CHAPTER III

EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Waste tire samples

Passenger car tire (Bridegestone TURANZA GR-80) samples were prepared by a cutting machine and then sieved into the particle size range of 8-18 mesh. The life time the tire was fixed at about 50,000-80,000 kilometers.

3.1.2 Equipment

1. Cutting Tool
2. Sieves, Mesh 8-18 and Mesh 40-60
3. Gas sampling bag
4. Rotary evaporator
5. Liquid chromatography column (Glass), 650 mm height, 26.6 mm inside diameter
6. Bench-scale autoclave reactor
7. A hydraulic pellet
8. Vacuum pump
9. Aquariums air pump
10. Ultrasonic bath
11. Agilent Technologies 6890, Gas chromatography (GC)
12. LECO® Elemental Analyzer (TruSpec®S)
13. X-ray Fluorescence (XRF)
14. Thermo Finigan TPDRO 1100 (Temperature Programmed Desorption/Reduction/Oxidation)
15. X-ray Diffraction (XRD)
16. Varian GC-3800 simulated distillation gas chromatograph (SIMDIST GC)
17. Gas Chromatography - Mass Spectrometry, Time of Flight (GC-TOF)

3.1.3 Chemicals and solvents

1. Methanol (CH_3OH, 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. Benzene (C_6H_6, Assay $\geq$ 99.8 %)
6. Neutral alumina for liquid chromatography (0.05-0.15mm; pH 7.0±0.5)
7. Silica for liquid chromatography (Particle size 0.063-0.200; 70-730 mesh ASTM)
8. N_2 gas
9. Carbon disulfide, CS_2
10. HBETA from Tosoh Company, Singapore
11. Metal precursors: Nickel nitrate hexahydrate ($Ni(NO_3)_2.(6H_2O)$
12. Metal precursors: Cobalt nitrate hexahydrate ($Co(NO_3)_2.(6H_2O)$
13. Metal precursors: Ammonium heptamolybdate ($(NH_4)_6Mo_7O_2$)
14. Metal precursors: Ammonium metatungstate hydrate $((NH_4)_6H_2W_{12}O_4)\cdot H_2O$

3.2 Methodology

3.2.1 Catalyst Preparation

3.2.1.1 Preparation of the support

The HBETA zeolite (Si/Al = 13.5) obtained from Tosoh Company in Singapore was calcined in order to remove the organic template from the zeolites. The calcination of HBETA would take place at 600 °C for 5 hrs with heating rate of 2 °C/min.

3.2.1.2 Preparation of the bimetallic catalysts

NiMo, NiW, CoMo and CoW were prepared by co-impregnation on the HBETA support using incipient wetness method. For NiMo, appropriate amount of nickel nitrate hexahydrate ($Ni(NO_3)_2.(6H_2O)$ and ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}$) were dissolved in distilled water, and then the solution was gradually dropped into the HBETA support. After that, the samples were dried at 110 °C for 3 hr in the oven, and then calcined at 500 °C for 5 hr with the heating rate of 5 °C/min to obtain the bimetallic catalysts in an oxide form. Finally, the oxide form was converted to the metal form, by reducing at 800 °C for 1 hr. For NiW, ammonium metatungstate hydrate ($(NH_4)_6H_2W_{12}O_4) \cdot H_2O)$ was used instead of ammonium heptamolybdate with the same as the above method. For CoMo and CoW, Cobalt nitrate hexahydrate ($Co(NO3)_2 \cdot 6H_2O$) was used instead of Nickel nitrate hexahydrate ($(Ni)(NO_3)_2.6H_2)$. The oxide form of Co was converted to the metal form, by reducing at 800 °C for 1 hr.

3.2.2 Reaction Equipment

There are 2 zones of the pyrolysis reactor; that are, catalytic zone (the upper zone) and pyrolytic zone (the lower zone). First, 30 g of the waste tire with sizes in the range of 8-18 mesh was loaded into the lower zone with a heating rate of 10 °C/min from the room temperature to final temperature. The final temperature of this zone was controlled at 500 °C and then kept for 90 minutes at the atmospheric pressure. In the same time, 7.5 g of pellet catalyst was loaded to the catalytic zone of the reactor which controlled temperature at 350 °C. N_2 was controlled at flow rate of 30 ml/min to purge the oxygen out of the system prior the pyrolysis and subsequently for carrying the pyrolysis product passed through condensers and a gas sampling bag. These condensers were placed into the ice bath in order to collect the condensable products. A gas sampling bag collected the non-condensable products.

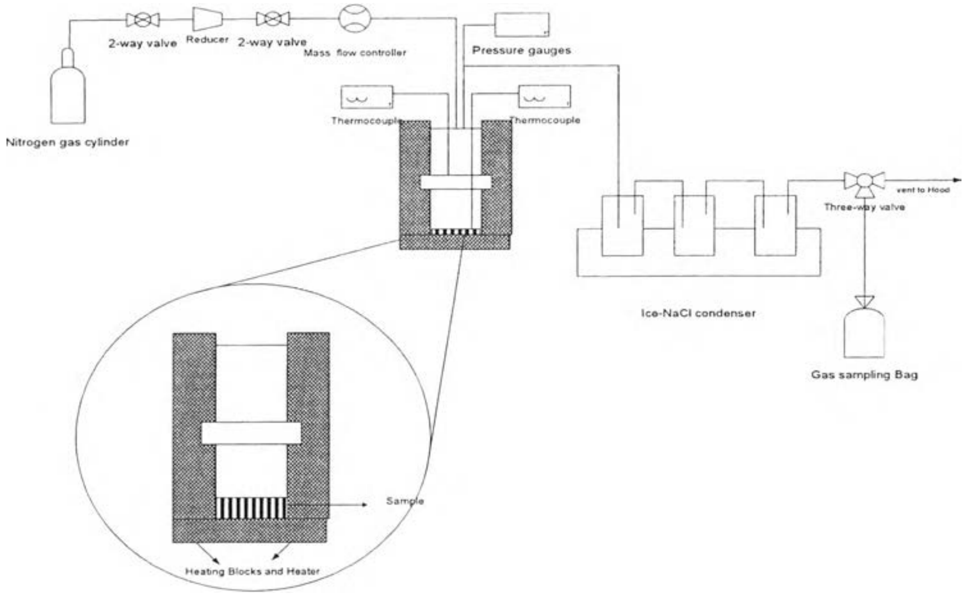


Figure 3.1 Diagram of the pyrolysis process (Mhodmonthin, 2005).

3.2.3 Catalyst Characterization

3.2.3.1 *X-ray Diffraction (XRD)*

X-ray Diffraction (XRD) was used to verify the metallic form of the catalysts. X-ray diffraction (XRD) patterns were taken by using a Bruker X-ray diffractometer system (D8 Advance) equipped with a 2.2 kW Cu anode long fine focus ceramic X-ray tube for generating a CuKα radiation (1.5405 Å). The detector scanned the peak position from the sample as a function of 2θ by starting at the 10° to 60° (2θ) range and a scan speed of 0.02° (2θ)/0.6 second. The XRD patterns were matched to the standards to identify crystalline phases.

3.2.3.2 *Temperature-Programmed Reduction (TPR)*

Temperature-programmed reduction (TPR) was used to identify the reducibility of the impregnated catalysts and the metal-metal interaction. The TPR experiments were conducted from 30 °C to 850 °C.

3.2.4 Product Analysis

3.2.4.1 *Oil Analysis*

i Asphaltene Precipitation

n-pentane was added into the oil product at the ratio of 40:1, and subsequently the mixture was shaken in an ultrasonic bath for 15 min at 30 °C and then left overnight. After that 0.45 um Teflon was used to filter the asphaltene out in a vacuum system. The membrane with precipitated material was dried in an oven at 110 °C over 6 hours. Finally, the asphaltene was weighed. The solution after filtration was evaporated by a rotary vacuum at 37 °C; thus, n-pentane was evaporated out to obtain a maltene solution.

ii Maltene Separation (Liquid Column Chromatography)

A liquid chromatography column (650 height x 26.6 mm. I.D.) was used to extract each functional group from the maltene solution. Prior to separation, the column had to be pre-wet with n-hexane overnight. Silica gel and alumina were packed on the top and in the bottom of the liquid chromatography column, respectively. The extraction was started by adding mobile phases, which are shown in Table 3.1. The flow rate of mobile phases was kept constant at 20 cm^3/min controlled by an aquarium pump. Then, the chemical fractions were separated from the mobile phases (solvents) by using a rotary vacuum evaporator at about 60°C.

Table 3.1 Optimized compositions and volumes of mobile phases for preparative separation of maltene 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

iii Simulated Distillation Gas Chromatography (SIMDIST GC)

All functional groups (saturated hydrocarbons, mono-aromatics, di-aromatics, poly-aromatics, and polar-aromatics) were analyzed by a Varian CP-3800 simulated distillation gas chromatography (SIMDIST GC), using ASTM D2887 method for true boiling point distillation curve. A liquid sample was injected to a SIMDIST GC after dilution (1:50) with carbon disulphide (CS_2). The condition was set 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

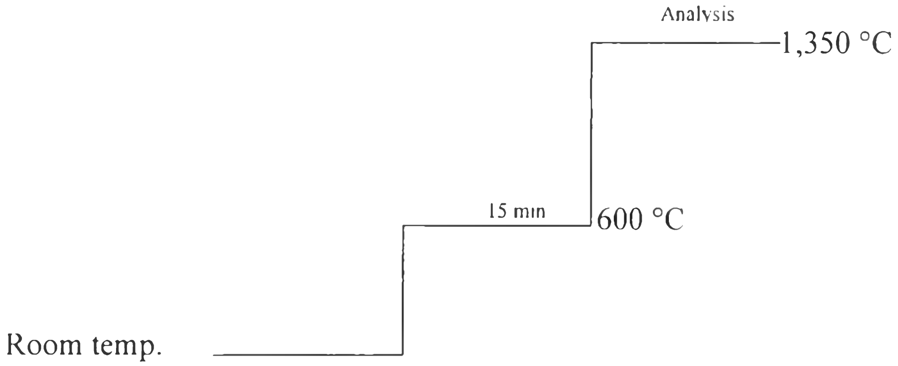
iiii Gas Chromatography-Mass Spectrometry, Time of Flight (GC-TOF)

Sulfur compounds in maltene solutions were determined by using Gas Chromatography-Mass Spectrometry, Time of Flight (GC-TOF), Agilent© 7890 with 2D dimension mode. Helium was used as a carried gas, and nitrogen was used for cooling. The conditions were set as follows:

Initial temperature	80 °C
Time at initial temperature	2 min
Heating rate	4 °C/min to 270 °C
Hold for	5 min
Split ratio	1:50

iiiii Sulfur content

The sulphur content in oil products was determined by using a LECO®Elemental Analyzer (TruSpec®S). The oil sample weight of 0.1 g was absorbed on an aid support, which was put in a ceramic boat. The temperature of furnace was 1,350 °C, which divided to 2 steps, as follows:



3.2.4.2 *Gas Analysis*

A gas sample from the pyrolysis process (non-condensable gas) was kept in a gas sampling bag, and 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. FID was used as a type of detector with He as the carrier gas. The conditions were set 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

3.2.4.3 *Residual Char and Spent catalyst Analysis*

The elemental analysis of residual char and spent catalysts was also carried out in the Elemental Analyzer (LECO, CHNS-932) for determining the content of sulfur.