

## CHAPTER III EXPERIMENTAL

### 3.1 Material

The side wall of a used automobile tire sample for pyrolysis, Bridgestone TURANZA GR-80, was first scraped and then sieved into a particle size range of 8-18 mesh.

### 3.2 Equipment

1. Grinding machine
2. Sieves, Mesh 8-18 and Mesh 40-60
3. Hydraulic pelletizer
4. Bench-scale autoclave reactor
5. Gas sampling bag
6. Ultrasonic Bath
7. Rotary evaporator
8. Aquariums air pump
9. Vacuum Pump
10. Liquid Chromatography Column (Glass), 650 mm height, 26.6 mm inside diameter
11. Agilent Technologies 6890, Gas chromatography (GC)
12. Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC)
13. Gas Chromatography-Mass Spectrometry, Time of Flight (GC-MS (TOF))
14. LECO® Elemental Analyzer (TruSpec®S)
15. X-ray fluorescence spectrometry (AXIOS PW4400)
16. Thermo Finnigan Sorptomatic 1990 (Surface Area Analyzer)
17. Temperature Programmed Desorption of isopropylamine (IPA-TPD)
18. Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA)

### 3.3 Chemicals and Solvents

1. Metal precursors, Rhodium(III) chloride hydrate, 38%Rh
2. Support KL, HY, HBETA
3. Spent NiMoS/Al<sub>2</sub>O<sub>3</sub> and fresh CoMoS/Al<sub>2</sub>O<sub>3</sub> commercial catalysts obtained from the hydrodesulfurization unit of a refinery in Thailand
4. Silica for liquid chromatography (Particle size 0.063-0.200; 70-730 mesh ASTM)
5. Neutral alumina for liquid chromatography (0.05-0.15mm; pH 7.0±0.5)
6. N<sub>2</sub> gas
7. n-Hexane (CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), Assay ≥ 99 %)
8. n-Pentane (CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, Assay ≥ 99 %)
9. Benzene (C<sub>6</sub>H<sub>6</sub>, Assay ≥ 99.8 %)
10. Diethyl ether ((C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O, Assay ≥ 99.5 %)
11. Methanol (CH<sub>3</sub>OH, Assay ≥ 99.8 %)
12. Carbon disulfide, CS<sub>2</sub>

### 3.4 Experiment Procedures

#### 3.4.1 Catalyst Preparation

##### 3.4.1.1 *Rh supported on various zeolites*

The zeolites, KL, HY and HBETA obtained from Tosoh Company in Singapore were dried first and calcined with different temperatures and heating rates. KL zeolite was calcined at 500 °C for 3 hours with the heating rate of 10 °C/min. HY zeolite was calcined at 500 °C for 3 hours with the heating rate of 5 °C/min and HBETA zeolite was calcined at 600 °C for 5 hours with the heating rate of 2 °C/min. Then, each type of zeolites was loaded with Rh by incipient wetness impregnation technique using Rhodium(III) chloride hydrate as the precursor. After that, the catalysts were dried at 110 °C overnight in an oven and subsequently calcined at 500 °C for 4 hours in a furnace (Sugioka *et al.*, 1996b). After that, these catalysts were pressed into a form of pellets by using a hydraulic pelletizer and sieved into the size range of 400-425 μm by using 40-60 mesh size of

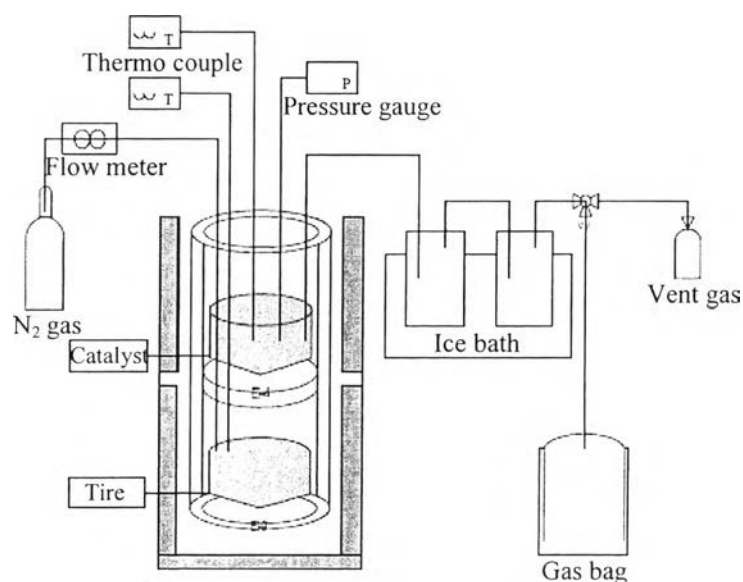
sieves. Finally, the catalysts were reduced at 450 °C for 1 hour with H<sub>2</sub> (Sugioka *et al.*, 1996b) so as to convert the metal oxide forms to metal forms.

#### 3.4.1.2 NiMoS/Al<sub>2</sub>O<sub>3</sub> and CoMoS/Al<sub>2</sub>O<sub>3</sub> commercial catalysts

The spent NiMoS/Al<sub>2</sub>O<sub>3</sub> and fresh CoMoS/Al<sub>2</sub>O<sub>3</sub> were obtained from the hydrodesulfurization unit of a refinery in Thailand. A regenerated commercial NiMoS/Al<sub>2</sub>O<sub>3</sub> was first screened for the clean pellets, then the two commercial catalysts were crushed, and sieved into the size range of 400-425 μm by using 40-60 mesh sizes of sieves.

#### 3.4.2 Pyrolysis Process

A waste tire sample was pyrolyzed in the lower zone of reactor with 500 °C final temperature while the catalytic reactions occurred in the upper zone with catalysts by controlling the temperature at 350 °C. The heating rate was controlled at 10 °C/min. The product effluent was carried by nitrogen carrier gas (oxygen inhibition) to the upper zone and then the liquid products were condensed from the effluent by using ice-salt condensers. The incondensable product was collected in a gas sampling bag. The liquid and solid products were weighed in order to determine the product distribution. The schematic of pyrolysis process was shown in Figure 3.1.



**Figure 3.1** Schematic of pyrolysis process (Saeah and Jitkarnka, 2012).

### 3.4.3 Product Analysis

#### 3.4.3.1 Asphaltene precipitation

Asphaltene is a non-desired product separated from pyrolysis oil products by adding a solvent such as n-pentane with the ratio of 1:40 (oil : n-pentane). The mixture was shaken in an ultrasonic bath at 30 °C for 15 min and left overnight. Then, the precipitate was separated from the pyrolysis oil by filtration using a 0.45 µm teflon membrane in a vacuum system. The membrane with filtrated asphaltene was dried at 110 °C for 6 hours before weighing the asphaltene. n-pentane was evaporated from the maltene by using a rotary vacuum evaporation at the temperature of 37 °C.

#### 3.4.3.2 Maltene Separation (Liquid Chromatography)

Maltenes were separated by using a liquid chromatography column (650 height x 26.6 mm. I.D.), packed firstly with alumina at the bottom, then silica gel at the top and of the column. The column had to be saturated with n-hexane overnight before pouring a maltene into the column. Then, the mobile phases (solvents) were passed through the stationary phase (maltene) by using an aquarium pump at 20 cm<sup>3</sup>/min. The five fractions; namely, saturated hydrocarbon, mono-, di-, poly-, and polar aromatic compounds, were eluted by using different compositions and volumes of the mobile phases shown in Table 3.1. After that, each mobile phase was recovered by a rotary vacuum evaporator at about 60 °C.

**Table 3.1** The optimized compositions and volumes of mobile phases for maltene separation of liquid chromatographic column (Šebor *et al.*, 1999)

Mobile phase	Volume (cm <sup>3</sup> )	Prevailing compounds type
Hexane	600	Saturated hydrocarbons
Hexane-benzene (24:1, v/v)	500	Mono-aromatics
Hexane-benzene (22:3, v/v)	500	Di-aromatics
Benzene	500	Poly-aromatics
Benzene-diethylether-methanol (1:1:3 v/v)	500	Polar-aromatics

### 3.4.3.3 Gas Chromatography

Incondensable gas products were collected by a gas sampling bag. Then, they were analyzed by using a Gas Chromatography, Agilent Technologies 6890 Network GC system, using HP-PLOT Q column: 30 m x 0.32 mm diameter (ID) and 20  $\mu\text{m}$  film thicknesses with FID detector and He carrier gas, as the following conditions.

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

### 3.4.3.4 Simulated Distillation Gas Chromatography (SIMDIST GC)

A varian CP-3800 simulated distillation gas chromatography (SIMDIST-GC) conformed with ASTM D2887 method was used to analyze the oils, for simulated true boiling point (TBP) curves and then carbon number distribution. The hydrocarbons were ranged into naphtha (<200 °C), kerosene (200–250 °C), light gas oil (250–300 °C), heavy gas oil (300–370 °C), and long residue (>370 °C). Prior to the analysis, a liquid sample was diluted with carbon disulphide ( $\text{CS}_2$ ) before being injected to a SIMDIST-GC using the conditions as following:

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

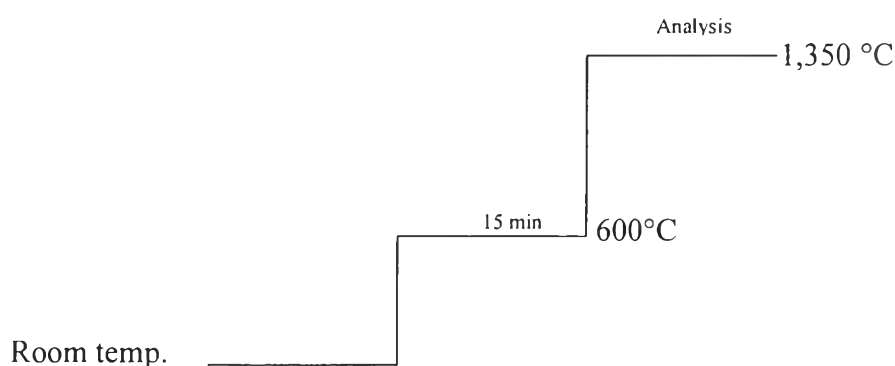
### 3.4.3.5 Gas Chromatography-Mass Spectrometry (Time of Flight), GC-MS (TOF)

The GC-TOF Mass analyzer, Agilent<sup>®</sup> 7890 with 2D dimension mode, was used to identify the components in a mixture by the difference of mass. Helium and Nitrogen were used as a carried and cooling gas. The liquid products were analyzed by this instrument to determine the most of sulfur compound that affected the tire-derived pyrolysis oil following the conditions below:

Initial temperature	80 °C
Time at initial temperature	2 min
Heating rate	4 °C/min to 270°C
Hold for	5 min
Split ratio	1:50

### 3.4.3.6 LECO<sup>®</sup> Elemental Analyzer, TruSpec<sup>®</sup>S

The waste tire samples, oil products, residual chars and spent catalysts were analyzed for the sulfur content in weight percentage by a using LECO<sup>®</sup> Elemental Analyzer, TruSpec<sup>®</sup>S. 0.1 g of sample was weighed in a ceramic boat. The temperature of furnace was 1,350 °C, divided to 2 steps, as shown in Figure 3.2. Then, sulfur balance was calculated.



**Figure 3.2** Temperature profile in the furnace of LECO<sup>®</sup> Elemental Analyzer, TruSpec<sup>®</sup>S.

### 3.4.4 Catalyst Characterization

#### 3.4.4.1 *X-ray fluorescence spectrometry (XRF)*

X-ray fluorescence spectrometry (AXIOS PW4400) is a non-destructive analytical technique used for qualitative and quantitative elemental analysis by identifying the concentrations of elements in the solid and powder samples. The conditions were set as follows: internal flow of 4.10 l/min, external flow of 2.49 l/min, cabinet temperature of 29.97 °C, primary temperature of 19 °C, vacuum of 10.10 Pa, x-ray generation of 50 kV (60 mA), 150 m of collimator, angle of 10.0002 degree, gas flow 0.90 l/h, and gas pressure of 1,020.8 hPa.

#### 3.4.4.2 *Thermo Finnigan Sorptomatic 1990 (Surface Area Analyzer)*

The specific surface area and total pore volume of the catalyst samples were determined by Brunauer-Emmet-Teller (BET) method using Thermo Finnigan/Sorptomatic 1990. The characterization was based on the physical adsorption of nitrogen gas on the catalyst surface. Before analysis, the samples were out gassed to eliminate volatile adsorbents on the surface at 150 °C with a helium flow at 300 °C for 4 hours. The calculation of specific surface area was determined by the BET model.

$$\frac{1}{V[(P_0/P)-1]} = \frac{C-1}{V_m C} \left( \frac{P}{P_0} \right) + \frac{1}{V_m C} \quad (1)$$

where  $V$  = volume of gas adsorbed at relative pressure  $P_0$

$V_m$  = volume of adsorbate containing a monolayer of surface coverage

$C$  = constant

And then the specific surface was calculated by

$$SS = \frac{S}{W} = \frac{S_0 \times V_m}{W} = \frac{Z \times a \times V_m}{W} \quad (2)$$

where  $SS$  = Specific surface

$W$  = Sample mass

$V_m$  = Monolayer volume

$Z$  = Avogadro number

$a$  = Average molecular area of adsorbate

$S$  =  $S_0 \times V_m$

$S_0$  =  $Z \times a$

#### *3.4.4.3 Temperature Programmed Desorption of isopropylamine (IPA-TPD)*

IPA-TPD was used to determine the acidity of a solid sample, performed by manual injection after the elimination of moisture in 0.05 g of the catalyst by He purging until no peak of water observed. The IPA-TPD was conducted from room temperature to 800 °C with a heating rate of 20 °C/min under He flow. The isopropylamine (C<sub>3</sub>H<sub>9</sub>N) is decomposed over Brønsted acid sites, in a narrow temperature range forming propylene and ammonia. The desorption of isopropylamine (m/e = 44), ammonia (m/e = 17) and propylene (m/e = 41) were detected by a mass spectrometer.

#### *3.4.4.4 LECO® Elemental Analyzer, TruSpec®S*

The sulfur content in tire derived oil and spent catalyst can be also determined by LECO® Elemental Analyzer, TruSpec®S, using the same procedure as shown previously in the product analysis.

#### *3.4.4.5 Thermogravimetric/Differential Thermal Analysis (TG/DTA)*

TG/DTA was used to determine the weight of coke formation on catalysts. About 4-7 mg of samples was heated from the room temperature to 700 °C with the heating rate of 10 °C/min. Oxygen flow rate was set about 50 ml/min.