



CHAPTER III EXPERIMENTAL

3.1 Materials

The tire used for pyrolysis was shredded and crumbed passenger car tire in the size range of 8-18 mesh (2.38-1.00 mm). The mileage of used tire was fixed to about 50,000 kilometers.

3.2 Equipment and Chemicals

3.2.1 Equipment

- 3.2.1.1 Bench-scale autoclave reactor
- 3.2.1.2 Agilent Technology, Gas Chromatography (GC)
- 3.2.1.3 Liquid Chromatography Column (Glass), 650 mm height, 26.6 mm. inside diameter
- 3.2.1.4 Varian GC-3800 stimulated distillation gas chromatography (SIMDIST GC)
- 3.2.1.5 Varian/SpectraAA 300 (Atomic Absorption Spectrometer, ASS)
- 3.2.1.6 Oxford/6111 (Scanning Electron Microscope, SEM)
- 3.2.1.7 Rigaku/Rint 2200HV (X-Ray Diffraction Spectroscopy)
- 3.2.1.8 Perkin Elmer/Pyris Diamond (Thermogravimetric /Differential Thermal Analysis, TG/DTA)
- 3.2.1.9 Temperature-programmed desorption (TPD)
- 3.2.1.10 Thermo Finnigan Sorptomatic 1990 (Surface Area Analyzer)
- 3.2.1.11 Gas-sampling bag
- 3.2.1.12 Aquarium Air pump
- 3.2.1.13 Vacuum Pump
- 3.2.1.14 Sieves, Mesh 8-18 and 40-60

3.2.2 Chemicals

- 3.2.2.1 Benzene (C_6H_6 , Assay $\geq 99.8\%$)
- 3.2.2.2 Diethyl ether ($(C_2H_5)_2O$, Assay $\geq 99.5\%$)
- 3.2.2.3 n-Pentane ($CH_3(CH_2)_3CH_3$, Assay $\geq 99\%$)
- 3.2.2.4 n-Hexane ($CH_3(CH_2)_4CH_3$, Assay $\geq 99\%$)
- 3.2.2.5 Methanol (CH_3OH , Assay $\geq 99.8\%$)
- 3.2.2.6 Carbon disulfide, CS_2
- 3.2.2.7 Silica for liquid chromatography (Particle size 0.063-0.200 mm; 70-230 mesh ASTM)
- 3.2.2.8 Neutral alumina for liquid chromatography (0.05-0.15 mm; pH 7.0 ± 0.5)
- 3.2.2.9 N_2 gas
- 3.2.2.10 KL and Y Zeolites Catalysts from Tosoh Company, Singapore
- 3.2.2.11 Metal precursor: hexachloroplatinic acid ($H_2PtCl_6 \cdot nH_2O$) from S.M. Chemical Company, Thailand.

3.3 Experimental Procedures

3.3.1 Catalyst Preparation

The KL and Y zeolites, obtained from TOSOH Company in Singapore, were first calcined at $500\text{ }^\circ\text{C}$ for 3 hours with the heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Then, the metal; Pt was loaded on the each zeolite by using the incipient wetness impregnation technique.

The precursor solution of hexachloroplatinic acid ($H_2PtCl_6 \cdot nH_2O$) was dropped onto calcined zeolite. Then, the impregnated catalyst was dried in an oven at $110\text{ }^\circ\text{C}$ for 3 hours. Next, the dried catalyst was calcined in the furnace at $500\text{ }^\circ\text{C}$ for 3 hours. After that, the catalyst was pelletized and sieved to obtain particle size in the range of $400\text{-}425\text{ }\mu\text{m}$. Finally, this catalyst was reduced with H_2 $500\text{ }^\circ\text{C}$ for 2 hour in order to convert metal oxide forms to metal elements before using in the experiments.

3.3.2 Pyrolysis Process

First, 30 g of scraped tires was loaded at the lower zone of the reactor. Prior to loading, these catalysts were mixed with various ratios (0.25 to 1.0). Then, for each experiment a catalyst mixture was loaded to the upper zone of the reactor in a “double bed” fashion. The so-called “double bed” schemes were classified into 3 cases as shown in Figure 3.1.

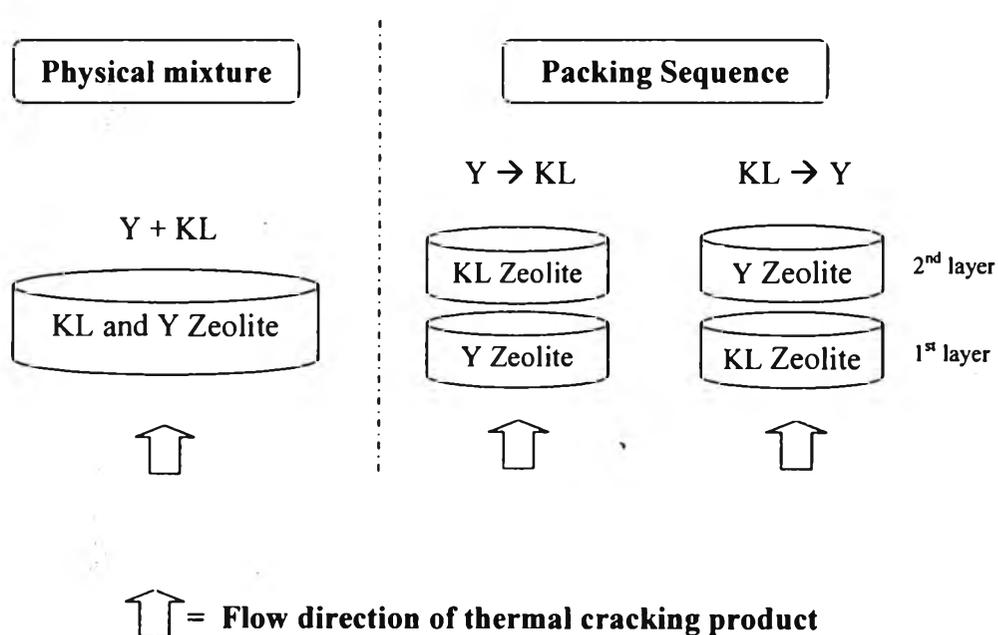


Figure 3.1 The order of catalyst packing in the reactor.

After that, the reactor (Figure 3.2) was closed and positioned in a furnace chamber as shown in Figure 3.3, and nitrogen was then passed through the reactor to purge oxygen inside the system at a flow rate 30 ml/min for 30 minutes. Heating via an external electrical heater was subsequently started, and the temperature was controlled to the final temperature of the upper zone of 300 °C, and the lower zone of 500 °C with the ramping rate of 10 °C/min. The temperature was held at the final temperatures for 90 minutes at the atmospheric pressure.

The liquid products were collected in the condensers placed into the iced-bath. And, the non-condensable products or gaseous products were collected in a gas-sampling bag. The mass of tires and liquid products, before and after pyrolysis,

were determined by weighing. The liquid products were analyzed by a SIMDIST Gas Chromatography (SIMDIST-GC). And, the gaseous products were analyzed by Gas Chromatography (GC).

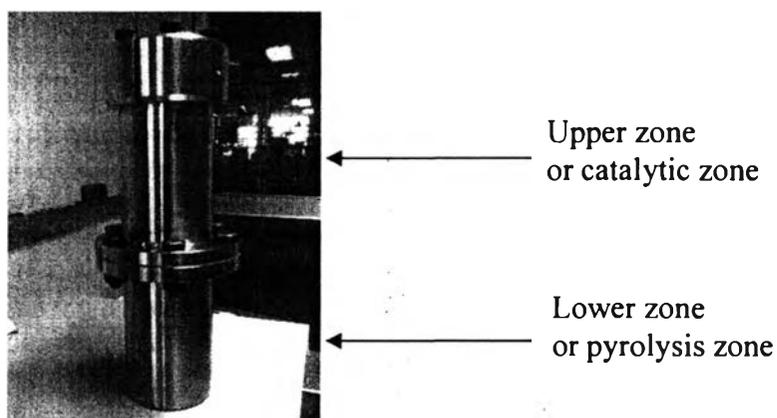


Figure 3.2 An autoclave reactor used in the experiment.

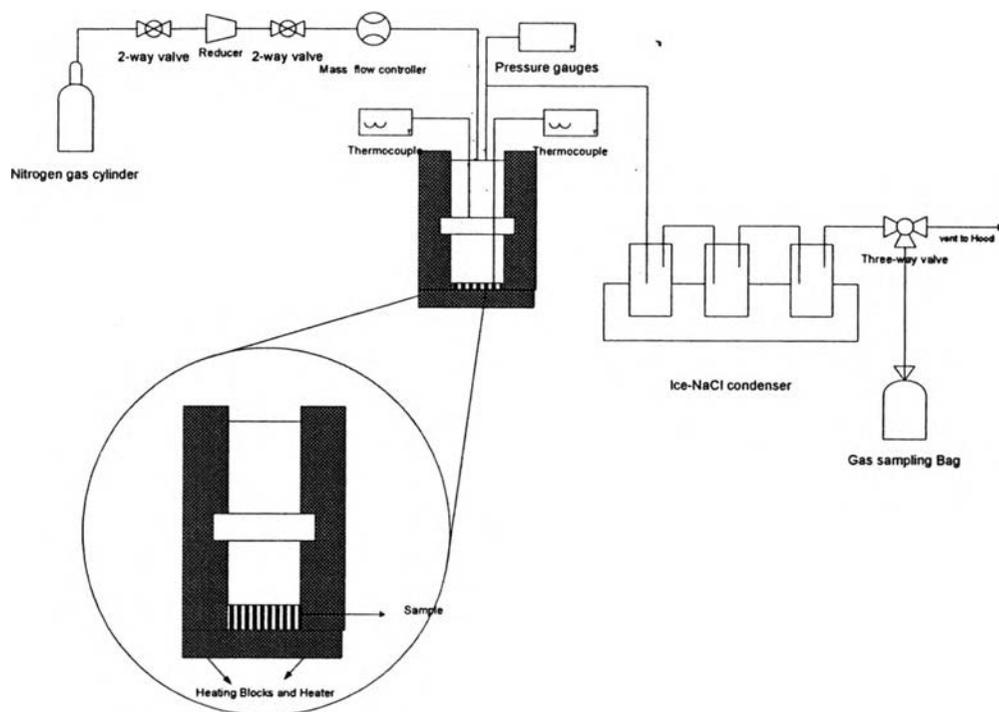


Figure 3.3 Schematic of the pyrolysis process (Mhodmonthin, 2005).

3.3.3 Product Analysis

3.3.3.1 *Gaseous Products*

The gaseous products were analyzed by 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 used as a detector with He as the carrier gas. The temperature program was as follows:

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

3.3.3.2 *Liquid Products*

The liquid products obtained from pyrolysis process were subject to be analyzed into 2 steps as follows:

a) Asphaltene Separation

The liquid products were first separated into maltene (n-heptane soluble) compounds and asphaltene (n-pentane insoluble) by adding n-pentane into the oils products at the ratio of 40:1, followed by shaking for 15 minutes in an ultrasonic bath and left overnight at room temperature. Then, the asphaltene was filtrated out by using 0.45 μm teflon membranes in a vacuum system. This membrane was then dried in an oven at 110 $^{\circ}\text{C}$ for 6 hours. Finally, the filter cake was weighed to determine the amount of asphaltene weight. The n-pentane solution was evaporated to seperate n-pentane from maltene by using rotary vacuum evaporator at 37 $^{\circ}\text{C}$.

b) Maltene Separation

The maltene solution (4.5 g mixed with 10 cm^3 n-hexane) was separated into five fractions: saturated hydrocarbon and aromatic compounds depending on their functional groups as shown in Table 3.1. The liquid chromatography column (650 height x 26.6 mm. I.D.) was packed with silica gel and alumina at the upper zone and lower zone of the column, respectively. Prior to

separation, the alumina and silica gel were activated at 160 °C for 18 hours. The column was pre-wetted with n-hexane overnight. The flow rates of the mobile phase were kept constant at 20 cm³/min controlled by using a fish pump. Then, each component was separated from mobile phase by using rotary vacuum evaporator at 60 °C

Table 3.1 The optimized composition and volumes of mobile phases for maltenes separation (Sebor et al., 1999)

Mobile phase	Volume (cm ³)	Prevailing type of 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 aromatic compounds

The obtained maltene and hydrocarbon fractions were also analyzed by a Varian CP-3800 stimulated distillation gas chromatography (SIMDIST GC), equipped with FID. The ASTM-conformed temperature program is shown 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

3.3.4 Catalyst Characterization

3.3.4.1 *Atomic Absorption Spectroscopy (AAS)*

Varian/SpectrAA 300 was used to identify and measure the metal content in catalysts. A sample must be digested with an *aqua regia* solution (3 conc. HNO₃: 1 conc. HCl) to a solution of the metal element and the zeolites.

3.3.4.2 *Surface Area Analyzer (SAA)*

The specific surface area and total pore volume of the prepared catalyst sample was determined by Brunauer-Emmet-Teller (BET) method using Thermo Finnigan/Sorptomatic 1990, which N₂ gas was used as the adsorbate. The characterization was based on the physical adsorption of nitrogen gas on the catalyst surface.

3.3.4.3 *X-Ray Diffraction (XRD)*

XRD patterns were obtained using Rigaku/Rint2200 HV. A prepared catalyst sample was packed in a glass specimen holder which was placed in the goniometer using CuK_α small radiation operated at 40 kV and 30 mA. The catalyst sample was scanned from 5 degrees to 90 degrees (2θ) with the scanning speed of 0.02 degrees/min.

3.3.4.4 *Hammett Indicators*

Acidic and basic strengths of each catalyst were determined by basic and acidic Hammett indicators, respectively. About 30 mg of a sample was shaken with 1 ml of a solution Hammett indicator diluted in 10 ml methanol and 10 ml benzene for acidic and basic tests, and left to equilibrate for 2 hours. The color of the catalyst was then noted (Singh and Fernando, 2008). In these experiments, the Hammett indicators that were used are listed in Table 3.2

Table 3.2 Hammett indicators used for the measurement of basic and acid strength (Ikemoto *et al.*, 1972 and Singh and Fernando, 2008)

Indicator	Color (Base Form)	Color (Acid Form)	H_0
p-Nitrotolulene	colorless	yellow	-10.8
2-Bromo-4,6-dinitroaniline	yellow	colorless	-6.6
Crystal violet	blue	yellow	0.8
p-Dimethylaminoazobenzene	yellow	red	3.3
Methyl red	yellow	red	4.8
Bromothymol blue	blue	yellow	7.2
Phenolphthalein	pink	colorless	8.2
2,4 Dinitroaniline	blue	red	15

The H_0 value of a sample at the acid sites was determined by the smallest value, which had been subjected to a color change and having a H_0 value less than 7.0. Moreover, the H_0 value of a sample at the basic sites was determined by the greatest H_0 , which had been subjected to a color change and having a H_0 value more than 7.0 (Singh and Fernando, 2008).

3.3.4.5 Thermogravimetric/Differential Thermal Analysis (TG/DTA)

The coke formation on a catalyst was determined by TG/DTA. The sample was heated from the room temperature to 800°C with the heating rate of 10°C/min. 99.9% nitrogen and 99.7% oxygen flow rate were controlled at 100 ml/min and 200 ml/min, respectively.