

CHAPTER IV

EXPERIMENTAL

This chapter describes the experimental procedures for the synthesis of ethyl *tert*-butyl ether from ethanol and *tert*-butyl alcohol in both batch reactor and the reactive distillation. Details are given for the catalyst and packing material preparation, kinetic study and reactive distillation study as follows.

4.1 Catalyst and packing material preparation

4.1.1 Preparation of Beta zeolite powder

The reagents used for the synthesis of Beta zeolite is shown in Table 4.1. The preparation processes consists of the following steps.

Table 4.1 Reagents used for the preparation of Na-Beta zeolite

Items	Weight x 10 ⁻³ (kg)
TEAOH	6.2
Cataloid for Si/Al = 50	6.7
KCl	0.5
NaOH	0.5
NaAlO ₂	0.7
NaCl	0.4

4.1.1.1 Gel preparation

Tetraethylammonium hydroxide (40% by weight aqueous solution) was mixed with sodium hydroxide and stirred until it became a homogeneous solution. The mixed solution was added with sodium aluminate (Al/NaOH about 0.81), potassium

chloride and sodium chloride. Then it was stirred to obtain a clear solution at the room temperature. Cataloid (SiO_2 30% by weight aqueous solution) was added dropwisely to the mixed solution. A vigorous stirrer was applied for one hour to obtain a gel.

4.1.1.2 Crystallization

The obtained gel was stirred thoroughly before transferring it to a stainless-steel autoclave. The gel was heated in the autoclave from the room temperature to 408 K in 1 hour under the nitrogen pressure of 3 kg/cm^2 (gauge) and maintained at this temperature for 40 hours. Then, the autoclave was immersed in cold water to start a crystallization process. The obtained solid material was centrifuged at 2,500 rpm (about 15 min.) and the recovered solid were washed and dried in an oven at 383 K overnight.

4.1.1.3 First calcination

The dry solid was calcined in an air stream at 913 K for 3.5 hours by heating it from the room temperature to 913 K in 1 hour. This step was to burn off the organic template and leave the cavities and channels in the crystals. Then, the calcined crystals were cooled to the room temperature in a desiccator. After this step, the crystals formed were called Na-Beta zeolite.

4.1.1.4 Ammonium ion-exchange

The ion-exchange step was carried out by mixing the calcined crystal with 2 M NH_4NO_3 (ratio of catalyst and solution is $1\text{g}:30 \text{ cm}^3$) and heated on a stirring hot plate at 353 K for 1 hour. The mixture was cooled down to the room temperature. Then, the ion-exchange crystal was washed twice with de-ionized water by using centrifugal separator. After that, the ion-exchange crystal was dried at 383 K for at least 3 hours in the oven. The dried crystals (NH_4 -Beta zeolite) were obtained.

4.1.1.5 Second calcination

The removable species, i.e. NH_3 and NO_x were decomposed by thermal treatment of the ion-exchange crystals in a furnace by heating them from the room temperature to 773 K in 1 hour in air stream and maintained at this temperature for 2 hours. After this step, the obtained crystals were H-Beta zeolite which was used for kinetic study.

4.1.2 Preparation of supported Beta zeolite

Supported Beta zeolite was used in reactive distillation studies. The catalyst was made by coating the obtained powder catalyst on a cordierite monolith obtained from N-COR Ltd., Nagoya, JAPAN. The procedures are as follows:

4.1.2.1 Preparation of monolith sample

The monolith test samples were prepared by cutting the cordierite monolith (400 cell/in²) into small cube support (0.5x0.5x0.5 cm³).

4.1.2.2 Surface treatment

The monolith supports were weighted and soaked in 2.5 wt % 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.

4.1.2.3 Preparation of slurry for washcoat

Beta zeolite powder was added into 2.5 wt % acetic acid solution to give 30-50 % wt/volume Beta zeolite washcoat and the obtained slurry was stirred for 5-10 min.

4.1.2.4 Monolith coating procedure

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 hours in air atmosphere.

4.1.3 Preparation of packing material

Stainless-steel sieves (30 mesh) with $0.7 \times 0.7 \text{ cm}^2$ size 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.

4.1.4 Characterization of the catalysts

4.1.4.1 X-ray diffraction patterns

X-ray diffraction (XRD) patterns of the catalysts were performed with SIEMENS XRD D5000, accurately measured in the $4\text{-}44^\circ$ 2θ angular region, at petrochemical Engineering Laboratory, Chulalongkorn University.

4.2 Kinetic study

4.2.1 Batch reactor apparatus

Kinetic study was carried out using a batch reactor. A 250 cm^3 three connected flask was used as the reactor. The middle connector was connected with a condenser using ice as a coolant to trap vapor from the reactor. The other connectors were connected with a thermometer and a liquid sampling syringe. The experimental set-up for the kinetic study are shown in Figure 4.1

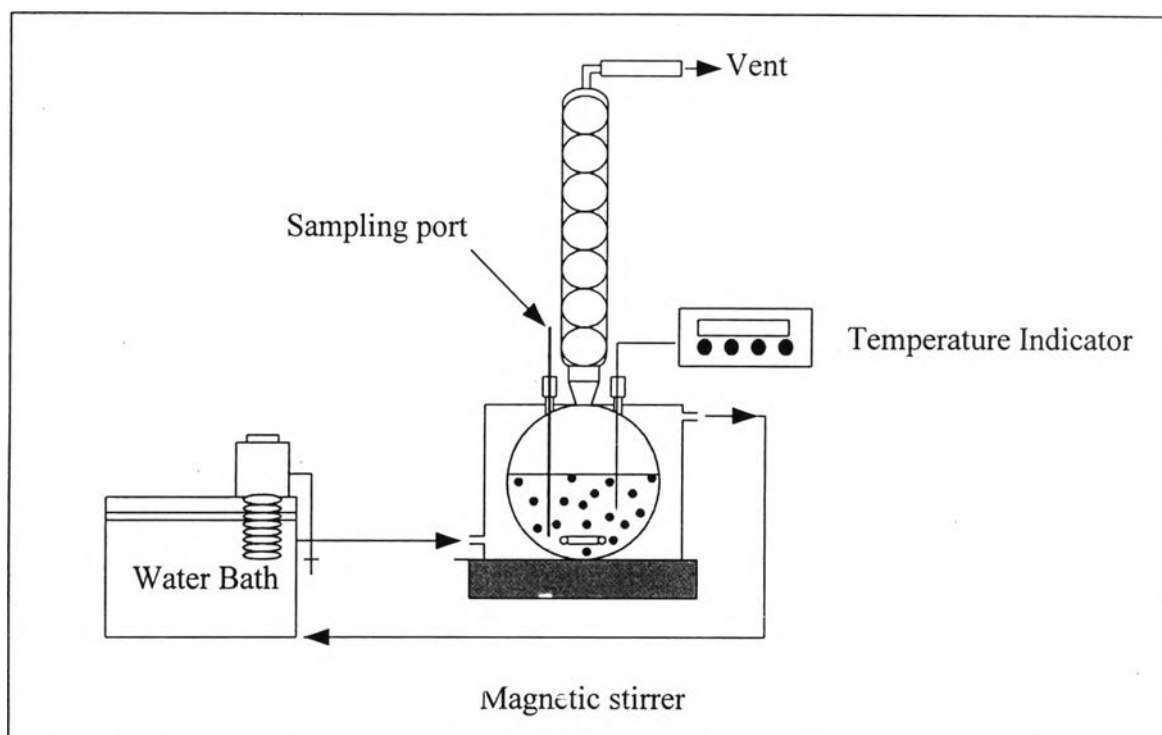


Figure 4.1 Schematic diagram of the kinetic studies experimental set-up

4.2.2 Experimental procedure

1. 30 grams of catalyst was weighted and left in the oven at 363 K overnight to remove moisture from the catalyst.
2. 0.5 mole of ethanol was mixed with TBA and placed into the 250 cm³ of three connected flask. Then, the mixture was stirred and heated up to desire temperature that shown in Table 4.2.
3. The reaction was started by adding a catalyst into the reaction mixture. Beta zeolite and the commercial Amberlyst-15 were used as catalysts in this study.
4. Liquid samples of 1 cm³ were at different reaction times; i.e. 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, 6, 7, 8 hours. They were analyzed by a gas chromatography. The operation condition of the gas chromatography was shown in Table 4.3.

Table 4.2 Operating condition for kinetic study

Catalyst weight	30 g
Reaction temperature	323, 333, 383 K
Atmospheric pressure	
Reaction time	0-8 hours
Mole of Ethanol	0.5 mole
Mole of TBA	0.5, 0.75, 1.0 mole
Speed Level of magnetic stirrer	300, 360, 450, 660 rpm

Table 4.3 Operating condition of gas chromatography

Model	GC 8A
Detector	TCD
Packed column	Gaskuropack 54
Column length	2.5 m
Mesh size of packing	60/80
Helium flow rate	30 cm ³ /min
Column temperature	443 K
Injector temperature	453 K
Detector temperature	443 K

4.3 Reactive distillation study

4.3.1 Reactive distillation apparatus

Figure 4.2 shows the schematic diagram of the reactive distillation experimental set-up. The height and diameter of the column are 70 cm and 3.5 cm, respectively. The upper section of the column was filled with $0.7 \times 0.7 \text{ cm}^2$ saddle of stainless-steel pieces. The middle section of the column was filled with the catalyst bed of $0.5 \times 0.5 \times 0.5 \text{ cm}^3$ supported Beta zeolite. Like the upper section, the lower section of the column was packed with $0.7 \times 0.7 \text{ cm}^2$ saddle of stainless-steel pieces. The heights of the sections were 10, 50, 10 cm, respectively. The temperature profile in the reactive distillation column was determined by using thermocouple 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 420 cm^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 measured 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 which took around 3 hours. Top and bottom products were sampled and their flowrate was measured every 30 min. 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.

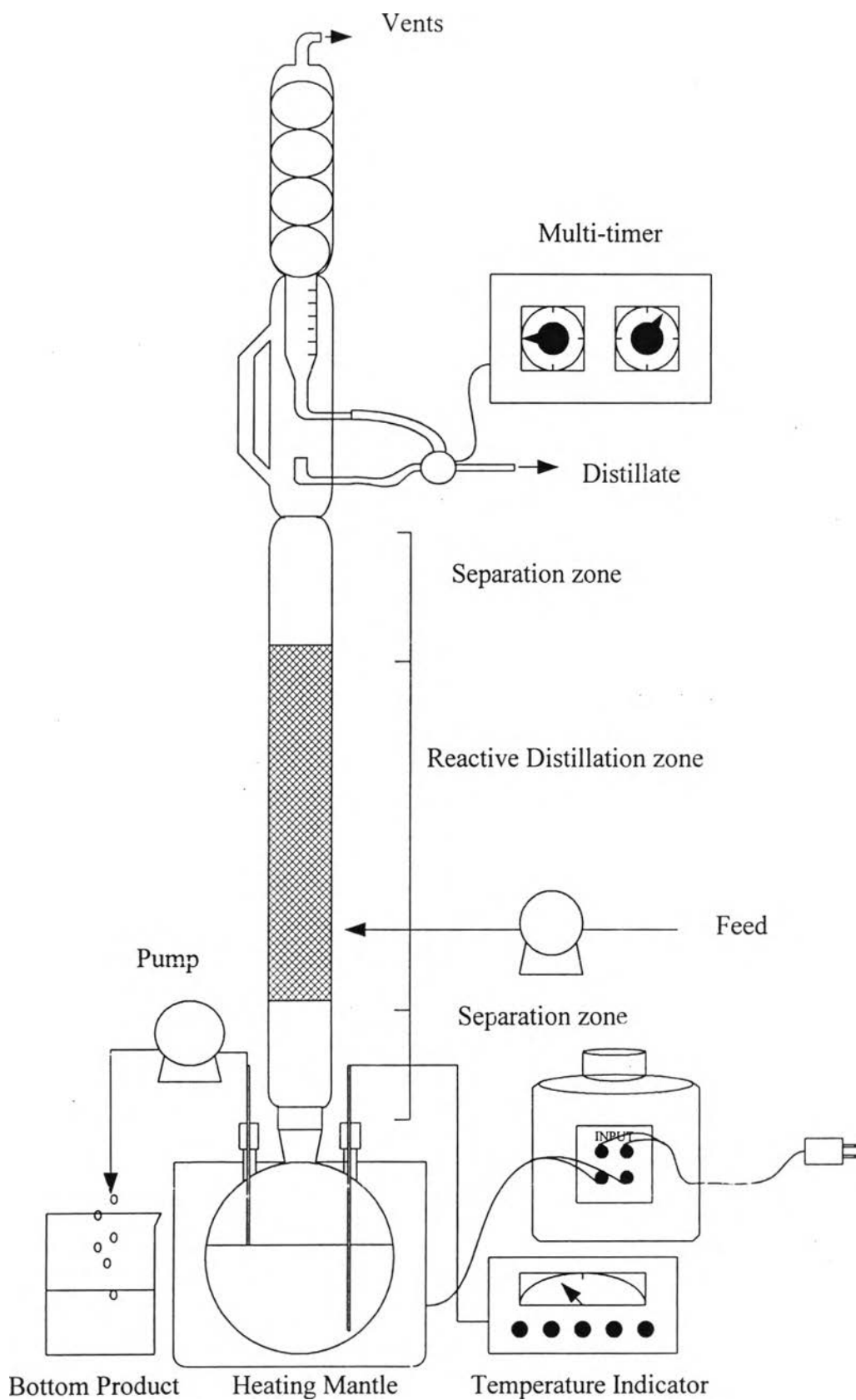


Figure 4.2 Schematic diagram of reactive distillation experimental system

4.3.2 Experimental conditions for the reactive distillation study

Table 4.4 shows lists of the experimental conditions for thirteen runs. Both top and bottom products were taken to measure the concentration of water, EtOH, TBA and ETBE at different reaction times and they were analyzed by Gas Chromatography.

Table 4.4 Lists of the experimental setting

No.	Heat duty (kW)	Feed			Operation
		Flow rate (ml/min)	TBA:EtOH:H ₂ O	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	1:1:38	1	Continuous
6	0.073	1	1:1:38	1	Continuous
7	0.105	1	1:1:38	1	Continuous
8	0.073	2	1:1:38	1	Continuous
9	0.073	4	1:1:38	1	Continuous
10	0.073	1	1:1:38	3	Continuous
11	0.073	1	1:1:38	5	Continuous
12	0.073	1	1:1:20	1	Continuous
13	0.073	1	1:1:10	1	Continuous