



CHAPTER III METHODOLOGY

3.1 Materials

The tread of used passenger tire tread, Bridgestone TURANZA GR-80, for pyrolysis was first shredded and crumbed to produce a size range of 8-18 mesh.

3.2 Equipment

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

3.3 Chemicals

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. Benzene (C_6H_6 , Assay $\geq 99.8\%$)
4. Diethyl ether ($(C_2H_5)_2O$, 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 (0.05-0.15mm ; pH 7.0 \pm 0.5)
9. N_2 gas
10. KL Zeolite Catalysts from Tosoh Company, Singapore
11. Metal precursors: Rhodium (III) chloride hydrate ($RhCl_3 \cdot xH_2O$), Cobalt (II) nitrate hydrate ($Co(NO_3)_2 \cdot 6H_2O$) and Nickel (II) nitrate hydrate ($Ni(NO_3)_2 \cdot 6H_2O$)

3.4 Experiment

3.4.1 Catalyst Preparation

(a) The Supported Monometallic Catalysts

The KL zeolite obtained from Tosoh Company, Singapore was calcined at 500°C for 3 hours with the heating rate of 10°C/min. After that the Rh, Ni and Co were loaded on KL by using the incipient wetness impregnation technique. First, the salt solution of rhodium (III) chloride hydrate ($RhCl_3 \cdot xH_2O$), cobalt (II) nitrate hydrate ($Co(NO_3)_2 \cdot 6H_2O$) and nickel (II) nitrate hydrate ($Ni(NO_3)_2 \cdot 6H_2O$) was individually dropped on the KL zeolite to obtain 1%wt of Rh and 1, 5, 10, 15, 20%wt of Ni and Co supported on KL catalysts. Then, the samples were dried in an oven at 100°C for 3 hours followed by calcination in a furnace at 500°C for 3 hours. Finally, the catalysts were reduced for 2 hours with H_2 at 400°C and 600°C for cobalt catalysts.

(b) The Supported Bimetallic Catalysts

The bimetallic of Rh-Ni/KL and Rh-Co/KL were prepared by impregnating KL zeolite with the mixed aqueous solution of $RhCl_3 \cdot xH_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$, and $Co(NO_3)_2 \cdot 6H_2O$, respectively. The salt solution of metal was dropped on the support according to the amount shown in Table 2.1 and then dried in

an oven at 100°C for 3 hours. After that the samples were calcined in a furnace at 500°C for 3 hours. Finally, the catalysts were reduced with H₂ at 400°C for 2 hours.

3.4.2 Pyrolysis Process

A catalyst was sieved into a particle size range of 300-425 μm and loaded to the upper bed of the reactor. The temperature of the catalytic zone and reactor zone were controlled at 350 and 500°C, respectively. Nitrogen was passed through the reactor in order to purge oxygen out of the system. The condensable products were collected in the condenser and the non-condensable products were passed through the condenser and collected in the gas-sampling bag.

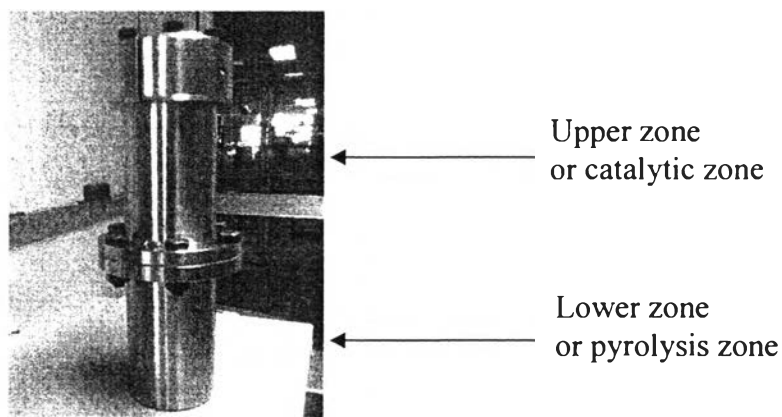


Figure 3.1 An autoclave reactor used in the experiment (Choosuton, 2007).

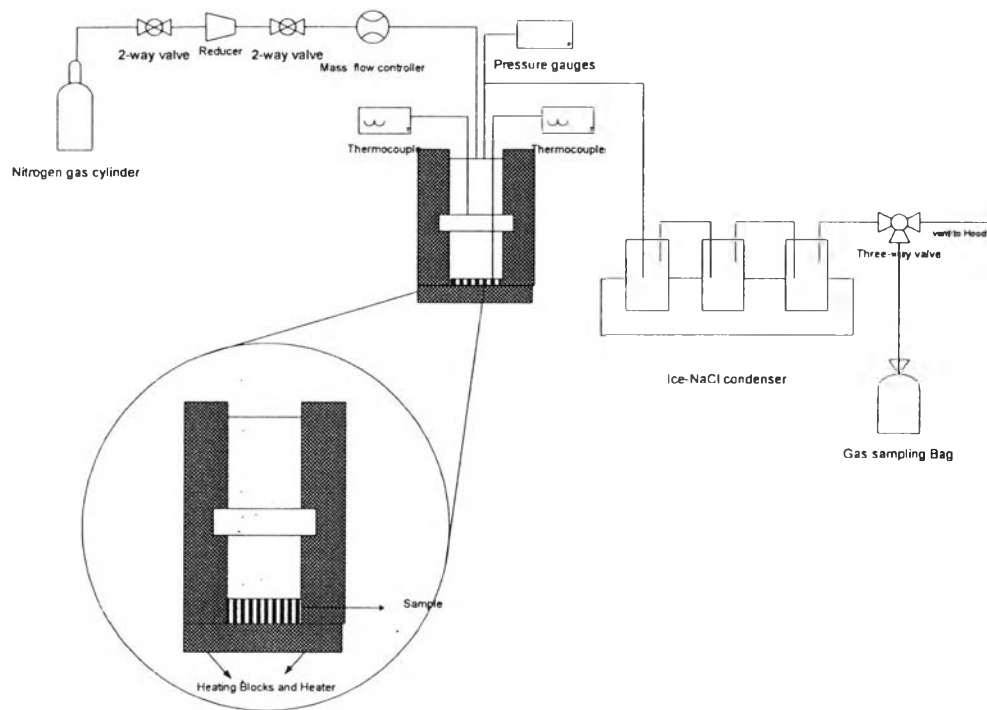


Figure 3.2 Schematic of the pyrolysis process (Mhodmonthin, 2005).

3.4.3 Product Analysis

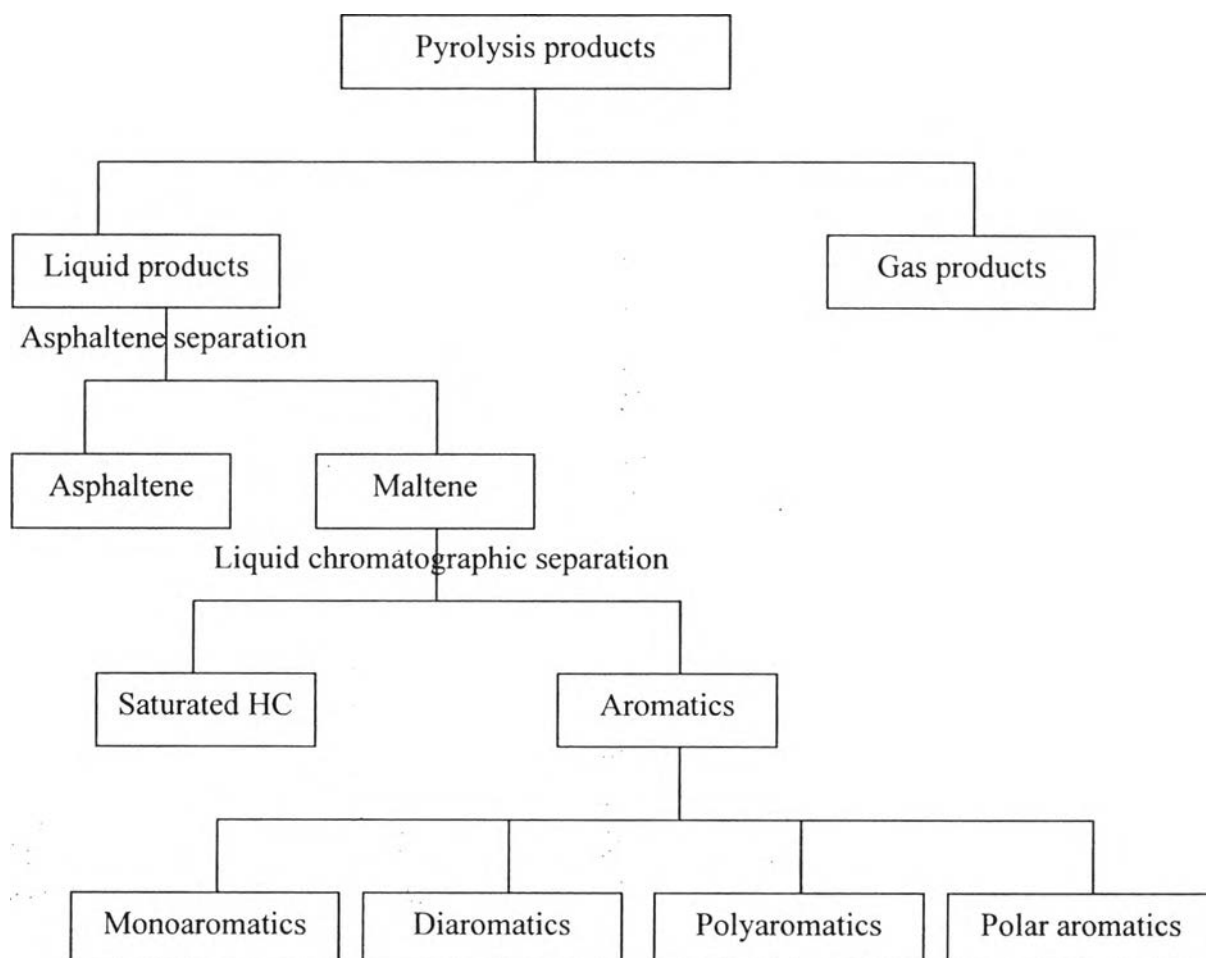


Figure 3.3 Block diagram of the product analysis.

(a) Liquid Analysis

1. Liquid Chromatography Column

The liquid product was separated into asphaltene (n-pentane insoluble) and maltene (n-pentane soluble). Firstly, n-pentane was added into the liquid fraction to separate asphaltene. Then, the maltene compound was fractionated into saturated hydrocarbons, monoaromatics, diaromatics, polyaromatics and polar aromatics by using Liquid Chromatography column, which was packed with silica gel and alumina. The column was pre-wetted with n-hexane overnight and preheated at 105°C for 2 hours with the following solvents as shown in Table 3.1

Table 3.1 The compositions and volumes of mobile phases used for separation of maltenes fraction by liquid chromatographic column (Sebor *et al.*, 1999)

Mobile phase	Volume (cm ³)	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

2. SIMDIST Gas Chromatography (SIMDIST-GC)

A liquid fraction was analyzed for the boiling point distribution of hydrocarbons by a Varian CP-3800 stimulated distillation gas chromatography (SIMDIST GC), equipped with an FID according to the ASTM D2887 method with the following conditions.

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 analysis

The gas product was analyzed by a Gas Chromatography, Agilent Technologies 6890 Network GC system, using HP-PLOT Q column: 30 m x 0.32 mm diameter (id) and 20 µm film thicknesses. FID was used as a detector with He as the carrier gas with 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

3.4.4 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 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.

(b) Temperature Program Reduction (TPR)

TPR was used to examine metal reducibility and metal-metal interaction of bimetallic catalysts. The instrument consists of TCD detector whose detected signal was sent online to the software. Approximately 0.05g of sample was weighed and packed in a quartz tube. Before analysis, the sample was pretreated with He at 150 °C for 30 minutes and then went to analysis step using 5 %H₂/N₂ with the heating rate of 10 °C/min from room temperature to 700°C for 1 hr.

(c) Elemental Analyzer

Elemental analyzer (LECO, CHNS-932) was used to determine the amount of sulfur deposition on spent catalysts and in derived oil.