

## CHAPTER III EXPERIMENTAL

### 3.1 Materials and Equipments

#### 3.1.1 Waste Tire Sample

Passenger car tire (Bridgestone TURANZA GR-80) samples were prepared by a cutting machine and then sieved into the particle size range of 20-40 mesh.

#### 3.1.2 Equipments

1. Cutting Tool
2. Sieves, Mesh 20-40 and Mesh 40-60
3. Gas sampling bag
4. Rotary evaporator
5. Bench-scale reactor
6. Hydraulic pellet
7. Vacuum pump
8. Ultrasonic bath
9. Agilent Technologies 6890, Gas chromatography (GC)
10. LECO<sup>®</sup> Elemental Analyzer (TruSpec<sup>®</sup>S)
11. X-ray Fluorescence (XRF)
12. Thermo Finigan TPDRO 1100 (Temperature Programmed Desorption / Reduction / Oxidation)
13. X-ray Diffraction (XRD)
14. Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC)
15. Two-dimensional Gas Chromatography - Mass Spectrometry with Time of Flight (GC×GC-TOF/MS)

#### 3.1.3 Chemicals and Solvents

1. *n*-pentane (CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, Assay ≥ 99 %)
2. Acetone
3. Carbon disulfide, CS<sub>2</sub>

4. Nitrogen gas
5. Helium gas
6. Air zero
7. HMOR (Si/Al = 9.5) from Tosoh Company, Singapore
8. HBeta (Si/Al = 13.5) from Tosoh Company, Singapore
9. HZSM-5 (Si/Al = 15) from Tosoh Company, Singapore
10. KL (Si/Al = 3) from Tosoh Company, Singapore
11. Metal precursors: Iron(III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ )
12. Metal precursors: Cobalt(II) nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ )

## 3.2 Experimental Procedures

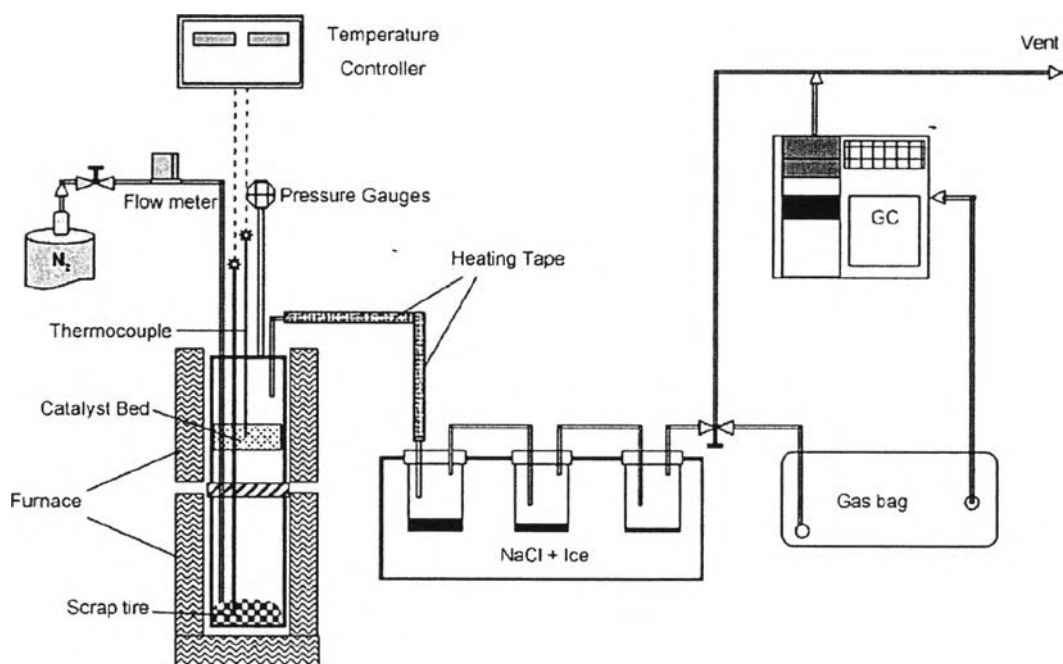
### 3.2.1 Catalyst Preparation

All zeolites (HMOR, HBeta, KL, and HZSM-5) were obtained from Tosoh Company in Singapore and Zeolyst International. In order to remove impurity from the zeolite, HMOR and HZSM-5 zeolites were calcined at 500 °C for 3 h with the heating rate of 10 °C/min. HBeta was calcined at 600 °C for 5 h with 2 °C/min., and KL was calcined at 500 °C for 3 h at 10 °C/min. Then, Co and Fe were loaded on the zeolite using incipient wetness technique. In this technique, an appropriate amount of iron(III) chloride hydrate hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) solution and cobalt (II) nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) solution were dropped on a zeolite to 5 wt.% loading. After that, the catalysts were dried at 100 °C for 3 h in an oven, and then calcined at 500 °C for 3 h in a furnace. The zeolite powders were pelletized, crushed, and sieved into the particle size range of 400-425  $\mu\text{m}$ . Finally, they were reduced at 800 °C for 2 h with  $\text{H}_2$  to convert the metal oxide forms to a metal element.

### 3.2.2 Reaction Equipment

There are 2 zones of the pyrolysis reactor, which are catalytic zone (the upper zone) and pyrolytic zone (the lower zone). Firstly, 30 g of the waste tire with sizes in the range of 20-40 mesh was loaded into the lower zone, and 7.5 g of pellet catalyst with sizes in the range of 40-60 mesh was loaded to the catalytic zone.

Then, the pyrolysis zone was heated with the rate of 10 °C/min from the room temperature to 500 °C, and then kept for 120 min at the atmospheric pressure. The temperature of pyrolysis zone was controlled at 350 °C. The flow rate of N<sub>2</sub> was controlled at 30 ml/min, continuously flown to purge the oxygen out of the system prior to pyrolysis and subsequently for carrying the pyrolysis products to condensers and a gas sampling bag. These condensers were placed into an ice bath in order to collect the condensable products. A gas sampling bag collected the non-condensable products.



**Figure 3.1** Diagram of the pyrolysis process (Dũng *et al.*, 2009b).

### 3.2.3 Catalyst Characterization

#### 3.2.3.1 X-ray Diffraction (XRD)

X-ray Diffraction (XRD) was used to verify the metallic form of the catalysts. X-ray diffraction (XRD) patterns were taken by using a Bruker X-ray diffractometer system (D8 Advance) equipped with a 2.2 kW Cu anode long in a long fine focus ceramic X-ray tube for generating a CuK $\alpha$  radiation (1.5405 Å). The detector scanned the peak position from the sample as a function of  $2\theta$  by starting at

the 5 ° to 100 ° (2 $\theta$ ) range and a scan speed of 5 °(2 $\theta$ )/min. The XRD patterns were matched to the standards to identify crystalline phases by using a PDXL2.

### 3.2.3.2 Temperature-Programmed Reduction (TPR)

Temperature-programmed reduction (TPR) is used to identify the reducibility of the impregnated catalysts and the metal-metal interaction. The temperature was ramped from 30 °C to 850 °C with a heating rate of 10 °C/min.

## 3.2.4 Product Analysis

### 3.2.4.1 Oil Analysis

#### i Asphaltene Precipitation

*n*-pentane was added into the oil product at the ratio of 40:1, and subsequently the mixture was shaken in an ultrasonic bath for 15 min at 30 °C and then left overnight. After that 0.45  $\mu$ m Teflon was used to filter the asphaltene in a vacuum system. The membrane with precipitated material was dried in an oven at 100 °C over 3 hours. Finally, the asphaltene was weighed. The solution after filtration was evaporated by a rotary vacuum at 37 °C; thus, *n*-pentane was evaporated to obtain a maltene solution.

#### ii Simulated Distillation Gas Chromatography

All functional groups (saturated hydrocarbons, mono-aromatics, di-aromatics, poly-aromatics, and polar-aromatics) were analyzed by a Varian CP-3800 simulated distillation gas chromatography (SIMDIST-GC), using ASTM D-2887 method based on true boiling point distillation. The liquid sample was injected to a SIMDIST-GC after dilution with carbon disulphide (CS<sub>2</sub>). The condition was set as follows:

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

iii Comprehensive Two-Dimensional Gas Chromatography with Time of Flight Mass Spectrometry (GC $\times$ GC-TOF/MS)

The hydrocarbon species containing in maltenes were identified by using Gas Chromatography-Mass Spectrometry (Agilent<sup>®</sup> 7890A), Time of Flight (PEGASUS<sup>®</sup>4D), with 2D dimension mode (GC×GC-TOF/MS). Helium was used as carried gas, and nitrogen was used in the cooling system. The conditions were set as follows:

1 <sup>st</sup> Column: Rtx 5, 30 m × 0.32 mm × 1.0 μm film thickness	
2 <sup>nd</sup> Column: Rtx 17, 1.8 m × 0.18 mm × 0.2 μm film thickness	
Helium flow rate	1.5 ml/min
Inlet temperature	250 °C
Time at initial temperature	2 min
Heating rate	5 °C/min to 270°C
Hold for	5 min
Electron impact ionization energy	70 eV

#### iii Sulfur content

The sulfur content in oil, char, and on spent catalyst were determined by using a LECO<sup>®</sup> Elemental Analyzer (TruSpec<sup>®</sup>S). 0.1 g oil and 1.0 g aid support were put in a ceramic boat, or 0.2 g char or spent catalyst was put in ceramic boat. The temperature of furnace was ramped two steps to 1,350 °C.

#### 3.2.4.2 Gas Analysis

A gas sample from pyrolysis (non-condensable gas) was kept in a gas sampling bag, and then was analyzed by using a Gas Chromatography, Agilent Technologies 6890 Network GC system, using HP-PLOT Q column: 30 m × 0.32 mm ID and 20 μm film thicknesses. FID was used as a type of detector with He as the carrier gas. The conditions were set 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
Cool down	50 °C