

## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Pyrolysis of Tires

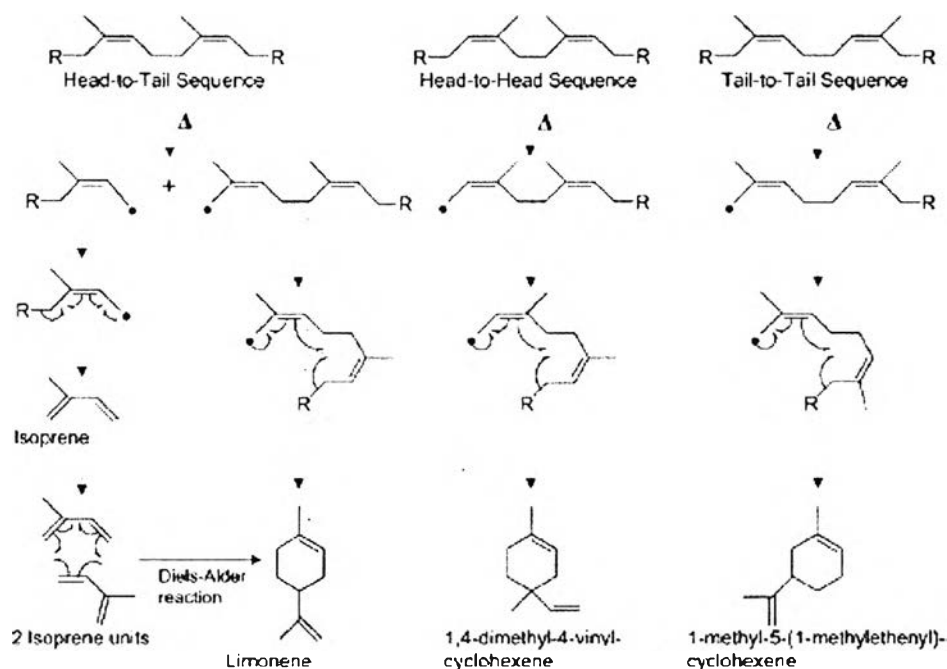
Pyrolysis technique is the thermal process with oxygen free atmosphere. The advantage of this process is low emission to the environment. Pyrolysis of tires generates gas, oil, char, and residual steel product. The gas product composes of hydrocarbons, which have carbon atoms varied from one to four, and other by-products such as hydrogen, carbon dioxide, carbon monoxide etc. The oil product consists of very complex mixtures of organic compounds with a high amount of aromatics such as benzene, toluene, xylene, polycyclic aromatics etc, and can be used as a fuel, a source of chemicals, or petrochemical feed stocks. Char is fine particulates composed of carbon black and ash (clay fillers, sulfur, zinc oxide etc.). And, other char by-products of pyrolysis may include steel. The yield and characteristics of pyrolysis products depend on feed stock, size and type of reactor, and operating conditions, such as temperatures, heating rate, pressure, and residence time, etc.

The probable pathways of degradation of tire by cracking reaction are explained in terms of natural rubbers (polyisoprene), polybutadiene rubbers, and styrene-butadiene rubbers as shown below;

##### 2.1.1 Polyisoprene (NR) Degradation

Sato *et al.*, 2003 studied the degradation of polyisoprene by lipid peroxidation. They reported that the major products formed from pyrolysis of polyisoprene were isoprene, limonene, 1,4-dimethyl-4-vinylcyclohexene, and 1-methyl-5-(1-methylethenyl) cyclohexene. The isoprene dimer species were formed by subsequent chain scission of  $\text{CH}_2\text{-CH}_2$  bond in the head-to-tail sequence of polyisoprene, while the limonene formed from the head-to-tail sequence of polyisoprene by inter molecular cyclization. The 1,4-dimethyl-4-vinylcyclohexene and the 1-methyl-5-(1-methylethenyl) cyclohexene were formed by cyclization from

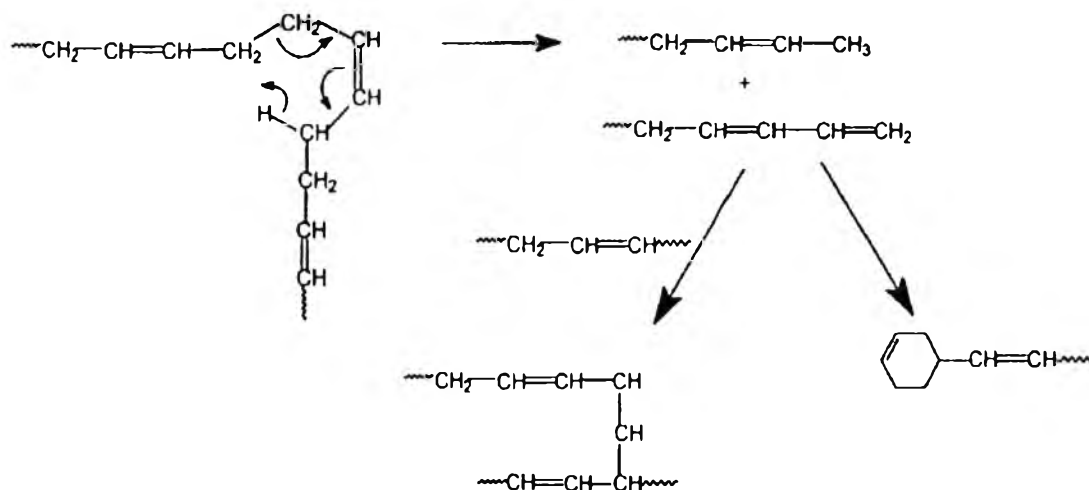
the head-to-head sequence and the tail-to-tail sequence of polyisoprene, respectively. As shown in Figure 2.1.



**Figure 2.1** Pathways for the formation of monomer and dimer components from polyisoprene rubbers by pyrolysis (Sato *et al.*, 2003).

### 2.1.2 Polybutadiene (BR) Degradation

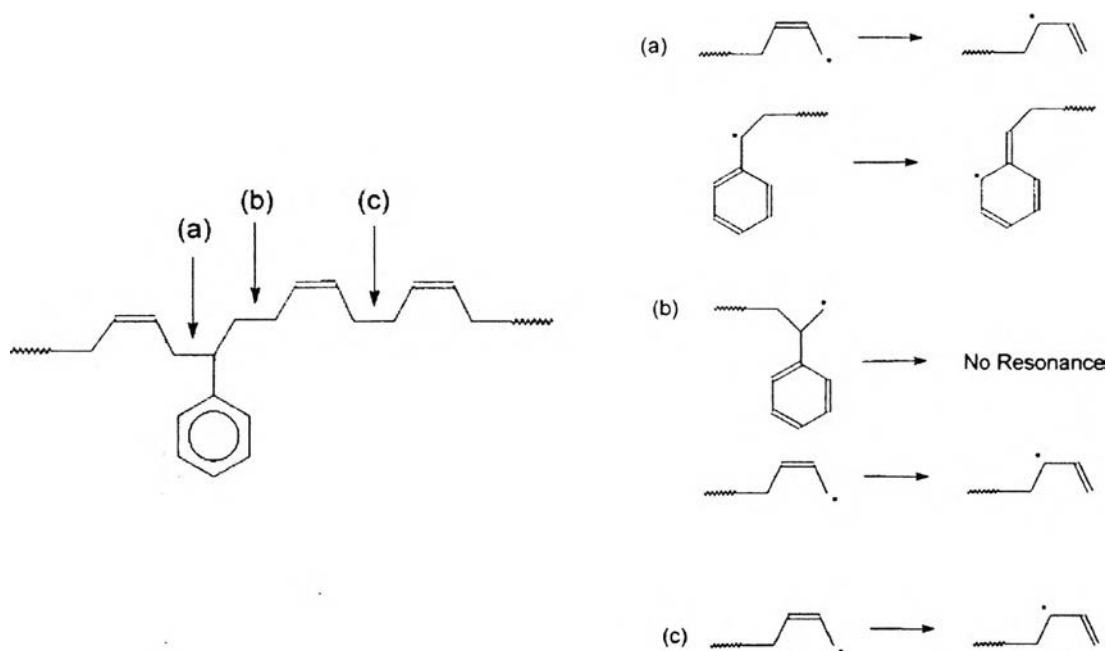
The thermal degradation of polybutadiene was studied by Chen and Qian in 2000. They concluded that at lower temperatures, the depolymerization of polybutadiene was the major reaction. At higher temperatures, the chain scission mainly occurred at the  $\beta$ -position of the C-C single bonds close to double bonds attended by cyclization and aromatization. Furthermore, the degradation of polybutadiene was occurred by hydrogen transfer reactions and led to chain scissions. The cyclization or branching reaction led to form vinyl chain ends and cross-linking. And, the possible reaction of polybutadiene degradation was proposed by Uhl *et al.* (2000) as shown in Figure 2.2.



**Figure 2.2** Possible mode of degradation of polybutadiene (Uhl *et al.*, 2000).

### 2.1.3 Styrene-Butadiene (SBR) Degradation

The most probable position dissociation sites in a SBR are shown in Figure 2.3. The dissociations of the positions (a) and (b) lead to the formation of radicals with the radical centers on styrene and butadiene units, while the dissociation of the position (c) results in the formation of radicals with the radical center on only butadiene units. The stability of the radicals formed by cleavage of positions (a) through (c) differs. The radical with the radical center on styrene, formed from the position (a), has very stable resonance forms due to the phenyl ring. Consideration of the stability of these radicals suggests that dissociation of the (a) linkage is more favorable than the dissociation of the (b) and (c) linkages reported by Choi in 2000.



**Figure 2.3** Styrene-Butadiene bond dissociation (Choi, 2000).

Many researchers have studied on the pyrolysis of waste tires. William *et al.* (1990) studied the influence of temperature and heating rate on the pyrolysis of scrap automotive tires, and found that the product yield increased with temperature, but no significance of heating rates was observed. Rodriguez *et al.* (2001) studied on the pyrolysis of car tires with different temperature conditions. They found that the tires were completely decomposed at 500°C. The oil pyrolysis products consisted of aromatics, and they were mixtures of C<sub>5</sub>-C<sub>20</sub> organic compounds of which 60 wt. % was in range of diesel oil. The gas products consisted of C<sub>1</sub> and C<sub>4</sub> hydrocarbons of high calorific values. Char was fine particulates as the original tire portion, and was easily crumbled into commercial carbon black. Barbooti *et al.* (2004) reported that the optimum pyrolysis condition of waste tire in a fixed-bed batch reactor (1.25 m length and 0.03 m o.d.), which gave the maximum yields of pyrolysis product, was the pyrolysis temperature of 430°C; the nitrogen flow rate of 0.35 m<sup>3</sup>h<sup>-1</sup>, and the particle size of 10 mm.

The effect of different types of reactors was investigated on the pyrolysis of tire. Different types of reactors have been used for waste tire pyrolysis, such as

autoclaves, fluidized bed reactors, fixed bed reactors, and moving bed reactors. Several research papers focused on the influence of type of pyrolysis reactor on the product yield and the characterization of pyrolysis products. Aylón *et al.* (2008) compared between a fixed bed reactor and a moving bed reactor in terms of the yield and the characterization of products. They found that the char yield was similar in both reactors. The oil yield obtained from the moving bed reactor was lower than that from the fixed bed reactor. In contrast, the gas yield in the moving bed reactor was higher than in the fixed bed reactor, and the light compounds were also higher than in the fixed bed reactor.

## 2.2 Catalytic Conversion

The catalytic conversion is another way to produce valuable pyrolysis products, and it also can control the selectivity to a desired product. Catalyst is an important parameter in the studies on catalytic pyrolysis.

As known, light olefins (ethylene and propylene) are the base feedstock for petrochemical industries. The major source of these olefins is the catalytic cracking of petroleum refineries products. Therefore, cracking catalysts for the production of light olefins are considered. There are three types of cracking catalysts for light olefins production. The first type is oxide supported metal catalysts, which the support can be  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , or other oxides and the metal are mainly selected from elements of IIB, VB, VIIB, and VIII groups. This type is only used for processing light feed stocks. The second type is oxide composites (such as a composite consisting of  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ , and alkaline metal oxides). This type of catalysts is used for liquid hydrocarbon feed stocks (including gasoline, kerosene, gas oil, or vacuum distillates). The third type is zeolite-containing catalysts (i.e. ZSM-5, Y) which an additive (such as alumina) can be added in the cracking catalysts. This type of catalysts is used for  $\text{C}_5$ - $\text{C}_{25}$  paraffinic hydrocarbons feedstocks. At present, an industrial catalyst for producing light olefins consists of 0-70% (based on the weight of the catalyst) of clays (such as kaolin and halloysite), 5-99% of inorganic oxides (such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$ ), and 1-50% of zeolite, wherein said zeolite is a mixture of 0-25 wt% of Y-zeolite and 75-100 wt% of phosphorus ( $\text{P}_2\text{O}_5$ ) and rare

earth ( $\text{Re}_2\text{O}_3$ ). These catalysts showed high  $\text{C}_2\text{-C}_4$  olefin yields in a cracking reaction (Zhicheng *et al.*, 1993).

There are many researchers to study the influence of matrix and binder in the cracking catalyst. Namely, Silverman *et al.*, 1986 studied matrix effect in catalytic cracking. They found that the matrix played a significant role in determining catalytic performance as well as affecting heat transfer in the FCC unit. The matrix was capable of cracking large feed molecules, which cannot readily diffuse into zeolite pores.

However, the other ways to improve the yield of light olefins was also studied by many researchers. For examples, Yoshimura *et al.*, 2000 studied a newly developed zeolite-based catalyst (ZSM-5, USY, and mordenite) for the catalytic cracking of naphtha to produce the light olefins as compared with commercial FCC catalysts. They concluded that the  $\text{La}_2\text{O}_3/\text{P}/\text{ZSM-5}$  zeolite exhibited a high activity and selectivity for light olefins (ethylene and propylene) production at low catalytic temperatures. Moreover, in 2002, Hollander *et al.* reported that the effect of additional ZSM-5 in fluid catalytic cracking (FCC) was to increase the olefins productions. Costa *et al.*, 2007 studied the use of BEA and MOR as additives in the fluid catalytic cracking (FCC) process for light olefins production. As a result, the addition of MOR (or BEA) in the common catalyst was effective to improve the light olefins production.

On the other hand, light olefins can be produced through the catalytic pyrolysis of waste tire. For examples, Olazar *et al.*, 2008 investigated the different shape selectivity of HY and HZSM-5 zeolite on the composition of tire pyrolysis products. They found that the HZSM-5 zeolite catalysts was significant for obtaining high yields of olefins (particularly ethene and propene), and for decreasing the yield of tar. In addition, both catalysts increased the yield of the aromatic fraction, but the HZSM-5 zeolite catalyst had a low capacity for PAH generation due to its shape selectivity. Nguyễn *et al.*, 2009 studied the production of light olefins and light oil from the catalytic pyrolysis of waste tire. And, they found that the Ru-supported MCM-41 was a good catalyst in the pyrolysis of waste tire because it gave a high yield of light olefins and a high concentration of single ring aromatics in light oil. Furthermore, light olefins can be produced from the pyrolysis of waste tire over Ru-

supported HMOR. As a result, Ru-supported HMOR can produce a high yield of light olefins (ethylene and propylene), reported by Choosuton (2007). Similarly, Kittikom (2008) investigated the effect of Ru-supported HMOR and Ru-supported HZM-5 on pyrolysis product. He found that the Ru-supported HMOR (at 0.7% loading of ruthenium metal) gave a high yield of gaseous product due to its high acidity for cracking reaction. So, Ru-supported HMOR was a good catalyst, which can improve the production of light olefins.

Moreover, in the catalytic cracking process, catalyst deactivation by coke deposit usually occurs with catalysts used in petrochemical industries. Coke deposits in the pores and on the surface of the catalysts lead to the loss of activity and product selectivity (Tailleur, 2008). There are researchers having studied the deactivation of catalysts. For example, Tailleur, 2008 studied the deactivation of catalyst during the upgrade of light catalytic cracking gas oil to low-sulfur and low-aromatic diesel by characterization of the catalysts before and after continuous operations. The results showed that the rate of ring opening decreased when the deactivation of catalyst by coke deposition occurred.

Since, mordenite is an acid catalyst that used for cracking, isomerization, and alkylation. It has 12 member rings with an opening of  $7.0 \times 6.5 \text{ \AA}$  (Auerbach, 2003). And, Ruthenium (Ru) is the most active metal for the hydroconversions of hydrocarbons and cracking reactions (Akhmedov *et al.*, 2000). The Ru containing catalyst showed the activity for the hydrogenation-dehydrogenation reactions (Betamcourt *et al.*, 1998). Ru supported catalyst can decrease saturates in the derived oils, but increase the gaseous product yield (Nguyễn *et al.*, 2009). Therefore, mordenite (HMOR) supported Ru catalyst is a selective cracking catalyst for the enhancement of light olefins productions. And, it needs to be further developed for a commercially scaled catalytic pyrolysis of waste tire.

From several research works, the most interesting issue is the development of Ru-supported HMOR catalyst as an industrial catalyst for the production of light olefins from waste tire. The catalysts consist of Ru/HMOR zeolite, clay, and  $\alpha$ -alumina. Therefore, this work investigates the optimum composition of modified catalyst, the effect of ratio of pellet diameter and reactor diameter, and the

deactivation of catalyst by coking on the quantity and quality of oil product obtained from the pyrolysis of used tire.

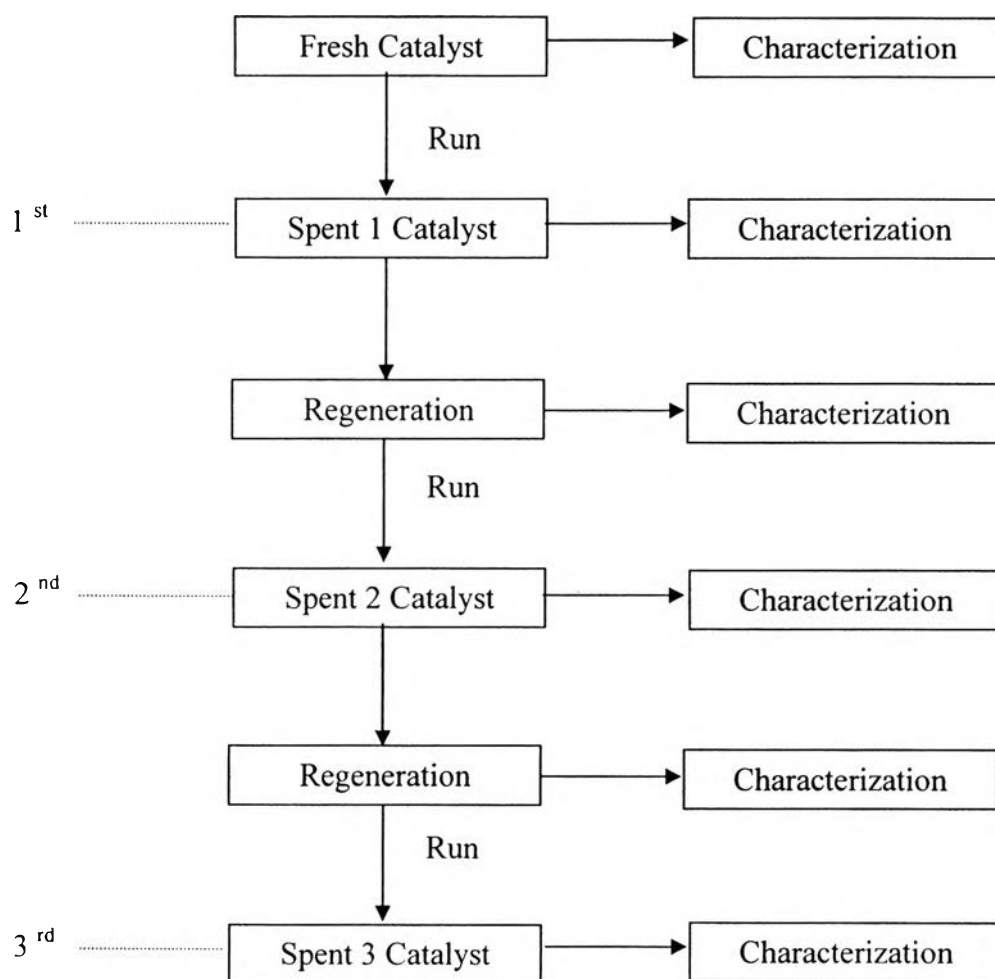
The objectives of this research work were: (1) to find the optimum composition of a being-developed Ru/HMOR catalyst for a commercial use, (2) to investigate the effect of ratio of  $D_{\text{pellet}}$  to  $D_{\text{reactor}}$  on pyrolysis products, and (3) to study the deactivation of catalyst by coking.

The scope of this research work covered: (1) the pyrolysis of scrap tires (life time more than 50,000 km) was performed in a bench-scaled autoclave reactor, (2) the holding time,  $N_2$  flow rate, pyrolysis temperature, catalytic temperature, heating rate, the amount of Ru loading, the amount of sample and catalysts were fixed to at 90 min, 30 ml/min, 500°C, 300°C 0, 10 °C/ min, 0.7 %wt, 30 g, and 7.5 g, respectively, (3) the optimum composition of the catalyst was determined by varying %wt of Ru/HMOR zeolite and clay (kaolin) at a fixed %wt of  $\alpha$ -alumina (a binder), as displayed in Table 2.1, (4) the influence of the ratio of pellet diameter to reactor diameter was studied by varying the size of pellet diameter (1.0, 2.0, 3.0, 4.0 mm), and (5) the deactivation of the spent catalyst by coke formation was studied for 1 to 3 cycles of operation. The spent catalysts were regenerated at 650°C for 30 mins. These catalysts were characterized before and after uses as shown in Figure 2.4

**Table 2.1** Varied compositions of a being-developed catalyst

<b>Components</b>	<b>Composition (%wt)</b>			
<b>Batch No.</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Ru/HMOR	20	30	40	50
Clay (Kaolin)	70	60	50	40
Binder ( $\alpha$ -alumina)	10	10	10	10





**Figure 2.4** Flowchart of steps in the study on catalyst deactivation by coke formation.