

CHAPTER III EXPERIMENTAL

3.1 Materials

A used passenger car tire (Bridgestone; Turanza GR-80) for pyrolysis was scraped by a grinder to produce a particle size range of 8-18 mesh. The mileage of tires was fixed at 50,000 kilometers (average life time of tires: 50,000-80,000 km).

3.2 Equipment

1. Bench-scale autoclave reactor
2. Varian GC-3800 simulated distillation gas chromatograph (GC-SIMDIST)
3. Liquid Chromatography Column (Glass), 650 height, 26.6 inside diameter
4. Gas Chromatography (GC)
5. Gas sampling Bags
6. Vacuum Pump
7. Aquarium Air pump
8. Ultrasonic Bath
9. Rotary evaporator
10. Sieves, Mesh 40-60
11. A grinder machine
12. A hydraulic pellet

3.3 Chemicals and Solvents

1. Pentane ($\text{CH}_3(\text{CH}_2)_3\text{CH}_3$, Assay $\geq 99\%$)
2. Hexane ($\text{CH}_3(\text{CH}_2)_4\text{CH}_3$, Assay $\geq 99\%$)
3. Carbon disulfide, CS_2
4. Silica 100 (Particle size 0.063-0.200 ; 70-730 mesh ASTM)

5. Neutral alumina for liquid Chromatography (0.05-0.15mm ; pH 7.0[±]0.5)
6. Benzene (C₆H₆, Assay ≥ 99.8 %)
7. Diethylether ((C₂H₅)₂O, Assay ≥ 99.5 %)
8. N₂ gas
9. Methanol (CH₃OH, Assay ≥ 99.8 %)
10. Catalysts
 - 10.1 Metal (Ag)
 - 10.2 Support (Beta, KL, MOR, and Y zeolite) from Tosoh Company, Singapore

3.4 Experimental Procedures

3.4.1 Catalyst Preparation

Catalysts in this experiment were prepared by the incipient wetness impregnation method. First, all of the zeolites (BETA, KL, HMOR, and Y) obtained from Tosoh Company in Singapore were calcined at 500 °C for 3 hours with the heating rate of 10 °C/min to remove the organic template from the zeolites, except the BETA zeolite, which was calcined at 600 °C for 5 hrs. Then, the silver nitrate (AgNO₃) solution was dropped onto the zeolites with various amounts of silver loading as 1, 2, 3 wt% on only Y zeolite. For BETA, KL, and HMOR zeolites, the amount of silver loading was fixed to 1% by weight. Before the catalysts were used in the pyrolysis reactor, they were pressed to pellets using a hydraulic pelletizer. Then, the pellets were crushed and sieved into the particle size between 400 and 425 μm using the mesh size between 40 and 60 of sieves. Finally, the catalysts were reduced with H₂ at 400 °C for 2 hrs in order to convert the metal oxide forms to metal elements.

3.4.2 Pyrolysis of Waste Tire

The diagram of waste tire pyrolysis process is shown in Figure 3.1. First, waste tire was loaded into the pyrolysis zone (the lower zone), and then the prepared catalyst was loaded into the catalytic zone (the upper zone). The reactor was heated by a furnace from room temperature to final temperatures (catalytic

temperature = 300 °C and pyrolysis temperature = 500 °C). The evolved product was transported by nitrogen to an ice bath condenser system containing 3 condensers in order to separate incondensable compounds from the liquid product. Non-condensable products or gaseous products were passed the condensers to a gas sampling bag. Table 3.1 shows all conditions in the experiment.

Table 3.1 Pyrolysis process conditions

Parameters	Conditions
Final temperature	500 °C
Catalytic temperature	300 °C
Holding time	1 hour
Nitrogen flow rate	30 ml/min
Heating rate	10 °C min ⁻¹
Waste tire sample weight	30 g
Catalyst weight	7.5 g

3.5 Products Analysis

3.5.1 Gas Analysis

Pyrolysis gas samples from the gas sample bag 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 µm film thicknesses. A detector is a FID type using He as the carrier gas.

3.5.2 Oil Analysis

(a) *Asphaltene Precipitation*

Oil products were mixed with n-pentane at the ratio of 40:1, and were shaken for 15 min in an ultrasonic bath. The solution was left overnight, after that asphaltene was filtrated out using a 0.45 µm Teflon membrane in a vacuum system. The membrane with the precipitated material was dried in a vacuum oven at

110°C overnight and finally weighted to determine the asphaltene. The solution after filtration was evaporated out by a rotary vacuum evaporator in 37 °C in order to remove n-pentane and obtain maltene solution.

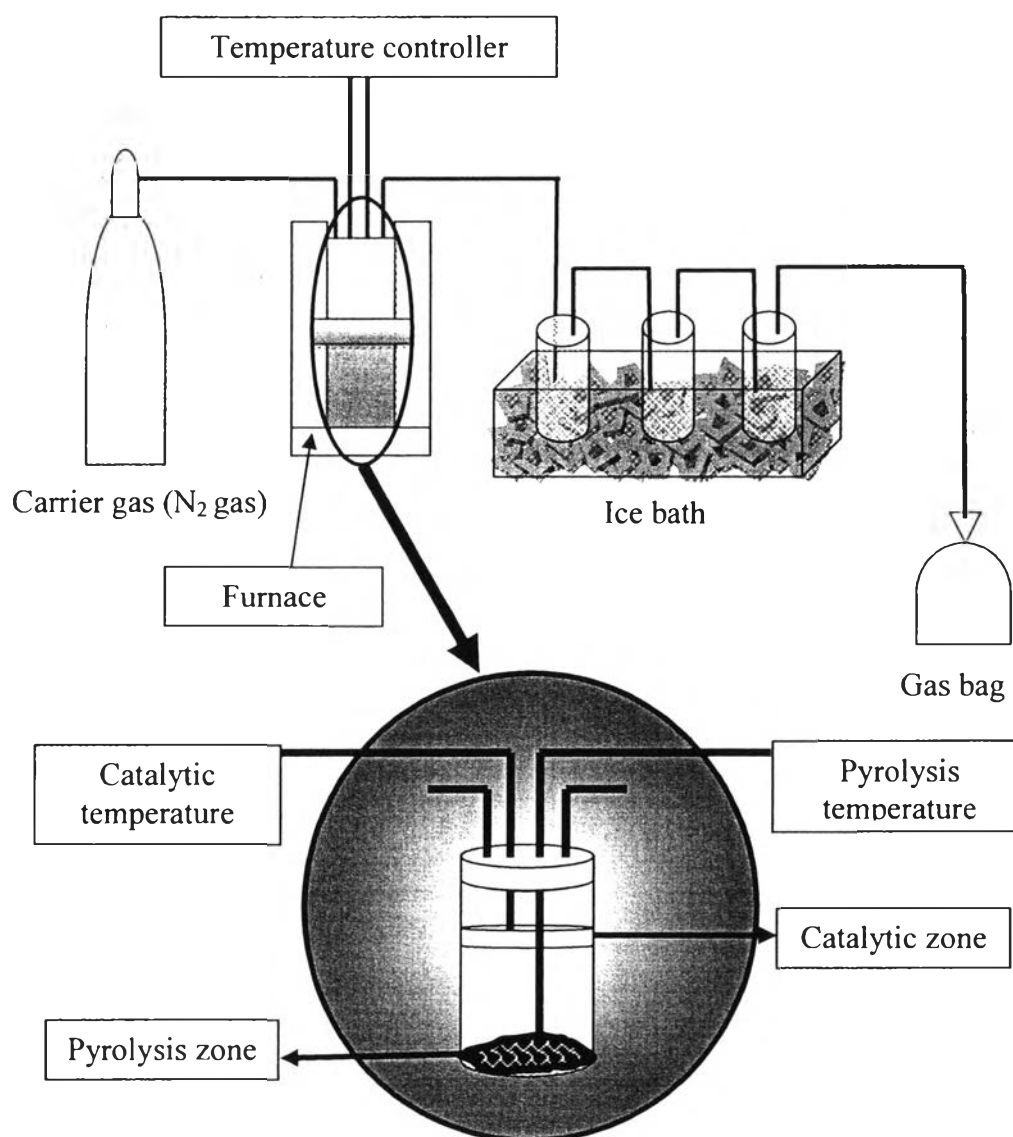


Figure 3.1 The reactor and the diagram of tire pyrolysis.

(b) Liquid Chromatography

Maltene solution was classified to each functional group as shown in Table 3.2 by using a liquid chromatography column (650 height x 26.6 mm. I.D.). The liquid chromatography column was packed with silica gel on the top and alumina in the bottom. The column was pre-wetted with n-hexane for overnight. The extraction was started with adding a mobile phase as shown in Table 3.2. The flow rate of the mobile phase was kept constant at 20 cm³/min controlled by an aquarium air pump. And then, the mobile phase was evaporated from each functional group by a rotary vacuum evaporator at about 60 °C. After extraction, the adsorbents were left overnight, and then were activated at 160 °C for 48 hr.

All functional groups (saturated hydrocarbons, mono-aromatics, di-aromatics, poly-aromatics, and polar-aromatics) obtained from the liquid chromatography process were analyzed the true boiling point distillation using a Varian GC-3800 simulated distillation gas chromatograph (SIMDIST GC). The liquid samples were injected to a SIMDIST GC after dilution in carbon disulphide (CS₂).

Table 3.2 Optimized composition and volumes of mobile phase for 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	

3.5.3 Catalyst Characterization

(a) Hydrogen Chemisorption

The samples were pretreated at 150 °C with the heating rate of 10 °C/min for 1 hour; under a flow of helium (helium flow rate was 10 ml/min). Hydrogen chemisorptions of the pretreated samples were carried out at room temperature in a chemisorption system equipped with a TCD. The hydrogen chemisorption was carried out with the hydrogen flow rate of 30 ml/min by hydrogen pulses. The hydrogen pulse was performed by released hydrogen to the system until the chemisorptions completed.

(b) Transmission Electron Microscope (TEM)

Electron microscopy measurements were performed by using a JEOL JEM 2010 instrument which was operated an accelerating at 200 kV. The sample was prepared by grinding, and ultrasonically dispersing in acetone. And then, a drop of suspension was put and evaporated on a copper grid. The TEM image was

recorded. The average particle size (d_{VA}) was determined by using the formula; $d_{VA} = \Sigma nd^3 / \Sigma nd^2$ (d refers to particle size (nm), and n refers to the number of particles of each size).

(c) Temperature Programmed Desorption (TPD)

TPD analysis was used to characterize the total acidity strength of the catalyst. The catalyst was first pretreated in He at 150 °C for 30 minutes. Then, the system was cooled to 100 °C, and the NH₃ adsorption was performed using 1.13% NH₃/N₂ for 1.5 hours (to make sure that the adsorption of NH₃ completed) followed by the introduction of He (helium flow rate was 30 ml/min) for 30 minutes at 100 °C to remove the physical adsorption of NH₃. Finally, the system was cooled to 50 °C, and then the temperature programmed desorption was started from 50 °C to 900 °C with the heating rate of 10 °C/min.

(d) Temperature Programmed Oxidation (TPO)

Temperature Programmed Oxidation was used to determine the amount and characteristics of coke which deposits on the spent catalysts. The spent catalysts were weighed at a suitable amount and placed in the quartz tube. 5% O₂/He was flown through the spent catalysts, while the temperature was increased from room temperature to 650 °C with the heating rate of 10 °C/min. Then, the final temperature was held for 30 minutes. The amount of coke was determined from the area under the curve and calculated using the software supplied with the machine.

(e) Temperature Programmed Reduction (TPR)

H₂-TPR profiles of the samples were recorded from room temperature to 600 °C with the heating rate of 10 °C/min using 5% H₂/N₂ after the pretreatment of the samples at 150 °C under helium flow at 30 ml/min for 30 minutes.

(f) Surface Area Analyzer (SAA)

The specific surface area and the pore size of catalyst were determined by Brunauer-Emmet-Teller (BET) technique by N₂ physical adsorption

using the Sorptomatic 2900 equipment. The specific surface area and the pore size of catalyst were obtained from the twenty-two-point nitrogen adsorption and desorption isotherm plot. The pore size distribution was calculated using the BJH method.

(g) X-ray Diffraction Spectroscopy (XRD)

X-ray diffraction (XRD) patterns were taken by using a Rigaku, Rint X-Ray diffractometer system (RINT 2200) using a Cu tube and nickel filter for generating the CuK α radiation (1.5406 Å). In this experiment, XRD was employed to obtain the structure of catalysts. A catalyst sample was ground to fine and homogeneous particles, and then was packed in a glass specimen holder. The data from XRD was analyzed and recorded by an on-line computer.