CHAPTER III
EXPERIMENTAL

3.1 Materials

A sample, used tire thread from a passenger car (Bridgestone TURANZA GR80), was cut by a cutting machine and then sieved to the particle size range of 20-40 mesh. The life time of this tire was fixed at about 50,000 kilometers.

3.2 Equipments

1. Cutting Tool
2. A hydraulic pellet
3. Sieves, Mesh 20-40 and Mesh 40-60
4. Bench-scale autoclave reactor
5. Gas sampling bag
6. Agilent Technologies 6890, Gas chromatography (GC)
7. Ultrasonic bath
8. Rotary evaporator
9. Liquid chromatography column (Glass), 650 mm height, 26.6 mm inside diameter
10. Vacuum pump
11. Aquariums air pump
12. Varian GC-3800 simulated distillation gas chromatograph (SIMDIST GC)
13. Perkiln Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA)
14. LECO® Elemental Analyzer (TruSpec®S)
15. Sorptomatic 1990 system

3.3 Chemicals and Solvents

1. Benzene (C_6H_6, Assay $\geq$ 99.8 %)
2. Diethyl ether ($(C_2H_5)_2O$, Assay $\geq$ 99.5 %)

3. n-pentane ($CH_3 (CH_2)_3CH_3$, Assay ≥ 99 %)
4. n-hexane ($CH_3 (CH_2)_4CH_3$), Assay ≥ 99 %)
5. Methanol (CH_3OH, Assay ≥ 99.8 %)
6. Carbon disulfide, CS_2
7. Silica for liquid chromatography (Particle size 0.063-0.200; 70-730 mesh ASTM)
8. Neutral alumina for liquid chromatography (0.05-0.15mm; pH 7.0±0.5)
9. N_2 gas
10. HBETA from Tosoh Company, Singapore
11. HY from Tosoh Company, Singapore
12. HZSM-5 from Tosoh Company, Singapore
13. Metal precursors: Palladium (II) nitrate dihydrate ($Pd(NO_3)_2.2H_2O$)

3.4 Experimental Procedures

3.4.1 Catalyst Preparation

3.4.1.1 Peparation of the Zeolite Catalysts

The zeolites (HBETA, HY, HZSM-5) obtained from Tosoh Company in Singapore were calcined in order to remove the organic template from the zeolites. For HBETA zeolite, the calcination took place at 600 °C for 5 hr with heating rate of 2 °C/min, 500 °C for 3 hr with heating rate of 5 °C/min, and 550 °C for 5 hr with heating rate of 10 °C/min for HBETA, HY, and HZSM-5, respectively.

3.4.1.2 Preparation of the Bi-functional Catalysts

The noble metal (Pd) was loaded on the zeolites (HBETA or HY) which act as the supports by using incipient wetness impregnation technique. Initially, the Pd precursor was dissolved by distilled water, and then, the obtained solution was gradually dropped into the zeolites. After that, these samples were dried at 110 °C for 3 hr in the oven, and were calcined at 500 °C for 3 hr with the heating rate of 5 °C/min to obtain the bifunctional catalyst in the oxide form. Finally, the oxide form was converted to the metal form by reduction at 400 °C for 1-2 hr before using in the experiments.

3.4.2 Reaction Equipment

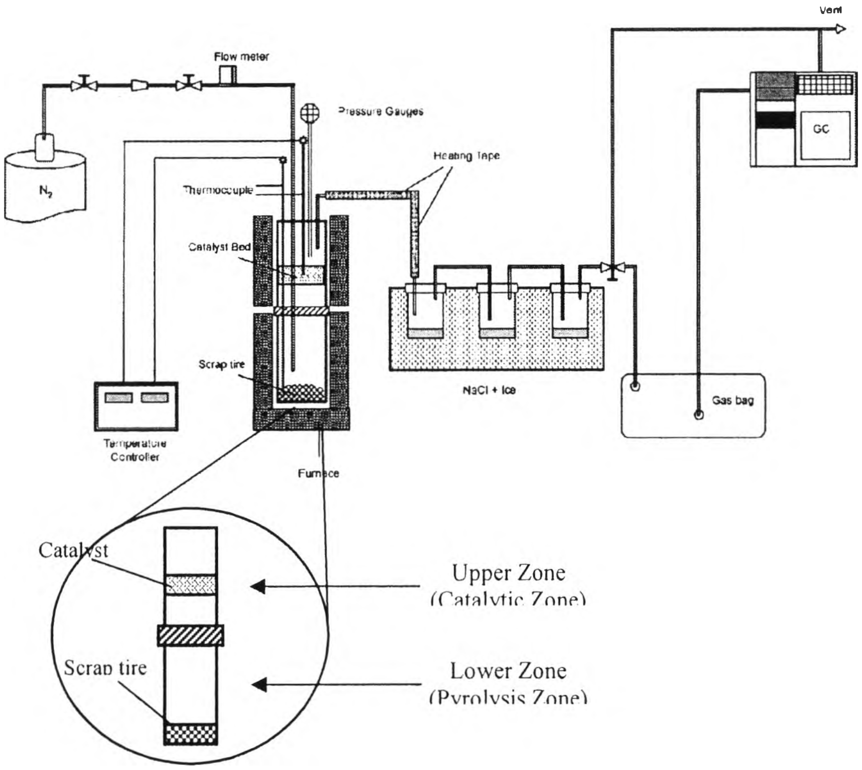

Figure 3.1 Schematic of experimental pyrolysis system (Dũng *et al.*, 2009).

Figure 3.1 shows the schematic of experimental pyrolysis system. The reactor was divided into two zones that are the lower zone (pyrolytic zone) and the upper zone (catalytic zone). The 30 g of a scrap tire sample was introduced to the lower zone of the reactor, while the upper zone contained 7.5 g of pellet catalysts. The temperature of pyrolytic zone was increased from room temperature to a final temperature with heating rate of 10 °C/min. The final temperature of this zone was controlled at 500 °C and kept for 90 minutes at the atmospheric pressure. For the catalytic zone, the temperature was controlled at 300 °C. The controlled N_2 flow rate of 30 ml/min was continuously flown to sweep the oxygen out of the system and to carry the pyrolytic products through a condenser system and a gas sampling bag. The condensers were placed into the ice-bath to collect the condensable products. The non-condensable products were passed through the condensers system and collected in the Tedlar® gas sampling bag.

3.4.3 Catalyst Characterization

3.4.3.1 Surface Area and Pore Size Distribution

The specific surface area, the total pore volume, and the pore size of catalyst were determined by Brunaueer-emmett-Teller (BET) technique and using Thermo Finnigan, Sorptomatic 1990 system. This technique based on the physical adsorption of nitrogen gas at 77 °K. Before starting, the catalyst sample was outgases by heating under vacuum at 300 °C for 6 hours in order to remove moisture. The specific surface area and the pore size of catalyst were obtained from the twenty-two-point nitrogen adsorption and desorption isotherm plot. The pore size distribution was calculated using the BET equation as shown in Equation 1.

$$\frac{1}{W\left(\frac{P}{P_o}-1\right)} = \frac{1}{W_m C} + \frac{(C-1)}{W_m C}\left(\frac{P}{P_0}\right) \qquad (1)$$

Where:

W = weight of gas adsorbed at relative pressure P_o

Wm = weight of adsorbate constituting a monolayer of surface coverage

P = pressure of gas

Po = saturated vapour pressure of the liquid at the operating temperature

C = constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction.

The surface area can be calculated by Equation 2.

$$A = \frac{W_m A_{nitrogen} \times 6.02 \times 10^{23}}{MW_{nitrogen}} \qquad (2)$$

Where:

A = surface area of sample

Anitrogen = cross-section area of one molecule nitrogen (0.162 nm^2 at -196 °C)

$MW_{nitrogen}$ = molecular weight of nitrogen (28 g/g-mol).

3.4.3.2 Thermogravimetric/Differential Thermal Analysis (TG/DTA)

The coke formation on catalysts will be determined by using the Thermogravimetric/Differential Thermal Analysis (TG/DTA). The samples were heated from the room temperature to 800 °C with the heating rate of 10 °C/min. Nitrogen and oxygen set flow rate about 100 ml/min and 200 ml/min, respectively.

3.4.4 Gas Analysis

Pyrolysis gas samples were analyzed by a Gas Chromatography, Agilent Technologies 6890 Network GC system, using HP-PLOT Q column: 30 m x 0.32 mm ID and 20 μm film thicknesses. A detector was FID type using Helium as the carrier gas.

The conditions were as follows:

Initial temperature	70	°C
Time at initial temperature	8	min
Heating rate	20	°C/min to 200 °C
Hold for	16	min
Final temperature	200	°C
Holding time	30	min

3.4.5 Oil Analysis

3.4.5.1 Asphaltene Precipitation

First, n-pentane was added into the oil products at the ratio of 40:1, then the mixture was shaken for 15 min in an ultrasonic bath and left overnight. After that asphaltene was filtrated out using 0.45 μm teflon membranes in a vacuum system. The membrane with the precipitated material was dried in an oven at 60 °C over 6 hours. The filter cake was weighed to determine the asphaltene weight. The n-pentane was evaporated from the solution by a rotary vacuum evaporator in 50 °C to obtain the maltene solution.

3.4.5.2 Maltene Separation (Liquid Adsorption Chromatography)

Liquid chromatography column (650 height x 26.6 mm. I.D.), which silica gel and alumina were packed at the upper and lower bed of the column, was used in this experiment. The column was pre-wetted with n-hexane overnight. The mixture of maltene solution (4.5 g mixed with 10 cm^3 n–hexane) was separated into five fractions according to their functional groups as shown in Table 3.1 by using the liquid chromatography technique. The flow rates of the mobile phases was kept constant at 20 cm^3/min controlled by an aquarium pump. And then the mobile phases (solvents) were separated from the chemical composition by a rotary vacuum evaporator at about 80 °C. After extraction, the adsorbents were dried at 50 °C for 8 hours and regenerated at 160 °C for 48 hours to remove hydrocarbon residuals.

Table 3.1 The optimized compositions and volumes of mobile phases for preparative separation of petroleum maltenes using the chromatographic column (Sebor *et al.*, 1999)

Mobile phase	**Volume (cm^3)**	**Prevailing Compounds Type**
Hexane	600	Saturated hydrocarbons
Hexane-benzene (24:1, v/v)	500	Monoaromatics
Hexane-benzene (22:3, v/v)	500	Diaromatics
Benzene	500	Polyaromatics
Benzene-diethylether-methanol (1:1:3 v/v)	500	Polar aromatic compounds

Finally, each functional group was analyzed by a Varian CP3800 Simulated Distillation Gas Chromatography (SIMDIST GC): ASTM D2887. This method at the following condition;

Initial temperature	30	°C
Time at initial temperature	0.01	min
Heating rate	20	°C/min
Final temperature	320	°C
Holding time	8.50	min

3.4.5.3 Sulfur Content

The percentage composition of sulphur in oil product was performed by using LECO®Elemental Analyzer (TruSpec®S). The 0.1-1 g of liquid oil product is absorbed on an aiding support that is put in a ceramic boat. The final temperature of furnace was raised to 1,350 °C, which the procedure was divided into 2 steps; firstly, the temperature was increased from room temperature to 600 °C and held for 15 min; then it was further ramped to the final temperature of 1,350 °C.