

CHAPTER III

EXPERIMENTS

3.1 Instruments, apparatus and analytical techniques

3.1.1 Oven and furnace

Crystallization of SBA-15 mother liquor was carried out at a temperature of 100°C in static condition using UM-500 oven as heater. Calcination of the white solid catalyst was attained in a Carbolite RHF 1600 muffle furnace with programmable heating for remove organic template.

3.1.2 X-ray powder diffractometer

Hexagonal XRD patterns were achieved by a Rigaku D/MAX-2200 Ultima⁺ X-ray diffractometer equipped with Cu target X-ray tube (40 kV, 30mA) at 2-theta ranged from 0.05 to 3.00 degree with a scan speed of 1.00 degree/min and sampling width of 0.02 degree. The scattering slit, divergent slit and receiving slit were fixed at 0.05 degree, 0.5 degree, and 0.15 mm, respectively. The measured diffractograms were analyzed using MDI software (Jade6.5).

3.1.3 Surface area analyzer

N₂ adsorption-desorption isotherms, BET specific surface area, and pore size distribution of the catalysts were performed using a BEL Japan, BELSORP-mini instrument. The samples were weighted exactly 40 mg and pre-treatment at 400°C for 3 h before each quantification.

3.1.4 ICP-AES spectrometer

Aluminium content in the synthetic materials were measured using the Perkin Elmer Plasma-1000 inductively coupled plasma-atomic emission spectrometer (ICP-AES).

3.1.5 AAS spectrometer

Sodium content in the catalyst was measured using the Varian, 280 FS atomic adsorption spectrometer.

3.1.6 ^{27}Al -NMR spectrometer

Solid state ^{27}Al -NMR spectra were performed using the Bruker Advance DPX 300 MHz NMR spectrometer.

3.1.7 Scanning electron microscope

Morphology and particle sizes of the catalysts were inspected using JEOL JSM-6480 LV scanning electron microscope. All samples were coated with spluttering gold under vacuum.

3.1.8 Gas chromatograph

Gas products from cracking process were analyzed using a Varian, GC CP3800 model, hydrocarbon (HC) gas chromatograph equipped with a 50 m length \times 0.53 mm inner diameter KCl/Al₂O₃-PLOT column, whereas permanent gas chromatograph equipped with a 2 m length \times 1mm inner diameter ShinCarbon ST 100/120-Micropacked column. On the other hand, liquid products were identified using the same instrument but equipped with a 30 m length \times 0.32 mm inner diameter CP-WAX 52-CB - column. Detector of HC gas and liquid samples was flame ionization detector (FID) using N₂ as carrier gas, while permanent gas detector was thermal conductivity detector (TCD) using He as carrier gas during analysis. The column oven heating programs of HC gas, permanent gas and liquid samples were shown in Figure 3.1, 3.2 and 3.3, respectively.

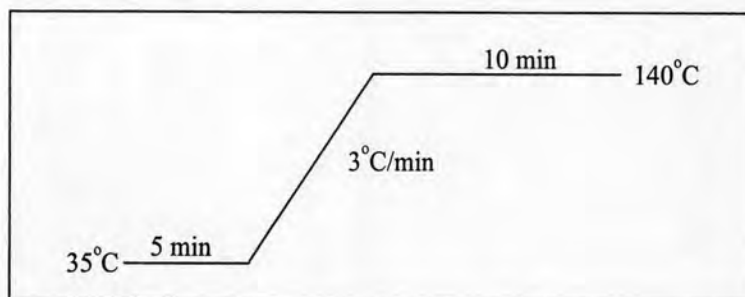


Figure 3.1 The GC heating condition for HC gas analysis.

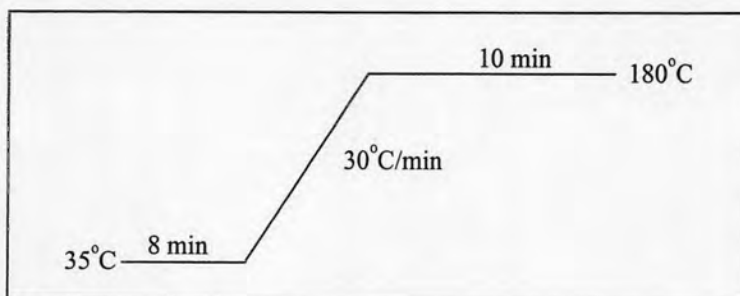


Figure 3.2 The GC heating condition for permanent gas analysis.

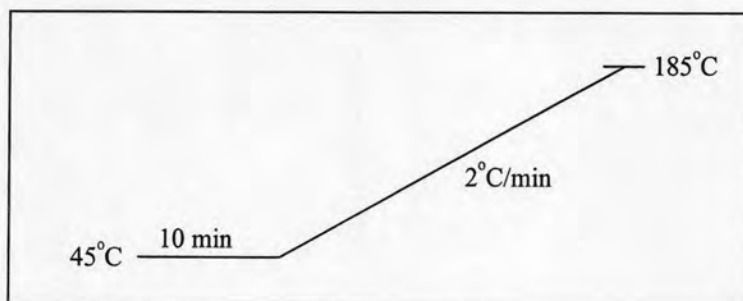


Figure 3.3 The GC heating condition for liquid samples analysis.

3.1.9 Gas chromatograph-Mass spectrometer

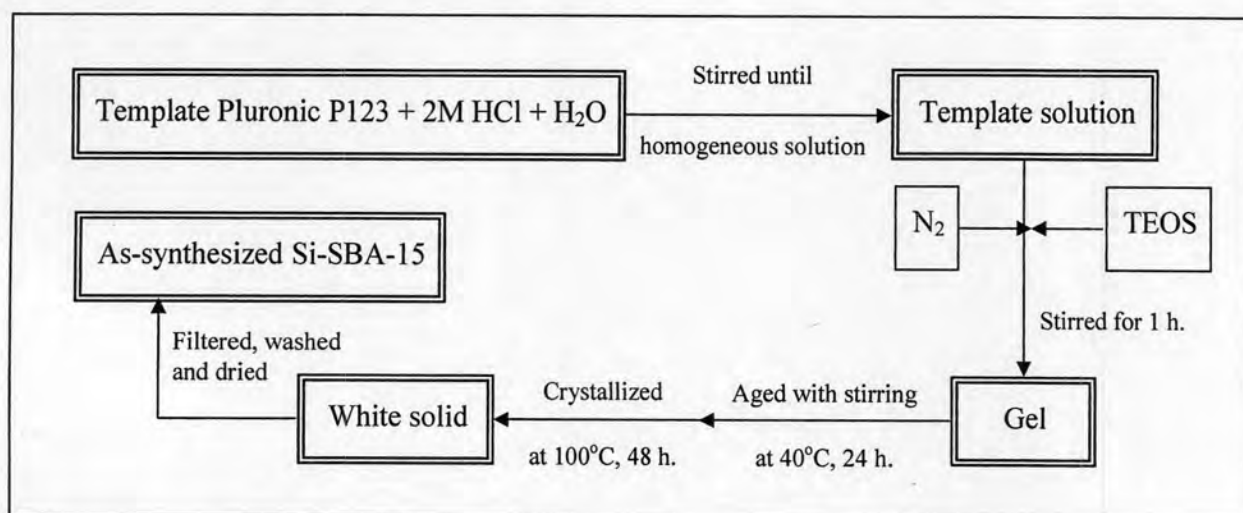
Qualitative analysis of liquid sample was confirmed with GC-MS technique. GC system network of Agilent 68090 N, Mass selective detector network of Agilent 5973 and injector of Agilent 7683 Series were used.

3.2 Chemical and gas

Tetraethyl orthosilicate, (98% TEOS) as Silica source was commercially available from Fluka. Sodium aluminate as alumina source was supplied from Riedel-de Haën. Triblock copolymer Pluronic P123 (PEO₂₀-PPO₇₀-PEO₂₀, average molecular weight = 5800) as template was available from Aldrich. Standard HC gas and waste from biodiesel production were kindly obtained from PTTCHEM and PTT Public Limited Company, respectively. Standard permanent gas mixture was kindly obtained from TIG. Other chemicals were provided from Merck or Fluka.

3.3 Synthesis procedure of Si-SBA-15 (pure SBA-15)

Pure Si-SBA-15, a mesoporous material was synthesized using a method reported by Stucky *et al.* [23, 56] using triblock copolymer Pluronic P123 as template. A 4.0 g of template was dissolved in 30 g of water and 120 g of 2M HCl solution. Subsequently, 8.5 g of tetraethyl orthosilicate (TEOS, Merck) was added and stirred for 1 h and then aged at 40°C for 24 h with stirring. The resulting gel was transferred into a Teflon PARR reactor and heated at 100°C for 48 h in static condition. As-synthesized SBA-15 was separated by filtration, washed with DI water for several times, and dried in the air. The white powder material was obtained. The procedure for synthesizing the Si-SBA-15 was shown in Scheme 3.1.



Scheme 3.1 Synthesis diagram for Si-SBA-15

3.3.1 Organic template removal

Pluronic P123, triblock-co-polymer template, was removed from the solid sample by calcination in a muffle furnace from room temperature to 550°C for 5 h as shown in Figure 3.4.

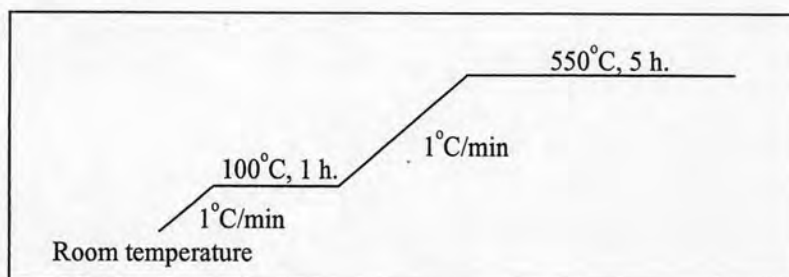


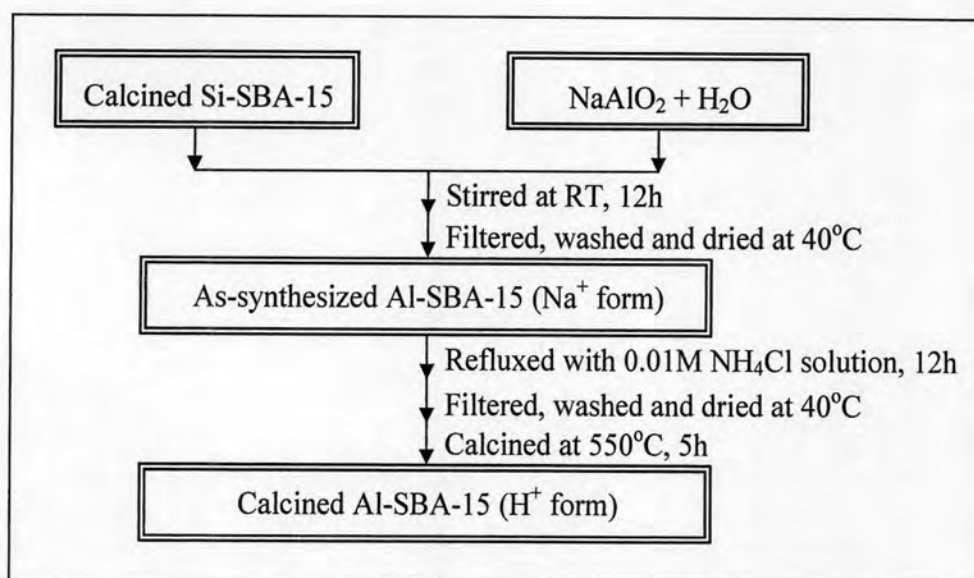
Figure 3.4 Calcination temperature program of SBA-15.

3.4 Synthesis of Al-SBA-15

In this work, mesoporous Si-SBA-15 was incorporated with aluminium *via* post synthesis. Alumination of SBA-15 was conducted by stirring 0.5 g of calcined SBA-15 in 50 mL of water containing various amounts of sodium aluminate at room temperature (RT) for 12 h which the stoichiometric amounts of sodium aluminate used were shown in Table 3.1. The solid material was then filtered, washed with distilled water, and dried at room temperature. Then sodium ion in post-synthesized Al-SBA-15 sample was removed by ion exchange with 0.01M NH_4Cl [24]. The alumination for preparing Al-SBA-15 was shown in Scheme 3.2.

Table 3.1 Stoichiometric amounts of sodium aluminate in alumination of Al-SBA-15 with various Si/Al ratios

Si/Al molar ratio in gel	NaAlO_2 dissolved in 50.0 mL H_2O (g)
10	0.1288
25	0.0515
50	0.0258
100	0.0129
200	0.0064



Scheme 3.2 Alumination of Al-SBA-15

3.5 Sample preparation for ICP-AES analysis

A 40 mg of calcined sample was soaking in 10 mL of 37% HCl and subsequently 10 mL of 48% HF (Merck) was added dropwise to remove silica in form of volatile SiF₄. The sample was heated until dryness and the fluoride treatment was repeated twice. Then, 10 mL of aqua regia (6M HCl : 6M HNO₃ at ratio 1 : 3) was added slowly and warmed until dryness again. An amount of 10 mL de-ionized (DI) water was added to and warmed to complete dissolution for a few minutes. The solution was transferred to a 50-mL polypropylene volumetric flask. This solution was diluted to the mark with 1000 ppm KCl. The flask was capped and shaken thoroughly. The solution was transferred into a plastic bottle with a treaded cap lined under with a polyethylene seal for analysis.

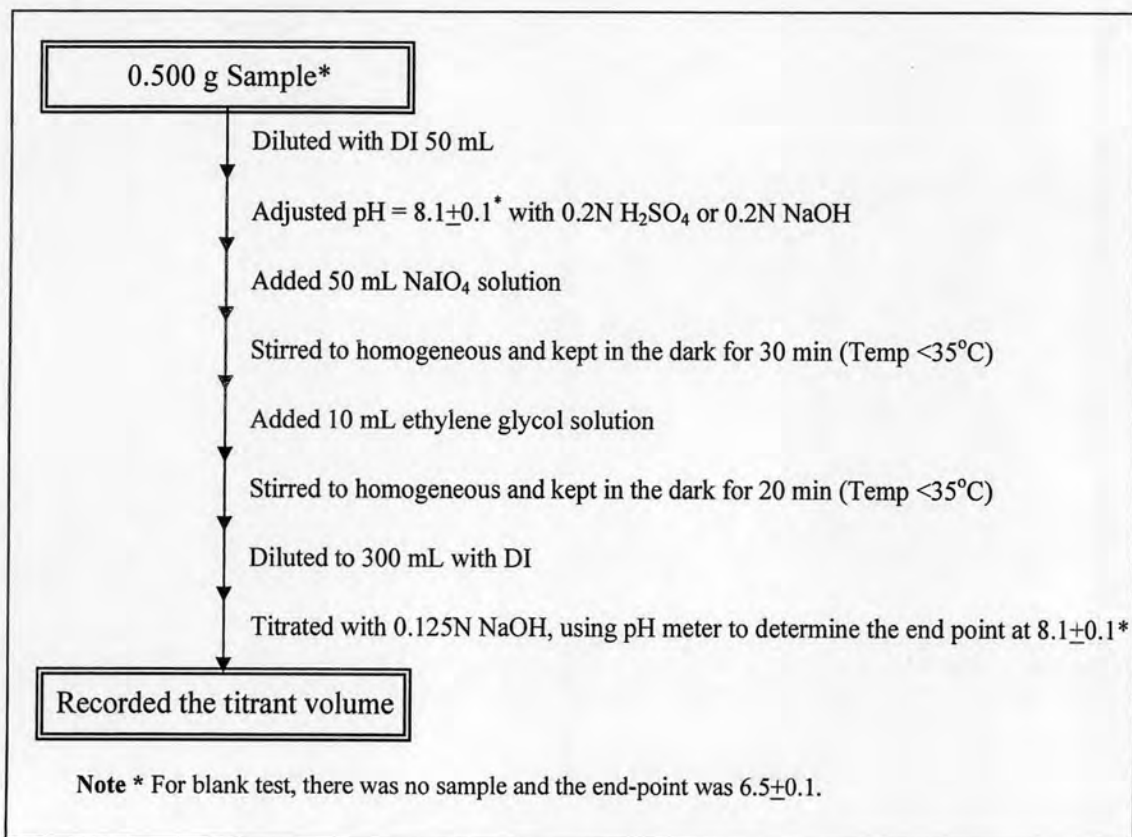
3.6 Determination of the composition of waste from biodiesel production (WBP)

3.6.1 Determination of glycerol content (follow BS 5711: Part 3: 1979 [57])

Weighed 0.50 g of waste from biodiesel production. Then, diluted the test portion to 50 mL with DI. Adjusted the pH of this solution to 8.1±0.1 with 0.2N H₂SO₄ or 0.2N NaOH using pH meter which equipped with the glass electrode for measurement. Next, transferred 50 mL of sodium periodate solution (NaIO₄) into the test solution, swirled gently, and kept in the dark at room temperature for 30 minutes. After that, added 10 mL of ethanediol solution, swirled mindly, and allowed to stand in the dark for other 20 minutes. At the end of this procedure, made the volume to 300 mL before titration to pH 8.1±0.1 with 0.125M standardized NaOH solution. For blank test, used the same steps, but 50mL of DI was instead the test sample, and pH of the end-point was 6.5±0.1. This procedure can be concluded in Scheme 3.3. The glycerol content was given, as a percentage by mass, by the following equation:

$$\text{glycerol content (\% by mass)} = 1.151 \times \frac{(V_0 - V_1)}{m} \times T$$

- where
- V_0 : the volume of the NaOH solution used as titrate in the test portion (mL),
 - V_1 : the volume of the NaOH solution used as titrate in the blank (mL),
 - T : the actual concentration of the NaOH solution used as titrate (M),
 - m : the mass of test portion (g).



Scheme 3.3 The flow-chart for determination of glycerol content

3.6.2 Determination of ash-gravimetric method (follow BS 5711: Part6: 1979 [58])

Heated the crucible at $750\pm 10^{\circ}\text{C}$ for a few minutes in the furnace. Then, cooled to room temperature in a desiccator. After that, weighed for empty crucible (M_1). For ash determination, put the sample into the crucible on the scale, and recorded the data (M_2). Next, gently heated and calcined this portion in a furnace controlled the end temperature at $750\pm 10^{\circ}\text{C}$ for 10 min. Finally, recorded the data of calcined crucible (M_3). Calculated ash as a percentage by mass, from the equation:

$$\text{Ash (\% by mass)} = \frac{(M_3 - M_1)}{(M_2 - M_1)} \times 100$$

where M_1 : the mass, in grams, of the empty crucible,

M_2 : the mass, in grams, of the sample and crucible,

M_3 : the mass, in grams, of the calcined test portion crucible.

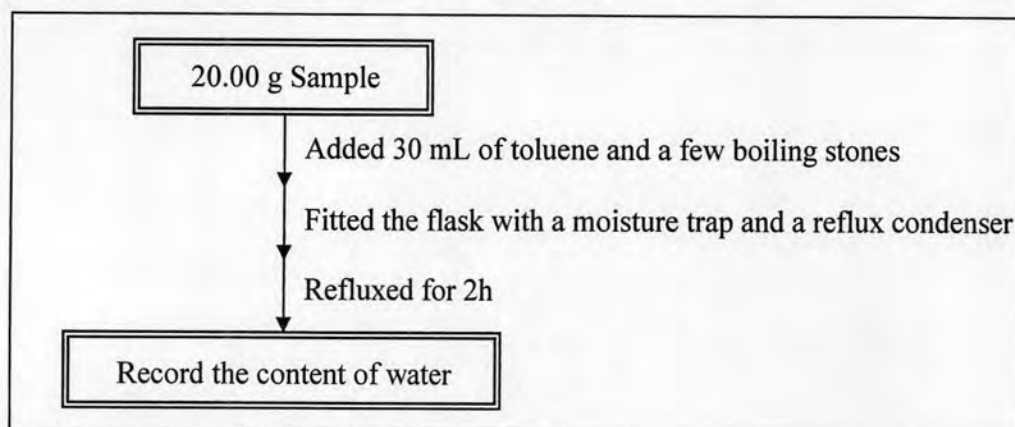
3.6.3 Determination of water content-Azeotropic distillation (follow D890-98(2003) [59])

Weighed 20.00 g of glycerol sample (W_1) in round-bottom flask and added 30 mL of toluene and boiling stones. Fitted the flask with a moisture trap (Dean-Stark trap) and condenser before refluxing for 2 h. Recorded the quantity of water in the trap (W_2). This method can be concluded in Scheme 3.4. The water content can be calculated as following equation:

$$\text{Water content (\% by mass)} = \frac{W_2}{W_1} \times 100$$

where W_1 : the mass (in grams) of the sample,

W_2 : the mass (in grams) of the water in trap.



Scheme 3.4 Procedure for determination of water content

3.6.4 Calculation of matter organic non-glycerol (MONG) (modified from BS 5711: Part9: 1979 [60])

The content of Matter Organic Non-Glycerol (MONG) was given, as a percentage by mass (express the result to decimals one place), by the equation:

$$\% \text{ by mass of MONG} = 100 - A - B - C$$

where A : the glycerol content (% by mass),

B : the ash (% by mass),

C : the water content (% by mass).

3.6.5 Determination of density at 20°C (follow BS 5711: Part4: 1979 [61])

Used the Gay-Lussac pyknometer for density determination. First, weighed the empty-pyknometer for blank weight. Second, weighed the DI pyknometer which filled the DI after keeping at 20°C for 10 min labeled W_1 . Finally, weighed the glycerol sample pyknometer which contained pure glycerol or the WBP, after stored at 20°C for 30 min denoted W_2 . Density of the sample at 20°C was given, in grams per milliliter, by the formula:

$$\text{Density at } 20^{\circ}\text{C (g/mL)} = \frac{W_2 + A}{W_1 + A} \times \rho_e$$

where W_1 : the apparent mass, in grams, of water contained the pyknometer at 20°C,
 W_2 : the apparent mass, in grams of the test portion,
 ρ_e : the density of water at 20°C, 0.9982 g/mL,
 A : the buoyancy correction given by : $\rho_a \times m_1$,
 ρ_a : the density of air, 0.0012 g/mL.

3.6.6 Determination of alkalinity (modified from BS5711: Part5: 1979 [62])

Weighed 10.0 g of the biodiesel waste sample and added 15.0 mL of water. Then, well-mixed stirred before measuring alkalinity with pH meter which equipped with glass electrode.

3.7 Catalyst performance testing

3.7.1 Procedure in catalytic cracking of waste from biodiesel production

The cracking of waste from biodiesel production was performed at 350-450°C in the upright cylindrical reactor under atmospheric pressure with continuous N_2 flow rate 20 mL/min (Figure 3.5). In each experiment, 5 g of waste sample was loaded into the reactor and mixed with 0.50 g of calcined catalyst powder. The reactor was heated to the desired reaction temperature at the rate of 20°C/min, and kept constant for a period of 40 min. During this time, the gaseous and liquid products coming out from the reactor were separated in a condenser which cooled at 1°C. The transformative products were classified into three groups, i.e. gases, liquid and

residue. The percentage of gaseous product was estimated by subtracting the weight of liquid products and residues from the starting material. Liquid product obtained from the reaction was separated into two fractions; light liquid and heavy liquid, by vacuum distillation using small distillation kit at the heater temperature of 200°C. The cracking procedure can be concluded in Scheme 3.5.

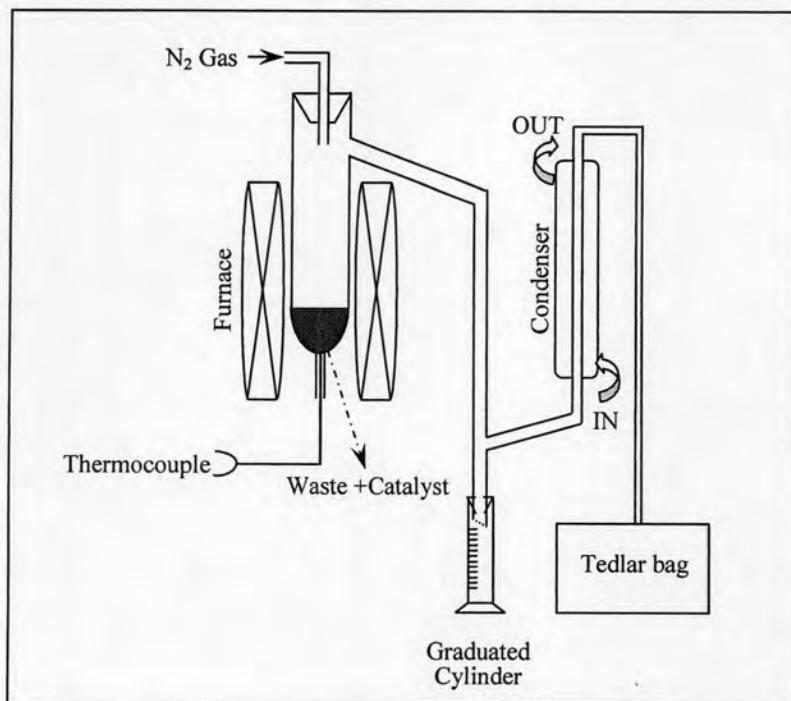


Figure 3.5 Equipments for cracking reaction.

The values of % conversion and % yield of products were calculated based on the equations as follows:

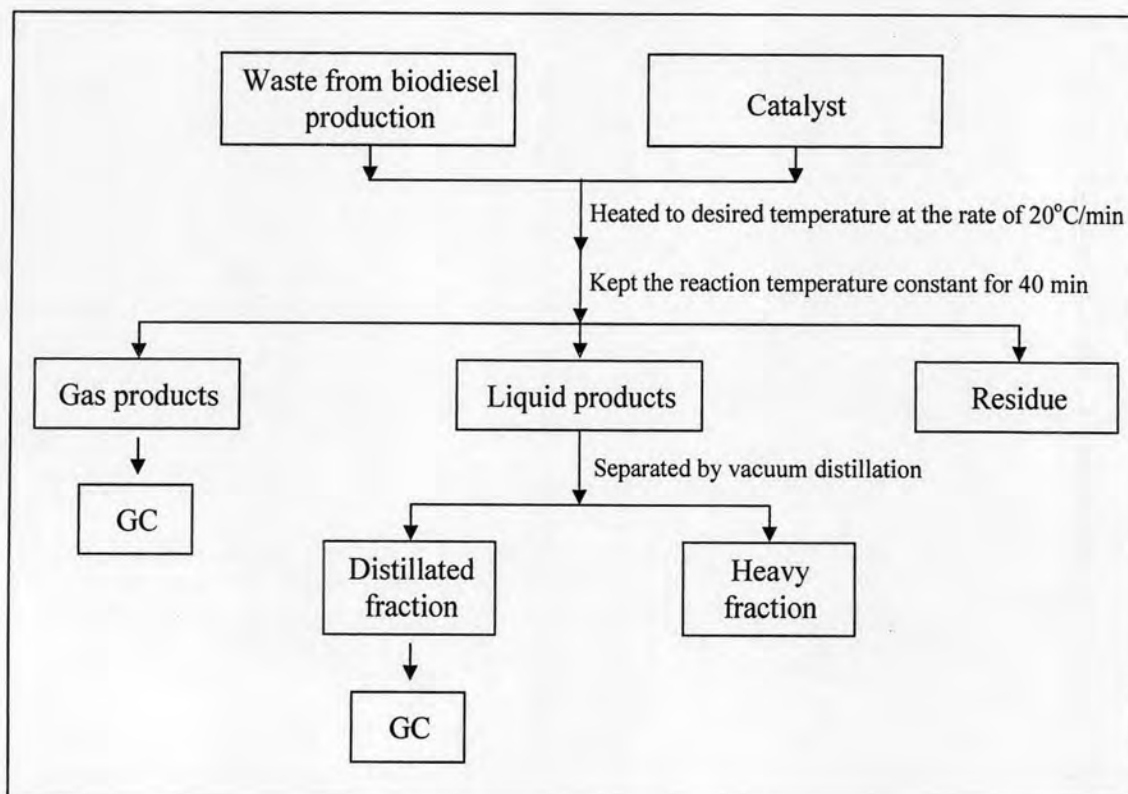
$$\% \text{ Conversion} = \frac{(\text{mass of liquid products} + \text{mass of gas products})}{\text{mass of waste from biodiesel}} \times 100$$

mass of gas fraction = mass of the reactor with waste from biodiesel production and catalyst before reaction – mass of the reactor with residue and used catalyst after reaction – mass of liquid fraction

$$\% \text{ Fraction yield} = \frac{\text{mass of product fraction}}{\text{mass of waste from biodiesel production}} \times 100$$

3.7.2 Thermal cracking and catalytic cracking over non-acidic SBA-15

In cracking process, the reaction temperature plays one of the important role, hence the thermal cracking of waste from biodiesel production is investigated and compared with cracking over non-acidic silica, SBA-15 in each reaction temperature.



Scheme 3.5 The overall cracking procedure of waste from biodiesel production

3.7.3 Study on the effect of Si/Al ratios in catalysts

The degradation of waste from biodiesel production was carried out using Al-SBA-15(H^+ form) with Si/Al ratios in gel of 10, 25, 50, 100, and 200 as catalysts. The reaction was performed according to the procedure above in Section 3.7.1.

3.7.4 Study on the effect of the reaction temperatures

In this topic, the effect of temperature on cracking of waste from biodiesel production was studied in the same way to general procedure, but the reaction temperature was varied to 350, 400, and 450°C.

3.7.5 Study on the effect of waste from biodiesel production to catalyst ratios

The catalytic cracking was carried out similar to the procedure in Section 3.7.1, but the amount of catalyst, Al-SBA-15 (H^+ form), was changed to 2.5wt%, 5wt%, 10wt%, and 15wt% catalyst of waste from biodiesel production.

3.7.6 Study on the effect of vapour-phase catalytic cracking

The catalytic cracking was carried out similar to the procedure in Section 3.7.1, but the position of the catalyst, Al-SBA-15 (H^+ form), was changed from liquid-phase (catalyst was mixed with starting material at the bottom of a 36 cm long reactor) catalytic cracking to vapour-phase (catalyst was placed on the 150 mesh sieve at 13 cm from the bottom of the reactor in order to contact vapour phase of starting material) catalytic cracking.

3.8 Catalyst regenerations

The spent catalyst of the first and the second use ($Si/Al=100$) was washed several times with n-hexane and dried in oven. The used catalysts were regenerated by calcination in air at $550^{\circ}C$ for 5h and characterized by XRD and surface area analysis before testing in the next reaction.