

## CHAPTER III

### EXPERIMENTAL SECTION

#### 3.1 Materials

##### 3.1.1 Catalyst

Zirconium oxide ( $ZrO_2$ ) was purchased from Riedel-deHaën.

##### 3.1.2 Reagent

Ammonium sulfate ( $(NH_4)_2SO_4$ ) was purchased from Asia Pacific Specialty Chemical Limited. Carbon disulfide ( $CS_2$ ) was purchased from Merck.

##### 3.1.3 Tire Tread

Waste passenger tire was received from Bridgestone Co., Ltd., and rubber compound was received from a well-known tire company.

##### 3.1.4 Crosslink Densities

Tetrahydrofuran (Assay 99.8%) and hexane (total isomer 100%) were purchased from J.T. Baker and Mallinckrodt, respectively. N-decane ( $C_{10}H_{22}>98\%$ ) was purchased from Fluka Chemical.

##### 3.1.5 Gas and Chemical Regents Used for GC Calibration

Standard refinery gas was purchased from Agilent Technologies (Manufactured for Agilent by Scott Specialty Gases). N-pentane ( $C_5H_{12}>99.0\%$ ) and n-hexane ( $C_6H_{14}>99.0\%$ ) were purchased from Lab-Scan, Analytical Sciences, n-heptane ( $C_7H_{16}>99.7\%$ ) and iso-pentane ( $C_8H_{18}>99.85\%$ ) were purchased from Carlo Erbe Reagent and Fisher Chemicals, respectively.

##### 3.1.6 Standard Solution for SIMDIST GC

ULTRA Standard (FM) solution was purchased from Ultra Scientific.

#### 3.2 Experimental Procedures

##### 3.2.1 Catalyst Preparation

The most common way of preparation  $SO_4^{2-}/ZrO_2$  was incipient wetness impregnation. An aqueous solution of  $(NH_4)_2SO_4$  was added to the metal

oxide, Zirconium oxide, in a certain amount followed by drying at 110°C for about 15 hours and calcined at 550°C for 2 hours before keeping in the desiccators.

### 3.2.2 Preparation of Scrap Tires

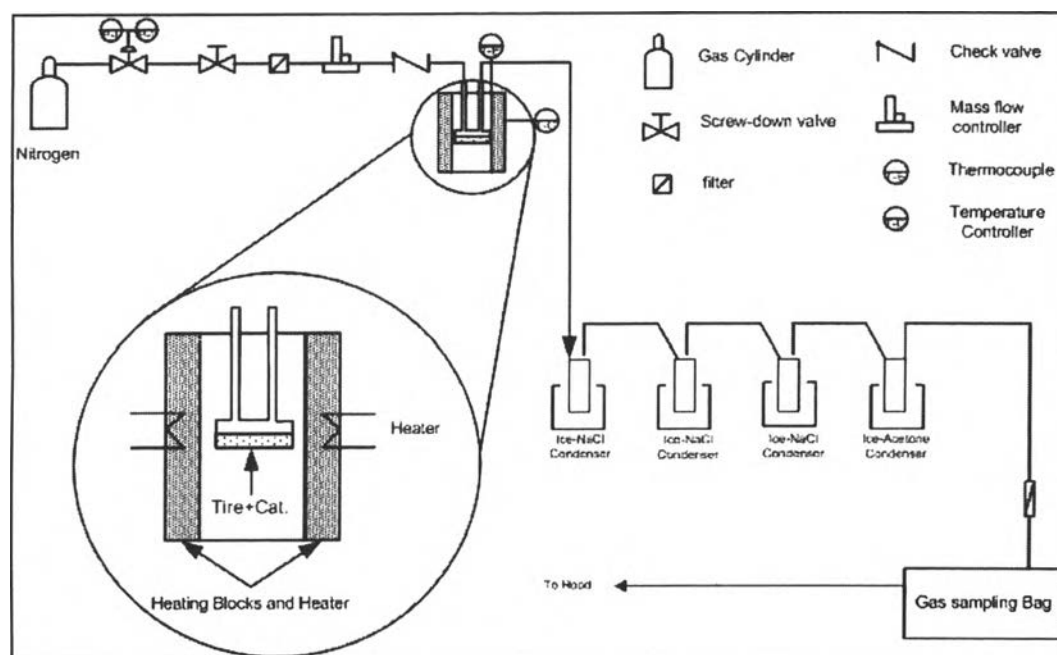
The tire tread for pyrolysis cut from passenger car tire was shredded and crumbed to small sizes. The shredded tire tread was sieved in the range of 0.5-1.4 mm. particle size diameters. The chopped material was stored under dry condition.

### 3.2.3 Preparation of Aged-Rubber Compounds

Tire tread rubber compounds, received from a well-known tire company, were molded. The sample sets were prepared in the size of 1.0x10.0 cm. before aging in the oven at 70°C under atmosphere at varied aging times from 1 to 4 weeks.

### 3.2.4 Pyrolysis Process

Two sets of experiments were performed: thermal and catalytic pyrolysis. For the first one, thermal pyrolysis was studied for the effect of tire aging on pyrolysis products. Catalytic pyrolysis experiments were performed to study the effect of catalyst acidity on pyrolysis products. One gram of chopped tire with 0.5-1.4 mm particle size diameter was loaded into U-tube reactor. Then, the reactor was positioned in the furnace reactor as shown in Figure 3.1 with a nitrogen flow 30 ml/min for 30 min in order to purge oxygen from the reactor line. The reactor was heated from room temperature to 500°C with the ramping rate of 10°C/min. The temperature was then stabilized at the final set point for 1 hour. Liquid products were trapped in NaCl-ice bath and ice-acetone condensers. Gas sampling bag, Dual-Valve Tedlar® PVF Bags (12x12 in) from Cole-Parmer, collected gaseous samples to be analysed off-line by GC. For catalytic pyrolysis experiments, a tire sample was mixed with catalyst with a certain tire to catalyst ratio. After all experiments, oil product was weighed. The product residue stored in the U-tube reactor was weighed, removed, and washed with tetrahydrofuran. Thus, the gas weight can be calculated by subtracting the oil weight and the residue weight from the total weight of initial tire.



**Figure 3.1** Schematic diagram of semi-batch fixed bed reactor for pyrolysis experiments.

### 3.3 Characterizations

#### 3.3.1 Physical Properties

##### 3.3.1.1 *Crosslink densities*

The crosslink densities of the samples were determined by the swelling method (Fan *et al.*, 2001). The procedure to measure the crosslink density was as follows: initially the samples were cut to  $\approx 10 \times 10 \times 2$  mm; then, organic additives in the samples were removed by extraction with THF and hexane for 2 days each and were dried for 2 days at room temperature; the organic material-extracted samples were then weighed; followed by soaking in n-decane for 1 day and the resulting samples were weighed; finally, the crosslink was calculated by the Flory-Rhener equation.

$$-\ln(1 - v_r) - v_r - \chi v_r^2 = \frac{2C_1 V_0 (v_r)^{1/3}}{RT}$$

Where  $v_r$  is the measure volume fraction of rubber in the swollen vulcanized samples;  $\chi$  is the interaction parameter between the rubber network and the swelling agent, n-decane, to be 0.43;  $V_0$  is the molar volume of n-decane,  $194.92 \text{ cm}^3 / \text{mol}$ ;  $R$  is the gas constant,  $8.29 \text{ N m}/(\text{mol K})$ ;  $T$  is the absolute temperature,  $298 \text{ K}$ . The  $C_1$  value calculated into the concentration of chemical crosslinks,  $[2M_{c,\text{chem}}]^{-1}$ , which is referred to as the crosslink density, using the equation

$$C_1 = \left( \frac{0.5\rho RT}{M_{c,\text{chem}}} + 0.78 \times 10^6 \right) \left( 1 - \frac{2.3M_{c,\text{chem}}}{M_n} \right)$$

Where  $\rho$  is the density of the rubber compound measured by BD210D as showed in Appendix B and  $M_n$  is the number-average molecular weight of masticated natural rubber before vulcanization, assumed to be  $5 \times 10^5 \text{ g/mol}$ . Experiments were carried out on three sets of samples, and the measured values were averaged.

### 3.3.1.2 Hardness

Hardness of the blends was measured using Durometer (Shore A), according to ASTM-D2240. Thickness of test specimens was 6 mm. The results were obtained from mean value of five measurements carried out on each sample.

### 3.3.2 X-Ray Diffraction (XRD)

XRD patterns were obtained using Rigaku D/Max 2200H. A sample was packed in glass specimen holder, which was placed in the goniometer using  $\text{CuK}_\alpha$  small radiation, and was operated at 40 KV and 30 mA. This prepared sample was scanned from 3 degrees to 90 degrees ( $2\theta$ ) with scanning speed of 0.02 degrees/min. The digital output of the proportional X-Ray detector and the goniometer angle measurements were recorded via an on-line computer for subsequent analysis.

### 3.3.3 Brunauer-Emmett-Teller (BET)

A surface area and pore size of catalysts was determined using the Brunauer-Emmer-Teller (BET) method. These characterizations are based on the physical adsorption of nitrogen gas through the Autosorb-1 Gas Sorption system (Quantachrome Corporation) at liquid nitrogen temperature of 77 K. Before starting characterization, catalyst samples were heated overnight in an oven at 250°C in order to remove moisture. A sample cell glass tube with 12 mm diameter was employed, and the sample was weighted for about 0.5 g. The net dried weight of catalysts was the weight after out-gassing. The specific surface area and pore size of catalysts were obtained from twenty-two-point nitrogen adsorption and desorption isotherm plot.

### 3.3.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis, the Dupont TGA 2590 equipped with a thermal analyzer 2000, measuring weight loss of a sample versus time and temperature, was employed to study thermal stability of rubber, solid residue and the kinetics of pyrolysis process. The chopped tire tread or rubber compound and catalysts were loaded in a platinum pan and pyrolyzed over 30 to 800°C with the heating rate of 10°C/min under an inert atmosphere of nitrogen gas to quantify the amount of rubber and other components. In oxygen atmosphere, the solid residue left after pyrolysis process was employed the same condition as inert atmosphere to quantify the carbon content.

### 3.3.5 Gas Chromatography (GC)

Gas-phase sample was analysed by gas chromatography, Agilent Technologies 6890 Network GC system, using HP-PLOT Q column: 30 m 0.32 mm i.d. 20 µm film. FID was used as a detector and He as carrier gas. The temperature programs were 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	220°C

Heating rate	10°C/min.
Hold for	30 min.

In this study, GC with FID analyzed the essential components collected in gas sampling bag for the composition. The standard refinery gas containing methane, ethylene, ethane, propylene, propane, C<sub>4</sub> and C<sub>5</sub>, was used for calibrating GC and examining the response factors. A mixture of n-pentane, n-hexane, n-heptane, and iso-octane in 25% volume used to calibrate C<sub>6</sub>, C<sub>7</sub>, and C<sub>8</sub> by n-pentane was applied as the standard. The response factors of gases on FID are calculated on the weight basis by the following equation using methane as the standard.

$$f_i = \frac{A_{std}}{A_i} \times \frac{G_i}{G_{std}} \times f_{std}$$

Where G<sub>i</sub> is the mass of the component, G<sub>std</sub> is the mass of methane, A is the area count from GC, i, std replaced each component in the standard. Finally, the mass fraction of any component, m<sub>i</sub> can be calculated as the following equation.

$$m_i = \frac{A_i \times f_i}{\sum A_i \times f_i}$$

The response factors are listed in Table 3.1.

**Table 3.1** Response factor of gases

Gas	Response Factor ( $f_i$ )
Methane	1
Ethylene	$0.94654 \pm 0.00217$
Ethane	$1.00996 \pm 0.00247$
Propylene	$0.97351 \pm 0.00324$
Propane	$0.98920 \pm 0.00390$
C <sub>4</sub>	$0.98242 \pm 0.00397$
C <sub>5</sub>	$0.98411 \pm 0.00472$
C <sub>6</sub>	$0.93943 \pm 0.00452$
C <sub>7</sub>	$0.91804 \pm 0.01078$
C <sub>8</sub>	$0.96873 \pm 0.01019$

### 3.3.6 SINDIST Gas Chromatography (SGC)

Liquid phase sample from the pyrolysis of used tires were analyzed directly by Varian CP-3800 Simulated Distillation Gas Chromatography (SGC), equipped with FID, using a 15m×0.25mm×0.25µm, WCOT fused silica capillary. The following temperature program, according to ASTM D 2887, was used:

Initial temperature	30°C
Time at initial temperature	0.01 min.
Heating rate	20°C/min.
Final temperature	320°C
Hold for	8.50 min.

The derived oils from the four glass condensers were bulked and analyzed together. They were diluted with a suitable solvent, CS<sub>2</sub>, to a known concentration, with an approximate ratio of 1:100. The standard volumes ULTRA standard solution, gravimetrically prepared, was used for calibrating SGC.