CHAPTER III
EXPERIMENTAL

3.1 Materials

The tread of a used passenger tire, Bridgestone TURANZA GR-80, for pyrolysis was first shredded and sieved to a size range of 8-18 mesh.

3.2 Equipment

1. Bench-scale autoclave reactor
2. Agilent Technology Gas Chromatography 7890 (GC)
3. Thermal modulator with Pegasus® 4D TOF-MS
4. VARIN INOVA 500 MHz spectrometer
5. Gas-sampling bag
6. Aquarium Air pump
7. Vacuum Pump
8. Sieves, Mesh 8-18 and 40-60

3.3 Chemicals

1. Carbon disulfide, CS_2
2. N_2 gas
3. KL Zeolite Catalysts from Tosoh Company, Singapore
4. Metal precursors: Rhodium (III) chloride hydrate ($RhCl_3 \cdot xH_2O$)
5. N-pentane ($CH_3(CH_2)_3CH_3$, Assay $\geq$ 99 %)

3.4 Experiment

3.4.1 Catalyst Preparation

The zeolite, Linde Type L (LTL, K-form, Si:Al = 3) supplied by the TOSOH Company (Singapore) was first calcined in air at 500 °C with the heating rate of 5 °C min^{-1} for 3 hours. Then, the KL catalyst was loaded with Rh using the incipient wetness impregnation technique to obtain 1 %wt Rh-supported catalyst. After that, the KL and Rh/KL were pelletized, ground, and then sieved to a specific particle size range of 400-425 μm before use.

3.4.2 Pyrolysis of Waste Tire

A used passenger tire tread. Bridgestone TURANZA GR-80, was shredded and sieved to a size range of 8-18 mesh. The tire pyrolysis experiments were conducted using the same pyrolysis system as in (Dũng *et al.*, 2009). The tire sample was pyrolyzed in the reactor where the temperature was ramped from room temperature to the final temperature of 500°C with the ramping rate of 10 °C min^{-1}, and kept at the final temperature for one hour to ensure the total conversion of tire. 7 grams of the KL and 1% Rh/KL catalysts were packed and heat at 350 °C in the catalytic zone. A 25 ml min^{-1} nitrogen was used to purge the reactor before the experiment and to carry the product out of the reactor. The obtained product was passed through the ice-salt condensing system containing two consecutive containers in order to separate the liquid product from incondensable compounds. After the experiment, the solid and liquid were weighed to determine the product distribution. The amount of gas was calculated from mass balance. Only the oil was brought to analysis in this study. It was first dissolved in n-pentane with the ratio of 40:1 (n-pentane:oil) to separate asphaltene. The clear solution after filtration is called maltene.

3.4.3 Product Analysis

3.4.3.1 Comprehensive 2D Gas Chromatography with Time-of-flight Mass Spectrometry (GC × GC- TOF/MS)

The GC × GC / TOF-MS system was composed of an Agilent gas chromatograph 7890 (Agilent Technologies, Palo Alto, CA, USA), a thermal modulator, and a Pegasus® 4D TOF-MS (LECO, St. Joseph, MI, USA). The GC was installed with two columns: the first column was a non-polar Rtx 5 silms® (30m x 0.25 mm i.d. x 0.25 μm film thickness), and the second column a Rxi®-17 ms (1.10 m x 0.10 mm i.d. x 0.10 μm film thickness). Both columns were made by Thames Restek (Sounderton, UK). The main GC oven was operated from at 50 °C with 2 minute holding at the beginning and then ramped to 310 °C at 5 °C min^{-1} with 10 minute holding at 310 °C, and the secondary oven was operated at 60 °C held for 2 minutes at the beginning and ramped to 320°C at 5 °C min^{-1} with 10 minute holding at the final temperature. One μl of the 10 mg/ml maltenes in carbondisulfide (CS$_2$)

was injected via a spiltless injector at 250 °C using He as the carrier and a constant column flow rate of 1.0 ml/min. The modulator was operated under modulation timing of 4-s cycle time and 0.5-s holding time in the release position. The nitrogen cryogen coolant maintained the temperature of the modulation trap to at lease 30 °C. A Pegasus 4D® TOF-MS instrument was used to acquire mass spectral data, using -70 V electron impact ionization. The ion source temperature was set at 250 °C. The detector voltage was set at 1600 V. The transfer line temperature was 250 °C. The mass rage collected was from 35 to 500 m/z, with 100 spectra/s transferred to the data station. The data processing was set S/N value of 10, match required to combine 500, and dt that was used to calculate the percentage area. Data were recorded and analyzed using the LECO ChromaTOF® software. The NIST library provided with the instrument was used for spectral searching. The analysis was repeated for 3 times.

3.4.3.2 Heteronuclear Single-Quantum Correlation-Nuclear Magnetic Resonance (HSQC-NMR)

NMR is a powerful tool that can reveal the environment of an atom in an organic hydrocarbon molecule. Besides qualitative information, NMR can provide valuable quantitative information about a sample. As the complexity of a sample increases, the analysis can be complicated by the spectra overlapped each other. In fact, the limitations of 1D NMR can be overcome by using modern two-dimensional (2D) NMR techniques. Two-dimension Heteronuclear Single-Quantum Correlation-Nuclear Magnetic Resonance (HSQC-NMR) has been successfully used to analyze pyrolysis oil from kraft lignin (Ben and Ragauskas, 2011). All NMR spectra were recorded using a VARIN INOVA 500 MHz spectrometer at 32 °C in deuterated ($CDCl_3$-d) chloroform as the solvent. 70 mg of maltenes from non-catalyst, KL and 1%Rh/KL batches was dissolved in 0.5 mL of $CDCl_3$-d. 2D HSQC-NMR spectra were recorded by employing a standard VARIAN pulse sequence "s2pul (gHSQC)" with 90° pulse, 3.0 s acquisition time, 3.0 s relax delay, $^1J_{C-H}$ 145 Hz, 48 scans, and the spectral widths were 8,000 and 32,000 Hz for the ^1H and ^{13}C dimensions, respectively. The central solvent ($CDCl_3$) peak was used as an internal chemical shift reference point ($\delta C/\delta H$ 77.2/7.26) (David *et al.*, 2010). Heteronuclear single-quantum coherence (HSQC) data processing and plots were carried out using

the default processing template and automatic phase and baseline correction of MestReNova, version 6.0.1. software. The analysis was repeated for 7 times.