

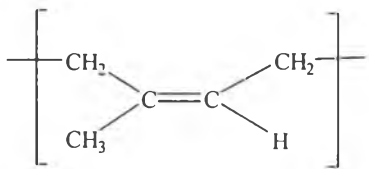
## CHAPTER II BACKGROUND AND LITERATURE REVIEW

### 2.1 Background

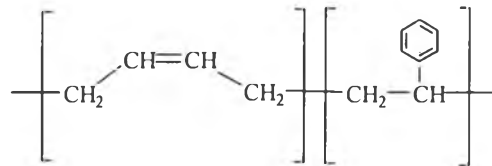
Natural rubber has been utilized in products for more than two hundred years. It is a material stored in bushes and trees and manufactured into products by original natives of Central and South America far back in the past. Until 1839, Charles Goodyear accidentally discovered that sulfur would crosslink the polymer chains, so rubber has become a widely usable material. Natural rubber is used in almost every part of the passenger car tires (tread surface, steel belts, nylon belt, side wall, inner liner etc.). One of the reasons for this wide use is its good building tack.

#### 2.1.1 Tires

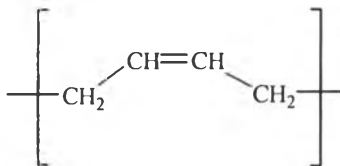
Tires contain vulcanized rubber in addition to the rubberized fabric with reinforcing textile cards, steel or fabric belts, and steel-wire bead. The most commonly used tire rubber is styrene-butadiene copolymer (SBR) containing about 25%wt styrene. Other rubbers used in tire manufacture include natural rubber (cis-polyisoprene), synthesis cis-polyisoprene, and cis-polybutadiene, as shown in Figures 2.1 to 2.3.



**Figure 2.1** Natural Rubber.



**Figure 2.2** Styrene Butadiene Rubber.



**Figure 2.3** Polybutadiene Rubber.

Another important component in tire manufacturing is carbon black, which is used to strengthen the rubber and aid abrasion resistance. In addition, extender oil, a mixture of aromatic hydrocarbons, is added to soften the rubber and to

improve workability. In the rubber vulcanization process, sulfur is used to crosslink the polymer chains within the rubber, and it also hardens and prevents excessive deformation at elevated temperature. In general, the sulfur content of rubber in tire is up to 1.5%. The composition of a typical passenger tire by weight (data received from a well-known tire company) is:

|   |     |
|---|-----|
| Synthetic Rubber (SBR, BR)              | 27% |
| Carbon Black                            | 28% |
| Natural Rubber                          | 14% |
| Oil Extender                            | 10% |
| Organic Fabric (e.g. nylon)             | 4%  |
| Steel Wire (reinforcement)              | 10% |
| Other Petrochemicals                    | 4%  |
| Fillers (S, ZnO, TiO <sub>2</sub> etc.) | 3%  |

### 2.1.2 Pyrolysis

In general, pyrolysis or thermal cracking can be defined as the decomposition of organic matters in the absence of oxygen or in an oxygen-starved atmosphere (Chang, 1996).

## 2.2 **Pyrolysis of Tires**

The main products of the tire pyrolysis process can be roughly categorized into three phases at room temperature: gas product, liquid oil, and solid residue or char. The volatile organic matters of tires consist of low molecules, carbon monoxide, carbon dioxide, and hydrogen, which can be useful as fuel or a source of chemicals. Moreover, the non-volatile carbon char remains as a solid residue which can be recycled in other proper applications.

There were many researchers attempting to find the optimum condition. Therefore, they were interested in parameters, such as temperature, heating rate, flow

rate of carrier, particle size, time, and sample weight that affected to the composition and distribution of products.

### 2.2.1 Thermal Degradation

In 1997, Roy *et al.*, studied the potential of polyisoprene rubber pyrolysis in order to make products to be able to replace commercial products. The conditions at 500°C and at total pressure varying between 0.8 and 28.0 kPa were applied to pyrolyze pure polyisoprene and a commercial rubber sample. A good quality pyrolytic carbon black (CBp) and pyrolytic oil were obtained from vacuum pyrolysis of polyisoprene rubber at low pressure. Most of aromatics and branched olefins can be used as gasoline additives. The rest was naphtha fraction. The surface chemistry of the organic portion of the recovered carbon black obtained at low pyrolysis pressure was closed to that of commercial carbon black, N330. Therefore, rubber pyrolysis should be performed at low pressure in order to obtain products with a higher commercial value.

In 1998, Roy *et al.*, focused on the development of a market for the pyrolytic oil and carbon black products obtained from a vacuum pyrolysis process. In the batch experiments, the feedstock was filled in the reactor at room temperature. Then, it was heated at a rate of 10°C/min to final selected pyrolysis temperature. The pyrolytic carbon black surface chemistry and activity were similar to the commercial carbon blacks such as grade N774. The total pyrolytic oil can be used as a liquid fuel or subjected to distillation. A gasoline additive can be replaced by a light fraction. The middle fraction was successfully tested as a plasticizer in rubbers. Road pavements can be added by the heavy fraction representing a good-quality feedstock. The pyrolytic gas can be used as a make-up heat source for the pyrolysis process.

The kinetic of the pyrolysis of four different tire powder sizes; 1.18-2.36 mm (40 mesh), 1.0-1.18 mm (16 mesh), 0.5-0.6 mm (30 mesh), and 0.355-0.425 mm (40 mesh) was investigated by Leung *et al.*, (1998) by using thermogravimetric and derivative thermogravimetric analysis method. They found that the DTG curve exhibited three different normalized weight loss rate regions over a temperature range of 150-600°C due to the lossing weight of main components; NR, SBR, BR or minor components; moisture, oil, plasticizer, and additive loss their weight at different rates and at different temperatures. Not only did the size of tire powder has

a significant effect on the pyrolysis process with increasing heating rate, but also the weight loss regions shift to higher temperature range or as well as the increase in the weight loss rate.

In 2000, Mastral *et al.*, had determined the influence of some important process variables (temperature, heating rate, time and hydrogen pressure) on yields of oils, gases and solid residue. The conversion products were comprised of oils and gases together with a solid that corresponded to the unconverted carbon black. The temperature was the main variable affected tire conversion. At 500°C, the conversion of scrap tire was always closed to the maximum, and the oil yield was always higher than 40%. However, hydrogen pressure was the most important variable regarding oil composition, with much lighter products being obtained at high pressure.

In 2000, Williams studied how the process of pyrolysis consumed heat without oxygen to break down a tire rubber. The tire was pyrolysed under temperatures between 450 and 700°C, leaving oil, a gas, a solid carbon and the steel casing of the tire. They had refined the process to produce mixtures of oils and chemicals with a real commercial value. Such high value products were aromatic chemicals, which were limonene, toluene, and xylene found in the oil used in the petrochemicals industry, and the residual carbon, which was upgraded to produce a high-grade activated carbon. Now, William and his assistant Alex Brindie have been working on methods to concentrate these chemicals using a novel application of catalyst technology. The catalysts promoted the formation of low molecular weight aromatic compounds in high yields. Fifteen to twenty percent of the tire rubber can be converted to limonene, toluene and xylenes.

In 2000, Laresgoiti *et al.*, pyrolysed car tires under nitrogen at 400-700°C. The compositions of gas generated during each pyrolysis run were analysed by gas chromatography with a Thermal Conductivity Detector (TCD) and a Flame Ionization Detector (FID) connected on-line. Tire pyrolysis gases composed of CO, CO<sub>2</sub>, H<sub>2</sub>S, and hydrocarbons such as CH<sub>4</sub>, C<sub>2</sub> (ethane, ethylene), C<sub>3</sub> (propane, propene), C<sub>4</sub> (butane, butene, etc.), C<sub>5</sub> (pentane, pentene, etc.), C<sub>6</sub> (hexane, hexene, etc.) and its unsaturated derivatives. Due to thermal cracking performed at higher temperatures, lighter gases were produced in higher amount, and the amount of

liquid was decreased. Since decomposition was completed and the same yields was obtained, the optimum temperature for recycling tire by pyrolysis was 500°C.

González *et al.*, (2001) found that the effect of temperature was similar to the effect of heating rate. As the temperature was increased, the yield of char decreased and the yield of gas increased. The yields of char, oil, and gas were 37-40%, ~55%, and 4-11%, respectively. A gas chromatography with a thermal conductivity detector was employed to analyze the gas composition, mainly H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>. The liquid fractions were aliphatic, aromatic and hydroxyl compounds characterized by FT-IR functional group analysis and chromatography. The kinetics of the thermal decomposition of the feedstock was studied using isothermal and non-isothermal thermogravimetric method at different temperatures (400-600°C) and heating rates (5-50K min<sup>-1</sup>). Not only did the particle sizes (0.2-1.6 mm. diameter) have no influence on the reaction but also the nitrogen flow rate and initial sample weight had no effect.

In 2002, Pantea *et al.*, examined the effect of a pyrolytic carbon black (CBp) post-pyrolysis heat treatment. At atmospheric pressure and under vacuum, truck tyre particles were pyrolysed at 490°C. Then, the recovered CBp was heated in a post-pyrolysis process at temperatures of 670-860°C. The CBp was recovered from carbonaceous deposits. The electrical conductivities depended on the CBp properties. The amount of carbonaceous deposits can be reduced at reduced pressure. By a post-pyrolysis heat-treatment of the CBp, a portion of the carbonaceous deposit was transformed into more polyaromatic structures, and the CBp conductivity was also increased.

In 2002, Choi studied pyrolysis patterns of SBR with different microstructures characterized by pyrolysis-gas chromatography. Butadiene, 4-VCH, and styrene were the major volatile pyrolysis products. The relative abundance of the styrene peak increased with an increase in the styrene unit content in SBR. The peak intensity ratio of 4-VCH/butadiene decreased with an increase in the 1,2-unit content, on the other hand, it increased with an increase in the *cis*-1,4, or *trans*-1,4-unit content.

Most researchers attempted to apply catalysts to overcome the faults of thermal cracking and receive more useful chemicals with narrow distribution.

### 2.2.2 Catalytic Degradation

In 2002, Williams *et al.*, maximised the concentration of single ring aromatic compounds from scrap tyres pyrolysed at 500°C in a fixed bed reactor. The catalysts used in this experiment were three types of zeolite catalysts. They were examined with different surface acidity and pore sizes. The results showed that the influence of the catalysts were to reduce the yield of oil with a consequent increase in gas yield. However, the concentrations of certain single ring aromatic compounds in the derived oils after catalysis were markedly increased. The different properties of the three catalysts such as pore size, influencing selectivity and the silica/alumina ratio, influencing the number of catalytically active sites on the catalyst surface caused the yield of aromatic hydrocarbons in the derived oil.

In 2002, Brebu *et al.*, had studied thermal and catalytic degradation of acrylonitrile-butadiene-styrene copolymer (ABS) performed at 450°C by semi-batch operation. For catalytic degradation, SA4 silica alumina and three SA4 iron oxide combinations (-Fe<sub>2</sub>O<sub>3</sub>, a Fe<sub>3</sub>O<sub>4</sub>-C composite and -FeOOH) were used. The quality of the degradation oil was affected by the heating rate, followed by heating program giving the lowest amount of heavy nitrogen-containing compounds. The SA4 iron oxide catalytic systems gave better results than the separate use of the catalysts, converting the heavy nitrogen (N)-containing compounds easily removed from the degradation oil by distillation. SA4-FeOOH system gave the best results in ABS degradation. The results related to experimental and mathematical modeling for constructing a breakthrough curve were summarized in their works.

Leung *et al.*, (2002) explored the effect of a pyrolysis temperature range of 500-1000°C and residence time on gas yield and composition. In addition, the effect of two natural catalysts, i.e. dolomite and limestone, on gas yield and composition was also studied. They found that the pyrolysed time decreased with increasing temperature. Due to stronger thermal cracking, the gas productivity increased dramatically from 5% to 25%, with increasing temperature from 500 to 1000°C while the tar yield decreased from 57% to 43% correspondingly. Beyond these temperatures, there was no significant change in the product yield. The main components consisted of H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>S and hydrocarbons such as CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>6</sub>, etc., which were the gases produced from the

pyrolysis process, in addition to a few other heavy hydrocarbons. With the use of catalysts, limestone exhibited similar trend as dolomite, the gas yield decreased slightly while tar yield increased slightly at both 700 and 800°C as compared to those without catalyst. The gas yield was increased sharply when the temperature was increased to 900°C. And the catalysts had capability of absorbing H<sub>2</sub>S. However, their life was limited by carbon black deposited on the surface and the poisoning of the catalyst by H<sub>2</sub>S.

From the previous works, researchers were interested in little catalytic cracking process. They were not clearly to summarize the differences in applications of series of acid catalysts to desired types of products. Thus, for this work, catalytic cracking of waste passenger tires using series of SO<sub>4</sub><sup>2-</sup> loading in ZrO<sub>2</sub> in a semi-batch reactor was performed to study the influence of catalyst on product distribution. Moreover, non-catalytic pyrolysis was also performed on aged rubber compounds for investigating whether or not pyrolysis of tires with different mileages would give the same product distribution.