



CHAPTER III EXPERIMENTAL

3.1 Materials

A used passenger car tire for pyrolysis, which life time was fixed at about 50,000 kilometers, was cut in pieces and ground to produce samples with a particle size range of 8-18 mesh.

3.2 Equipment

- a. Bench-scale autoclave reactor
- b. Gas sampling bag
- c. Agilent Technologies 6890, Gas chromatography (GC),
- d. Liquid chromatography column (Glass), 650 mm height, 26.6 mm inside diameter
- e. Varian GC-3800 simulated distillation gas chromatograph (SIMDIST GC)
- f. Varian / SpectrAA 300 (Atomic Absorption Spectrometer, AAS)
- g. Oxford/6111 (Scanning Electron Microscope, SEM)
- h. Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA)
- i. Sieves, Mesh 8-18 and Mesh 40-60
- j. Aquariums air pump

3.3 Chemicals and Solvents

- a. Benzene (C_6H_6 , Assay $\geq 99.8\%$)
- b. Diethyl ether ($(C_2H_5)_2O$, Assay $\geq 99.5\%$)
- c. N-pentane ($CH_3(CH_2)_3CH_3$, Assay $\geq 99\%$)
- d. N-hexane ($CH_3(CH_2)_4CH_3$, Assay $\geq 99\%$)
- e. Methanol (CH_3OH , Assay $\geq 99.8\%$)
- f. Carbon disulfide, CS_2
- g. Silica for liquid chromatography (Particle size 0.063-0.200 ; 70-730 mesh ASTM)
- h. Neutral alumina for liquid chromatography (0.05-0.15mm ; pH 7.0 ± 0.5)

- i. N₂ gas
- j. Beta Zeolite Catalysts from Tosoh Company, Singapore
- k. Metal precursor, Palladium (II) nitrate dehydrate (Pd(NO₃)₂·2H₂O)

3.4 Methodology

3.4.1 Catalyst Preparation

First, Beta zeolite obtained from Tosoh Company in Singapore was calcined at 600°C for 5 hours with the heating rate of 2°C/min to remove the organic template from the zeolites. After that, palladium (Pd) was loaded on the zeolites by using the incipient wetness impregnation and ion exchange technique.

An appropriate amount of palladium (II) nitrate hydrate (Pd(NO₃)₂·2H₂O) dissolved in distilled water was dropped onto calcined zeolites. And then, the impregnated catalyst was allowed to stand for 3 hours at room temperature. After that the sample was dried in oven at 110°C for 3 hours. Finally, this catalyst was calcined in a furnace at 500°C for 3 hours with the heating rate of 5°C/min to obtain bifunctional catalysts in oxide forms. This catalyst was reduced with H₂ at 400°C for 1-2 hours due to convert the metal oxide forms to metal elements before using in the experiments.

For an ion-exchanged catalyst, the calcined zeolites was kept under agitation at room temperature for 8 hrs in the solution of Pd(NO₃)₂·2H₂O. Next, the suspension was filtered and thoroughly washed with deionized water. The final catalyst was dried overnight at 110 °C and then calcined at 500 °C for 2 hour. Finally, the catalyst was reduced with the same condition of impregnated Pd /H-Beta zeolite.

3.4.2 Pyrolysis Process

The reactor and the diagram of tire pyrolysis in the experiment are shown in Figures 3.1. The reactor is separated into 2 zones: the lower zone is pyrolysis zone where waste tire is loaded and the upper zone is catalytic zone as shown in Figure 3.1

The catalyst powder was pelletized and sieved to the particle size between 300 to 425 μm . Then, it was loaded to the reaction zone of the reactor. For pyrolysis zone, The temperatures was increased from room temperature to final temperatures with heating rate of $10^\circ\text{C}/\text{min}$. The final temperature of pyrolysis zone was controlled at 500°C and kept for 90 minutes at the atmospheric pressure. At 500°C , the all composition in tire sample was completely decomposed to lower molecular weight products (Miguel et al, 2006). In the bottom zone or catalytic zone of pyrolysis reactor, the temperature was varied in the range between 350 to 450°C .

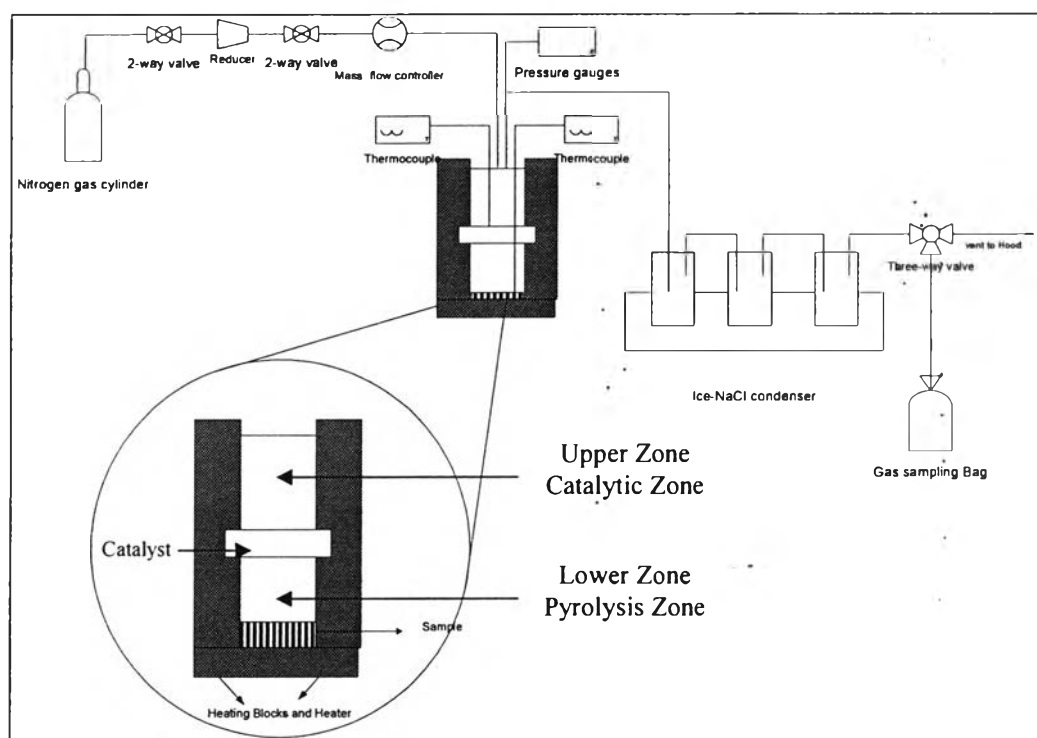


Figure 3.1 Schematic diagram of the pyrolysis process (Mhodmonthin, 2005)

The N_2 flow rate was flown to sweep the pyrolysis products to condensers and a gas sampling bag. The condensers were placed into the iced-bath to collect the condensable products. The non-condensable products or gaseous products were passed through the condensers and be collected in the gas sampling bag.

3.4.3 Oil Analysis

The oil products obtained from the pyrolysis process were classified into two steps as shown Figure 3.2;

3.4.3.1 Asphaltene Precipitation, and

3.4.3.2 Maltene Separation (Liquid Adsorption Chromatography).

3.4.3.1 Asphaltene Precipitation

For asphaltene precipitation, n-pentane was added into the oil products at the ratio of 40:1 before shaking 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 a oven at 100°C over 6 hrs. Finally, 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.

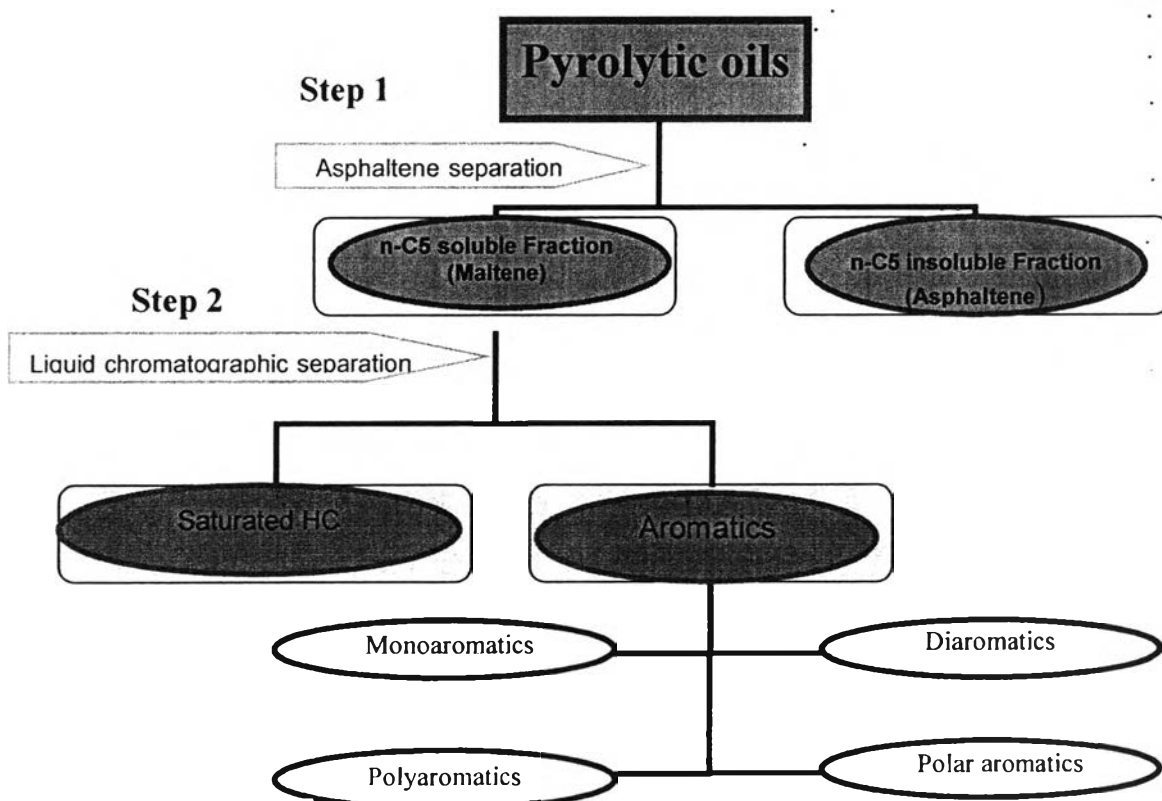


Figure 3.2 The schematic diagram of the oil analysis. (Mhodmonthin, 2005).

3.4.3.2 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. After that the mixture of Maltene solution (4.5 g mixed with 10 cm³ 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 were kept constant at 20 cm³/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 110°C for 8 hours and generated at 160°C for 48 hr 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 were analyzed by a Varian CP3800 Simulated Distillation Gas Chromatography (SIMDIST GC): ASTM D2887

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 He as the carrier gas.

3.4.5 Catalyst Characterization.

3.4.5.1 *Atomic Absorption Spectrometer (AAS)*

The amounts of palladium (Pd) metal loading on zeolite were obtained by using Atomic Absorption Spectrometer (Varian, SpecterAA 300 model). Aqua regia (3 HCl : 1 HNO₃) was used to digest the ion-exchanged catalyst.

3.4.5.2 *X-ray Diffraction Spectroscopy (XRD)*

X-ray diffraction (XRD) patterns were taken by using a Rigaku, Rint X-Ray diffractometer system (RINT 2200) with Cu tube for generating CuK α radiation (1.5406 Å) and nickel filter. In this experiment, XRD was employed to obtain the structure of catalysts and metal dispersion on zeolite supports. A catalyst sample was ground to fine and homogeneous particles, and then packed in glass specimen holder. The data from XRD were analyzed and recorded by an on-line computer.

3.4.5.3 *Surface Area and Pore Size Distribution*

The specific surface area and the pore size of catalyst were determined by Brun-aueer-emmett-Teller (BET) technique and using Thermo Finnigan, Sorptomatic 1990. This technique was based on the physical adsorption of nitrogen gas at 77°K. 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 BJH method.

3.4.5.4 *Temperature Programming Oxidation (TPO)*

Temperature Programming Oxidation can be used to determine the amount and characteristics of coke which deposits on the spent catalysts. The spent catalysts were weight with suitable amounts and placed in the quartz tube. 5% O₂/He was flown through the spent catalyst, while the temperature linearly increased with the heating rate of 10°C/min. The coke was oxidized and the carbon dioxide was generated. This gas was monitored by TCD detector. The exact amount to oxidized coke was calibrated using the pulses of pure CO₂.

3.4.5.5 *Transmission Electron Microscope (TEM)*

Electron microscopy measurements were performed by using a JEM 2100 Transmission electron microscope (TEM) equipment which operated an accelerating at 200 kV. The sample were prepared by grinding, ultrasonically dispersing in acetone. And then a drop of suspension were evaporated and put on the copper grid. The TEM image were recorded and calculated the particle size diameters from equation $d_{avg} = \sum (n_i d_i) / \sum n_i$.