



CHAPTER III EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Waste Tire Sample

The waste passenger car tire (Bridgestone TURUNZA GR-80) thread was used in this pyrolysis study. Then, the waste tire was scraped by a grinder, and sieved to obtain a particle size range of 8-18 mesh.

3.1.2 Equipment

1. Bench-scale autoclave reactor
2. Thermo Finnigan Sorptomatic 1990 (Surface Area Analyzer)
3. Oxford/6111 (Scanning Electron Microscope, SEM)
4. Thermo Finigan TPDRO 1100 (Temperature Programmed Desorption/ Reduction/Oxidation)
5. Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC)
6. Liquid Chromatography Column (Glass), 650 mm height, 26.6 mm inside diameter
7. Agilent Technology Gas Chromatography (GC)
8. Gas sampling Bags
9. Vacuum Pump
10. Aquarium Air pump
11. Ultrasonic Bath
12. Rotary evaporator
13. Sieves, Mesh 8-18 and Mesh 40-60
14. A grinder machine
15. A hydraulic pellet

3.1.3 Chemicals and Solvents

1. n-Pentane ($\text{CH}_3(\text{CH}_2)_3\text{CH}_3$, Assay $\geq 99\%$)
2. n-Hexane ($\text{CH}_3(\text{CH}_2)_4\text{CH}_3$, Assay $\geq 99\%$)
3. Carbon disulfide, CS_2
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. Benzene (C_6H_6 , Assay $\geq 99.8\%$)
7. Diethyl ether ($(\text{C}_2\text{H}_5)_2\text{O}$, Assay $\geq 99.5\%$)
8. N_2 gas
9. Methanol (CH_3OH , Assay $\geq 99.8\%$)
10. Catalysts
 - 10.1 Metal precursors:
 - Palladium(II)nitrate dihydrate ($\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$)
 - Ruthenium(III) chloride hydrate ($\text{RuCl}_3 \cdot \text{aq}$)
 - Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
 - Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$)
 - 10.2 Support HMOR and HBeta zeolite from Tosoh Company, Singapore

3.2 **Experimental Procedures**

3.2.1 Catalyst Preparation

The catalysts were prepared based on HMOR and HBeta zeolites, which were supplied by Tosoh Company (Singapore). The HMOR zeolites was calcined at $500\text{ }^\circ\text{C}$ for 3 hours the heating rate of $5\text{ }^\circ\text{C}/\text{min}$ and Beta zeolite was calcined at $600\text{ }^\circ\text{C}$ for 5 hours with the heating rate of $2\text{ }^\circ\text{C}/\text{min}$. The Pd, Ru, Ni and Fe catalyst were prepared by impregnating the zeolites support with a precursor aqueous solution of palladium(II) nitratedihydrate ($\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$), ruthenium(III) chloride hydrate ($\text{RuCl}_3 \cdot \text{aq}$), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$)

The amount of noble metal (Pd and Ru) loading was fixed to 1 wt%, and that of non-noble metals (Ni and Fe) was varied 5, 10, and 20 wt%, respectively. Then, the samples were dried in an oven at 110°C for 3 hours followed by calcination in a furnace at 500 °C for 3 hours with the heating rate of 5 °C/min. Before the catalysts were used in the pyrolysis reactor, they were pressed to pellets using a hydraulic pelletizer. Then, the pellets were crushed and sieved into the particle size between 400 and 425 µm using the mesh size between 40 and 60 of sieves. Finally, the catalysts were reduced for 2 hours with H₂ in order to convert the metal oxide forms to metal elements.

3.2.2 Pyrolysis of Waste Tire

The diagram of waste tire pyrolysis process is shown in Figure 3.1. First, the scraped waste tire was loaded into the pyrolysis zone (the lower zone), and the prepared catalyst was loaded into the catalytic zone (the upper zone). The reactor was heated by a furnace from room temperature to a final temperature with the heating rate 10 °C/min. The final catalytic temperature was 300 °C, and the final pyrolysis temperature was 500 °C. The evolved product was transported by nitrogen to an ice bath condenser system containing two condensers in order to separate non-condensable compounds from the liquid product. Non-condensable products or gaseous products were passed through the condensers to a gas sampling bag.

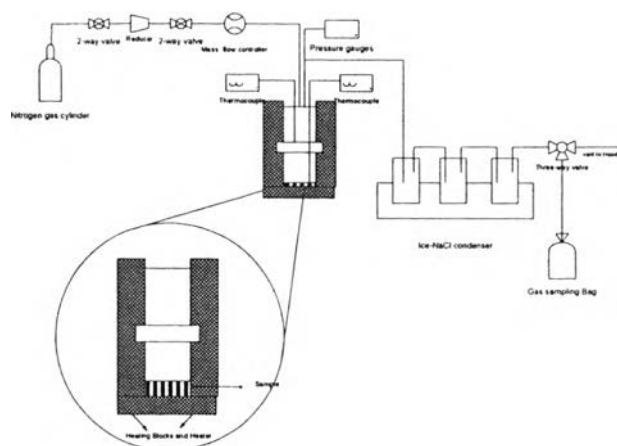


Figure 3.1 Schematic of the pyrolysis process (Mhodmonthin, 2005).

3.2.3 Products Analysis

3.2.3.1 *Gas Analysis*

The non-condensable gas sample was collected in a gas sampling bag. The non-condensable gas product was analyzed by using 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 a FID type using He as the carrier gas. The temperature was programmed as follows:

Initial temperature	70	$^{\circ}\text{C}$
Time at initial temperature	8	min
Heating rate	20	$^{\circ}\text{C}/\text{min}$ to 200 $^{\circ}\text{C}$
Hold for	16	min
Final temperature	220	$^{\circ}\text{C}$
Holding time	30	min

3.2.3.2 *Oil Analysis*

i Asphaltene Precipitation

Oil products were mixed with n-pentane at the ratio of 40:1, and were shaken for 15 min in an ultrasonic bath. The solution was left overnight, after that asphaltene was filtrated out by using a 0.45 μm Teflon membrane in a vacuum system. The membrane with the precipitated material was dried in a vacuum oven at 110 $^{\circ}\text{C}$ overnight and finally weighted to determine the asphaltene. The solution after filtration was evaporated out by a rotary vacuum evaporator in 37 $^{\circ}\text{C}$ in order to remove n-pentane and obtain maltene solution.

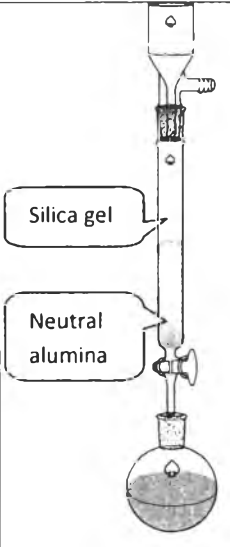
ii Liquid Chromatography

Maltene solution was extracted to each functional group as shown in Table 3.1 by using a liquid chromatography column (650 height x 26.6 mm. I.D.). The liquid chromatography column was packed with alumina firstly in the bottom and silica gel on the top. The column was immersed with n-hexane for overnight. The extraction was started with adding a mobile phase as shown in Table 3.1. The flow rate of the mobile phase was kept constant at 20 cm^3/min controlled by an aquarium air pump. And then, the mobile phase was evaporated from each functional group by a rotary vacuum evaporator at about 60 $^{\circ}\text{C}$ (Sebor *et al.* 1999).

All functional groups (saturated hydrocarbons, mono-aromatics, di-aromatics, poly-aromatics, and polar-aromatics) obtained from the liquid chromatography were analyzed for the true boiling point distillation curves using a Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC). The liquid samples were injected to a SIMDIST GC after dilution in carbon disulphide (CS₂), dilution ratio was 1:200 (liquid Sample: CS₂). The temperature of the oven was programmed 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

Table 3.1 Optimized compositions and volumes of mobile phases for 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	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-aromatic compounds	

3.2.3.3 Residual Char Analysis

The elemental analysis of residual char was carried out in an Elemental analyzer (LECO, CHNS-932) for determining the content of sulfur.

3.2.4 Catalyst Characterization

3.2.4.1 *Thermogravimetric/Differential Thermal Analysis (TG/DTA)*

The coke formation on catalysts was determined by a TG/DTA machine. The spent catalysts were weighed and placed in a Pt pan followed by heating 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.

3.2.4.2 *Temperature Programming Reduction (TPR)*

H₂-TPR profiles of the samples was recorded from room temperature to 600 °C with the heating rate of 10 °C/min using 5 %H₂/N₂ after the pretreatment of the samples at 150 °C under helium flow at 30 ml/min for 30 minutes.

3.2.4.3 *Elemental Analyzer*

Elemental analyzer (LECO, CHNS-932) was used to determine the sulfur content in derived oils and sulfur deposition on spent catalysts