of feed molar ratio of water

Figure 5.16 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.

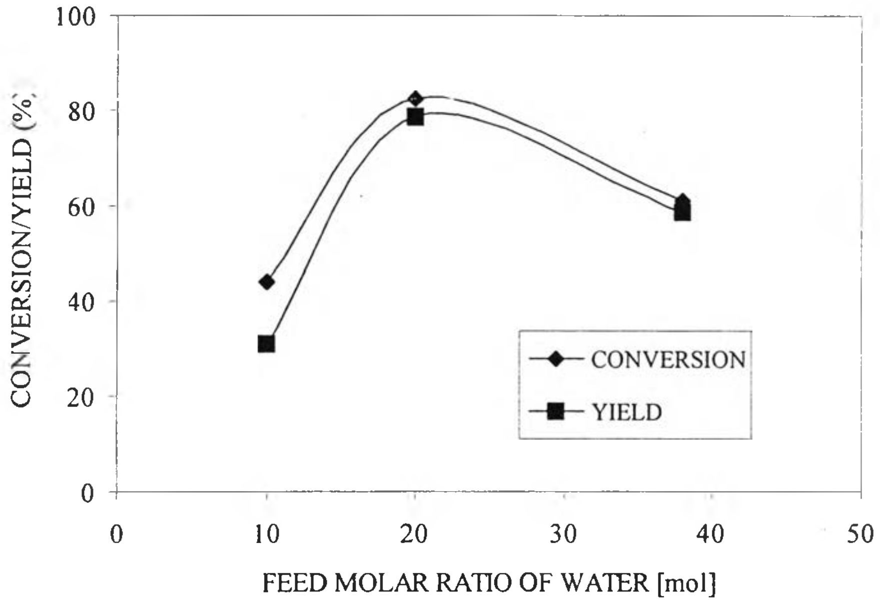


Figure 5.16 Effect of feed molar ratio of water on the conversion and yield of reactive distillation. (Catalyst =Beta zeolite, catalyst weight=50 g, heat duty=0.073 kW, reflux ratio=1, feed flow rate=1 cm^3/min)