

CHAPTER III EXPERIMENTAL

3.1 Materials

Waste tires (Bridgestone Turanza GR-80) were cut into pieces by a grinding machine and then sieved to obtain the particle sizes of 20-40 mesh (425 -850 μm).

3.2 Equipment

1. Grinding Machine
2. Bench-scale autoclave reactor
3. Thermo Finigan TPDRO 1100 (Temperature Programmed Desorption/Reduction/Oxidation)
4. RINT-2200 Rigaku X-Ray diffractometer system (XRD)
5. Thermo Finnigan Sorptomatic 1990 (Surface Area Analyzer)
6. LECO® Elemental Analyzer (TruSpec®S)
7. Agilent Technologies 6890 (GC) with FID detector
8. Varian GC-3800 simulated distillation gas chromatograph (SIMDIST GC) with FID detector
9. Gas Chromatography-Mass Spectrometry, Time of Flight (GC-TOF)
10. PerkinElemer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA)
11. Rigaku D/MAX 2200H X-Ray diffractometer system (XRD)
12. FEI Tecnai G² 20 200kV TEM/STEM/EDX/Tomography
13. Water bath
14. Gas sampling bag
15. Aquariums air pump
16. Hydraulic pelletizer
17. Rotary Evaporator
18. Vacuum Air Pump
19. Sieves (20,40 and 60 U.S. mesh (ASTM))

3.3 Chemical and Solvents

1. n-pentane ($\text{CH}_3(\text{CH}_2)_3\text{CH}_3$, Assay $\geq 99\%$)
2. Carbon disulfide (CS_2)
3. Nitrogen gas
4. Sulfuric acid (H_2SO_4 , Assay $\geq 98\%$)
5. Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
6. HBETA, HY, HMOR and KL zeolite
7. MCM-41 molecular sieve
8. Cetyltrimethyl ammonium bromide (CTABr)
9. Sodium silicate hydrate

3.4 Experimental Procedures

3.4.1 Synthesis of HY- MCM-41 Composites

The core-shell structure composites of HY zeolite and MCM-41 were synthesized by the method in Li *et al.* (2009). 4.25 g of CTABr was dissolved in 40 mL of deionized water, and 1.2 g of HY was added to the solution at 25 °C with stirring for 24 h to form Slurry A. Solution B was prepared by dissolving 9.79 g of sodium silicate in 100 mL of deionized water, and the pH is adjusted to 11 by adding 6 M H_2SO_4 . After stirring for 10 min, Slurry A was added drop by drop to Solution B. After that, the mixture was stirred at room temperature for 2 h and kept into an autoclave at 120 °C for 72 h. Then, the solid product was filtered, washed, dried, and calcined at 540 °C for 6 h.

3.4.2 Synthesis of HBETA-MCM-41 Composites

The core-shell structure composites of HBETA zeolite and MCM-41 were synthesized by the method in Li *et al.* (2009). 4.25 g of CTABr was dissolved in 40 mL of deionized water, and 1.2 g of HBETA was added to the solution at 25 °C with stirring for 24 h to form Slurry A. Solution B was prepared by dissolving 9.79 g of sodium metasilicate in 100 mL of deionized water, and the pH was adjusted to 11 by adding 6 M H_2SO_4 . After stirring for 10 min, Slurry A was added drop by drop to Solution B. After that, the mixture was stirred at room temperature for 2 h and kept

into an autoclave at 120 °C for 72 h. Then, the solid product was filtered, washed, dried, and calcined at 540 °C for 6 h.

3.4.3 Synthesis of Mesoporous MCM-41

The 4.25 g of CTABr was dissolved in 40 mL of deionized water, followed by the addition of the solution containing 9.79 g sodium silicate and 100 mL of deionized water. The solution of sodium silicate was priorly stirred until the solution was clear before addition to the CTABr solution. After stirring at 25 °C for 2 h, the mixture of CTABr, sodium silicate and DI water was transfer into an Teflon line autoclave at temperature 120 °C for 3 days. Then, the solid product was filtered, washed, dried, and calcined at 540 °C for 6 h.

3.4.4 Metal Loading on Supports

The HMOR, HY, HBETA, HZSM-5 and KL zeolites obtain from Tosoh Company, Singapore. HMOR, HZSM-5, and HY zeolites are calcined at 500 °C for 3 h with heating rate 10 °C/min. HBETA is calcined at 600 °C for 5 h with heating rate of 2 °C /min, and KL zeolite is calcined at 500 °C for 3 h with heating rate 10 °C/min. Then, the nickel precursor ((Ni(NO₃)₂ •6H₂O)) is loaded on the all zeolites by the incipient wetness impregnation method. After that, catalysts are dried at 100 °C for 3 h and calcined at same condition of fresh zeolites. Next, catalysts are reduced at 500 °C for 2 h with H₂ gas at atmospheric pressure. Finally, the all catalysts are pelletized, crushed and sieved to obtain the particle size 40-60 mesh.

3.4.5 Pyrolysis of Waste Tire

The pyrolysis system is displayed in the Figure 3.1. The 30 g of waste tire with particle size of 20-40 mesh is pyrolyzed in the lower zone of the pyrolysis reactor with heating rate 10 °C/min from room temperature to final temperature. After the reaching the final temperature, the temperature is held on at 500 °C for 2 hr. The 7.5 g of catalyst is loaded to the upper zone of the pyrolysis reactor that is heated at 350 °C. The nitrogen gas is flown with flow rate 30 ml/min for carrying the pyrolysis products passed through an ice-salt condensing system and a gas sampling bag. The condenser system condenses the condensable products and collected in the condenser. And, the non-condensable products pass through to the gas sampling bag.

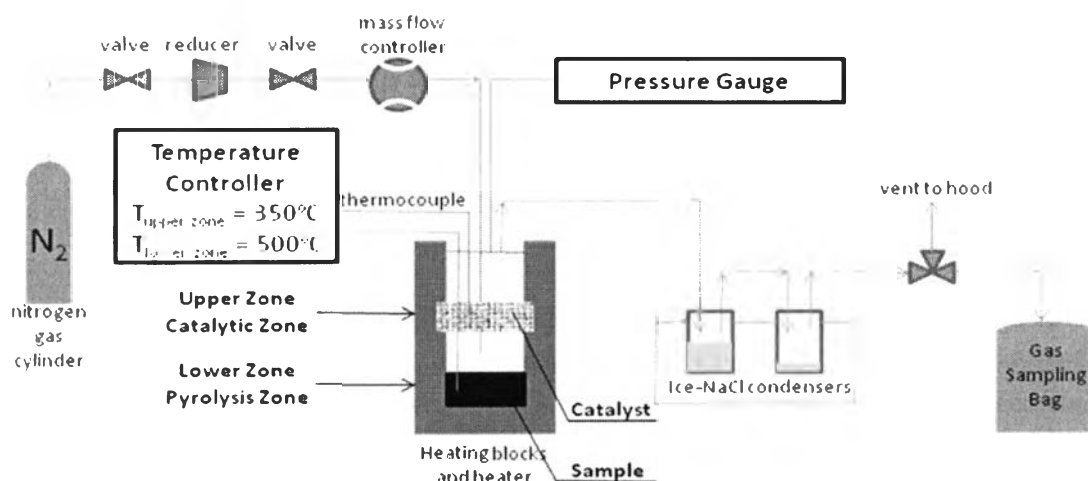


Figure 3.1 The schematic of the pyrolysis process. (Yuwapornpanit, 2014)

3.4.6 Gas Analysis

The gas products in the gas sampling bag are analyzed by a Gas Chromatography, Agilent Technologies 6890 Network GC system, using HP-PLOT Q column 30m x 0.32 mm internal diameter and 20 μm film thicknesses. A detector was flame ionization detector (FID) using helium as a carrier gas. The analyzing condition was displayed below:

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

3.4.7 Tire-derived Oil Analysis

There are two steps of tire-derived oil analysis. The first step is asphaltene separation and the second step is maltene analysis.

3.4.7.1 Asphaltene Separation

For the asphaltene separation, the n-pentane is added to oil products with ratio of 40:1. After that the mixture of n-pentane and oil product is shaken by ultrasonic bath at 30 $^{\circ}\text{C}$ for 15 min, and leaves the mixture overnight at

room temperature. The asphaltene is filtered using 0.45 μm Teflon membrane in a vacuum system. The filtered membrane is dried in the vacuum oven at 0.1 barg and 60 $^{\circ}\text{C}$ for 6 h. After that, the dried asphaltene is weighed to determine the amount of asphaltene. Finally, the n-pentane in the solution is evaporated by rotary vacuum evaporator at 50 $^{\circ}\text{C}$.

3.4.7.2 Maltene Analysis

The maltene solution after maltene separation is used to identify the hydrocarbon species by GC-TOF, Agilent©7890 with 2D dimension mode. After the analyzing process, the hydrocarbon species are categorized into 5 groups, which are saturated hydrocarbon, mono-aromatics, di-aromatics, poly-aromatics, and polar aromatics.

3.4.7.3 Simulated Distillation Gas Chromatography (SIMDIST GC)

The maltene and hydrocarbon fractions are analyzed for simulating true boiling point curves and carbon number distribution by Varian GC-3800 Simulated Distillation Gas Chromatograph (SIMDIST GC): ASTM D2887 method following this condition below:

Initial temperature	30	$^{\circ}\text{C}$
Time at initial temperature	0.01	min
Heating rate	20	$^{\circ}\text{C}/\text{min}$
Final temperature	320	$^{\circ}\text{C}$
Holding time	8.50	min

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

The GC-TOF, Agilent©7890 with 2 dimension mode is used to identify the sulfur compound. Helium is used as carrier gas and nitrogen is used for cooling system. The analyzing condition was set as follows:

Initial temperature	80	$^{\circ}\text{C}$
Time at initial temperature	2	min
Heating rate	4	$^{\circ}\text{C}/\text{min}$
Final temperature	270	$^{\circ}\text{C}$
Split ratio	1.50	

3.4.8 Residual Char Analysis

The LECO® Elemental Analyzer is used to determine the sulfur content in residual char. The 0.1 g of residual char is added to ceramic boat. After that, the ceramic boat is heated from room temperature to 600 °C for 15 min. Finally, the ceramic boat is heated up to 1350 °C for analyzing step.

3.4.9 Catalyst Characterization

3.4.9.1 *X-Ray Diffraction (XRD)*

X-Ray Diffraction is used to analyze the structure of catalyst and dispersion of metal on the supports. XRD patterns are observed from Ringku/Rint2200 HV.

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

The coke formation on catalysts is determined by TG/DTA machine. The spent catalysts are weighed and placed in a sample pan followed by heating from the room temperature to 700 °C with the heating rate of 10 °C /min. Oxygen flow rate is controlled at 50 ml/min.

3.4.9.3 *Temperature Program Reduction (TPR)*

Temperature program reduction is used to determine metal reducibility and metal-metal interaction of bimetallic catalysts.

3.4.9.4 *Elemental Analyzer*

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

3.4.9.5 *Thermo Finnigan Sorptomatic 1990 (Surface Area Analyzer)*

Thermo Finnigan Sorptomatic is used to determine the surface area and total pore volume by Brunauer-Emmet-Teller method. The glass tube contained of sample is out gassed at 150 °C. After that helium gas is flown through the tube at 300 °C for 4 h.

3.4.9.6 *Transmission Electron Microscopy (TEM)*

Transmission electron microscopy is used to observe the core - shell structure of composite material and selected area electron diffraction (SEAD) image is used to identify the core structure of composites.

3.4.9.7 X-Ray Photoelectron Spectroscopy (XPS)

XPS spectra were carried out using an AXIS ULTRADLD to determine the species of metal in a fresh catalyst.