# CHAPTER III
# EXPERIMENTAL

## 3.1 Materials

### 3.1.1 Waste Tire Samples

Rubber particles was prepared by a cutting machine in the range of 8–18 mesh, using passenger car tire for catalytic pyrolysis, which life time was fixed at about 50,000 kilometers. The elemental composition of the waste tire used in this study was summarized in Table 3.1.

**Table 3.1** Elemental composition of waste tire (Dũng *et al.*, 2009)

| Element | C | H | S | Other |
|---|---|---|---|---|
| %wt | 87.4 | 7.2 | 1.7 | 4.7 |

### 3.1.2 Clay (Kaolin)

The kaolin used in this work obtained from Sibelco Minerals (Thailand) Co., Ltd. The chemical properties of the kaolin were summarized in Table 3.2.

**Table 3.2** Chemical compositions of kaolin

| Composition | $SiO_2$ | $Al_2O_3$ | $TiO_2$ | $Fe_2O_3$ | CaO | MgO | $K_2O$ | LOI |
|---|---|---|---|---|---|---|---|---|
| % | 47.39 | 37.79 | 0.90 | 0.59 | 0.03 | 0.07 | 0.73 | 12.65 |

## 3.2 Equipments

1. Bench-scale autoclave reactor
2. Gas sampling bag
3. Cutting Tool
4. Agilent Technologies 6890, Gas chromatography (GC),
5. Liquid chromatography column (Glass), 650 mm height, 26.6 mm inside diameter
6. Varian GC-3800 simulated distillation gas chromatograph (SIMDIST GC)
7. Varian / SpectrAA 300 (Atomic Absorption Spectrometer, AAS)
8. Oxford/6111 (Scanning Electron Microscope, SEM)
9. Aquariums air pump
10. Thermo Finigan TPDRO 1100 (Temperature Programmed Reduction/Oxidation)
11. Perkiln Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA)
12. LECO® Elemental Analyzer (TruSpec®S)
13. Sorptomatic 1990 system

## 3.3 Chemicals and solvents:

1. Benzene ($C_6H_6$, Assay $\geq$ 99.8 %)
2. Diethyl ether ($(C_2H_5)_2O$, Assay $\geq$ 99.5 %)
3. N-pentane ($CH_3(CH_2)_3CH_3$, Assay $\geq$ 99 %)
4. N-hexane ($CH_3(CH_2)_4CH_3$), Assay $\geq$ 99 %)
5. Methanol ($CH_3OH$, Assay $\geq$ 99.8 %)
6. Carbon disulfide, $CS_2$
7. Silica for liquid chromatography (Particle size 0.063–0.200 ; 70–730 mesh ASTM)

8. Neutral alumina for liquid chromatography (0.05–0.15mm ; pH 7.0±0.5)
9. $N_2$ gas
10. Catalysts from Tosoh Company, Singapore : HMOR
11. α-alumina
12. Metal precursors: Ruthenium (III) chloride hydrate ($RuCl_3.aq$)

## 3.4 Methodology

### 3.4.1 Catalyst Preparation

*3.4.1.1 Preparation of catalysts to find the optimize component*

The HMOR zeolite used in this work obtained from Tosoh Company; Singapore was calcined at 500°C for 3 hours with the heating rate of 10°C/min. Then, the zeolite was loaded with 0.7 %wt ruthenium by using the incipient wetness impregnation technique. The precursor solution of ruthenium (III) chloride hydrate was dropped on an individual zeolite by a microsyring for 1-2 hours. After that, the wet zeolite was dried in oven at 110°C for 3 hours and calcined in a furnace at 500°C for 3 hours with the heating rate of 10°C/min to obtain the bifunctional catalyst in an oxide form. Then, the catalyst was reduced with $H_2$ at 400°C for 2 hours in order to convert the metal oxide form to metal element (Ru-supported HMOR zeolite) as shown below.

$$RuO_2 + H_2 \longrightarrow Ru + 2H_2O$$

After that, Ru/HMOR zeolite with the %wt in that range 20–50 %wt was mixed with 40–70 %wt the clay (kaolin), which was pre-calcined at 550°C for 2 hours, and 10 %wt α-alumina in deionized water. The mixture was homogenized. Then, the paste was extruded through a hole of 2 mm diameter. The extrudates was dried in an oven at 110°C for 3 hours and subsequently calcined in a furnace at 250°C for 2 hours with the heating rate of 10°C/min to get the catalyst for catalytic pyrolysis.

#### *3.4.1.2 Preparation of catalyst for studying the effect of ratio of pellet diameter and reactor diameter and the deactivation of catalyst*

Ru-supported HMOR zeolite (prepared as section 3.4.1.1) was mixed with clay (kaolin) and α-alumina based on the optimized composition in deionized water. The mixture was homogenized. Then, the paste was extruded through holes of 1 to 4 mm diameter. The extrudates was dried in oven at 110°C for 3 hours and subsequently calcined in a furnace at 250°C for 2 hours with the heating rate of 10°C/min to get the catalyst for catalytic pyrolysis process.

### 3.4.2 Reaction Equipment

Figure 3.1 shows a scheme of pyrolysis unit. First, 30 g of waste tire sample was introduced to the lower zone of autoclave reactor. And, 7.5 g of pellet catalyst was loaded to the upper zone of reactor. For the pyrolysis zone, the temperatures were increased from room temperature to final temperatures with heating rate of 10°C/min. The final temperature of pyrolysis zone was controlled at 500°C and kept for 90 minutes at the atmospheric pressure. In the catalytic zone of pyrolysis reactor, the temperature was controlled at 300°C. The $N_2$ with flow rates were controlled at 30 ml/min flown to carry along 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 collected in the gas sampling bag.

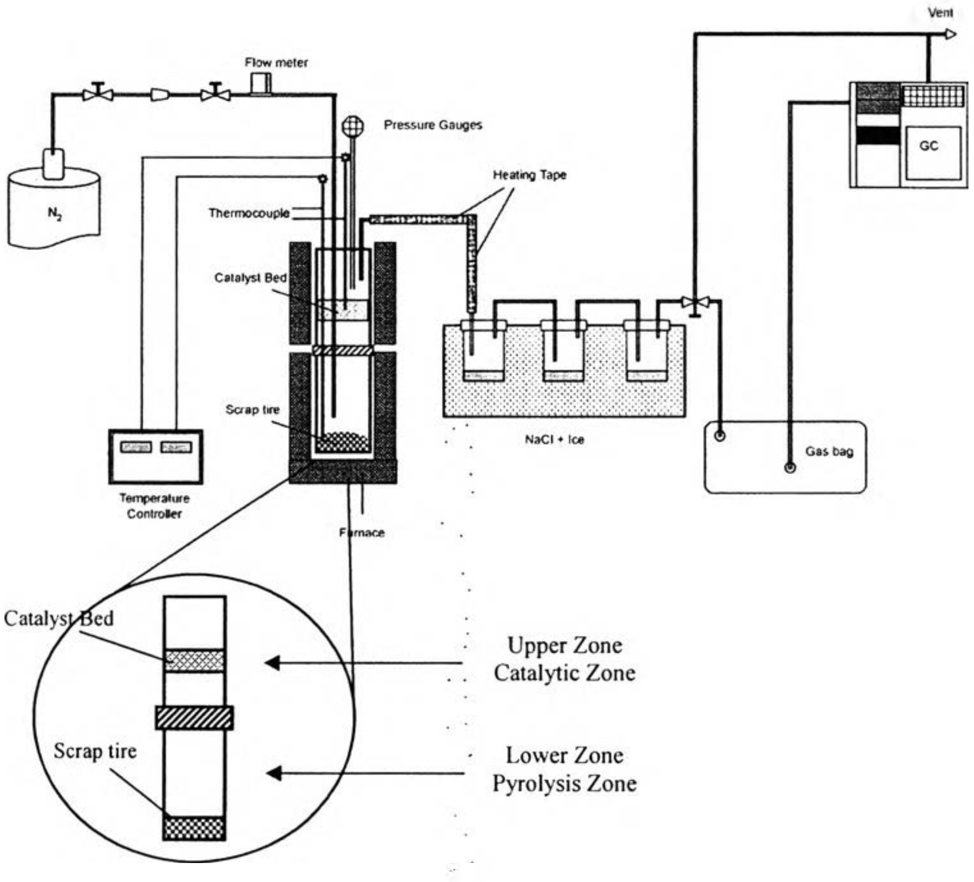


**Figure 3.1** Schematic of experimental pyrolysis system (Dũng *et al.*, 2009).

### 3.4.3 Catalyst Characterization

*3.4.3.1 Atomic Absorption Spectrometer (AAS)*

The amounts of Ruthenium (Ru) metal loading on zeolite were obtained by using Atomic Absorption Spectrometer (Varian, SpecterAA 300 model).

*3.4.3.2 X-ray Diffraction Spectroscopy (XRD)*

X-ray diffraction (XRD) patterns was taken by using a Rigaku, Rint X-Ray diffractometer system (RINT 2200) with Cu tube for generating CuKα 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 was analyzed and recorded by an on-line computer.

### *3.4.3.3 Surface Area and Pore Size Distribution*

The specific surface area, the total pore volume, and the pore size of catalyst was determined by Brunaueer-emmett-Teller (BET) technique and using Thermo Finnigan, Sorptomatic 1990 system. This technique was based on the physical adsorption of nitrogen gas at 77°K. Before starting, the catalyst sample was outgassed by heating under vacuum at 300°C for 6 hours in order to remove moisture. 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 BET equation as shown in Equation 1.

$$\frac{1}{W\left(\frac{P}{P_o}-1\right)}=\frac{1}{W_m C}+\frac{(C-1)}{W_m C}\left(\frac{P}{P_0}\right) \qquad (1)$$

Where:

W = weight of gas adsorbed at relative pressure $P_o$

$W_m$ = weight of adsorbate constituting a monolayer of surface coverage

P = pressure of gas

$P_0$ = saturated vapour pressure of the liquid at the operating temperature

C = constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction.

The surface area was calculated by Equation 2.

$$A=\frac{W_m A_{nitrogen}\times 6.02\times 10^{23}}{MW_{nitrogen}} \qquad (2)$$

Where:

A = surface area of sample

$A_{nitrogen}$ = cross-section area of one molecule nitrogen (0.162 $nm^2$ at -196°C)

$MW_{nitrogen}$ = molecular weight of nitrogen (28 g/g-mol).

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

The coke formation on catalysts was determined by Thermogravimetric/Differential Thermal Analysis (TG/DTA). The samples was heated from the room temperature to 800°C with the heating rate of 10°C/min. Nitrogen and oxygen set flow rate about 100 ml/min and 200 ml/min, respectively.

### 3.4.4 Oil Analysis

#### *3.4.4.1 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 an oven at 60°C over 6 hours. 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.

#### *3.4.4.2 Maltene Separation (Liquid Adsorption Chromatography)*

Liquid chromatography column (650 height x 26.6 mm. I.D.) which silica gel and alumina was packed at the upper and lower bed of the column was used in this experiment. The column was pre-wetted with n-hexane overnight. The mixture of maltene solution (4.5 g mixed with 10 $cm^3$ n-hexane) was separated into five fractions according to their functional groups as shown in Table 3.3 by using the liquid chromatography technique. The flow rates of the mobile phases was kept constant at 20 $cm^3$/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 50°C for 8 hours and generated at 160°C for 18 hours to remove hydrocarbon residuals.

**Table 3.3** The appropriate compositions and volumes of mobile phases for preparative separation of petroleum maltenes using the chromatographic column (Sebor *et al.*, 1999)

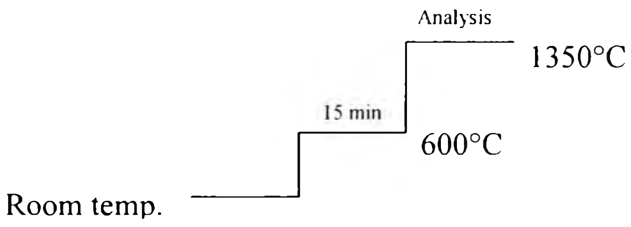
| **Mobile phase** | **Volume (cm$^3$)** | **Prevailing compounds type** |
|---|---|---|
| Hexane | 600 | Saturated hydrocarbons |
| Hexane-benzene (24:1, v/v) | 500 | Monoaromatics |
| Hexane-benzene (22:3, v/v) | 500 | Diaromatics |
| Benzene | 500 | Polyaromatics |
| Benzene-diethylether-methanol (1:1:3 v/v) | 500 | Polar aromatic compounds |

Finally, each functional group was analyzed by a Varian CP3800 Simulated Distillation Gas Chromatography (SIMDIST GC): ASTM D2887. This method at the following condition;

| | |
|---|---|
| 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 |

### *3.4.4.3 Sulfur content*

The percentage composition of sulphur in oil products was performed by using a LECO®Elemental Analyzer (TruSpec®S). The oil product of 0.1–1 g was absorbed on an aid support, which was put in a ceramic boat. The temperature of furnace was raised to a final temperature of 1,350°C via 2 steps, as follows:



### 3.4.5 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 Helium as the carrier gas.

The conditions were 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 |