



CHAPTER III EXPERIMENTAL

3.1 Materials

A used passenger car tire with a life time of about 50,000 kilometers for pyrolysis 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. Varian GC-3800 simulated distillation gas chromatograph (SIMDIST GC)
- c. Liquid chromatography column (Glass), 650 mm height, 26.6 mm inside diameter
- d. Gas chromatography (GC)
- e. Oxford/6111 (Scanning Electron Microscope, SEM)
- f. Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA)
- g. Thermo Finigan TPDRO 1100 (Temperature Programmed Reduction/Oxidation)
- h. RINT-2200 Rigaku X-Ray diffractometer system (X-Ray Diffraction, XRD)
- i. Sorptomatic 1990 system
- j. Gas sampling bag
- k. Aquariums air pump
- l. Sieves, Mesh 8-18 and Mesh 40-60

3.3 Chemicals and Solvents

- a. N-pentane ($\text{CH}_3(\text{CH}_2)_3\text{CH}_3$, Assay $\geq 99\%$)

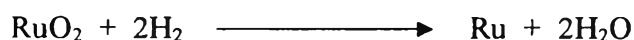
- b. N-hexane ($\text{CH}_3(\text{CH}_2)_4\text{CH}_3$), Assay $\geq 99\%$
- c. Carbon disulfide, CS_2
- d. Silica for liquid chromatography (Particle size 0.063-0.200 ; 70-730 mesh ASTM)
- e. Neutral alumina for liquid chromatography (0.05-0.15mm ; pH 7.0 ± 0.5)
- f. Benzene (C_6H_6 , Assay $\geq 99.8\%$)
- g. Diethyl ether ($(\text{C}_2\text{H}_5)_2\text{O}$, Assay $\geq 99.5\%$)
- h. N_2 gas
- i. Methanol (CH_3OH , Assay $\geq 99.8\%$)
- j. Catalysts from Tosoh Company, Singapore : HMOR
- k. Metal precursors: Ruthenium (III) chloride hydrate ($\text{RuCl}_3 \cdot \text{aq}$)

3.4 Methodology

3.4.1 Catalyst Preparation

The zeolite catalysts (HMOR and HZSM5) obtained from Tosoh Company, Singapore were calcined at 500°C for 3 hours with the heating rate of $5^\circ\text{C}/\text{min}$. After that, these zeolites were loaded with ruthenium by using the incipient wetness impregnation technique. Firstly, the salt solution of ruthenium was dropped on an individual zeolite. And then, the sample was dried in oven at 110°C for 3 hours. Finally, the catalyst was calcined in a furnace at 500°C for 3 hours with the heating rate of $5^\circ\text{C}/\text{min}$ to obtain the bifunctional catalyst in an oxide form.

The catalysts were reduced with H_2 at 400°C for 1-2 hrs in order to convert the metal oxide form to metal element before using in the experiments as shown below.



3.4.2 Pyrolysis Process

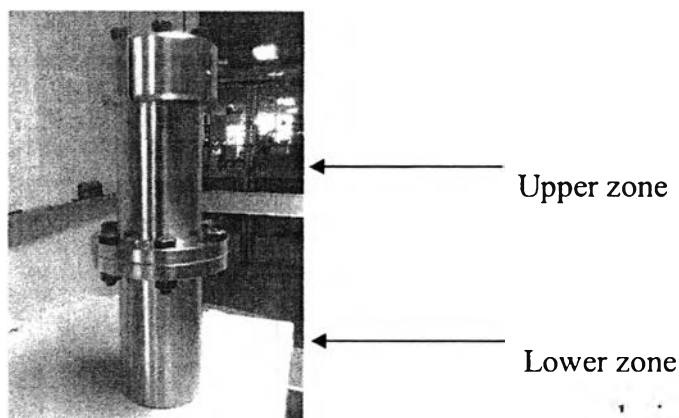


Figure 3.1 The autoclave reactor used in the experiment (Choosuton, 2007).

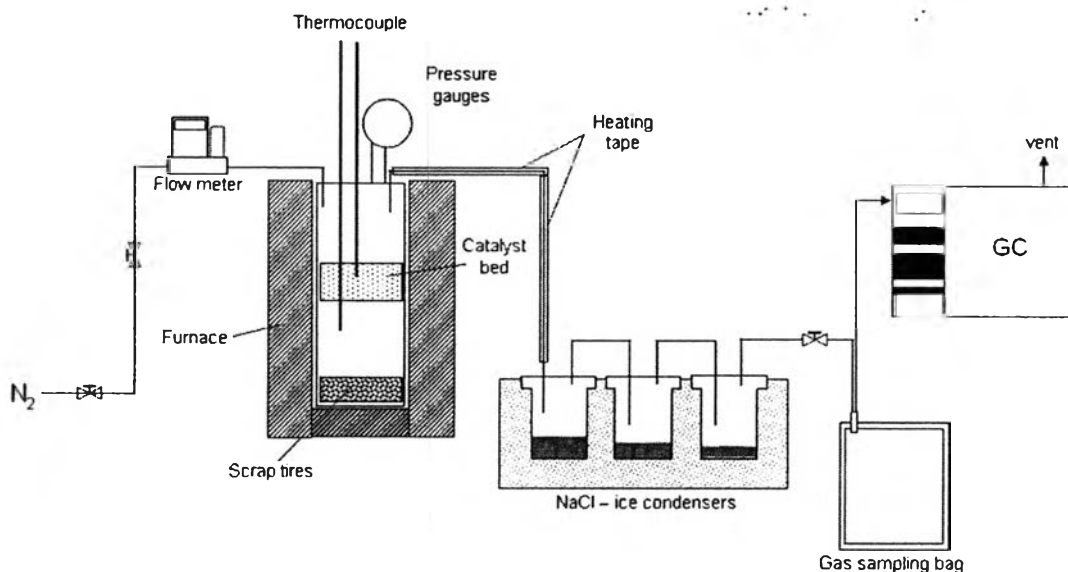


Figure 3.2 The diagram of the pyrolysis process.

Figures 3.1 and 3.2 show the pyrolysis reactor and schematic diagram for tire pyrolysis. The reactor is separated into 2 zones: the upper zone is catalytic zone and the lower zone is pyrolysis zone where waste tires are loaded. The total volume of the reactor is 750 ml and separates the volume by 400 and 350 ml for pyrolysis

zone and catalytic zone, respectively. The catalyst powder was pelletized and sieved to the particle size between 300 to 425 μm . Then, it was loaded to the upper bed of the reactor. The final temperature of the upper zone was 300°C, and the lower zone was varied from 400 to 700°C. The reactor was heated from room temperature to final temperatures with the ramping rate of 10°C/min and kept for 90 minutes at the atmospheric pressure. The N₂ gas with various flow rates varied from 10 to 30 ml/min is flown to sweep the pyrolysis products to condensers and a gas sampling bag. The condensers were placed into the iced-bath in order to collect the condensable products, therefore, non-condensable products or gaseous products were passed from condensers to the Tedlar gas sampling bag. The pyrolysis residue and liquid were weighted to determine yields. Pyrolysis gas yield was determined by the difference from liquid and solid for all runs.

3.4.3 Oil Analysis

The condensed liquids obtained from the pyrolysis process were collected in the glass condensers. The components have been classified into two steps as

a) Asphaltene Precipitation

For asphaltene precipitation, n-pentane was added into the oil products at the ratio of 40:1 before being shaken for 15 min in an ultrasonic bath and left overnight. After that, the asphaltene was filtrated out by a vacuum system. The filter membrane with the precipitated material was dried in a vacuum oven at 0.1 barg and 60 °C for 6 hrs. Then, the weight of asphaltene was determined. Finally, n-pentane was evaporated from the solution by a rotary vacuum evaporator to obtain the maltene solution.

b) Maltene Separation Using Liquid Adsorption Chromatography

For maltene separation, 4.5 g of maltene was mixed with 10 cm³ n-hexane and then separated into five fractions according to their functional groups (as shown in Table 3.1) by using liquid chromatography column. (650 height x 26.6 mm. I.D.) The column was filled with silica gel packed at the upper column and alumina packed at the lower column. The column was prewetted with n-hexane, and the neutral alumina was activated at 400°C for 8 hrs before used. The flow rates of

the mobile phases were kept constant at 20 cm³/min and control by an aquariums air pump. And then the mobile phases (solvents) were separated from the chemical composition by a rotary vacuum evaporator at about 80°C and a pressure of 4.4 kPa. After extraction, the adsorbents were dried at 50°C for 8 hrs. And then they were regenerated to remove hydrocarbon residuals.

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

Mobile phase	Volume (cm ³)	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, a SIMDIST GC was used to determine the boiling point distributions of hydrocarbons according to ASTM D2887 method at the following conditions;

Initial temperature	30	°C
Heating rate	20	°C/min
Final temperature	320	°C

3.4.4 Gas Analysis

The pyrolysis gas stream that leaves the condensers 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 is FID type using Helium as the carrier gas in order to detect the hydrocarbon components. The conditions were as follows:

Initial temperature	70	°C
Heating rate	20	°C/min to 200°C
Final temperature	200	°C

The integration of the peak from chromatogram can be used to estimate the percent weight and the concentration of components in gaseous products.

3.4.5 Catalyst Characterization

(a) Surface Area Measurement (BET)

The surface area, total pore volume, and average pore size diameter of the catalyst sample were determined by using the Brunauer-Emmer-Teller (BET) method. These characterizations are based on the physical adsorption of nitrogen gas through the Sorptomatic 1990 system at liquid nitrogen temperature of -196°C. The pore size distribution was calculated by using the BJH method.

(b) Transmission Electron Microscopy (TEM)

The electron microscopy (JEM 2100) was used to identify the microstructure of the samples. The sample was 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 $d_{avg} = \sum (n_i d_i) / \sum n_i$.

(c) Powder X-ray diffraction (XRD)

The XRD measurements were carried out with a RINT 2000 diffractometer (Rigaku) using Cu K α radiation. The sample in the powder form was packed as a thin layer into a shallow sample holder backed with a glass slide. The XRD patterns were recorded at a rate of 5 min⁻¹ with a step size $2\theta = 0.02$.