



CHAPTER III METHODOLOGY

3.1 Materials

The preparation of the tire sample for pyrolysis was done by a four blade-cutting machine. The passenger car tire with an average mileage of 50,000 km was shredded and ground in pieces to acquire a sample with a particle size between 8-18 mesh.

3.2 Equipment

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. Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA)
12. Micromeritics, TPD/TPR 2900 Analyzer
13. LECO[®] Elemental Analyzer (TruSpec[®]S)
14. Sorptomatic 1990 system

3.3 Chemicals and Solvents

1. Benzene (C₆H₆, Assay ≥ 99.8 %)
2. Diethyl ether ((C₂H₅)₂O, Assay ≥ 99.5 %)
3. N-pentane (CH₃ (CH₂)₃CH₃, Assay ≥ 99 %)
4. N-hexane (CH₃ (CH₂)₄CH₃, Assay ≥ 99 %)
5. Methanol (CH₃OH, Assay ≥ 99.8 %)
6. Carbon disulfide, CS₂
7. Silica for liquid chromatography (Particle size 0.063-0.200 ; 70-730 mesh ASTM)
8. Neutral alumina for liquid chromatography (0.05-0.15 mm ; pH 7.0±0.5)
9. N₂ gas
10. Catalysts from Tosoh Company, Singapore : Beta zeolite (Si/Al = 13.5 and 250)
11. Natural Clays (Bentonite, Ball Clay)
12. α-alumina
13. Metal precursors: Palladium (II) nitrate dihydrate (N₂O₆Pd.H₂O)

3.4 Experimental

3.4.1 Catalyst Preparation

In this work, Beta zeolites with Si/Al = 13.5 and 250 (supplied by Tosoh Company, Singapore) were used as the palladium metal supports for the preparation of the agglomerated Pd/Beta-based catalysts. First, the Beta zeolites were precalcined at 500°C for 3 hours with the heating rate of 10°C/min in order to remove the impurity and organic templates which may contaminate in the zeolites. Next, a precalcined zeolite was loaded with Pd by using incipient wetness impregnation technique, to obtain the zeolite with 0.25 wt. % palladium loading. The impregnated catalyst was then dried in an oven at 110°C for 3 hours followed by calcination at 500°C for another 3 hours with the heating rate of 10°C/min to obtain the oxide catalyst which was ready to be mixed with the binder and a matrix. The commercial ball clay and bentonite were first pre-calcined at 500°C for 2 hours and

then mixed with the binder (α -alumina) and a zeolite at different weight ratios to produce the agglomerated catalysts with different active component weight percentages. The mixtures were then homogenized and extruded to produce catalyst extrudates. The extrudates were finally dried in oven at 110°C for 3 hours and subsequently calcined in a furnace at 500°C for 2 hours with the heating rate of 10°C/min. Lastly, the catalysts were reduced under H₂ at 400°C for 4 hours to convert the metal oxide to metal.

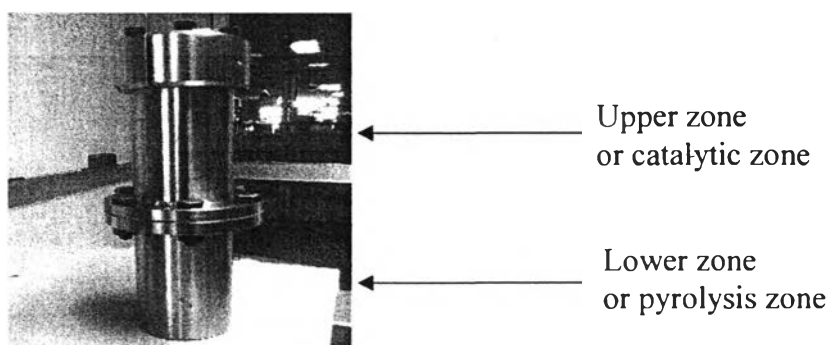


Figure 3.1 Autoclave-type pyrolysis reactor (750 ml) (Mhodmonthin, 2005).

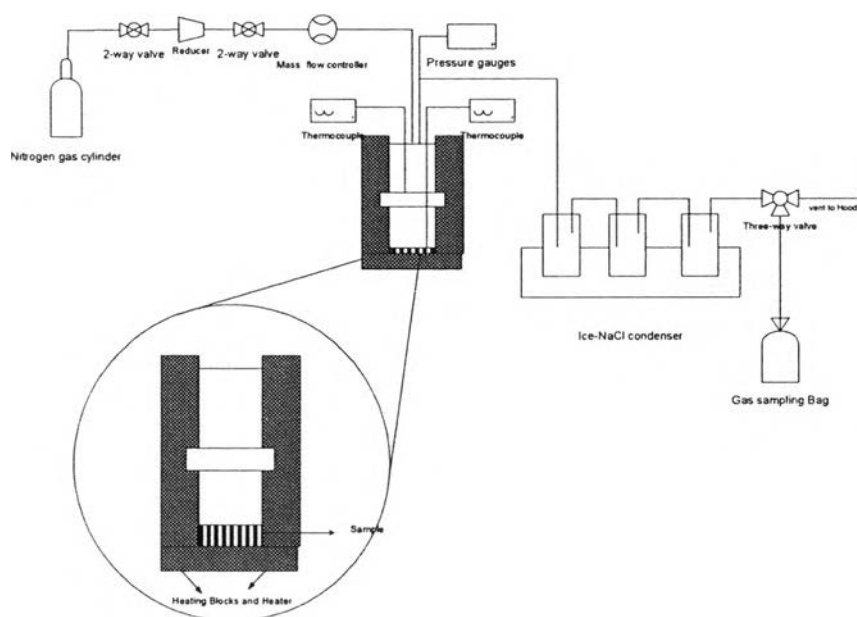


Figure 3.2 Process flow scheme of waste tire pyrolysis (Mhodmonthin, 2005).

3.4.2 Pyrolysis Process

The reactor and the process flow scheme in the experiment are shown in Figures 3.1 and 3.2, respectively. The autoclave reactor with a total volume of 750 ml is divided into two zones; the first is the upper zone (350 ml) or catalytic zone, and the lower zone (400 ml) or the pyrolysis zone. The waste tire sample with a particle size between 8-18 mesh was loaded first in the bottom of the reactor, followed by the addition of the prepared catalyst, which was loaded afterward on the top zone. Nitrogen gas with a flow rate of 50 ml/min was allowed to purge through the system fifteen minutes before, and throughout the experiment, in an attempt to maintain an oxygen free atmosphere and sweep out the pyrolysis products. The reactor was heated with the ramping rate of 10°C/min from room temperature to the final temperature (350°C on the top and 500°C in the bottom) and kept constant for 90 minutes to ensure the complete conversion of the feed tire. The product evolved during the pyrolysis was passed through a series of condensers where the heavy products are condensed and trapped. The remaining part of the product which still remained in the gas phase was collected later in a gas sampling bag.

3.4.2 Product Analysis

a. Liquid Analysis

The analysis of oil products can be separated into two main sections, which are asphaltene precipitation and maltene separation.

Asphaltene Precipitation

In this section, n-pentane was added into the oil products at the ratio 40:1 followed by shaking at 30°C for 15 minutes in an ultrasonic bath. The solution was then left overnight to allow total separation. After that, the asphaltene was filtrated out by using a teflon membrane filter and dried in a vacuum oven for six hours at a condition of 0.1 barg and 110°C. Finally, the dried asphaltene was weighed to verify the asphaltene content. After the asphaltene was removed, the n-pentane in the liquid fraction was then evaporated out using a rotary vacuum evaporator at 37 °C to obtain the maltene.

Maltene Separation

Liquid adsorption chromatography technique was employed to separate maltene into five different compound fractions in accordance to their functional groups (Saturated hydrocarbons, Mono-Aromatic, Di-aromatic, Poly-aromatic and Polar-aromatic). The column with a 650 mm. height and 26.6 mm. I.D. was used for the separation. Silica and alumina gel were activated at 400°C for 8 hrs before packing separately into the lower part and the upper part of the column, respectively. Before each experiment, the prepared column was pre-wetted overnight with pure n-hexane. Maltene sample was prepared by adding 10 cm³ n-hexane into 5 g of maltene. Then, the sample was added into the column with a flow rate of 20 cm³ /min, controlled by using an aquarium pump. After that, five different compositions of mobile phase solutions were sequentially introduced into the column in order to extract each compound fraction according to their functional group types (The detailed composition for each mobile phase solutions used is shown in the Table 3.1). Finally, all the mobile phases were removed from the product fractions by means of a rotary vacuum evaporator at 60°C and 4.4 kPa. After each experiment, the adsorbents (silica and alumina gel) was dried at 50°C for 8 hours followed by regeneration at 160°C for 48 hr to get rid of the remaining hydrocarbon residuals.

Table 3.1 The optimized compositions and volumes of mobile phases for preparative separation of petroleum maltenes using the chromatographic column (Šebor *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	Polararomatic compounds

Finally, each liquid fractions from pyrolysis of used tire was analyzed by a Varian CP-3800 Stimulated Distillation gas chromatography (SIMDIST-GC), equipped with FID. The ASTM D2887 temperature program is described 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

b. Gas Product Analysis

Pyrolysis gas sample was 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 thickness. A detector used was FID type using Helium as the carrier gas. The conditions used were as follows:

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

3.4.4 Catalyst Characterization

a. Surface Area Analyzer (SAA)

The specific surface area and total pore volume of the prepared catalyst sample were determined by Brunauer-Emmet-Teller (BET) method using Thermo Finnigan/Sorptomatic 1990, which N₂ gas was used as the adsorbate. The characterization was based on the physical adsorption of nitrogen gas on the catalyst surface.

b. Thermogravimetric/Differential Thermal Analysis (TG/DTA)

The coke formation on catalysts was determined by TG/DTA. The sample was heated from the room temperature to 800°C with the heating rate of 10°C/min. Nitrogen and oxygen flow rate were controlled at 100 ml/min and 200 ml/min, respectively.

c. X-Ray Diffraction (XRD)

An XRD pattern was obtained using Rigaku/Rint2200 HV. A prepared catalyst sample was packed in a glass specimen holder which was placed in the goniometer using CuK_α small radiation operated at 40 KV and 30 mA. This prepared catalyst sample was scanned from 5 degrees to 60 degrees (2θ) with the scanning speed of 0.02 degrees/min.

d. Elemental Analyzer

The amount of sulfur content in the tire derived oil was determined by using an elemental analyzer (LECO, CHNS-932).