CHAPTER III
METHODOLOGY

3.1 Materials

Waste tires were cut in pieces and ground to be samples in the particle size range of 20-40 mesh (425-850 μm).

3.2 Equipment

1. Grinding Machine
2. Bench-Scale Autoclave Reactor
3. Thermo Finigan TPDRO 1100, Temperature Programmed Desorption/Reduction/Oxidation
4. RINT-2200 Rigaku X-Ray Diffractometer System, X-Ray Diffraction (XRD)
5. Thermo Finnigan Sorptomatic 1990, Surface Area Analyzer
6. LECO®Elemental Analyzer (TruSpec®S)
7. Agilent Technologies 6890, Gas Chromatography (GC)
8. Varian GC-3800, Simulated Distillation-Gas Chromatograph (SIMDIST-GC)
9. Gas Chromatography-Mass Spectrometry, Time of Flight (GC-TOF)
10. PerkinElmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA)
11. Varian/SpectraAA 300 (Atomic Absorption Spectroscopy, AAS)
12. X-Ray Photoelectron Spectroscopy (XPS)
13. Water Bath
14. Gas Sampling Bag
15. Hydraulic Pelletizer
16. Ultrasonic Bath
17. Rotary Evaporator
18. Sieves (20, 40 and 60 U.S. Mesh (ASTM))

3.3 Chemicals and Solvents

1. Metal precursors: Copper (II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) and Zinc (II) nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$)
2. Supports from Tosoh Company, Singapore: BETA, Y, MOR and KL zeolites
3. *n*-pentane ($CH_3(CH_2)_3CH_3$, Assay $\geq$ 99 %)
4. Carbon disulfide (CS_2)
5. High purity nitrogen and hydrogen gases

3.4 Experimental Procedures

3.4.1 Catalyst Preparation

The MOR, Y, KL zeolites obtained from Tosoh Company, Singapore, was calcined in a furnace at 500 °C for 3 hr with the heating rate of 5 °C/min (MOR and Y) and 10 °C/min (KL) to remove organic templates and some impurities. The BETA zeolite obtained from the same company was calcined in the furnace at 600 °C for 5 hr with the heating rate of 2 °C/min, and then the calcined zeolite was impregnated with the solution of a metal precursor, $Cu(NO_3)_2.3H_2O$ or $Zn(NO_3)_2.6H_2O$. After that, the catalysts were dried in an oven at 110 °C for 3 hr and calcined in the furnace at the same conditions of fresh zeolites. Then, the Cu- and Zn-loaded catalysts were reduced in hydrogen atmosphere at 600 °C and 500 °C, respectively, for 2 hr with the heating rate of 10 °C/min. Finally, the last step was to pelletize, crush and sieve the catalysts to the particle size in the range of 40-60 mesh (250-425 μm).

3.4.2 Pyrolysis Process

The pyrolysis process was shown in Figure 3.1. The reactor was divided into two zones: the lower zone was the pyrolysis zone where waste tire sample was placed, and the upper zone was the catalytic zone where a catalyst was packed. The reactor was heated from room temperature with 10 °C/min to the final temperature at 500 °C and 350 °C for lower and upper zones, respectively, and kept for 120 min at atmospheric pressure. Nitrogen gas was flown all the time at a flow

rate of 30 ml/min to sweep the pyrolysis products to condensers and a gas sampling bag. The condensers were immersed in an ice-salt bath to collect the condensable products while the non-condensable products were passed through the condensers and collected by the gas sampling bag.

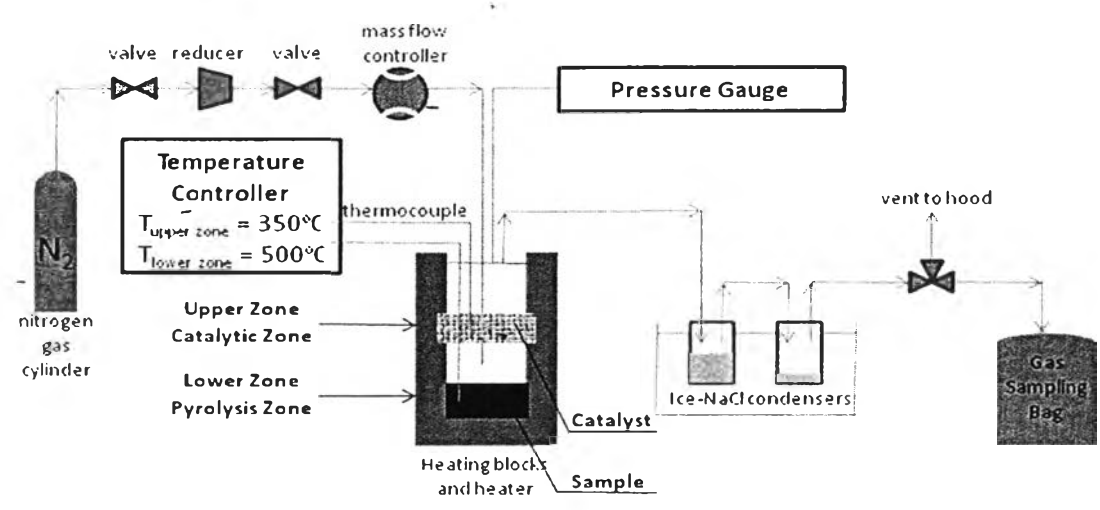

Figure 3.1 Schematic of the pyrolysis process.

3.4.3 Gas Analysis

Gas Chromatography, Agilent Technologies 6890 Network GC system, using HP-PLOT Q column: 30 m × 0.32 mm internal diameter (ID) and 20 μm film thicknesses, FID detector and He carrier gas, was used to analyze the composition of pyrolysis gas products. The conditions are shown below:

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

3.4.4 Oil Analysis

An oil product obtained from the pyrolysis process was mixed with the *n*-pentane at the weight ratio of 40:1. Then, the mixture was sonicated at room temperature for 15 min in an ultrasonic bath before leaving overnight. After that the asphaltene was filtered out by using 0.45 μm a teflon membrane in a vacuum system. The membrane and asphaltene were dried in an oven at 60 °C for 6 hr and weighed to determine the asphaltene content. Then, the *n*-pentane was evaporated from the maltene solution obtained after filtering by using a rotary vacuum evaporator at 50 °C. The remained oil was analyzed by using the LECO®Elemental Analyzer for sulfur content. The maltene was also diluted with carbon disulfide before analyzing by SIMDIST-GC and GC×GC-TOF/MS.

3.4.4.1 Simulated Distillation-Gas Chromatography (SIMDIST-GC)

The maltene was analyzed for simulating true boiling point curves using a Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC) equipped with a 15 m × 0.25 mm × 0.25 μm WCOT fused silica capillary column and FID. The maltene was analyzed according to the ASTM D2887 method with the conditions below:

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

3.4.4.2 Gas Chromatography-Mass Spectrometry, Time of Flight (GC×GC-TOF/MS)

Gas Chromatography-Mass Spectrometry (GC×GC-TOF/MS) was used to analyze the maltene compositions and average carbon numbers. GC×GC-TOF/MS apparatus equipped an Agilent gas chromatograph 7890 (Agilent Technologies, Palo Alto, CA, USA), a Pegasus® 4D TOF/MS (LECO, St. Joseph, MI, USA) and a thermal modulator was used to analyzed oil compositions.

The instrument operated by the cooperation of two GC columns (Thames Restek, Sounderton, UK). The 1st GC column is a non-polar Rtx®-5Sil MS, 30 m × 0.25 mm ID × 0.25 μm film thickness, that it was operated at the temperature of 50 °C which was held for 2 min at the beginning of analysis and ramped to 310 °C with 5 °C/min, and held at the final temperature for 10 min. The 2nd GC column is an Rxi®-17 MS, 1.10 m × 0.10 mm ID × 0.10 μm film thickness, that it was started at 60 °C held for 2 min and heated to 320 °C with 5 °C and held for 10 min when the final temperature was reached. Maltene solution samples were prepared by adjusting 1 μL of maltene with CS_2 into 2 mL, and analyzed by injecting them into the instrument via a splitless injector operated at 250 °C using 1.0 mL/min of helium as a carrier gas. The modulator timing condition was set at the cycle time of 4 s and holding time of 0.5 s in the release position. Nitrogen (UHP) was used as a cryogen coolant set at least -80 °C of the modulation trap temperature. The TOF/MS instrument using the electron impact ionization of -70 V was used to provide mass spectral data collected in the range of 35 to 500 m/z with the data transfer of 100 spectra per second. The temperatures of ion source and detector voltage were operated at 250 °C and 1,600 V, respectively. The transfer line was heated to 250 °C. The Signal/Noise value of data processing was set at 10. The LECO ChromaTOF® software was used to recorded and analyzed data, and spectral searching can be provided by the NIST library.

3.4.4.3 Elemental Analyzer

A ceramic boat filled with nickel boat was added with com-aid and 0.1 gram of an oil sample, and then the ceramic boat was put in the LECO®Elemental Analyzer. The temperature of furnace was raised from room temperature to 600 °C and held for 15 min in the first step, and then raised again to 1,350 °C in the analyzing step.

3.4.5 Residual Char Analysis

After the end of pyrolysis process, the residual char was weighed for calculating the conversion of waste tire. To find the sulfur content and calculate the sulfur balance, 0.2 gram of residual char was added on the ceramic boat, and then the boat was put in the LECO®Elemental Analyzer operated at the same conditions as in the oil analysis.

3.4.6 Catalyst Characterization

3.4.6.1 X-Ray Diffraction (XRD)

XRD patterns of catalysts were determined using Riguku/Rint2200 HV. For characterization procedures, a catalyst sample in powder form was packed in a glass specimen holder that was placed in the goniometer using CuK_α small radiation (1.5406 Å) operating at 40 kV and 30 mA. The XRD patterns were recorded from 5° to 65° of 2θ with a step size 2θ = 0.02° at the scanning speed of 5°/min

3.4.6.2 Thermo Finnigan Sorptomatic 1990 (Surface Area Analyzer)

The catalyst samples, before and after loading metals, were determined for their specific surface area and total pore volume by using Thermo Finnigan Sorptomatic 1990. At the first step, the glass tube containing a sample was out-gassed to eliminate some volatile adsorbents on the catalyst surface at 300 °C for 5hr. After that helium gas was flown into the tube as a blank analysis. The specific surface area and total pore volume were obtained from calculating the amount of nitrogen physisorption on the catalyst surface.

3.4.6.3 Elemental Analyzer

The sulfur content on the spent catalysts was determined using elemental analyzer. The characterization was operated at similar conditions to residual char analysis as mentioned above.

3.4.6.4 Thermogravimetric/Differential Thermal Analysis (TG/DTA)

PerkinElmer/Pyris Diamond TG/DTA was used to determine the amount of coke deposited on the catalysts. The approximately 8 mg of a spent catalyst sample was loaded on a sample pan, and then the sample was heated from room temperature to 900 °C with the heating rate of 10 °C/min and oxygen flow rate of 20 ml/min.

3.4.6.5 Temperature Programmed Reduction (TPR)

Thermo Finigan TPDRO 1100 was used to determine metal-support interaction of the catalysts. A catalyst was weighed and placed in the quartz tube. The instrument recorded TPR profiles from room temperature to 950 °C under 4.99 % H_2/N_2 flow at 20 ml/min.

3.4.6.6 Temperature Programmed Desorption (TPD)

Thermo Finigan TPDRO 1100 was used to determine basicity of the KL, Cu/KL, and Zn/KL catalysts. A catalyst was weighed and placed in the quartz tube. The catalyst adsorbed 99.999 %CO_2 at room temperature for 30 min. The instrument recorded CO_2-TPD profiles from room temperature to 600 °C under 99.999 % He flow at 10 ml/min with heating rate of 10 °C/min.

3.4.6.7 X-Ray Photoelectron Spectroscopy (XPS)

XPS spectra were carried out using an AXIS ULTRADLD to determine the species of metal in a fresh catalyst. The system was equipped with a monochromatic Al X-ray source and a hemispherical analyzer. The spectrometer was operated with the pass energy of 160 eV and 40 eV when recording wide scan and core level spectra, respectively. All peaks were calibrated from referring C1s spectra located at 284.6 eV.

3.4.6.8 Atomic Absorption Spectrometer (AAS)

The metal loading on zeolites were determined by using Atomic Absorbtion Spectrometer (Varian, SpecterAA 300 medel) ULTRADLD. A sample was digested with an acid solution (1 conc. HCl: 1 conc. HF: 1 conc. H_2O) to a solution of the metal element.