



CHAPTER III EXPERIMENTAL

3.1 Materials

A used passenger car rubber tire tread, Bridgestone TURANZA GR-80 195/65R15, was cut and grated into small pieces to produce samples with a particle size range of 8-18 mesh for pyrolysis.

3.2 Equipments

1. Grinder machine
2. Bench-scale autoclave reactor
3. Gas sampling bag
4. Liquid chromatography column (Glass), 650 mm height, 26.6 mm inside diameter
5. Agilent Technologies 6890, Gas chromatography (GC),
Varian GC-3800 simulated distillation gas chromatograph (SIMDIST GC)
6. Varian / SpectrAA 300 (Atomic Absorption Spectrometer, AAS)
7. Oxford/6111 (Scanning Electron Microscope, SEM)
8. Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA)
9. Thermo Finnigan Sorptomatic 1990 (Surface Area Analyzer)
RINT-2200 Rigaku X-Ray Diffractometer system (X-Ray Diffraction, XRD)
10. Sieves, Mesh 8-18 and Mesh 40-60
11. Ultrasonic Bath
12. Evaporator
13. Aquariums air pump
14. Vacuum Pump

3.3 Chemicals and Solvents

1. n-Hexane ($\text{CH}_3(\text{CH}_2)_4\text{CH}_3$), Assay $\geq 99\%$
2. n-Pentane ($\text{CH}_3(\text{CH}_2)_3\text{CH}_3$, Assay $\geq 99\%$)
3. Benzene (C_6H_6 , Assay $\geq 99.8\%$)
4. Diethyl ether ($(\text{C}_2\text{H}_5)_2\text{O}$, Assay $\geq 99.5\%$)
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 (0.05-0.15 mm ; pH 7.0 ± 0.5)
9. Catalysts from Tosoh Company, Singapore : Beta, USY and HMOR
10. N_2 gas
11. Metal precursor, Cobalt (II) nitrate hydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)

3.4 Methodology

3.4.1 Catalyst Preparation

All zeolites (HBETA, HY, HMOR and HZSM-5) obtained from Tosoh Company in Singapore. SAPO-34 was obtained from Tianjin Chemist Scientific in China. HY, HMOR, and HZSM-5 zeolites were calcined at $500\text{ }^\circ\text{C}$ for 3 hours with the heating rate of $10\text{ }^\circ\text{C}/\text{min}$, but HBETA and SAPO-34 were calcined at $600\text{ }^\circ\text{C}$ for 5 hours. Then, Co was loaded on the zeolite using incipient wetness technique. In this technique, cobalt (II) nitrate hydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) solution was dropped on a zeolite to 5 wt% loading. After that, catalysts were dried at $100\text{ }^\circ\text{C}$ for 3 hours in an oven, and then calcined at $500\text{ }^\circ\text{C}$ for 3 hours in a furnace. Finally, they were reduced at $500\text{ }^\circ\text{C}$ for 2 hours with H_2 to convert the metal oxide forms to a metal form. To prepare a binary supported catalyst, 5 %Co was loaded separately

on each zeolite, and then the loaded catalysts were physically mixed to a desired ratio prior to use.

3.4.2 Pyrolysis Experiment

Waste tire with the size range of 8-18 mesh was loaded into the lower zone of the reactor, and a catalyst was loaded into the upper zone of the reactor. The temperature was controlled at 350 °C for the catalytic zone and 500 °C for the pyrolytic zone. Oxygen was purged out of system by using nitrogen. The pyrolysis product was passed through an ice-salt condensing system. In this step, the condensable products were condensed, and became liquid products. The non-condensable products were passed through the condensers, and collected in a gas sampling bag. The schematics of reactor and pyrolysis process are shown in Figure 3.1

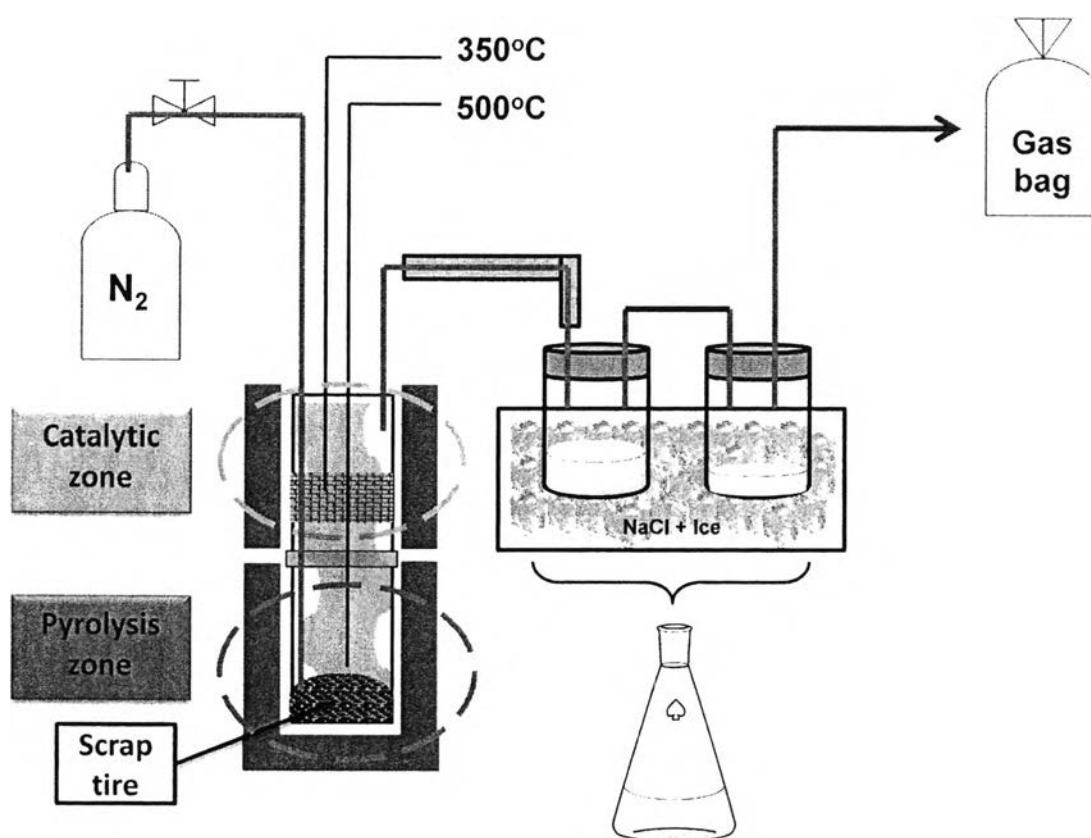


Figure 3.1 Schematic of the pyrolysis experiment.

3.4.3 Product Analysis

The products from pyrolysis are classified as shown in Figure 3.2.

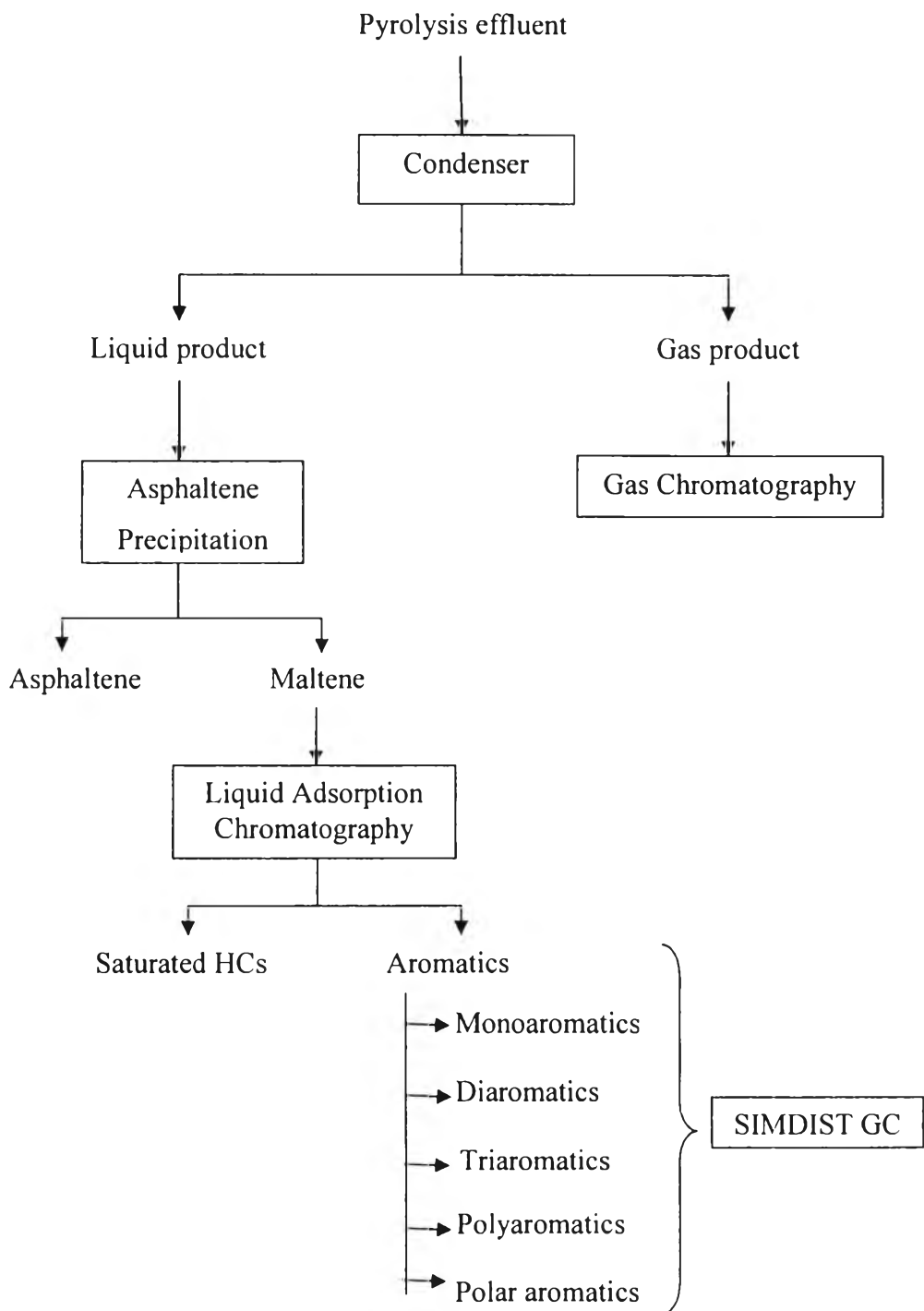


Figure 3.2 Pyrolysis products.

3.4.3.1 Liquid Analysis

(a) Asphaltene Precipitation

N-pentane was added into the liquid products with the ratio of 40:1 for the separation of asphaltene. Next, the solution was shaken in an ultrasonic bath for 15 min and left overnight. And then, asphaltene was filtered by using a 0.45 μm teflon membrane and a vacuum system. After that, the membrane with asphaltene precipitate was dried in an oven at 60 °C for 6 hours. The asphaltene weight in the maltene solution was determined by weighing the filter cake and evaporating n-Pentane.

(b) Maltene Separation (Liquid Adsorption Chromatography)

Maltenes were separated by liquid chromatography column chromatography (650 height x 26.6 mm. I.D.) packed with silica gel on the top and alumina in the bottom of the column. The column must be pre-wet with n-Hexane overnight before separating maltene fractions. A sample of maltenes was separated into five fractions by using different compositions and volumes of the mobile phases shown in Table 3.1. After that, a mobile phase eluted with each functional group was recovered by a rotary vacuum evaporator at about 60 °C.

Table 3.1 Optimized compositions and volumes of mobile phases for maltene separation by using liquid 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

(c) *Simulated Distillation Gas Chromatography (SIMDIST GC)*

Liquid samples from pyrolysis were analyzed by a Varian CP-3800 simulated distillation gas chromatography (SIMDIST GC), using ASTM D2887 method for true boiling point curves. Liquid samples were diluted with carbon disulphide (CS₂) before being injected to a SIMDIST GC. The conditions were listed 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

This ULTRA standard (TMP) solution was purchased from Varian, and the compositions are shown in Table 3.2.

Table 3.2 Standard solution for calibrating SIMDIST GC (ASTM Method D2887)

Components	Carbon number	% By weight
n-Hexane	6	6.0
n-Heptane	7	6.0
n-Octane	8	8.0
n-Nonane	9	8.0
n-Decane	10	12.0
n-Undecane	11	12.0
n-Dodecane	12	12.0
n-Tetradecane	14	12.0
n-Hexadecane	16	10.0
n-Octadecane	18	5.0
n-Eicosane	20	2.0
n-Tetracosane	24	2.0

n-Octacosane	28	1.0
n-Dotriacontane	32	1.0
n-Hexatriacontane	36	1.0
n-Tetracontane	40	1.0
n-Tetratetracontane	44	1.0

3.4.3.2 Gas Analysis

Gas samples from pyrolysis 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 μ m film thicknesses. The type of detector was FID with using Helium as the carrier gas. The conditions were listed 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

3.4.4 Catalyst Characterization

(a) 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 50 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) Temperature Programmed Reduction (TPR)

A sample was pretreated at 150 °C under helium flow at 30 ml/min for 30 minutes. After that, 5 %H₂/N₂ was flown through the sample. H₂-TPR profiles of the samples were recorded from room temperature to 600 °C with the heating rate of 10 °C/min.

(d) Surface Area Analyzer (SAA)

The specific surface area and the pore size of catalyst were determined by Brunauer-Emmett-Teller (BET) technique. Thermo Finnigan, Sorptomatic 1990 and physical adsorption of nitrogen gas at 77 °K was used in this technique. The specific surface area and the pore size of a catalyst were obtained from the twenty-two-point nitrogen adsorption and desorption isotherm plot. The pore size distribution was calculated using the BJH method.

(e) Elemental Analyzer

The amount of sulfur deposit on the catalyst and sulfur in the oils were determined by using an elemental analyzer (LECO, CHNS-932).