



CHAPTER III EXPERIMENTAL

3.1 Materials

Used passenger car tire (Bridgestone Turanza GR80) in life time about 50,000 kilometers was cut in pieces and ground to produce samples with a particle size range of 8-18 mesh.

3.2 Equipments

1. Aquarium Air pump
2. Agilent Technology, Gas Chromatography (GC)
3. Bench-scale autoclave reactor
4. Gas-sampling bag
5. Liquid Chromatography Column (Glass), 650 mm height, 26.6 mm inside diameter
6. Perkin Elmer/Pyris Diamond (Thermogravimetric /Differential Thermal Analysis, TG/DTA)
7. Rigaku/Rint 2200HV (X-Ray Diffraction Spectroscopy)
8. Sieves, Mesh 8-18 and 40-60
9. Thermo Finnigan Sorptomatic 1990 (Surface Area Analyzer)
10. Varian GC-3800 stimulated distillation gas chromatography (SIMDIST GC)
11. Varian/Spectra AA 300 (Atomic Absorption Spectrometer, AAS)
12. Vacuum Pump
13. Elemental Analyzer (LECO, CHNS-932)

3.3 Chemicals and Solvents

1. Benzene (C_6H_6 , Assay $\geq 99.8\%$)

2. Carbon disulfide, CS₂
3. Diethyl ether ((C₂H₅)₂O, Assay ≥ 99.5 %)
4. KL Zeolite Catalysts from Tosoh Company, Singapore
5. Metal precursors: Ammonium Perrhenate (NH₄ReO₄), Ammonium Molybdate Tetrahydrate (NH₄)₆Mo₇O₂₄·4H₂O), (from S.M. Chemical Company, Thailand)
6. Methanol (CH₃OH, Assay ≥ 99.8 %)
7. n-pentane (CH₃(CH₂)₃CH₃, Assay ≥ 99 %)
8. n-hexane (CH₃(CH₂)₄CH₃), Assay ≥ 99 %)
9. Neutral alumina for liquid chromatography (0.05-0.15mm ; pH 7.0±0.5)
10. N₂ gas
11. Silica for liquid chromatography (Particle size 0.063-0.200 ; 70-730 mesh ASTM)

3.4 Methodology

3.4.1 Catalyst Preparation

3.4.1.1 Preparation of KL Zeolite

KL zeolite obtained from Tosoh Company Singapore was calcined at 500 °C for 3 hours with the heating rate of 10 °C/min to remove the organic content from zeolite.

3.4.1.2 Preparation of %MoO₃/KL Catalysts

Molybdenum supported on KL zeolite was prepared by the incipient wetness impregnation with an aqueous solution containing ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O)). The impregnated catalysts were dried at 110 °C for 3 hours and calcined at 500 °C for 4 hours.

3.4.1.3 Preparation of %Re/KL Catalysts

Rhenium supported on KL zeolite was prepared by the incipient wetness impregnation with different percentages using an aqueous solution of ammonium perrhenate (NH₄ReO₄). The impregnated catalysts were dried at 110 °C for 3 hours and calcined at 500 °C for 4 hours. Finally, all of Re/KL catalysts were reduced at the reduction temperature as shown in Appendix J for 4 hours.

3.4.1.4 Preparation of %Re-1%MoO₃/KL Catalysts

The catalysts were prepared by incipient wetness impregnation of KL zeolite using (NH₄)₆Mo₇O₂₄·4H₂O and NH₄ReO₄. There were 2 preparation steps. In the first step, 1wt% of MoO₃/KL was prepared as indicated above, and followed by rhenium loading in the second step. The co-loaded precursors were dried and calcined again, then they were reduced at the reduction temperature of Re/KL at different percentages for 4 hours to produce the Re metallic clusters, while MoO₃ still remained in the oxide form on the catalysts.

3.4.2 Pyrolysis Process

The pyrolysis was carried out in an autoclave reactor. The reactor and diagram of pyrolysis are shown in Figures 3.1 and 3.2, respectively. The reactor is separated into 2 zones; the lower zone for the pyrolysis of raw material and the upper for catalytic pyrolysis zone. A weight of scrap tire material in each batch pyrolysis was 30 g. All catalysts were pelletized and sieved to the particle size between 300 μm to 425 μm and loaded to the upper zone of reactor. Nitrogen gas was passed through the reactor to purge oxygen gas inside the reactor system at a flow rate of 30 ml/min for minutes. The temperature of both zones was heated from room temperature to final temperature with heating rate of 10 °C/min and hold at the final temperature for 90 minutes at atmospheric temperature. The final temperature of pyrolysis zone and catalytic zone were 500 °C and 300 °C, respectively. The liquid product from pyrolysis was condensed into the condensers, and the gaseous product was passed to a gas-sampling bag. The liquid product and pyrolysis residue (char) were determined by weighing, and then gas products were determined by mass balance.

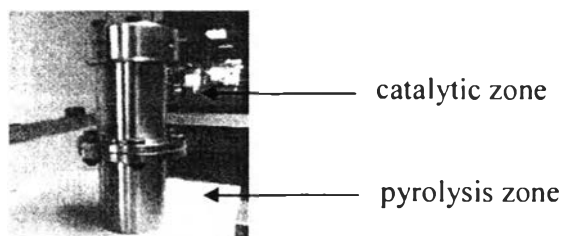


Figure 3.1 An autoclave reactor (Choosuton, 2007).

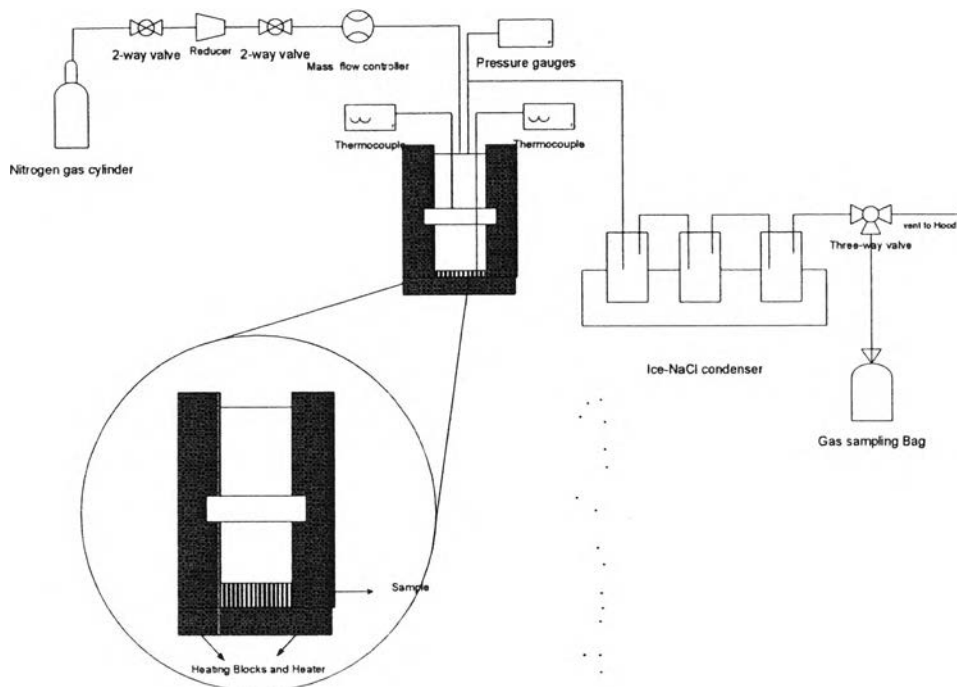


Figure 3.2 Schematic of the pyrolysis process (Mhodmonthin, 2005).

3.4.3 Product Analysis

3.4.3.1 *Liquid Product Analysis*

The liquid product in the glass condensers from pyrolysis process was analyzed into 2 steps as follows:

a) Asphaltene Precipitation

Asphaltene was precipitated from maltene by adding *n*-pentane into the liquid product and then shaking at 30 °C for 15 minutes in an ultrasonic bath, and after that asphaltene was filtrated in a vacuum system by using 0.45 μm teflon membrane. The membrane with filtered was dried at 100 °C for 6 hours, and then it was weighed

b) Maltene Separation

Maltene was separated into saturated hydrocarbons and aromatic compounds as shown in Table 3.1 by using liquid chromatography column (650 height × 26.6 mm. I.D.). The column was packed with silica gel and alumina in the upper half zone and the lower half zone, respectively. The adsorbent column was prewetted with *n*-hexane for a night before its use for separation. The flow rate of

mobile phase was controlled by a fish pump, and was kept at a constant of 20 cm³/min. Then, the mobile phase in each prevailing compound was evaporated at about 60 °C by a rotary vacuum evaporator. After extraction, the adsorbents were dried and regenerated to remove hydrocarbon residuals at 160 °C for 18 hr.

Table 3.1 The optimized composition and volumes of mobile phases for maltenes separation by liquid adsorption chromatography (Šebor *et al.*, 1999)

Mobile phase	Volume (cm ³)	Prevailing compounds
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 aromatics

The liquid fractions from liquid chromatography were analyzed by a Varian CP-3800 stimulated distillation gas chromatography (SIMDIST-GC). It was used to determine the boiling point distribution of hydrocarbon according to ASTM D2887 method at 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

3.4.3.2 Gaseous Products Analysis

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

3.4.4.1 *Coke Formation Analysis*

Thermogravimetric/Differential Thermal Analysis (TG/DTA) was used for coke formation analysis on the catalysts. A sample was heated from the room temperature to 800°C with the heating rate of 10°C/min, and it was held at this temperature for 30 minutes. Nitrogen and oxygen flow rate were controlled at 100 ml/min and 200 ml/min, respectively.

3.4.4.2 *Elemental Analyzer*

Sulfur content in the pyrolytic oil and on the spent catalysts was analyzed by an elemental analyzer (LECO, CHNS-932).

3.4.4.3 *Temperature Programmed Reduction (TPR)*

The TPR profile of the catalysts was obtained using a Thermo Finnigan, TPDRO1100 analyzer with MS. 0.1 g of catalysts was loaded in a quartz tube, and then this tube was heated from room temperature to 900 °C at 10 °C/min under a flow of 4.95%H₂ in N₂ (20 ccm/min).