



## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Background

Rubber has been invented since 1839 by Charles Spencer Goodyear and his work was patented on June 15, 1844. With this invention, rubbers became a popular material for transportation industry, especially for the passenger car tires. A tire is made of rubber compounds, steel and fibers. The principal element of the tire is rubber, which has a structure intermediate between thermosets and thermoplastics with molecular chains crosslinked by sulphur bridges during vulcanization reaction. This crosslinked network can resist heat softening, creep and solvent attack, but cannot be thermally re-processed. Such properties of rubber make it possible to use rubber tires under severe conditions. The other elements, such as steel and fibers, are also required in tire component in order to have durability and strength, and all components are chemically or physically bonded together.

Due to the growth of rubber tire product and the rapid development of technology, rubber tires are generated in a large amount every year, causing the disposal of waste tires more than 5 million tons per year. Most of the waste tires are usually dumped in landfill sites, thereby discarding the large amount of energy production potential of scrap tires and providing breeding grounds for some insects. Moreover, open dumping area can result in accidental fires with high pollutant emissions. Therefore, several utilization processes for waste tires such as retreading, reclaiming, incineration, gasification, and pyrolysis have been developed to maximize the potential economic recovery of energy and chemical materials from waste tires.


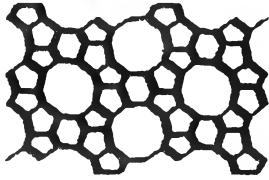
Among the utilization alternatives, pyrolysis is very interesting process to handle this kind of wastes because it seems to be an appropriate process for complex materials such as tires that cannot be remolded. Pyrolysis, also termed thermolysis is a process of chemical and thermal decomposition, usually resulting in smaller molecules. In most pyrolysis processes, air is excluded, for reasons of safety, product quality and yield.

In tire pyrolysis, the main material is tire rubber, a compound of styrene-butadiene and isoprene-based rubber (SBR), carbon black, sulphur, vulcanization aids, and zinc oxide. The rubber polymers are decomposed to low molecular weight products, liquids or gases, which can be useful as fuels or chemicals sources. The inorganic components, mainly steel and the nonvolatile carbon black, remain as solid residue that can be recycled in worthwhile applications such as smokeless fuel, carbon black or low-grade activated carbon.

The use of catalysts in pyrolysis process, so called catalytic pyrolysis, has been studied for a long time. The advantages of this process are lower operating temperature for degradation reaction, so it can save energy consumption and it also can control the selectivity to desired products, which has high market values. There are many types of catalyst used in this process such as zeolites catalysts and bifunctional catalysts. Mordenite zeolites are famous catalysts for cracking and isomerization and their proton forms are widely used in catalytic industrial processes due to its high acidity and thermal stability. Mordenite is comprised of two channel types: (i) larger channels, or main channels, which can access through twelve member rings of oxygen with an opening of  $7.0 \times 6.5 \text{ \AA}$ , and (ii) smaller channel, or side-pockets, which include eight member oxygen rings with  $3.4 \times 4.8 \text{ \AA}$ . These channels allow mono-dimensional diffusion for larger molecule such as Xe,  $C_3H_8$ , pyridine, etc., and three-dimensional for small molecule such as  $N_2$ , CO,  $NH_3$ , etc (Macedo *et al.*, 2004). Another type of zeolite also widely used in petrochemical process is ZSM-5 zeolite. This zeolite has been proven to have an excellent catalytic efficiency on cracking, degradation, isomerization and aromatization due to its crystalline microporous structure and strong acidity for the carbon-carbon bond scission. Protonic form of ZSM-5 presents an excellent stability due to its particular structure, which can prevent the formation of coke. Moreover, the opportunity of pore blocking is low due to the intersecting connection of the channels (Mastral *et al.*, 2006). ZSM-5 catalyst is an MFI type with intersecting of  $5.4 \times 5.6 \text{ \AA}$  and  $5.1 \times 5.5 \text{ \AA}$  channels. The structures of these two zeolites are shown in the Table 2.1.

Another type of catalysts is bifunctional catalysts. It usually comprises of two functional sites such as metal site for dehydrogenation reaction and acid site for cracking reaction.

**Table 2.1** Zeolites structure

Zeolites	Dimension	Si/Al
 MOR	1 D	38
 ZSM-5	3 D	23

## 2.2 Literature Reviews

Many researchers have studied on the pyrolysis of waste tire. Rodriguez *et al.* (2001) studied on pyrolysis of scrap tire at the temperatures between 300 to 700°C under nitrogen atmosphere in an autoclave. They found that the temperatures over 500°C did not affect to product yield, but produced a lot of aromatic hydrocarbons in the liquid fractions. The results were similar to Laresgoiti *et al.*(2004), who pyrolysed the whole car tire under nitrogen atmosphere in an autoclave at the temperatures between 300 to 700°C. It was found that temperature affected to the yield of liquid and gas obtained from the process. And, the aromatic hydrocarbons also increased with the increase of pyrolysis temperature. They also concluded that every 100°C of increasing temperature in the reactor, the yield of solid decreased. However, the yield of gas and liquid increased only at the pyrolysis temperature range from 300 to 500°C. Many authors reported about the influence of temperature to yield of pyrolysis product compositions. William *et al.*(1990) studied pyrolysis of scrap automotive tires under nitrogen atmosphere in a static-bed reactor, and found that gas and oil yield increased until the pyrolysis temperature reached 600 °C. They concluded that the increase in pyrolysis temperature affected to the amount of

hydrocarbons in oil fraction, that is, the aliphatic hydrocarbons were decreased whereas aromatic hydrocarbons were increased. The compositions of pyrolysis product are solid char (35 wt. %), liquid fractions such as alkane, alkenes, ketone and aldehyde, aromatic and poly aromatic (55 wt. %), and gas fractions such as H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>6</sub> (10 wt. %). González *et al.* (2001) studied pyrolysis of waste tire in a nitrogen atmosphere at the temperature range between 350–700°C and the heating rate 5-10 K/min. They found that the yield of solid char decreased, and the yield of gas increased as the pyrolysis temperature was increased. The yield of oil reached a maximum at the temperature around 550-575°C, and then declined at higher temperatures due to the strong cracking leading to the formation of the gas. And the compositions of oil and gas were the similar to William *et al.* (1990). Diez *et al.* (2004) also reported likewise, that is, the higher the pyrolysis temperature, the higher the liquid and gas yields were obtained. They concluded that the composition of gaseous fraction highly depended on the final temperature of pyrolysis; therefore, the high temperatures favored the presence of hydrogen and methane, while low temperatures favored a higher proportion of heavier hydrocarbons. Dai *et al.* (2001) studied on pyrolysis of waste tire in a fluidize-bed reactor, and found that at a long residence time, secondary cracking reactions occurred. At high temperatures and long residence time, the yield of CH<sub>4</sub>, H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and CO was increased. And, at the lower temperatures and heating rates, the pyrolysis favored carbonization, which reduced the yield of oil. This also reported by Ferrueco *et al.* (2005), who studied tire plrolysis in an atmospheric static-bed batch reactor under nitrogen atmosphere at the temperature range of 400-700°C. Liquid yield was increased at the temperatures of 400-500°C and remained constant until 700°C, whereas the gas yield slightly increased from 2.4% to 4.4% at the temperature range of 400 to 700°C. They concluded that the yield of light gas (H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub>) increased at high pyrolysis temperature. In the contrary, Lee *et al.* (1995) studied the effect of the feed rate of waste tire at the pyrolysis temperature range 700 to 880°C. They found that the gas product increased while the liquid product decreased with the increasing temperature. They concluded that the product yields, compositions and heating value were independent of feed rate of waste tire. Likewise, Cunliffe *et al.* (1998) studied waste scrap tire pyrolysis in a static-bed reactor at the temperature range 450-600°C.

Their results showed that the increase in final pyrolysis temperature led to the increase in gas yield and the decrease in liquid yield and poly aromatics hydrocarbons.

There were several authors having studied on the effect of different tire types in the pyrolysis process. Ucar *et al.* (2005) studied on the pyrolysis product of passenger car tire and truck tire. They found that the compositions of pyrolysis products of both tire types were similar. They also found that the passenger car tire had higher aromatics and sulphur content than the truck tire. But the solid product obtained from pyrolysis of truck tire was more suitable for producing activated carbon than that from the passenger car tire. Chen *et al.* (2001) also studied on the pyrolysis of passenger tire and truck tire. They found that the reaction rate increased when the temperature was increased.

Although the pyrolysis process can reduce the amount of waste disposed to the environment, but it also has some disadvantages: Firstly, the primary products obtained from pyrolysis such as low molecular weight olefins and char have low prices. Another is high operating cost in purification of the high molecular weight substances. So, the development of pyrolysis technology has been widely studied on the aim to improve the product quality or to reduce process cost. Vacuum pyrolysis, which has been studied by many researchers, is the way to improve product quality. Not only is the product quality improved, but also the energy is saved because it needs low temperature and residence time. And, it also gets rid of undesired reactions occurring during pyrolysis such as carbonization and secondary decomposition of valuable products. Murena *et al.* (2000) studied hydrogenative pyrolysis of scrap tire in liquid phase in the presence of hydrogen donating compound using a lab scale autoclave at 380 and 400°C. They concluded that hydrogenative pyrolysis required low temperature, and maximized the yield of liquid product. Also, high quality of products was also obtained because of the lack of coking and repolymerization reactions. The hydrogenative pyrolysis gave the same products yield as those obtained from vacuum pyrolysis.

Another way to improve either the quantity or quality of pyrolysis product is the use of a process called catalytic pyrolysis. Catalyst is the most important parameter in the studies on catalytic pyrolysis. Not only does the pyrolysis product

distribution vary, but also operating conditions are different for different types of catalysts. Generally, pyrolysis catalysts should have high activity and selectivity. They should be selected to ensure that they can produce a high amount of light products, as well as less hydrogen, methane and coke, and have high stability. At present, there are two types of pyrolysis catalysts; one is metal oxide based catalysts and another is based molecule sieve catalysts.

There has been great interest in studying of metal oxide catalysts for catalytic pyrolysis. Kolts *et al.* (1986a, 1986b, 1987) have developed metal oxide catalysts comprising of such mixed oxides as manganese oxide, magnesium oxide, iron oxide, together with alkaline-earth metals and rare-earth metals. Kolombos *et al.* (1978a, 1978b) have developed a manganese oxide catalyst used as an active component with titanium oxide and zirconium oxide as a carrier. Molecule sieve catalysts have attracted great interest in recent years. Pop *et al.* (1979) have investigated synthetic mordenite zeolite modified by Cu, Ag, and Co to produce a high yield of ethylene. Qu *et al.* (2006) have studied scrap tire pyrolysis catalysts utilizing ZSM-5 molecule sieve with lubricant base oil in order to enhance the degradation rate and improve the yield of oil product.

There were many researchers having reported the catalytic pyrolysis technology. Li *et al.* (2005) studied the influencing factor on catalytic pyrolysis process. They found that the keys to get high productivity were the properties of feedstock and types of catalyst. They also concluded that for difference cracking feedstock, the yield of light olefins can increase over the same types of catalyst. William *et al.* (1995) have studied the pyrolysis of biomass in a fluidized bed at 550°C by using H-ZSM-5, Y-zeolite and activated alumina. The results showed that ZSM-5 gave the highest yield of hydrocarbons, and all zeolites were found to produce polyaromatic hydrocarbons. They also reported that the coke formation was increased in Y-zeolite and activated alumina. Bagri *et al.* (2002) studied the influence of zeolite catalysts on upgrading pyrolysis gas derived from polyethylene. They found that oil products mainly consisted of aliphatic hydrocarbons, and ZSM-5 produced a high concentration of gas while Y-zeolite produced a high amount of aromatic hydrocarbons. They concluded that the higher yield of aromatic compounds using the Y-zeolite compared to the ZSM-5 catalyst was subjected to the difference

in pore size, surface acidity and surface area of the two catalysts. These results were similar to Marcilla *et al.* (2003) Moreover, catalyst can help reducing temperature in degradation process. For catalytic pyrolysis of waste tire, many reports stated the advantages of this process: (1) saving energy, (2) expanding the scope of pyrolysis feedstock and lowering demand of pyrolysis feed stock, (3) reducing cost and consumption of equipment, (4) increasing selectivity of light olefin, and (5) flexibility to adjust the yield distribution of light olefins (Meng *et al.*, 2004). Shen *et al.* (2006) studied pyrolysis of scrap tire using USY zeolite catalyst. They investigated the influence of pyrolysis temperature, catalytic temperature, catalyst/tire ratio and heating rate, and found that when the temperature and catalyst/tire ratio were increased, high gas yield and coke formation were observed. The results were similar to the report of William *et al.* (2003) and Meng *et al.* (2004) Moreover, they found that a high catalyst/tire ratio favored in the increase of the concentration of light naphtha in oils. They also reported that the amount of oil produced using the USY zeolite was less than ZSM-5 and Y-zeolite catalysts, but the products from USY zeolite had higher total concentration of benzene, toluene and xylene. Heating rate was also investigated and found to affect to aromatics, olefins, and coke formation.

From the recent work, Choosuton (2007) studied the pyrolysis of scrap tire in a bench-scale autoclave reactor. The pyrolysis temperature was increased from room temperature to 500°C with the heating rate of 10°C/min and kept in atmospheric pressure for 90 min. He tested 16 catalysts (the combination of USY, Beta, MOR and KL catalysts with noble metals of Pt, Pd and Ru). He found that gas yield was increased, resulting in a reduction of oil yield, in the presence of catalysts. Moreover, all catalysts can reduce polyaromatics by 50-70 %wt, approximately, and can produce higher quality gasoline and kerosene than pure zeolites and much higher than a non-catalytic case. Moreover, the quality of diesel was also improved because polyaromatics were highly reduced, although the quantity of diesel decreased.

One of the most interesting results by Choosuton (2007) is on the gas yield obtained from Ru/MOR, which was produced about 3 times as much as being produced from the non-catalytic case, resulting in the significant decrease of oil yields due to its highest cracking ability. Methane, ethylene and also propylene were

the main components in gaseous products. In-depth information of these results can be further studied for the effects and the role of ruthenium supported mordenite catalysts on the yield of pyrolysis products.