

# CHAPTER III

## EXPERIMENTS

### 3.1 Instruments and Apparatus

#### Ovens and Furnaces

During the synthesis course, the starting mixture was heated in a Memmert UM-500 oven. Heating of any solid sample at 100°C was carried out using the same oven. Calcination of the solid catalysts at 550°C was achieved in a Carbolite RHF 1600 muffle furnace with programmable heating rate of 1°C/min.

#### X-ray Powder Diffractometer (XRD)

The structure of synthesized Si-SBA-15 and zeolite beta were identified by using a Rigaku, Dmax 2200/ultima plus X-ray powder diffractometer with a monochromator and Cu K<sub>α</sub> radiation (40 kv, 30 mA). The 2-theta angle was ranged from 0.5 to 3.0 degree for analyzed SBA-15 phase and 3.0 to 45 degree for zeolite beta phase with scan speed of 5 degree/min and scan step of 0.02 degree. The scattering slit, divergent slit and receiving slit were fixed at 0.5 degree, 0.5 degree, and 0.15 mm for Si-SBA-15 and the scattering slit, divergent slit and receiving slit were fixed at 0.5 degree, 0.5 degree, and 0.3 mm for zeolite beta, respectively.

#### NMR Spectrometer

Solid state <sup>27</sup>Al-MAS-NMR spectra were performed using the Bruker Advance DPX 300 MHz NMR spectrometer

#### Scanning Electron Microscope (SEM)

JEOL JSM-6480L V scanning electron microscope was used to examine the morphology and particle size of Si-SBA-15 and zeolite beta. In order to avoid charging of samples and obtain good quality of micrographs, the catalysts were dispersed in absolute ethanol in ultrasonic water bath before gradually evaporated on glass slide and coated with sputtering gold under vacuum prior to the SEM measurements.

### **Nitrogen Adsorptometer**

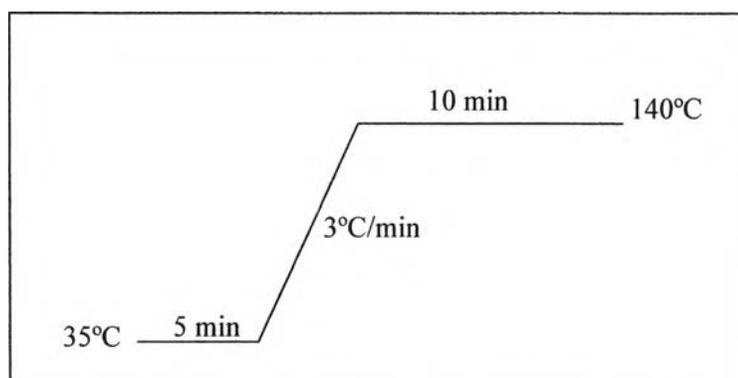
Characterization of catalyst porosity in terms of nitrogen adsorption-desorption isotherms, BET specific surface area, and pore size distribution of the catalysts was carried out using a BEL Japan, BELSORP-II instrument. The sample near 40 mg was pretreatment at 400°C 3 h under vacuum and weighed for the accurate amount before each measurement. Surface areas and micropore volume of catalysts were calculated by using the BET equation. The external surface areas were obtained from the analysis of adsorption branch of the isotherm by the t-plot method.

### **NH<sub>3</sub> TPD Instument**

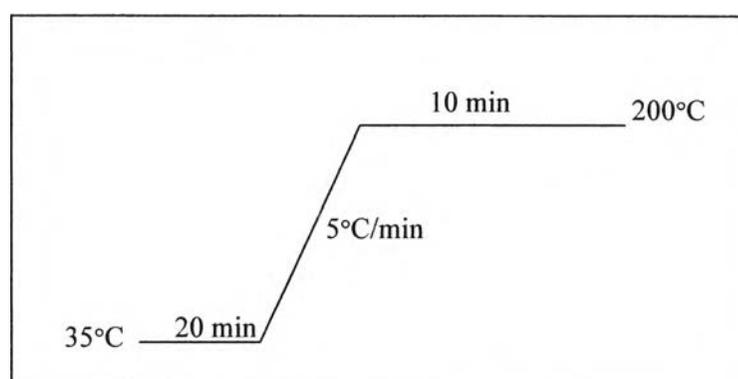
Acid strength of catalysts was determined using the BEL Japan, BELCAT. Before adsorption, the sample weight about 100 mg was dried in flowing He at 400°C for 20 min. Adsorption go pure NH<sub>3</sub> until saturation took place at 100°C until saturated, then the catalyst was flush with He at the same temperature. TPD measurements were done from 100°C to 600°C, with He as the carrier gas. The amount of desorption ammonia was detected by a thermal conductive detector. The TPD thermogram (derivative plot) was obtained from the plot of the amount of ammonia desorption as a function of temperature.

### **Gas Chromatograph**

Hydrocarbon gases from cracking reaction were analyzed by using a Varian CP-3800 gas chromatograph equipped with a 50 m length x 0.53 mm outer diameter Alumina-KCl PLOT column. Liquid products from cracking the same instrument but equipped with a 30 m length x 0.25 mm outer diameter CP-sil 5 (0.25 µm film thickness) column (equivalent to DB-1 column). All GC detectors are flame ionization detectors (FID). The column heating programs for gas and liquid analysis are shown in Schemes 3.1 and 3.2, respectively. The sample volumes are 3.00 µl of gas and 1.00 µl of liquid injection.



**Scheme 3.1** The GC heating program for gas analysis.



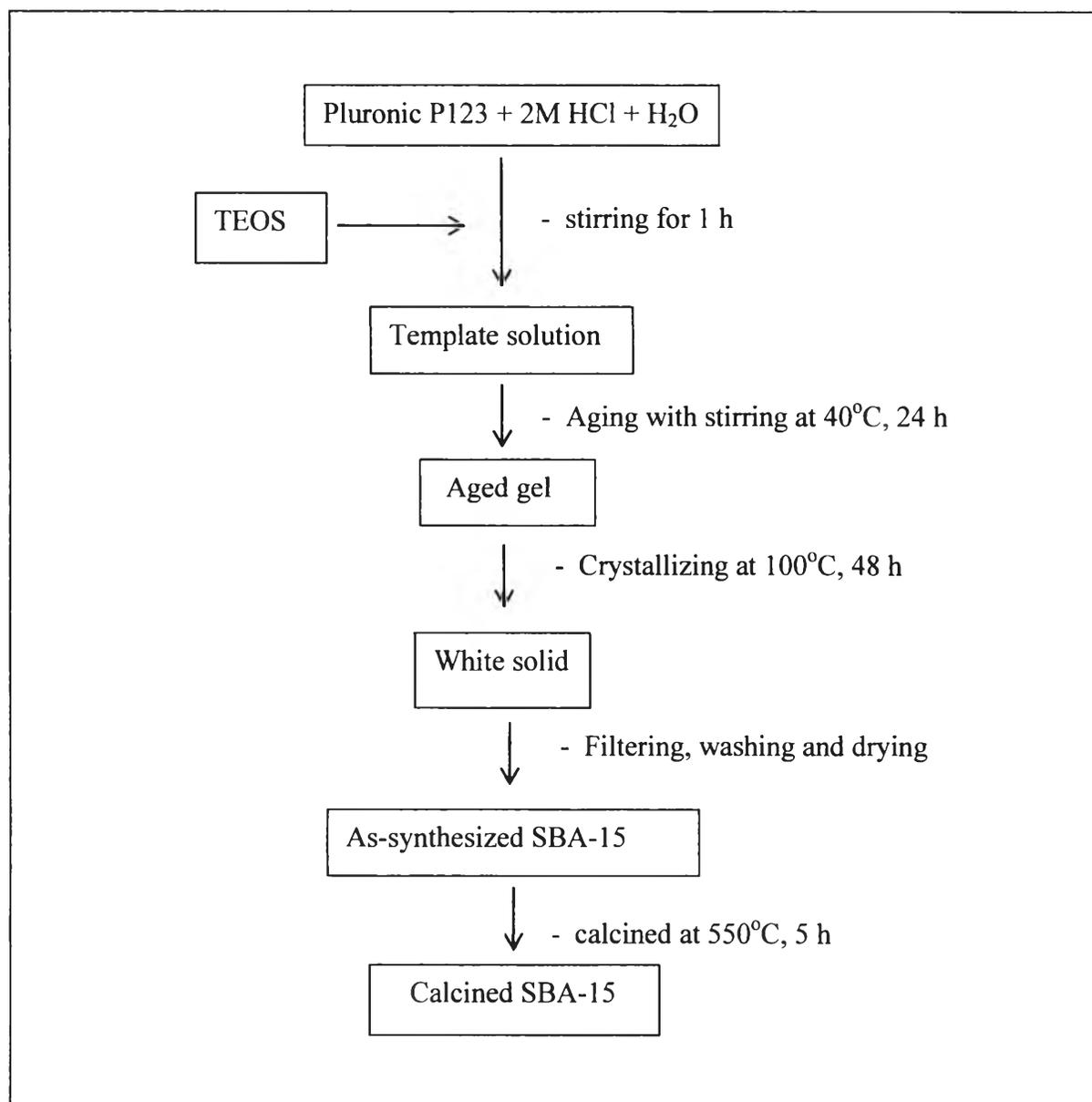
**Scheme 3.2** The GC heating program for liquid analysis.

### 3.2 Chemicals and Gases

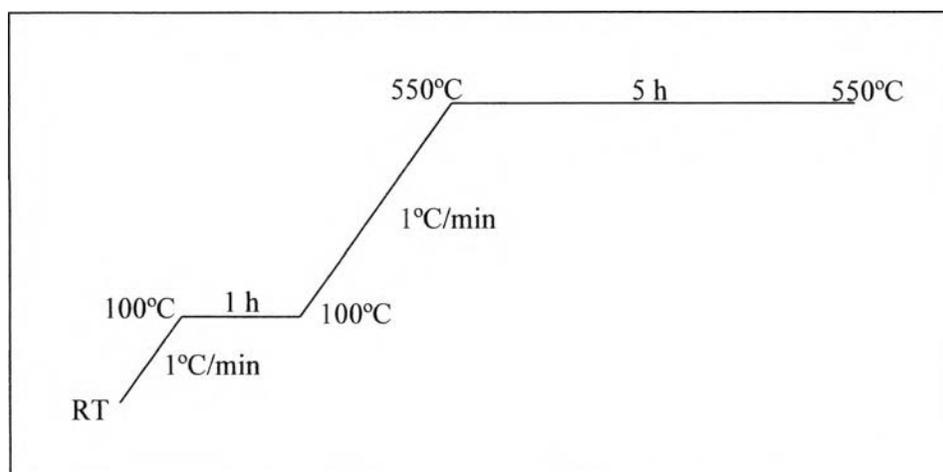
1. Tetraethylammonium hydroxide, TEAOH (Fluka, 40 wt%)
2. Tetraethylorthosilicate, TEOS (Aldrich, 98 wt%)
3. Aluminium isopropoxide, AIP (Aldrich)
4. Hydrochloric acid, HCl (Fluka, 37 wt%)
5. Triblock copolymer Pluronic P123 ,PEO<sub>20</sub>-PPO<sub>70</sub>-PEO<sub>20</sub>, average molecular weight = 5800 (Aldrich.)
6. Standard gas mixture and liquid mixture for GC analysis were kindly obtained from PTT Chemical Public Company Limited.
7. Standard liquid mixture (Restek)
8. Nitrogen gas, N<sub>2</sub> (Thai Industrial Gases (TIG), highly pure grade )
9. Ammonia gas, NH<sub>3</sub> (Linde Gas Thailand, highly pure grade)

### 3.3 Preparation of SBA-15

Pure silica SBA-15 to be used as a silica source in the synthesis of zeolite beta, was prepared in an acidic media using a triblock copolymer Pluronic P123 as a structure directing agent following a method in literature reported by Zhao et al. [84]. The template Pluronic P123 was dissolved in water and acidified with 2 M HCl. Then TEOS was added and the solution was stirred for 1 h and then aged at 40°C for 24 h. The solution was transferred into a Teflon-lined autoclave and heated in an oven preset at 100°C for 48 h. As-synthesized SBA-15 was separated as a white solid by filtration, washed several times with deionized and dried by air suction through the solid. The structure directing agent was removed from the pores of SBA-15 by calcination in a muffle furnace at 550°C for 5 h. The white powder material was obtained and characterized by using XRD, SEM and nitrogen adsorption-desorption instruments. The procedure for preparing the SBA-15 is shown in Scheme 3.3. The heating program for template removal is shown in Scheme 3.4. The calcined sample was kept in desiccators prior to use.



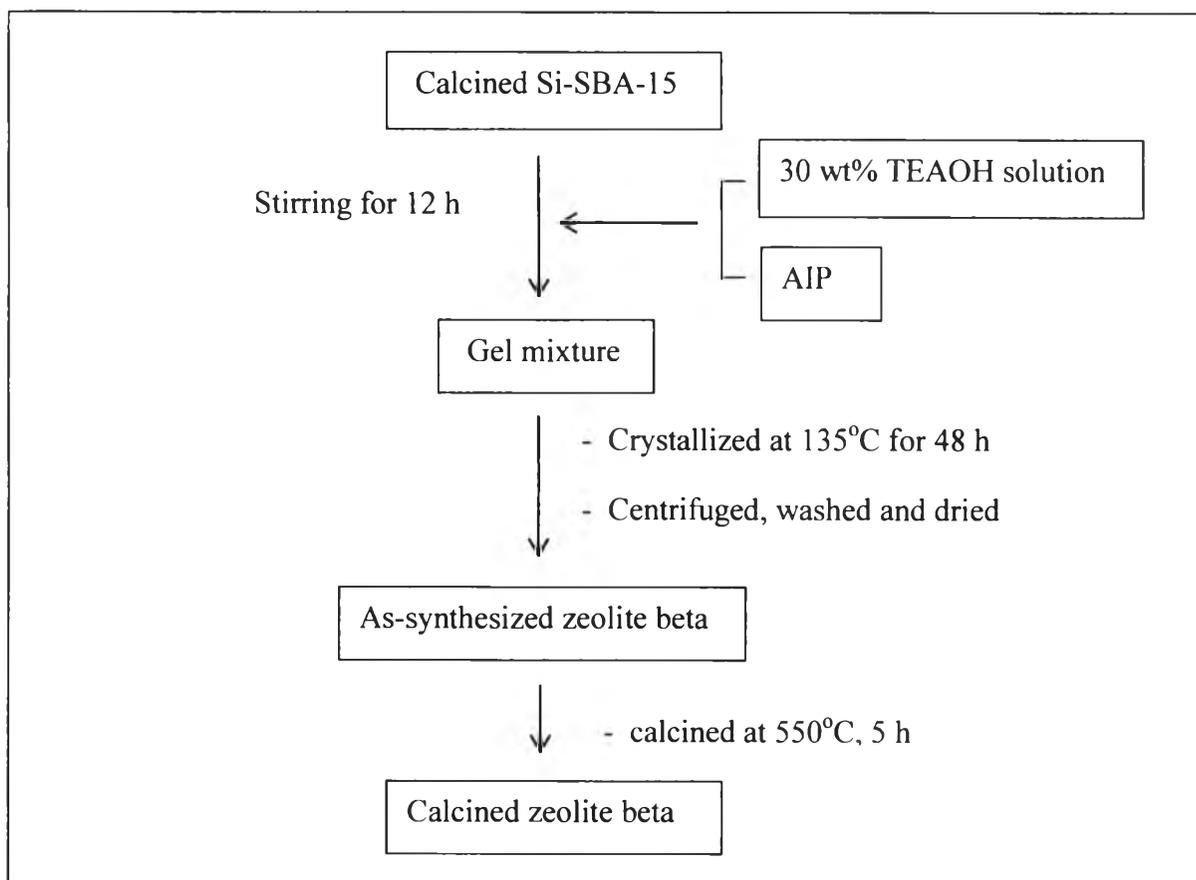
**Scheme 3.3** Systemization diagram for SBA-15



**Scheme 3.4** A heating program for removal of organic template from the pores of SBA-15

### 3.4 Transformation of SBA-15 into Zeolite Beta

Transformation of SBA-15 into BEA structure was performed typically as follows: The molar composition of reaction mixture was:  $\text{SiO}_2$ :  $x\text{Al}_2\text{O}_3$ :  $y\text{TEAOH}$ :  $5.0\text{H}_2\text{O}$  when ( $x = 0.0055$ - $0.049$ ) and ( $y = 0.10$ - $0.39$ ). The mixture of 0.7376 g of AIP and 41.88 g of 30 wt% aqueous TEAOH solution was drop wise added to a  $500\text{ cm}^3$  4-necked round bottom flask containing the 13.00 g of calcined SBA-15 with stirring under nitrogen atmosphere. Then the mixture was aged by stirring under nitrogen atmosphere for 12 h. The gel mixture was transfer into a stainless-steel autoclave containing Teflon cup and kept in the oven at  $135^\circ\text{C}$  for 6-48 h. After that the autoclave was quenched, white solid sample was separated by centrifugation, washed several times with deionized water and dried in the oven at  $110^\circ\text{C}$  overnight. The white solid product was characterized by XRD. The schematic diagram of this whole procedure is shown in Scheme 3.5. The solid samples were denoted as Run No. The conditions of synthesis are showed in Table 3.1.



**Scheme 3.5** Diagram of the synthesis procedure of zeolite beta

**Table 3.1** The condition of zeolite beta synthesis

Sample	Silica source	TEAOH/SiO <sub>2</sub> ratio	SBA-15/AIP ratio in gel	Crystallization period (h)
Run No.1	SBA-15	0.39	60	6
Run No.2	SBA-15	0.39	60	12
Run No.3	SBA-15	0.39	60	24
Run No.4	SBA-15	0.39	60	48
Run No.5	SBA-15	0.26	60	48
Run No.6	SBA-15	0.20	60	48
Run No.7	SBA-15	0.10	60	48
Run No.8	SBA-15	0.26	10	48
Run No.9	SBA-15	0.26	30	48
Run No.10	SBA-15	0.26	90	48
Run No.11	xerogel	0.26	60	48

### 3.5 Preparation of Zeolite Beta with Various Crystallization Time

Zeolite beta with SBA-15/AIP ratios in gel of 60 and TEAOH/SiO<sub>2</sub> ratio of 0.39 was synthesized using the similar method to that described in Section 3.4 with various crystallization periods of 6, 12, 24 and 48 h. All samples were characterized by XRD, XRF, SEM and nitrogen adsorption-desorption instruments.

### 3.6 Preparation of Zeolite Beta with Various TEAOH/SiO<sub>2</sub> Ratios

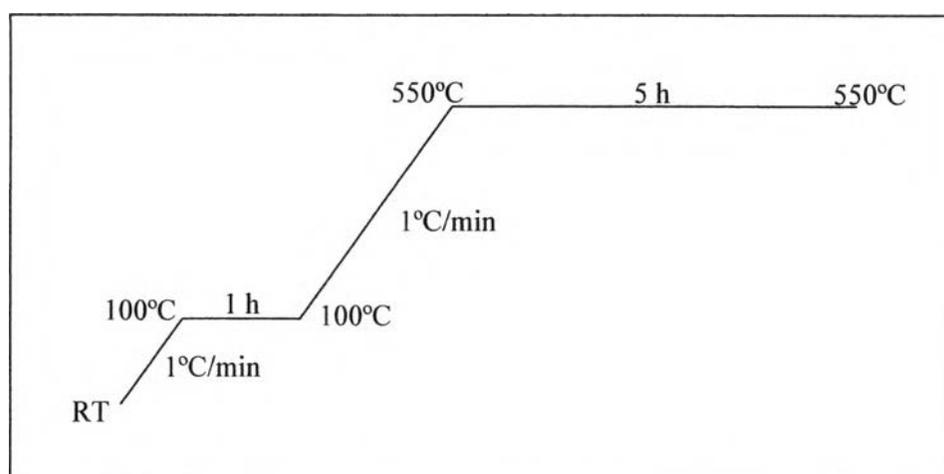
Zeolite beta samples with SBA-15/AIP ratio in gel of 60 were synthesized with various TEAOH/SiO<sub>2</sub> ratios in gel of 0.10, 0.20, 0.26 and 0.39, using crystallization time of 48 h. The zeolite beta was synthesized using the similar method to that described in section 3.4 and 3.5. The code of each sample was used as indicated in Table 3.1. All samples were characterized using XRD, SEM and nitrogen adsorption-desorption instruments.

### 3.7 Preparation of Zeolite Beta with Various SBA-15/AIP Ratios

Zeolite beta was synthesized with various SBA-15/AIP ratios in gel of 10, 30, 60 and 90, fixed TEAOH/SiO<sub>2</sub> ratio of 0.26 and crystallization time of 48. The zeolite beta was synthesized using the similar method to that described in Section 3.4, 3.5 and 3.6. Different conditions of synthesis were used as shown in Table 3.1. All catalysts were characterized using XRD, ICP-AES, SEM, <sup>27</sup>Al-MAS-NMR, NH<sub>3</sub>-TPD, and nitrogen adsorption-desorption instruments.

### 3.8 Removal of Organic Template from the Zeolite Beta Catalysts

To make room in the catalyst structure, the organic template must be removed by oxidation to carbon dioxide at elevated temperature depending on the catalyst. An as-synthesized zeolite beta was calcined in a muffle furnace using the heating program for the template removal as shown in Scheme 3.6. The calcined sample was characterized using XRD, SEM, <sup>27</sup>Al-MAS-NMR, NH<sub>3</sub>-TPD and nitrogen adsorption-desorption instruments. All samples were kept in a desiccator prior to use.



**Scheme 3.6** A heating program for removal of organic template from the pore of zeolite beta.

### 3.9 Activities of Various Zeolite Beta Catalysts in Plastic Waste Cracking

#### 3.9.1 General Procedure in Catalytic Cracking of Plastic

Degradation of plastic waste (PP or HDPE) was performed using zeolite beta catalysts. All catalysts were freshly calcined at 550°C for 5 h before test activity. Thermal and catalytic cracking activities were carried out in glass reactor (4.4 cm. *i.d.* and 37 cm. length) under a continuous nitrogen flow by batch operation as shown in Figure 3.1 and Scheme 3.7. A total of 5.0 g of waste plastic and 0.5 g of catalyst were loaded into the reactor. In a typical run, the reactor was set up, and purged with N<sub>2</sub> at flow rate of 20 ml/min to remove the air. The reactor was heated to a required temperature (350°C or 420°C) in 20 min (20°C/min) using a split-tube furnace equipped with a programmable temperature controller and a K-type thermocouple. The temperature was maintained constant at the reaction temperature for 40 min. The gas fraction which flowed from the reactor with the nitrogen stream was passed through a condenser cooled by cold water. The gas fraction was collected into a Tedlar bag since the start of heating while the liquid fraction was condensed and collected in a 10 cm<sup>3</sup> graduated cylinder. After completion of the reaction, the reactor was cooled down to room temperature and weighed. The values of %conversion and % yield were calculated based on the equations as follows:

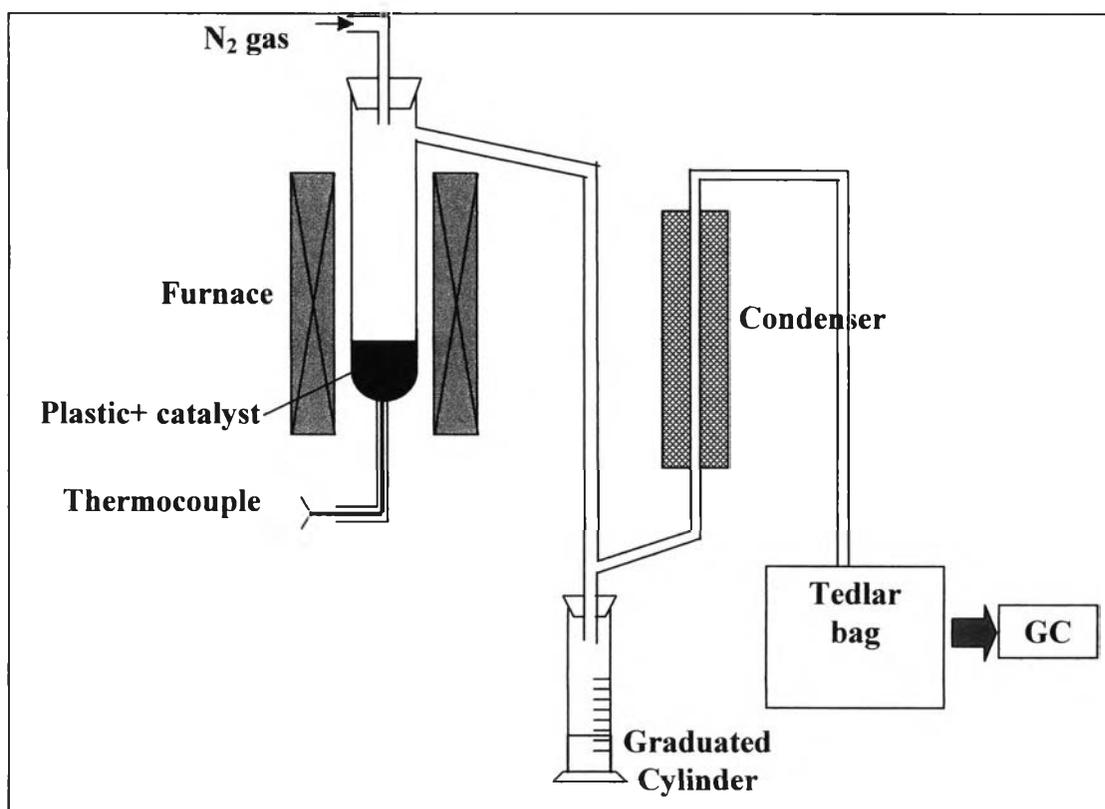
$$\% \text{ Conversion} = \frac{(\text{mass of liquid fraction} + \text{mass of gas fraction}) \times 100}{\text{mass of plastic}}$$

mass of gas fraction = mass of the reactor with plastic and catalyst before reaction –  
mass of the reactor with residue and used catalyst after reaction

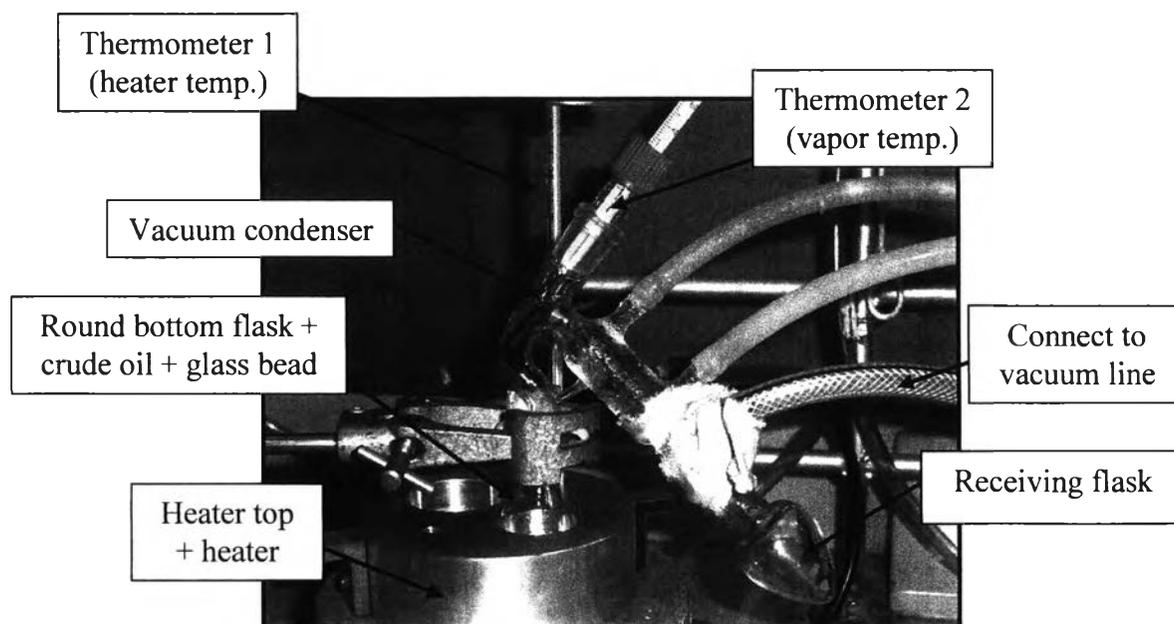
$$\% \text{ Yield} = \frac{\text{mass of product fraction} \times 100}{\text{mass of plastic}}$$

The degradation products were divided into three fractions: gas fraction (products which were not condensed at water cooling temperature), liquid fraction and residue. The gas products were analyzed by a gas chromatography. Liquid fraction obtained from the reaction was separated into two fractions, distillate oil and heavy oil, by vacuum distillation using small distillation kit at the heater temperature of 200°C as shown in Figure 3.2. The distillate oil was analyzed by a GC. The values of

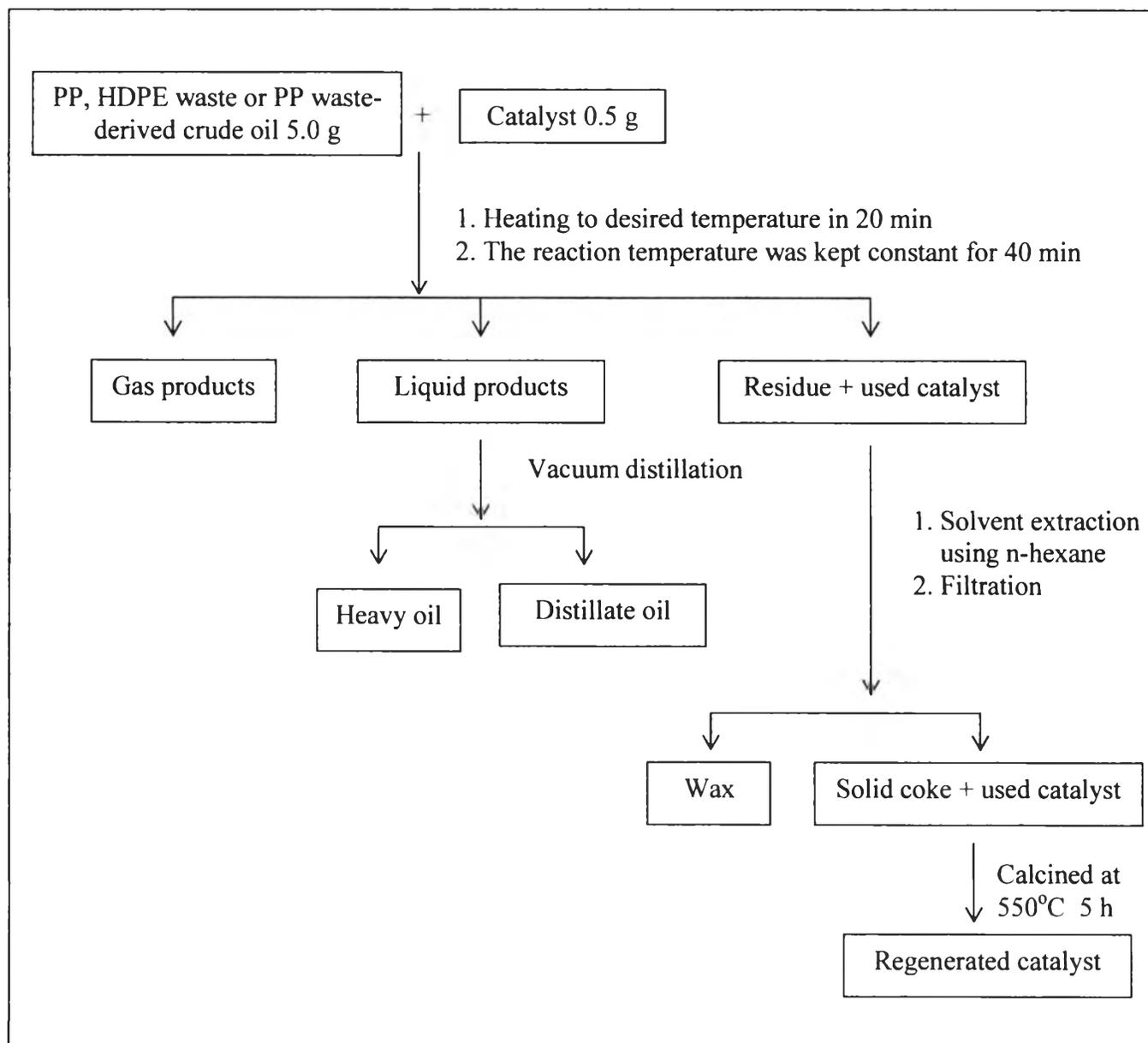
retention time of components in the distillate oil on a gas chromatogram were compared to those of reference compounds in form of n-paraffins. The value of %coke formed on the catalyst was determined by the weight loss upon thermal regeneration of the used catalyst after leaching out of waxes by n-hexane. The heating program for regeneration of the used catalyst is the same as the program for removal of template as shown in Scheme 3.4.



**Figure 3.1** Apparatus for catalytic cracking.



**Figure 3.2** Apparatus for vacuum distillation.



**Scheme 3.7** Catalytic cracking of PP, HDPE waste or PP waste-derived crude oil using zeolite beta as catalyst

### 3.9.2 Effect of SBA-15/AIP Ratios in Catalyst

The catalytic cracking of plastic waste was carried out using zeolite beta catalysts with various SBA-15/AIP ratios of 30, 60 and 90 (denoted Run No.9, Run No.5 and Run No.10, respectively). The reaction was performed in the similar way to what described in Section 3.9.1. The experiments were set up at reaction temperature of 350°C in order to reduce the effect of thermal reaction.

### 3.9.3 Effect of Reaction Temperature

The effect of temperature on catalytic cracking of plastic waste was studied in the similar method that described in Section 3.9.1, but the SBA-15/AIP ratio of catalyst was 30 for PP and 60 for HDPE. The reaction temperature was varied to 350, 380, 400 and 420°C.

### 3.9.4 Effect of Plastic Waste to Catalyst Ratios

The catalytic cracking reaction was carried out according to the procedure above in 3.9.1, but the amount of catalyst (Run No.9 or Run No.5) was changed to 0.5 wt%, 1.0 wt%, 3.0 wt%, 5.0 wt% and 10.0 wt% catalyst of plastic waste at the reaction temperature of 380 or 400°C.

### 3.9.5 Regeneration of Catalyst

The spent catalyst of single use (SBA-15/AIP = 30 ) was subjected to be reused with and without regeneration and used PP waste to catalyst ratio of 5.0 wt%. The spent catalyst for HDPE waste cracking was SBA-15/AIP ratio of 60 and used plastic to catalyst ratio of 3.0 wt%. The spent catalyst was regenerated by washing several times with n-hexane to remove wax, drying in an oven at 110°C overnight, and calcining in air at 550°C for 5 h. The regenerated catalyst was characterized by XRD, SEM and surface area analysis before testing for its activity, catalytic cracking of PP at reaction temperature 380°C and 400°C for HDPE cracking. The test reaction was performed in the similar way to what described in Section 3.9.1.

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### **3.10 Activities of Various Zeolite Beta Catalysts in PP Waste-Derived Crude Oil Cracking**

PP-Waste-Derived Crude Oil was prepared by thermal cracking of PP waste at 400°C. The catalytic cracking reaction of PP-Waste-Derived Crude Oil over a selected catalyst (Run No.9) was carried out similarly to the procedure in Section 3.9 at various conditions.