

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

##### 3.1.1 Starting material and chemicals

Waste lubricating oil was obtained from the Bang-Sue Train Maintenance Shop in Thailand and was used after standing for 2 weeks and screening through a 200 mesh sieve.

Hexane ( $C_6H_{14}$ ) was purchased from LAB-SCAN Co., Ltd., Thailand and carbon disulfide ( $CS_2$ ) was supplied by MERCK Co., Ltd., Thailand. These reagents were used as analytical grade.

Toluene ( $C_7H_8$ ) was commercial grade (purity 80% minimum) from S.R. Lab Co., Ltd., Thailand. This reagent was used without further purification.

Hydrogen gas (purity 99.5% minimum) was supplied by ENVIROMATE Co., Ltd., Thailand.

##### 3.1.2 Catalysts

The types of catalysts used in this study were Cobalt-Molybdenum loaded on alumina ( $CoMo/Al_2O_3$ ), Iron loaded on activated carbon ( $Fe/AC$ ) and HZSM-5. These

catalysts were obtained from Assoc. Prof. Tharapong Vitidsant's Fuel Research Laboratory, Chulalongkorn University.

### **3.2 Apparatus**

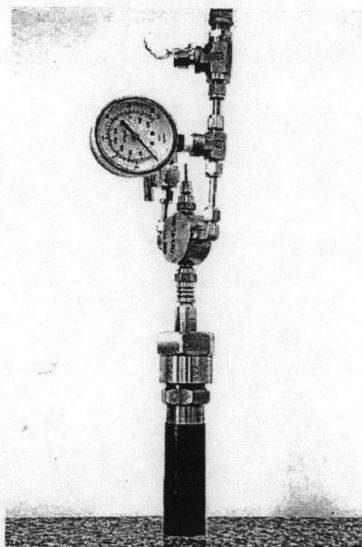
The catalytic cracking reactions were carried out in a micro-cylindrical reactor, tightly sealed tubing bomb, constructed of stainless steel 316. The micro-reactor had volume capacity of 70 ml. with inside diameter of 30 mm. A needle valve was connected to the top of the tube through which gases could be charged. The reactor was attached to a horizontal motion oscillator and was heated to the desired temperature by a 400 watts heater. The reaction temperature was measured by a sheathed thermocouple attached to the tubing bomb and controlled by a PID temperature controller. The micro-cylindrical reactor and accessories are shown in Figure 3.1 and 3.2, respectively.

### **3.3 Experimental procedure**

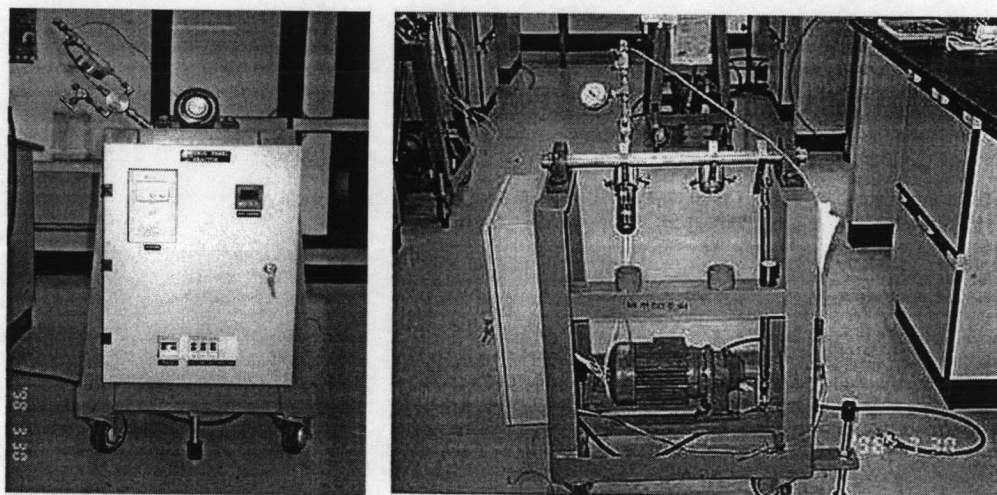
Twenty grams of waste lubricating oil and the required amount of catalyst were charged into the micro-reactor under hydrogen atmosphere. The heating coil, insulator and thermocouple were parted around the reactor. The reactor was fixed on a shaker at 100 rpm while its reaction corresponded to a required time. At the end of the reaction time, measured from the time at which reaction temperature was reached, the reactor was cooled down to room temperature. After that, the micro-reactor was opened to allow gases to evolve gently. The oil and solid product mixture remaining

in the reactor were separated by vacuum filtration. For each run, the inside surface of the reactor and spent catalyst were washed with hexane. The hexane-soluble portion was recovered by evaporation. Liquid yield was defined as  $(\text{weight of oil from filtration} + \text{weight of oil that soluble in hexane}) \times 100 / (\text{weight of feed})$ . The solid yield was defined as  $(\text{weight of hexane insoluble}) \times 100 / (\text{weight of feed})$ , while the gas yield was defined as  $(100 - \text{liquid yield} - \text{solid yield})$ . The flow diagram of the experimental procedure is shown in Figure 3.3.

Kinetic experiments were carried out at different temperature (390, 420 and 425 °C) and reaction times (10, 20, 30, 40, 50, 60 and 90 min). The reactor was loaded with 20 g of waste lubricating oil and optimum amount of each catalyst.

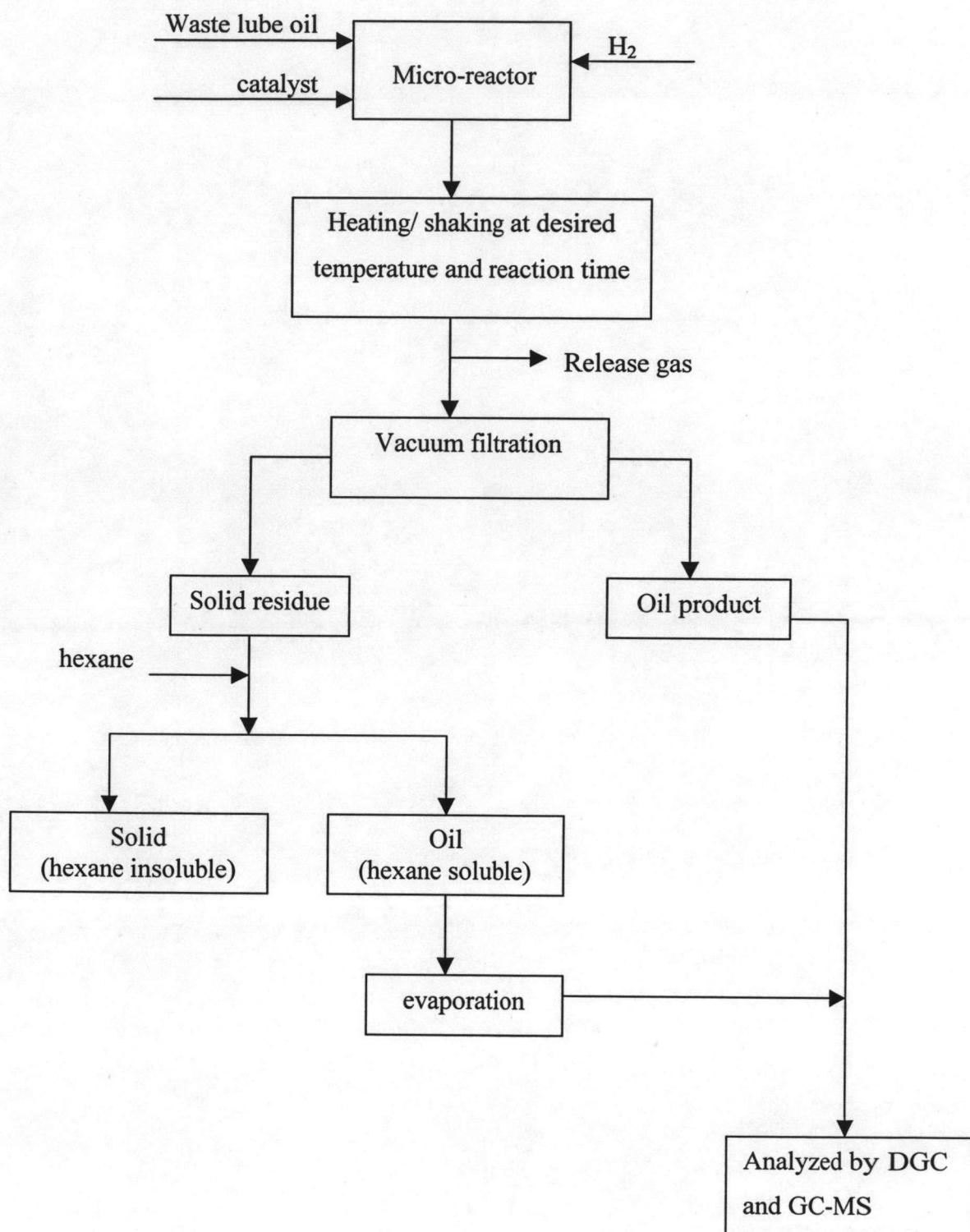


**Figure 3.1** Micro-cylindrical reactor



**Figure 3.2** The reaction unit





**Figure 3.3** Flow diagram of the experimental procedure

### **3.4 Product analysis**

#### **3.4.1 Boiling range distribution**

The boiling range distribution of oil products from the catalytic cracking reaction was analyzed by a Simulated Distillation Analyzer followed the ASTM method D2887. The system consisted of Varian CP-3800 gas chromatograph equipped with an automatic sampler and a flame ionization detector (FID) at the Department of Chemical Technology, Chulalongkorn University. Capillary column (15 m x 0.25 mm, i.d. 0.25  $\mu\text{m}$  film thickness) CP-SIL 5CB was employed with a programmed temperature from 30 to 320  $^{\circ}\text{C}$ . The gas chromatography was calibrated by analyzing a mixture of normal paraffins with known boiling points and samples were injected in the  $\text{CS}_2$  solution. Gasoline, kerosene, light gas oil, gas oil and long residue fractions in product oils were referred to by boiling point in each fraction as follows: under 200  $^{\circ}\text{C}$  (gasoline), 200-250  $^{\circ}\text{C}$  (kerosene), 250-350  $^{\circ}\text{C}$  (light gas oil), 350-370  $^{\circ}\text{C}$  (gas oil) and over 370  $^{\circ}\text{C}$  (long residue).

#### **3.4.2 Gas chromatography –mass spectrometry (GC-MS)**

Information on molecular structures of oil products obtained were only available in terms of analyses in the GC-MS at Department of Chemical Technology, Chulalongkorn University. A SHIMADZU GC-MS QP2010 equipped with DB-1 capillary column (30 m x 0.25 mm, i.d. 0.25  $\mu\text{m}$  film thickness), and a 1:30 split ratio was used. The GC column was ramped at 20  $^{\circ}\text{C min}^{-1}$  from 40 (hold 2 min) to 320  $^{\circ}\text{C}$ .

Helium gas was used as the carrier gas with a flow rate 1.5 ml/min. Sample was injected into a CS<sub>2</sub> solution.

### **3.5 Characterization of materials**

#### **3.5.1 Characterization of waste lubrication oil**

Feed waste lubricating oil was characterized by simulated distillation (SIMDIST) followed ASTM D2887 [31] and gas chromatography. Density and dynamic viscosity were also detected. The waste lubricating oil properties is presented in Table 3.1.

#### **3.5.2 Characterization of the catalysts**

The chemical composition of the catalysts were analyzed by XRF (SIEMENS SRS 3400) at the Scientific Instruments Science Centre, Faculty of Science, King's Mongkut Institute of Technology Ladkrabang.

The shape and size of the crystals of catalysts were observed with a LEO 1455VP Scanning Electron Microscope (SEM) at the Scientific Instruments Science Centre, Faculty of Science, King's Mongkut Institute of Technology Ladkrabang.

The N<sub>2</sub> adsorption-desorption isotherms was measured by using Quantachrome Autosorb 1 at The Petroleum and Petrochemical College, Chulalongkorn University. The surface area was calculated by the BET equation.

Chemical composition and surface area of the catalysts are shown in Table 3.2

**Table 3.1** Properties of waste lubricating oil

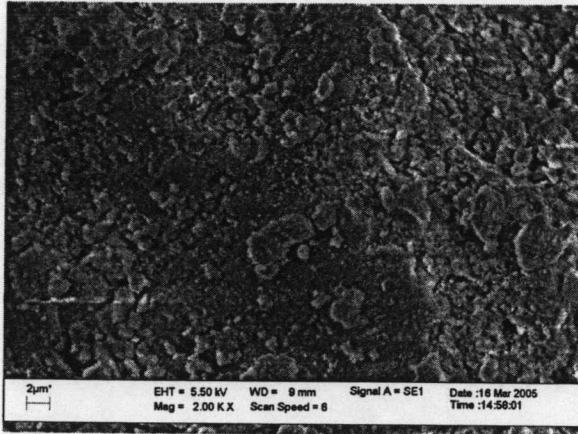
Properties	Results
Dynamic viscosity (cSt)	18.24
Density (g/cm <sup>3</sup> )	0.89
SIMDIST distillation fractions	
Gasoline (wt%)	0.00
Kerosene (wt%)	0.50
Light gas oil (wt%)	3.77
Gas oil (wt%)	8.48
Long residue (wt%)	87.25

**Table 3.2** Properties of catalysts

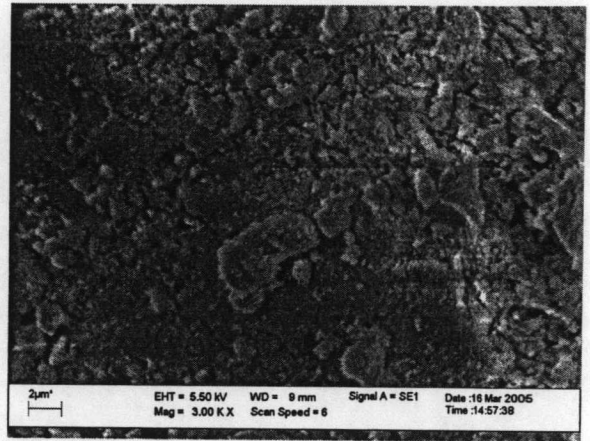
Catalyst type	CoMo/Al <sub>2</sub> O <sub>3</sub>	Fe/AC	HZSM-5
Chemical composition (wt%)			
Cobalt (Co)	8.55	-	-
Molybdenum (Mo)	55.90	-	-
Iron (Fe)	-	9.25	-
Silicon (Si)	-	-	97.60
Aluminium (Al)	28.40	-	2.25
Sulfur (S)	6.89	0.12	-
Potassium (K)	-	0.95	-
Carbon (C)	-	89.68	-
Physical Properties			
Surface area (m <sup>2</sup> /g)	229	654	374



From the experimental results in Table 3.2, Fe/AC has a highest surface area of 654 m<sup>2</sup>/g. HZSM-5 and CoMo/Al<sub>2</sub>O<sub>3</sub> have a surface area of 374 and 229 m<sup>2</sup>/g, respectively. Analysis of chemical composition by using XRF technique, CoMo/Al<sub>2</sub>O<sub>3</sub> consisted of a ratio of Mo to Co of 6.5/1, a ratio of Si to Al in HZSM-5 is 43/1 and %Fe loaded on activated carbon is 9.25%. Figure 3.4 to Figure 3.6 illustrated scanning electron micrographs of CoMo/Al<sub>2</sub>O<sub>3</sub>, Fe/AC and HZSM-5 catalysts, respectively at various magnifications.



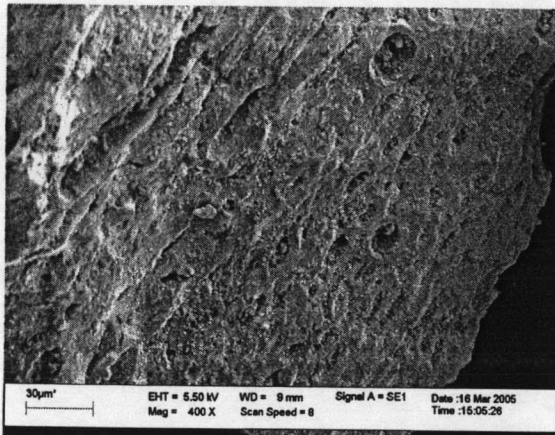
(a)



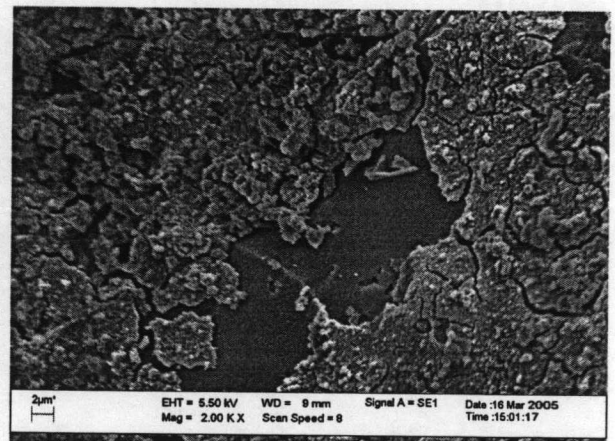
(b)

**Figure 3.4** Scanning electron micrographs of CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst

(a) Magnification 2000 (b) Magnification 3000



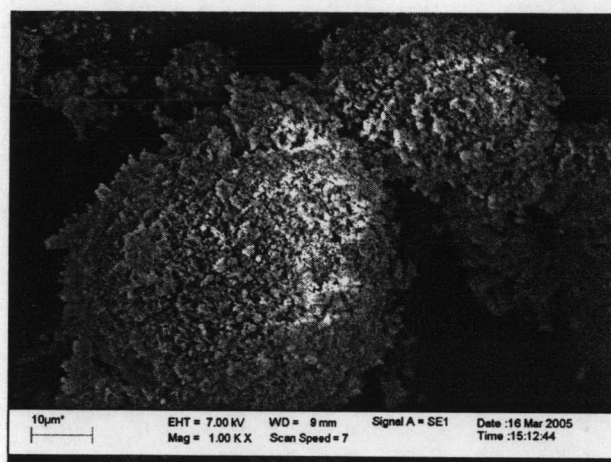
(a)



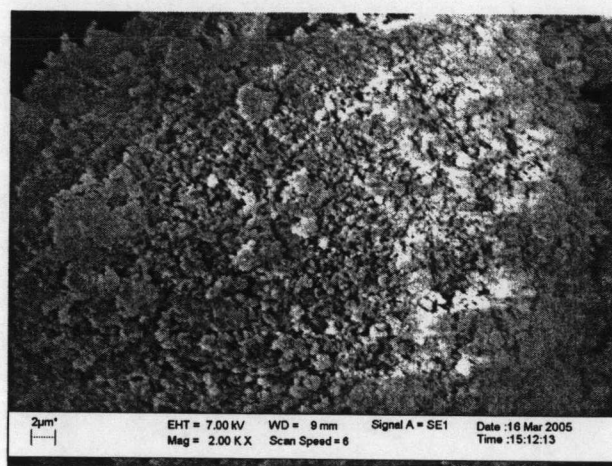
(b)

**Figure 3.5** Scanning electron micrographs of Fe/Ac catalyst

(a) Magnification 400 (b) Magnification 2000



(a)



(b)

**Figure 3.6** Scanning electron micrographs of HZSM-5 catalyst

(a) Magnification 1000 (b) Magnification 2000