



CHAPTER III

EXPERIMENTS

3.1 Instruments and apparatus

3.1.1 Oven and furnace

Crystallization of SBA-15 mother liquor was executed at a temperature of 100°C using UM-500 oven as heater. Organic template was removed from SBA-15 channels by calcination at 550°C for 5 h in a Carbolite RHF 1600 muffle furnace with programmable heating rate of 1°C/min.

3.1.2 X-ray powder diffractometer (XRD)

The structure of synthesized SBA-15 was determined by a Rigaku D/MAX-2200 Ultima⁺ X-ray diffractometer equipped with Cu target X-ray tube (40 kV, 30mA) at 2-theta between 0.5 to 3.00 degrees. The scattering slit, divergent slit and receiving slit were fixed at 0.5 degree, 0.5 degree, and 0.15 mm, respectively.

3.1.3 Surface area analyzer

The specific surface area, pore size distribution, and N₂ adsorption-desorption isotherms of the catalysts were identified using a BEL Japan, BELSORP-mini instrument. The catalysts were outgassed at 400°C at 3 h before the surface area measurements.

3.1.4 ICP-AES spectrometer

The chemical compositions of the catalysts were analyzed using the Perkin Elmer Plasma-1000 inductively coupled plasma-atomic emission spectrometer (ICP-AES).

3.1.5 ^{27}Al -NMR spectrometer

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

3.1.6 Scanning electron microscope (SEM)

The morphology and particle size of SBA-15 supported were analyzed by JEOL JSM-6480 LV scanning electron microscope. All samples were coated with sputtering gold under vacuum. The scanning electron microscope and energy dispersive spectrometer (SEM-EDS) was used to measure the metal loading in the support.

3.1.7 Transmission electron microscope (TEM)

The microstructure and particle size of metal on supported SBA-15 were investigated by JEOL; JEM-2100 transmission electron microscopy.

3.1.8 Gas chromatograph (GC)

Gaseous and liquid products were analyzed with Varian CP-3800 gas chromatograph (GC) equipped with 50 m length \times 0.53 mm inner diameter Alumina-PLOT column connected to a flame ionization detector (FID) detector using N_2 as carrier gas for hydrocarbon gas analysis. ShinCarbon ST 100/120-Micropacked column (equipped with a 2 m length \times 1mm inner diameter) was connected to a thermal conductivity detector (TCD) using He as carrier gas during analysis which permanent gases were analyzed. Moreover, liquid product was analyzed via CP WAX 52CB column (equipped with a 30 m length \times 0.32 mm inner diameter) connected to a FID detector using N_2 as carrier gas. The column heating programs for hydrocarbon gas, permanent gas and liquid analysis were shown in Figure 3.1, 3.2 and 3.3, respectively.

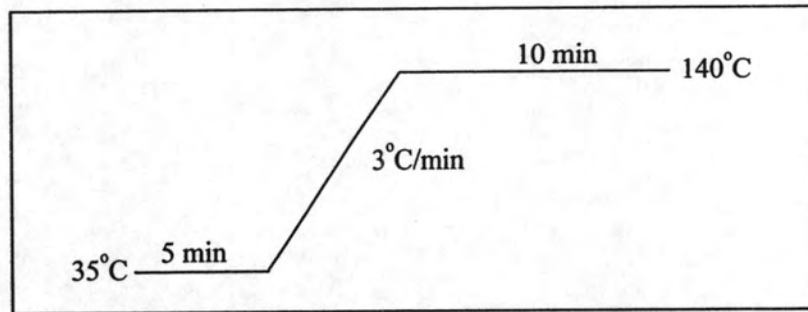


Figure 3.1 The GC heating condition for HC gas analysis.

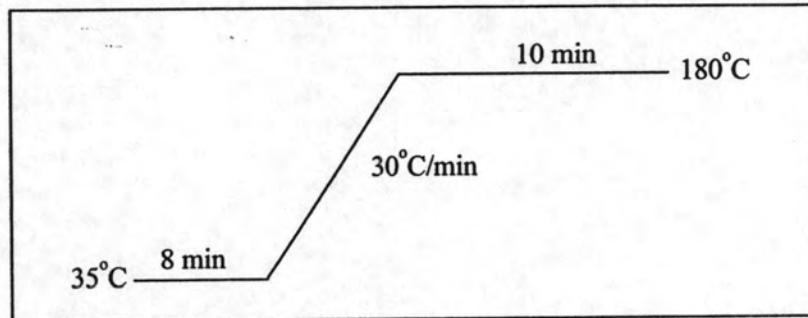


Figure 3.2 The GC heating condition for permanent gas analysis.

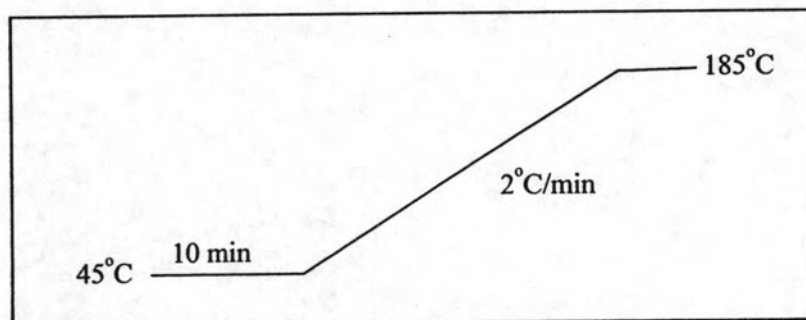


Figure 3.3 The GC heating condition for liquid samples analysis.

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.

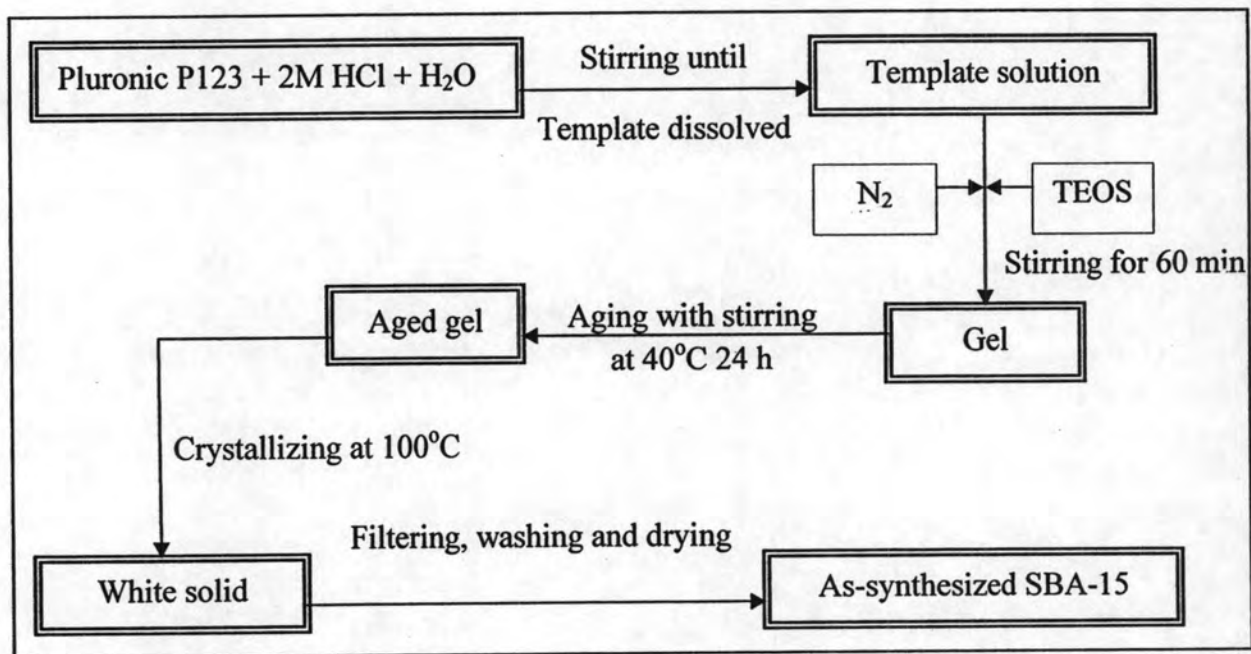
3.2 Chemicals

1. Triblock copolymer pluronic P123 (PEO₂₀-PPO₇₀-PEO₂₀, average molecular weight = 5800) (Aldrich)
2. Tetraethyl orthosilicate, TEOS (Fluka, 98 wt %)
3. Sodium aluminate, NaAlO₂ (Riedel-de Haën)
4. Hydrochloric acid, HCl (Fluka, 37 wt %)
5. Chloroplatinic acid hexahydrate, H₂PtCl₆ (Fluka)
6. Palladium chloride, PdCl₂ (Aldrich)
7. Ruthenium chloride hydrate, RuCl₃.xH₂O (Aldrich)
8. Nickel nitrate hexahydrate, Ni(NO₃)₂.6H₂O (Merck)
9. Standard gas mixtures (for GC analysis, kindly obtained from PTT Chemical Public Company Limited) (See appendices: 117)
10. Nitrogen gas, N₂ (Thai Industrial Gases (TIG), highly pure grade)
11. Helium gas, He (Thai Industrial Gases (TIG), ultra highly pure grade)

3.3 Synthesis of SBA-15

SBA-15 was synthesized by conventional hydrothermal method [14, 85] using 4 g of triblock copolymer pluronic P123 was dissolved with stirring in 120 g of 2M hydrochloric acid and subsequently added 30 g of deionized water and then stirred at ambient temperature. The above clear solution was added 8.5 g of tetraethylorthosilicate and stirred for another 1 h. The silicate fluid gel was formed and thoroughly stirred at 40 °C for 24 h and then transferred to a teflon-lined autoclave for hydrothermal crystallization at 100 °C for 48 h. After crystallization, the autoclave was quenched with cold water and the solids were separated from mother

liquor by vacuum pump. The recovered solids were washed till pH 6 -7, dried overnight at 100 °C The white powder material was obtained. The procedure for synthesizing the SBA-15 was shown in Scheme 3.1



Scheme 3.1 Synthesis diagram for SBA-15.

3.3.1 Organic template removal

To remove the template, (EO₂₀PO₇₀EO₂₀), the solid sample was calcined in a muffle furnace from temperature to 550°C for 5 h as shown in Figure 3.4.

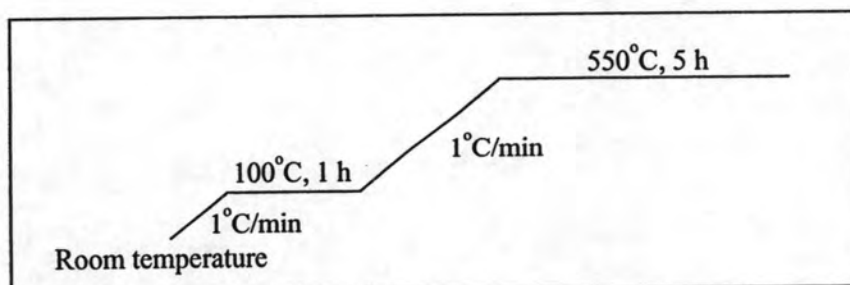
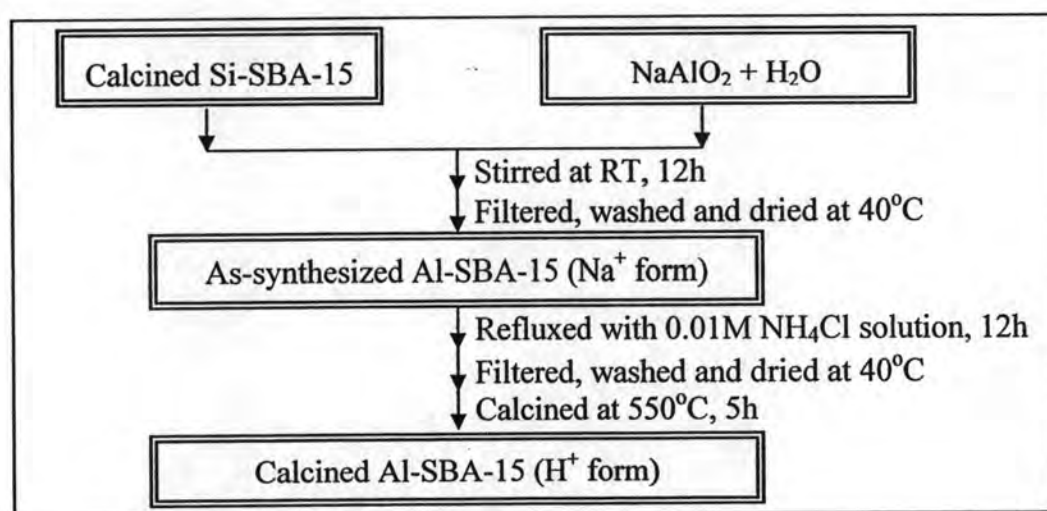


Figure 3.4 Calcination temperature program of SBA-15.

3.4 Synthesis of Al-SBA-15

In this work, mesoporous Si-SBA-15 was incorporated with aluminium *via* post synthesis. Post-synthesized of Al-SBA-15 following Luan *et al.* method [5, 6] was conducted by stirring 0.5 g of calcined SBA-15 in 50 ml of water containing 0.1288 g of NaAlO_2 at room temperature for 12 h. The Al-containing mesoporous material was filtered and thoroughly washed with deionized water and then dried at room temperature. After post-treatment, the remained Na^+ ion was removed by ion-exchange with of 0.01M NH_4Cl solution for 24 h. Then material was calcined at 550 °C for 5 h. The solid was designated as Al-SBA-15 at Si/Al mole ratio = 10. The procedure for preparing Al-SBA-15 was shown in Scheme 3.2.



Scheme 3.2 Alumination of Al-SBA-15.

3.5 Preparation of metal supported SBA-15 (M-SBA-15) [26]

The metal supported on siliceous SBA-15 of various metals ($M = \text{Ni}, \text{Pt}, \text{Pd}$, and Ru). Supported metal catalysts were also prepared by aqueous wet impregnation method using metal salt ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, PdCl_2 , $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, NiNO_3) aqueous solution, the amount of metal loading was 5 wt%. PdCl_2 was dissolved in 1M HCl because PdCl_2 did not dissolve completely in water. After impregnation, the samples were dried at 120 °C followed by calcination at 500 °C for 4 h as shown in Figure 3.5.

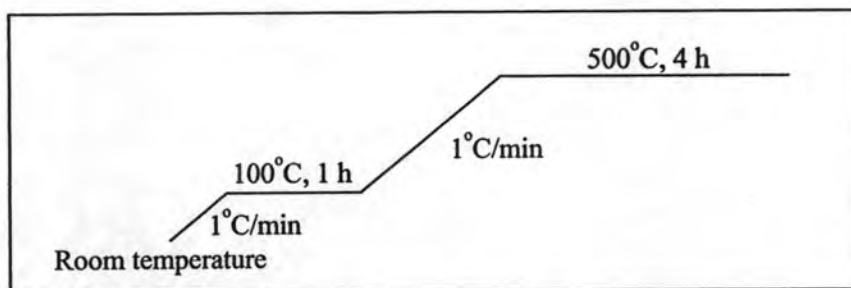


Figure 3.5 Calcination temperature program of M-SBA-15.

3.6 Preparation of nanoparticle of metal on supported SBA-15

The metal nanoparticles were prepared by reducing metal ion in D-glucose aqueous solution as the stabilizer and using sodium borohydride (NaBH_4) as the reducing agent. For the synthesis of metal nanoparticles, metal aqueous solution was added in D-glucose aqueous solution and then NaBH_4 was added to the system under constant stirring at room temperature for 24 h. After that the resultant metal nanoparticles were impregnated on supported SBA-15.

3.7 Sample preparation for ICP-AES analysis

Elemental analysis was performed to determine Si/Al in catalyst. Aluminum (Al) content was determined by ICP-AES. The content of silica (SiO_2) was obtained by difference of catalyst weight and Al_2O_3 weight calculated from ICP-AES. For sample preparation, 0.0400 g of a calcined catalyst (Al-SBA-15) was soaked with 10 cm^3 of 6 M HCl. Then 10 cm^3 of 48% hydrofluoric acid was dropwise added to the mixture to get rid off silica in the form of volatile SiF_4 species. The sample was heated but not boiled until it was dried on a hot plate. Then the fluoride treatment was repeated twice before 10 cm^3 of reverse aqua regia containing 6M HCl: 6M HNO_3 at a ratio of 1:3 was added slowly and warmed until dried again. After that 10 cm^3 deionized water was added to and warmed for 5 min. The sample solution was transferred to a 50- cm^3 polypropylene volumetric flask. The solution in the flask was

brought to the mark with 1000 ppm KCl. The flask was capped and shaken before transferred into a plastic bottle for analysis.

3.8 Pure glycerol cracking over modified SBA-15 catalyst

The thermal cracking using pure glycerol (Fluka, 99.5%) as starting material was investigated and compared with cracking over Al-SBA-15 and M-SBA-15 (M= Pt, Pd, Ru and Ni) at the reaction temperature of 400 °C. Thermal and catalytic cracking activities were carried out in a tubular reactor made of stainless steel (grade 316) with a under a continuous nitrogen flow by batch operation as shown in Figure 3.6.

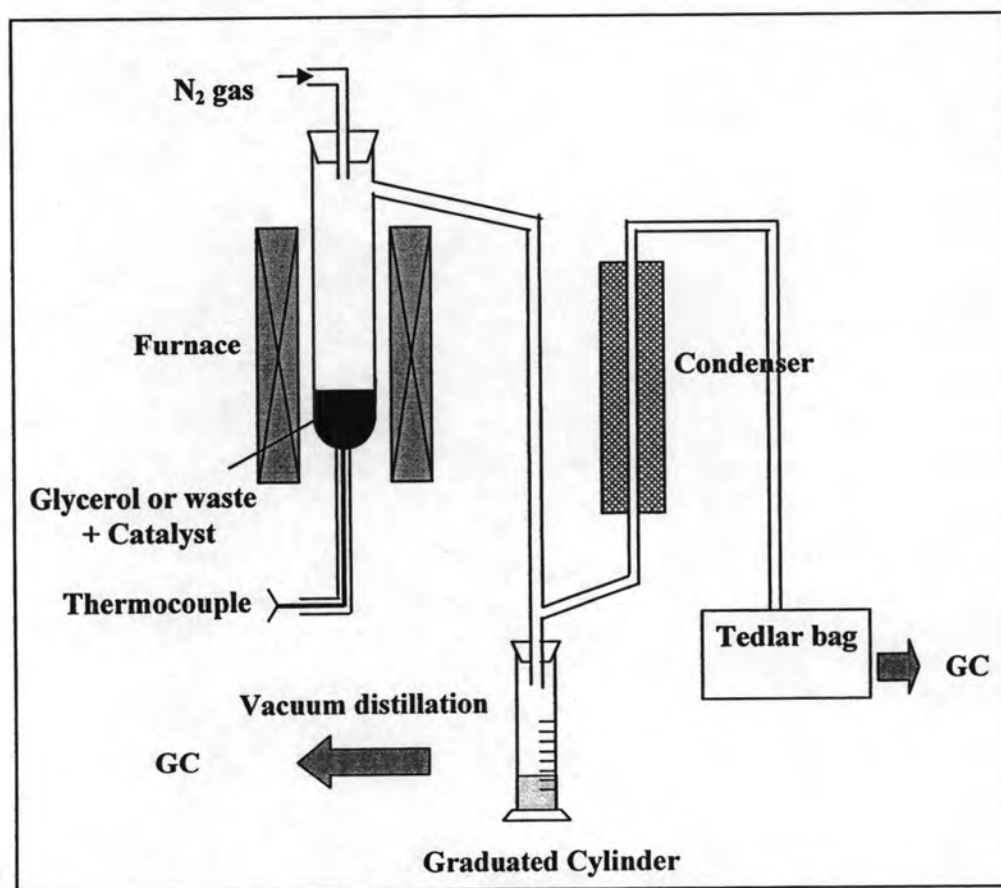


Figure 3.6 Apparatus for thermal and catalytic cracking.

Initially, 0.50 g of catalyst and 5.00 g of the glycerol were loaded into the reactor and mixed thoroughly. Afterward, the reactor was set up, purged with N₂ at flow rate of 20 ml/min to remove the air, and heated with a rate of 20°C/min up to 400°C, keeping it constant for 40 min. This temperature was continually monitored by a programmable temperature controller equipped with a K-type thermocouple in direct contact with the reaction mixture. The gaseous products at the reaction temperature were swept out from the reactor by the nitrogen stream and separated into liquid and gaseous fractions in a condenser cooled by a chiller. The gas fraction was collected into a Tedlar bag since the start of heating while the liquid fraction was collected in a 10 cm³ graduated cylinder. After completion of the reaction, the reactor was cooled down to room temperature and weighed. The values of % conversion were defined as the sum of collected gaseous and liquid products with regard to the initially loaded glycerol. The solid remaining in the reactor was considered as a residue, not being included in the conversion.

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

$$\% \text{ Conversion} = \frac{(\text{mass of liquid products} + \text{mass of gas products})}{\text{mass of starting glycerol}} \times 100$$

$$\text{mass of gas fraction} = \text{mass of the reactor with glycerol and catalyst before reaction} \\ - \text{mass of the reactor with residue and used catalyst after} \\ \text{reaction} - \text{mass of liquid fraction}$$

$$\% \text{ Fraction yield} = \frac{\text{mass of product fraction}}{\text{mass of starting glycerol}} \times 100$$

The alternative products were classified into three groups that were gas fraction, liquid fraction and residue. The gas products were analyzed by a gas chromatography. The liquid fraction was distilled under vacuum as shown in Figure 3.7. The cracking procedure can be concluded in Scheme 3.3.

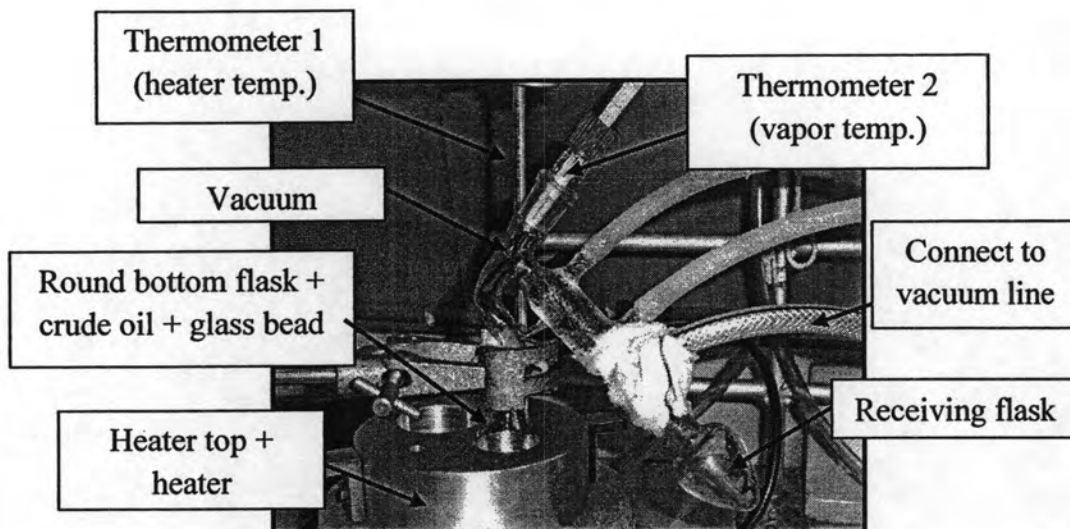
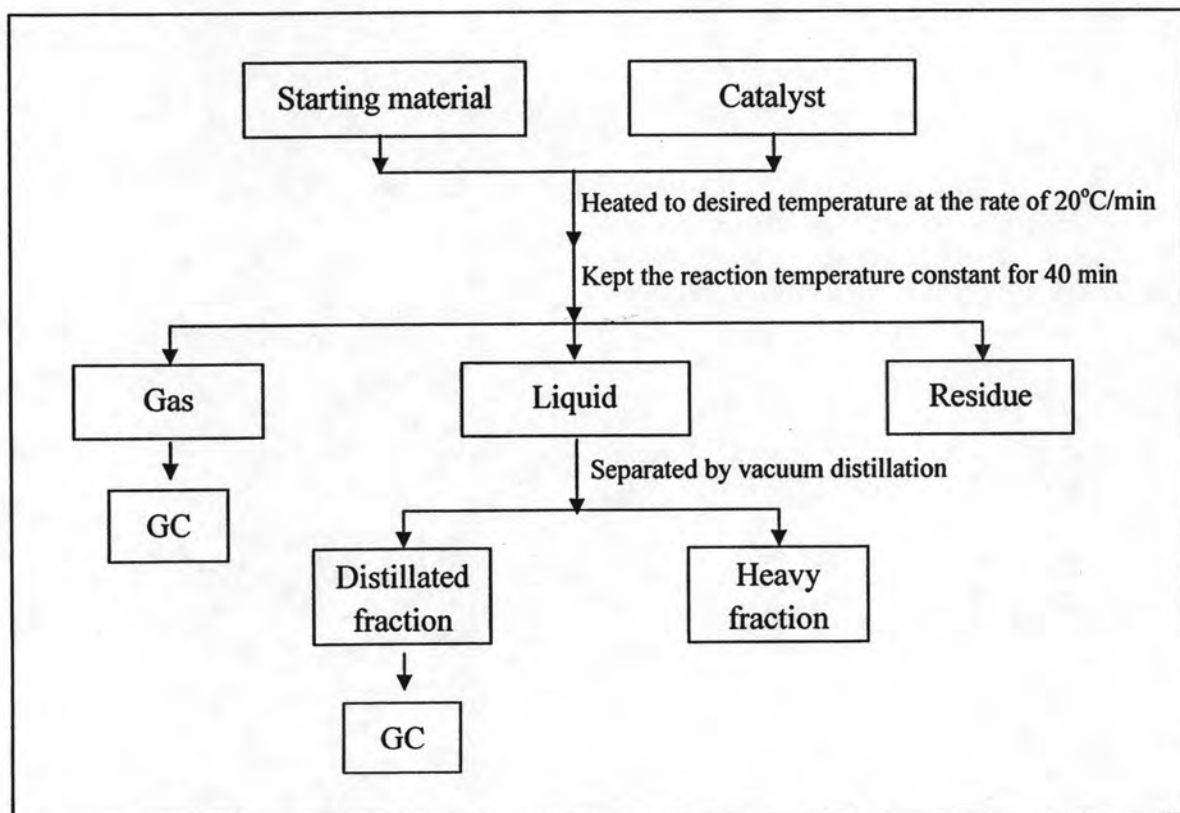


Figure 3.7 Apparatus for vacuum distillation.



Scheme 3.3 The overall cracking procedure.

3.9 Glycerol waste cracking over Al-SBA-15 catalyst

In cracking process was used glycerol waste from biodiesel production as starting material. The reaction was performed in the same way as what described in Section 3.8.

3.9.1 Effect of reaction temperature

The catalytic cracking of glycerol waste was carried out using Al-SBA-15 with different temperature reactions. The reaction was performed using the same way to general procedure, but the experiments were set up at reaction temperatures as 400 to 800°C.

3.10 Glycerol cracking over metal on supported SBA-15 catalysts

3.10.1 Effect of reaction temperature

In this topic, the catalytic cracking of glycerol waste was carried out using M-SBA-15 (M = Pt, Pd, Ru and Ni) catalysts were also prepared by aqueous wet impregnation method. The activity of glycerol waste cracking was measured under condition of reaction temperature of 400°C, 650°C and 800°C

3.10.2 Effect of glycerol waste to catalyst ratio

The M-SBA-15 sample was used for studying the effect of glycerol waste from biodiesel production to catalyst ratio on its activity. The amounts of glycerol waste to catalyst ratio were 5%, 10% and 15% catalyst of glycerol waste. The experiments were set up at the reaction temperature, which was the optimum reaction temperature from Section 3.10.1. The reaction was performed using the same method as that described in Section 3.8.

3.10.3 Effect of particle size of Pd on supported SBA-15

3.10.3 Effect of particle size of Pd on supported SBA-15

The degradation of glycerol waste from biodiesel production was carried out using nanoparticle of metal supported on SBA-15 prepared by reduction method. The experiments were set up at the reaction temperature and catalyst ratio, which was the optimum reaction temperature and catalyst ratio from Section 3.10.1 and 3.10.2, respectively. The reaction was performed using the same method as that described in Section 3.8.

3.10.4 Effect of position of catalyst

The experiments were set up at the reaction temperature and catalyst ratio, which was the optimum reaction temperature and catalyst ratio from Section 3.10.1 and 3.10.2, respectively. The catalytic cracking was carried out similar to the procedure in Section 3.8 but the position of the catalyst was changed from liquid-phase (catalyst was mixed with starting material at the bottom of a 36 cm long reactor) catalytic cracking to vapor-phase (catalyst was placed on the 150 mesh sieve at 13 cm from the bottom of the reactor in order to contact vapor phase of starting material) catalytic cracking.

3.11 Regeneration of catalyst

The used M-SBA-15 catalyst of the first and second runs were washed several times with n-hexane and dried in oven. The used catalysts were regenerated by calcination in air at 500°C for 4h and characterized by XRD, surface area analysis and SEM-EDS before testing in the next reaction.