



CHAPTER III EXPERIMENTAL

3.1 Materials

Used passenger car tire in the experiment is supported by Renewable Energy Company to produce within a particle size range of 8-18 mesh. The mileage of tires is fixed at 50,000 kilometers.

3.2 Equipments

1. Autoclave reactor
2. Varian GC-3800 simulated distillation gas chromatograph (Sim-Dist GC)
3. Liquid Chromatography Column (Glass), 650 height, 26.6 inside diameter
4. Gas Chromatography (GC)
5. Thermo Finnigan sorptomatic 1990 (Surface Area Analyzer)
6. Varian/SpectrAA 300 (Atomic Absorption spectrometer, AAS)
7. Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA)
8. Rigaku/Rint 2200HV (X-ray Diffraction Spectroscopy)
9. Gas sampling Bags
10. Aquariums Air Pump
11. Vacuum Pump
12. Ultrasonic Bath
13. Evaporator
14. Furnace

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. Aluminum oxide Fluka for Chromatography (0.05-0.15mm ; pH 7.0 ± 0.5)
6. Benzene (C_6H_6 , Assay $\geq 99.8\%$)
7. Diethylether ($(\text{C}_2\text{H}_5)_2\text{O}$, Assay $\geq 99.5\%$)
8. N_2 gas
9. Methanol (CH_3OH , Assay $\geq 99.8\%$)
10. Catalysts
11. Metal precursors ($\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ and $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$)

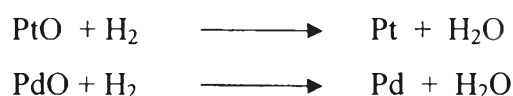
3.4 Methodology

3.4.1 Bimetallic Catalyst Preparation

3.4.1.1 *Co-impregnation Method*

Y zeolite was obtained from Tosoh Company, Singapore. The zeolite was calcined at $500\text{ }^\circ\text{C}$ for 3 hours with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ to remove organic residues from the zeolite. After that, the zeolite was loaded with Pt and Pd by an incipient wetness technique composing of 4 steps. Firstly, individual $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ and $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ compounds were dissolved in deionized water, and the solutions were mixed to get a solution. Secondly, the mixed solution was dropped on the zeolite using a micro syringe. Thirdly, the wet zeolite was dried in an oven at $110\text{ }^\circ\text{C}$ for 3 hours. Finally, catalyst was calcined in a furnace at $500\text{ }^\circ\text{C}$ for 3 hours with the heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Then, a catalyst was obtained in metal oxide forms.

Before using, the catalyst had to be reduced with H_2 at $500\text{ }^\circ\text{C}$ for 2 hours in order to convert metal oxide to metal.



3.4.1.2 *Successive-impregnation Method*

i. Loading Pt first

Y zeolite was obtained from Tosoh Company, Singapore. The zeolite was calcined at 500 °C for 3 hours with the heating rate of 10 °C/min to remove organic residues from the zeolite. After that, the zeolite was loaded with Pt and Pd by incipient wetness technique composing of 5 steps. Firstly, $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ was dissolved in deionized water to get a $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ solution. Secondly, the $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ solution was then dropped on the zeolite using a micro syringe. Thirdly, the wet zeolite was dried in an oven at 110 °C for 3 hours. Next step, the $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was dissolved in deionized water, and then was dried in an oven at 110 °C for 3 hours. Finally, the catalyst was calcined in a furnace at 500 °C for 3 hours with the heating rate of 10 °C/min. Then, a catalyst was obtained in metal oxide forms.

Before using, the catalyst was reduced with H_2 at 500 °C for 2 hours in order to convert metal oxide to metal.

ii. Loading Pd first

Y zeolite was obtained from Tosoh Company, Singapore. The zeolite was calcined at 500 °C for 3 hours with the heating rate of 10°C/min to remove organic residues from the zeolite. After that, the zeolite was loaded with Pt and Pd by incipient wetness technique composing of 5 steps. Firstly, $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was dissolved in deionized water to get a $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ solution. Secondly, the $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ solution was then dropped on the zeolite using a micro syringe. Thirdly, the wet zeolite was dried in an oven at 110 °C for 3 hours. Next step, an appropriate amount of $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ solution ($\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ precursor was dissolved in deionized water) was dropped on the zeolite, and then the zeolite was dried in an oven at 110 °C for 3 hours. Finally, all prepared catalysts were calcined in a furnace at 500 °C for 3 hours with the heating rate of 10 °C/min. Then, a catalyst was obtained in metal oxide forms.

Before using, the catalyst was reduced with H_2 at 500 °C for 2 hours in order to convert metal oxide to metal.

3.4.2 Pyrolysis Process

The system of experiment was shown in Figure 3.2. The reactor is autoclave reactor which has 2 zones: the upper zone (catalytic zone) and the lower zone (pyrolysis zone), as shown in Figure 3.1. Waste tire of 30 g was loaded in the lower zone and 7.5 g catalyst, which had particle size between 300 – 425 μm , was loaded in the upper zone. Before pyrolysis, nitrogen 30 ml/min was passed through the reactor to remove oxygen and moisture. The desired temperature of lower zone and upper zone were fixed at 500 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$, respectively. During pyrolysis the temperature increased from room temperature to desired temperature with the heating rate of 10 $^{\circ}\text{C}/\text{min}$ and held at the desired temperature for 90 minutes to ensure complete conversion. The liquid product was collected in condensers, and the gas product was collected in the gas bag. The solid product was located at the lower zone of the reactor.

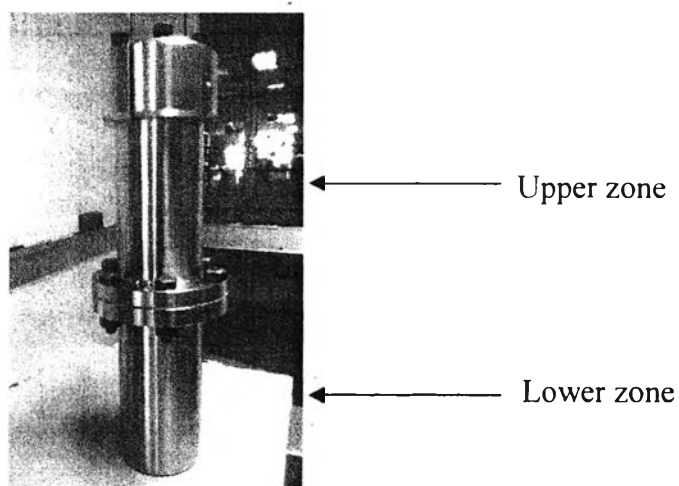


Figure 3.1 An autoclave reactor in the experiment.

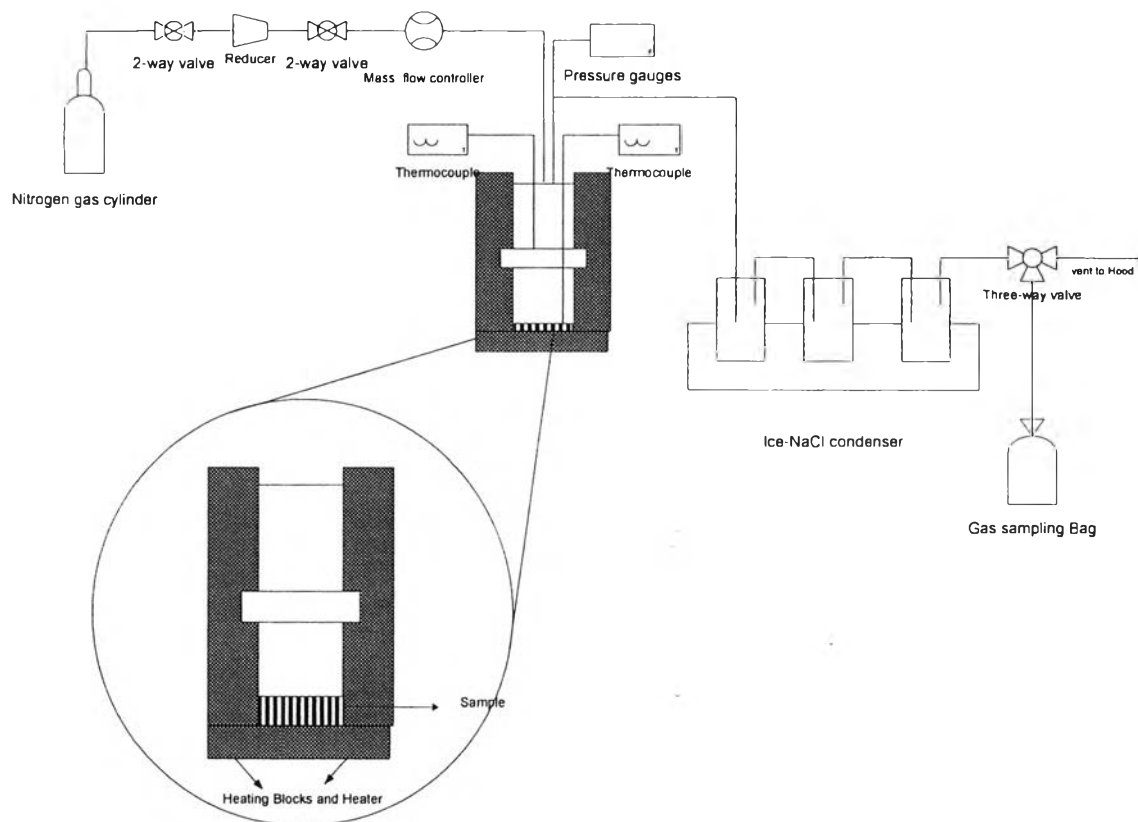


Figure 3.2 Diagram of the pyrolysis process (Mhodmonthin, 2005).

3.4.3. Catalyst Characterization

3.4.3.1 *Atomic Absorption Spectroscopy (AAS)*

The amount of metal loading on the zeolite was determined using an Atomic Absorption Spectrometer (Varian SpecterAA 300 model). The sample digested with *aqua regia*.

3.4.3.2 *Transition Electron Microscopy (TEM)*

Morphology characterization was performed by using a TEM. The TEM images of the catalyst samples were taken using a JEOL JEM 2010 instrument, working at 200 kV and equipped with an EDAX spectrometer for measuring X-ray energy dispersive data. The catalyst powders were dispersed in ethanol, and then the suspension was dropped on a carbon film supported on a 300 mesh Cu grid.

3.4.3.3 X-Ray Diffraction (XRD)

XRD patterns were measured by using the Rigaku Rint 2200. The profiles were recorded on a standard diffractometer using CuK radiation (1.5406 Å). The catalyst sample was scanned in the 2θ range of 5° to 90° . This system was operated at 40 kV and 30 mA. The catalyst sample was ground and packed in glass holder; then it was analyzed from $(2\theta/\theta)$ with the scan speed of $5^\circ/\text{min}$ and the scan step of 0.02.

3.4.3.4 Temperature Program Reduction (TPR)

The metal reduction and bimetallic interaction was examined by the Temperature Program Reduction method. The instrument was a conventionally made up system connected to a TCD detector, and the detected signal was sent online to the software. The experiments were performed in a quartz tube containing 0.05 g of sample. Before analysis, the catalyst sample was pretreated with He at 150°C for 30 minutes. After cooling, TPR patterns were recorded from room temperature to 600°C by using 5 % H_2/N_2 with the heating rate of $10^\circ\text{C}/\text{min}$.

3.4.3.5 Hydrogen Chemisorption

Hydrogen chemisorption was obtained by using a conventionally made up system connected to a TCD detector. The catalyst sample of 0.05 g was reduced at 500°C with the heating rate of $10^\circ\text{C}/\text{min}$ by using 5 % H_2/N_2 before any measurement. Hydrogen chemisorption was determined at room temperature with the purified H_2 pulsed of 20 μl . The result was detected with the TCD connected online to software to determine metal dispersion on the catalyst from the amount of H atoms adsorbed on the metals. For the calculation of metal dispersion, it was assumed the ratio of $\text{H}/\text{Metal} = 1$. And the metal particle size was measured by using the equation from Blomsma *et al.*, (2001).

3.4.3.6 Elemental Analyzer

The amount of sulfur deposit on the catalyst was determined by using an elemental analyzer (LECO, CHNS-932).

3.4.3.7 Thermo Gravimetric Analysis (TGA)

The amount of coke formation on the spent catalyst was determined by using Perkin Elmer, METTLER TG/DTA 851e. The sample was weighed and placed in a Pt pan. The samples were heated from the room temperature to 800°C with the heating rate

of 10°C/min. The nitrogen and oxygen flow rate were fixed at 100 ml/min and 200 ml/min, respectively.

3.4.4. Oil Analysis

Oil products produced from the pyrolysis process were classified into two steps;

3.4.4.1 *Asphaltene Precipitation*

For asphaltene precipitation, n-pentane was added to oil products at the ratio 40:1 and shaken for 10 min in ultrasonic bath. The solution was left overnight. After that, asphaltene was filtered out using 0.45 µm Teflon membrane in a vacuum system. The membrane with the precipitated material was dried in a vacuum oven at 0.1 bar and 333 K for 6 hours and finally weighed to determine asphaltene. N-pentane is evaporated from the solution by a rotary vacuum evaporator in 50 °C to obtain maltene.

3.4.4.2 *Maltene Classification using Liquid Adsorption*

Chromatography

The maltene solution (4.5 g of maltene mixed with 10 cm³ n – hexane) was analyzed for chemical compounds, as shown in Table 3.1 by using a liquid adsorption chromatography column (650 height x 26.6 mm. I.D.) in which silica gel and alumina was packed at the upper and lower bed of the column, respectively. (The column was prewetted with n-hexane, and the neutral alumina was activated at 160 °C for 18 hours prior to use). After extraction, the adsorbents were dried at 50 °C under vacuum 4.4 kPa for 8 hours, and then activated at 160 °C for 48 hours. The flow rate of the mobile phase was kept constantly at 20 cm³/min controlled by a pump. And then, the mobile phase was separated from each compound by a rotary vacuum evaporator at about 80 °C and a pressure of 4.4 kPa.

Table 3.1 Optimized composition and volumes of mobile phased for preparative separation of petroleum maltenes on used 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

Finally, SIMDIST GC was used to analyze each functional group: ASTM D2887 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

3.4.5. Gas Analysis

Pyrolysis gas fractions were analyzed by a gas chromatography, Agilent Technologies 6890 Network GC system, using HP-PLOT Q column: 30m x 0.32 mm i.d. and 20 µm film. FID was used as a detector with carrier He gas. The temperature program was 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	10	°C/min
Holding time	30	min