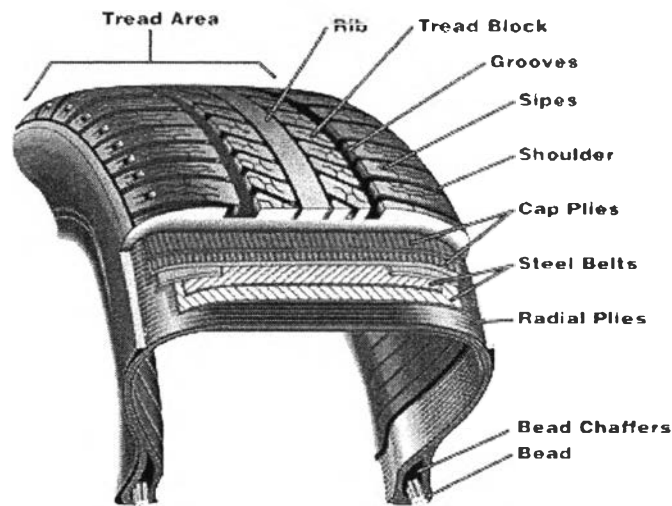


## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

Nowadays, the current oil price is still relatively high from the decreasing reserve oil around the world. Therefore, alternative fuels from natural sources and wastes are one of the interesting substitutes for petroleum fuels. Waste tires are one of the largest wastes in the environment, and cause a big serious environment problem because a huge amount of waste tires on the landfills make breeding sites for insects, and also cause fire that affects to the inhalation system of human. Tires consist of many components such as belts, casing, inner liner, plus sizing, tread, base, rib, shoulder and insulation as shown in Figure 1. It is hard to recycle because of sulfur that crosslinks the polymer chains in the vulcanization process that makes tires has chemically and physically resistant properties are difficult to be decomposed. There are many ways to recycle waste tires, such as retreading, grinding, pyrolysis, and reclaiming. Pyrolysis process offers a convenient way to decompose waste tires to petroleum products. Adrian *et al.* (1997) found that the oil produced from the pyrolysis process had similar properties to those of a light petroleum fuel.



**Figure 2.1** Components of a tire.

(<http://www.offroaders.com/tech/AT-MT-Tires/tire-tech.htm>)

## 2.1 Waste Tire Pyrolysis

Owing to the large amount of waste tires in the world, pyrolysis is a proper way to minimize the waste tires disposal problem. Pyrolysis is one of the thermal degradation processes in the absence of oxygen. It is a nice way to reprocess the waste tires to obtain an alternative fuel. The primary products from pyrolysis process consist of gas, oil and solid residue (char). Pyrolytic gas product is a mixed hydrocarbon gas, mainly in the carbon atoms from  $C_1$ - $C_5$ , such as methane, ethane, ethylene, propylene and butane; nevertheless, byproducts such as  $CO_2$  can also slightly obtain from pyrolytic gases. Pyrolytic oil can be further used as a fuel, which largely contains aromatics such as benzene, toluene and xylene. Solid residue can be used in combustion and gasification processes to produce fuels or high value materials (Zaboniotou *et al.*, 2003). Rodriguez *et al.* (2001) studied the pyrolysis process in an autoclave at 300 °C to 700 °C, and they found no significant influence of temperature on the yield of pyrolytic product at the temperatures above 500 °C. The pyrolytic liquid was the complex mixture of hydrocarbon in the carbon atoms between  $C_5$ - $C_{20}$ . Aromatics were the main component in the liquid product. When the temperature was increased, the yield of aromatic compounds increased because at a high temperature the recombination of free-radical fragments with one another would be occurred, and many aliphatic links with aromatic compounds were obtained. Laresgoiti *et al.* (2004) also studied on the influence of temperature on the pyrolytic product. They characterized the pyrolytic oil product using a GC/MS analysis, elemental analysis, gross calorific values and distillation. They concluded that the yield of the liquid product increased when the temperature increased up to 500 °C; then, it is constant at temperature from 500 °C to 700 °C. The solid yield was not also significantly changed at 500 °C to 700 °C. Therefore, the decomposition of waste tires completed at 500 °C and at this temperature, the optimum pyrolytic product was obtained. They also reported that there was almost no effect of temperature (500 °C to 700 °C) on the composition of oil because the H/C atomic ratio of each temperature are around 1.4, which indicated that pyrolytic oil was the

mixture of aromatic and aliphatic compounds. and the elemental composition of oil was not significantly changed.

Diez *et al.* (2003) determined the possibility of the product from pyrolysis for use as a fuel, and also determined the sulfur and chlorine content in all fractions. They concluded that the compositions of each fraction (gas, liquid, and solid) depended mainly on the final temperature in the pyrolytic process. The solid had carbon content around 80%, and it had the properties as good as coal's quality. For the oil, they showed that the calorific value increased up to 40 MJ/kg when the final temperature was increased from 350°C to 550°C. The amounts of sulfur and chlorine in each fraction of the pyrolytic product were different; that is the solid had the highest amount of sulfur contents when compared to sulfur contents in oil and gas. However, its sulfur contents were still lower than that in the original tire. The lowest amount of sulfur was found in the gas fraction in the form of hydrogen sulfide. Moreover, the chlorine was only found in the solid fraction, but not in the oil and gas fractions. In 2008, Islam *et al.* studied the oil products which were obtained from bicycle/rickshaw tires. They found that the properties of liquid such as density, viscosity, carbon and hydrogen content were almost similar to the commercial automotive diesel fuel, but the oil still had higher sulfur content and low flash point. The pyrolytic liquid of this work mainly contained a large amount of olefins, limestone and light aromatics which had higher values as chemical feedstock rather than being used as fuels. In the work of Jitkarnka *et al.* (2007), they studied the effect of thermal aging on the product in pyrolysis process. A tire compound was aged at 70 °C in an environmentally-controlled oven for 0-4 weeks. They found that in the range of 1-3 weeks, when the aging time increased, the liquid yield increased while the gas yield decreased. The gas component and carbon number distribution in the liquid products were not altered by the aging time. The amount of gas oil in the liquid product decreased with the aging time while the other fractions were not significantly changed. However, after 4 weeks, C-C bonds in the rubber chains were weakened which made easier for cracking the rubber chains. The gas and gas oil yields rapidly increased whereas the liquid yield suddenly decreased.

Waste tires contain large molecules of rubbers. For breaking the bonds of these rubbers in the waste tires, cracking is the most important reaction in the waste tires pyrolysis process. Catalysts have been chosen for being used in the pyrolysis process, called catalytic pyrolysis. Acidic sites increase the cracking activity, and the micro-pore of the acid catalyst can improve the selectivity to the desired product. There are several researchers who studied the effect of zeolite on the pyrolytic product. Olazar *et al.* (2007) used acid catalysts (HZSM-5, HY and HBETA) in pyrolysis process, and compared the results with the thermal pyrolysis. They found that the difference in shape selectivity and acidity of zeolites had the effect on the pyrolytic product. HBETA had the highest silica to alumina ratio among all tested zeolites, which led to the highest conversion of liquid fraction to the gas fraction. HY zeolite had high total acidity, high hydrogen transfer, and large pore sizes, which resulted in some heavy products (char, aromatic C<sub>10</sub>-). HZSM-5 also had a high silica to alumina ratio; therefore, the products from HZSM-5 and HBETA zeolites were similar. The product obtained from HZSM-5 and HBETA were light gas with a high yield of light olefins, non-aromatic C<sub>5</sub>-C<sub>10</sub>, and a high yield of BTX due to the Diel-Alder condensation of olefins. But the heavy aromatics from HBETA and HZSM-5 were obtained in very small amounts because shape selectivity of the zeolites.

The difference in the properties of the zeolite such as acidity, pore size, silica to alumina ratio and hydrogen transfer, therefore, had the influence to the pyrolytic products. HBETA has the Si/Al ratio of 13.5, 12-membered ring channel, three-dimensional micro-porous structure, and one opening intersection of 5.6 x 6.5 Å with two channels of 5.6 x 5.6 Å and 7.6 x 6.4 Å (<http://people.bath.ac.uk/cesoc/homepage/mtbe.htm>). The dimension of the zeolite can control the diffusion rate; for example, one-dimension structure has higher diffusion than the others. The pyrolytic products obtained from HBETA zeolite were mainly in light gases such as methane, ethane, ethylene, propylene and butane (Olazar *et al.*, 2007). The acidity and activity depended strongly on the alumina content because dealumination during the activation process has the effect to the activity of HBETA zeolite (<http://pubs.rsc.org>). Choosuton (2007) studied the effect

of the catalyst on the pyrolytic product, and he found that using HBETA zeolite gave a high amount of di-aromatic and low saturated hydrocarbons due to the high acid strength of HBETA. Costa *et al.* (2006) worked on the use of BETA to improve the efficiency of light olefin production in catalytic cracking process. The result showed that using BETA as an additive can improve the efficiency of H-MFI zeolite by increasing the yield of light olefins.

## 2.2 Bifunctional catalysts

Bifunctional catalysts (metals supported on zeolites) can improve the quality and quantity of the pyrolysis process. Du *et al.* (2005) reported that the acidic sites of a catalyst promoted cracking, dehydrogenation and isomerization, and metal sites promoted isomerization, ring-opening and hydrogenation. The activity on the ring-opening of a catalyst mainly depended on the properties of the metal and the support, such as the type of metal, particle size of metal, acidity of support zeolite, pore size and the interaction between metal and support. The main purpose of ring-opening is to decrease the ring structure without changing the carbon number in the product. Noble metals are normally used to promote hydrogenation and ring-opening, but they have low resistance to the sulfur poisoning. The noble metals are the metals which have high corrosion and oxidation resistant properties, including copper (Cu), ruthenium (Ru), rhodium (Rh), palladium (Pd), Silver (Ag), rhenium (Re), osmium (Os), iridium (Ir), platinum (Pt), gold (Au) and mercury (Hg). ([http://en.wikipedia.org/wiki/Noble\\_metal](http://en.wikipedia.org/wiki/Noble_metal)). In the work of Choosuton (2007), he also concluded that noble metals on acid zeolites can improve the hydrogenation and ring-opening of aromatic hydrocarbons. Using Pd/Beta, the quality and quantity of gasoline and kerosene were improved as compared to the BETA alone by the reduction of large amount of aromatic contents. He found out that Ru/MOR was the good catalyst for the production of gases such as methane; ethylene and propylene because it had the highest cracking activity. Dũng *et al.* (2010) studied the effect of Pt supported on BETA and MOR zeolites on polar-aromatic reduction. They suggested Pt/BETA represented a good catalyst for polar-aromatic reduction, which

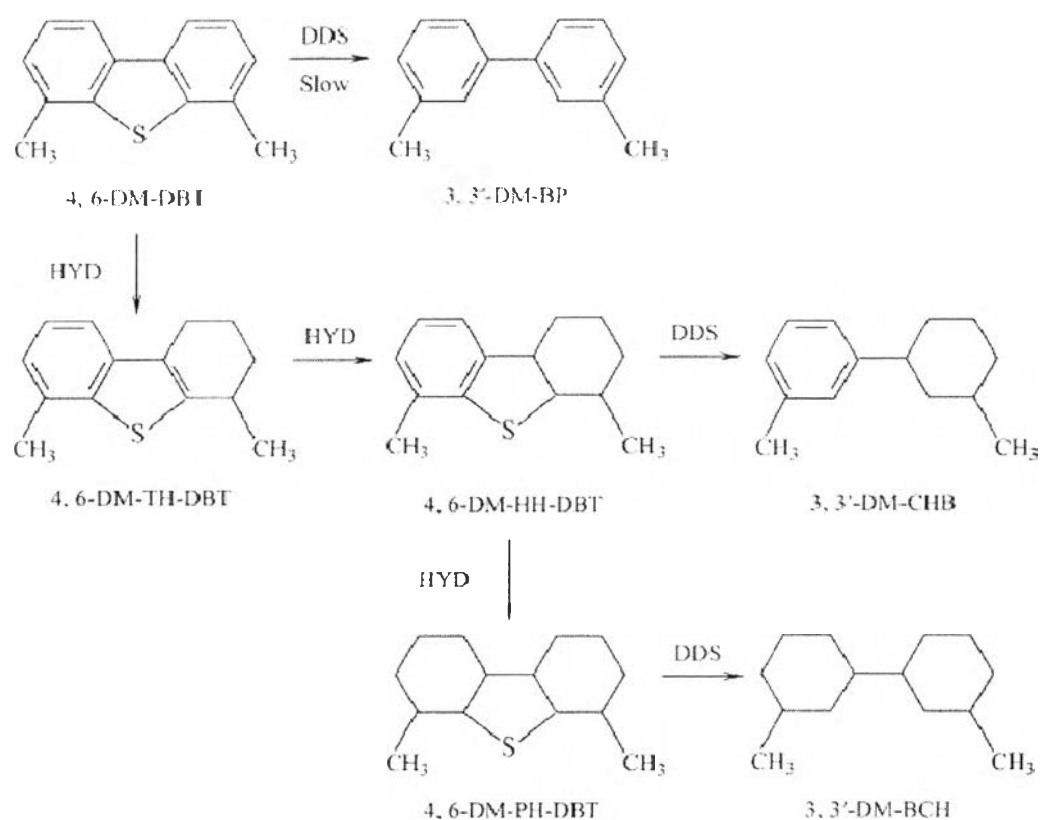
was better than Pt/MOR because BETA zeolite had higher dispersion of Pt on the HBETA zeolite than MOR zeolite. Moreover, they concluded that a high hydrogenation activity of Pt could prevent the polar-aromatic formation.

Castano *et al.* (2005) used noble metals (Pt, Pd, Ir and Ni) supported on HY zeolite in a fixed-bed reactor to study the hydrodearomatization of pyrolysis gasoline. The result showed that the activity depended on the total acidity under a severe condition. Ir/HY had the highest hydrogenation and ring-opening activity than the other noble metals (Pd and Pt) because it showed the best metal dispersion and stronger acidity. Ni/HY had the lowest activity due to the high amount of unreduced Ni after activation with hydrogen. In 2005, Aboul-Gheit *et al.*, studied the effect of noble metals (Pt, Pd, Ir or Re) loaded on HZSM-5 the hydroconversion of cyclohexane. The hydrocracking process consists of two activities; that are, hydrogenation activity from metal sites and cracking activity from acid sites. The results showed the acid strength was ranked in the order: H-ZSM-5 > Re/H-ZSM-5 > Pt/H-ZSM-5 > Pd/H-ZSM-5 > Ir/H-ZSM-5 whereas the hydrogenation activity was in this following order: Pd/H-ZSM-5 > Pt/H-ZSM-5 > Ir/H-ZSM-5 > H-ZSM-5 > Re/H-ZSM-5 but the hydrocracking activity was found in this order: Pt/H-ZSM-5 > Pd/H-ZSM-5 > Ir/H-ZSM-5 > H-ZSM-5 > Re/H-ZSM-5. They concluded that the hydrogenation of the metal sites had more pronounced effect on the hydrocracking than the acid strength.

### 2.3 Hydrodesulfurization

Noble metals on acidic zeolites showed good activity on cracking, but it is easy for them to be deactivated by sulfur compounds. These sulfur compounds can be removed from oil or gas by a hydrotreating process, called hydrodesulfurization. The main purpose for removing sulfur content from a fuel in the hydrodesulfurization process is to reduce sulfur dioxide (SO<sub>2</sub>), which is produced during the combustion of the fuel. The inhalation of SO<sub>2</sub> into the human body would affect the respiratory system; for example, nose and throat can be burnt, making difficulty to breath. If SO<sub>2</sub> is being released into the air, sulfuric acid, sulfurtrioxide

and sulfates can be formed. If it gets in to water, it can convert to sulfurous acid (<http://www.atsdr.cdc.gov>). With these reasons, many countries limit the amount of sulfur content in the product of transportation fuels. Tang *et al.* (2008) investigated Pd/H-Beta and Pd/Al-MCM-41 to evaluate the hydrodesulfurization activities on the conversion of 4,6-dimethyldibenzothiophen (4,6-DMDBT). There are two routes during hydrodesulfurization process as shown in Figure 2. One is direct desulfurization (DDS) to directly diminish 4,6-DMDBT, and another one is first hydrogenation (HYD), then followed by direct desulfurization (DDS). In Tang *et al.* (2008), the rate of direct desulfurization was very slow because there was no detection of 3,3'-dimethylbiphenyl product. The result showed that Pd/H-BETA had greater hydrodesulfurization activity than Pd/Al-MCM-41 because of the difference in support acidity. HBETA zeolite exhibited higher acidic site and higher strong acidic than Al-MCM-41.



**Figure 2.2** Hydrodesulfurization of 4,6-DM-DBT (Tang *et al.* 2008).

Noble metals supported on acidic zeolites are not only used for promoting hydrogenation, but somehow they can also promote hydrodesulfurization. Yasuda *et al.* (1999) studied the effect of acidity of the zeolites (HY and USY) on sulfur tolerance and aromatic hydrogenation. They used bimetallic Pd-Pt (mole ratio of Pd: Pt = 4:1) supported on HY and USY under a wide range of SiO<sub>2</sub> /Al<sub>2</sub>O<sub>3</sub> ratio from 5.6-480. They found that Pd-Pt/HY and Pd-Pt/USY showed high activities in hydrogenation and hydrodesulfurization. The hydrogenation activity of tetralin and hydrodesulfurization of dibenzothiophene mainly depended on the ratio of SiO<sub>2</sub> /Al<sub>2</sub>O<sub>3</sub>. With increasing the ratio of SiO<sub>2</sub> /Al<sub>2</sub>O<sub>3</sub> in the range of 14-50, the activity increased. They suggested in the range of SiO<sub>2</sub> /Al<sub>2</sub>O<sub>3</sub> 15-40, the Lewis acid sites increased whereas the Bronsted acid sites decreased. After increasing the ratio of SiO<sub>2</sub> /Al<sub>2</sub>O<sub>3</sub> from 40 to 680, the activity decreased and the Lewis acid sites also decreased due to the disappearance of the electron-deficient Pd-Pt.

#### 2.4 Non-noble metals

Due to the limitation sulfur content in the petroleum products and the high price of a noble metal, non-noble metals can be used in the pyrolysis process. Saeaeah *et al.* (2012) studied the effect of non-noble metal, Ni, on HBETA and HMOR zeolite on the quality and quantity of pyrolytic product as compared with the noble metal (Pd). They found that 5% Ni/HBETA produced high saturated hydrocarbons with low sulfur contents, and could be used to substitute 1% Pd/HBETA for naphtha production because 5% Ni/HBETA produced the similar quality and quantity of the full range naphtha as 1% Pd/HBETA. Moreover, they also found that 20% Ni/HMOR could be used to substitute 1% Pd/HMOR due to the high hydrogenation and cracking activity, which can produce the similar product as 1% Pd/HMOR.

Bifunctional metallic catalysts such as NiMo, NiW, CoMo, and CoW are normally used in hydrodesulfurization process. Aksoylu *et al.* (1988) used Ni-Mo supported on Al<sub>2</sub>O<sub>3</sub> catalysts to study the activity/selectivity of CO hydrogenation and the effect of interaction between Ni and Mo. They varied the amount of Ni and



Mo from 0-15 wt%, and they found that the activity of CO hydrogenation depended on the metal loading. When the amount of Mo increased, the hydrogenation of CO increased. They concluded that the presence of Mo as the second metal increased the total hydrocarbon production mainly in C<sub>2</sub>-C<sub>4</sub>. Metal surface area increased with the increasing amount of Mo (5-10 wt%), leading to the good dispersion of Ni. With the amount of Mo more than 10 wt%, Ni metal on the surface decreased because Mo covered the Ni sites. Alibouri *et al.* (2009) studied the hydrodesulfurization of dibenzothiophene over CoMo/Al-HMS nanocatalyst. They also reported that the efficiency of catalyst (conversion of dibenzothiophene) depended on the dispersion of metal on the support with increasing the active surface area. In 2010, Wang *et al.* used NiW supported on USY zeolite and Al<sub>2</sub>O<sub>3</sub> to determine the effect of hydrogenation and ring-opening of light cycle oil. They found that NiW supported on USY gave the higher hydrogenation activity and ring-opening than that supported on Al<sub>2</sub>O<sub>3</sub> because USY zeolite had higher acidity than Al<sub>2</sub>O<sub>3</sub>. Since the acidity of the zeolite favored the migration of hydrogen spillover over acid surfaces, the conversion of tetralin depended on the acidity of the zeolite. Therefore, they concluded that medium to strong zeolite acidity was the key factor to the ring-opening selectivity of tetralin. They suggested that the good ring-opening activity depended on the use of catalyst with high hydrogenation activity.

Ding *et al.* (2008) studied the effect of particle size of zeolite beta to the light cycle oil (LCO) hydrotreating. They used Mo-Ni and W-Ni supported on nano-sized and micro-sized beta to investigate the effect of hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydroaromatization (HDA) of LCO. The HDS, HDN, and HAD activities of the catalysts were determined by the following equation;  $\frac{\bar{x}_F - \bar{x}_P}{x_F} \times 100\%$  where X<sub>F</sub> and X<sub>P</sub> stand for the sulfur, nitrogen, and saturate contents in the feed and the product, respectively. The results showed that the catalysts had a high activity on HDN (92-97% conversion of nitrogen compounds) and HDS (92-94% conversion of sulfur compounds), and the liquid yield was 90-93 wt% with 9-15% HDA (conversion of saturated hydrocarbons). All used catalysts showed 13.3-15.5% conversion of poly-aromatics and about 22.8-26.4% of di-aromatics were converted to monoaromatics. In addition, the HDS, HDN and

HDA activities of Mo-Ni catalysts were shown similar in both nano-size and micro-size cases whereas the W-Ni catalyst on the nano-sized zeolite beta had higher activities of HDS, HDN and HNA than on the micro-sized zeolite beta. Okamoto *et al.* (2005) studied the intrinsic activity of Co-Mo and Co-W for hydrodesulfurization thiophene. The result of this work showed that the difference in intrinsic activities (conversion of thiophene) of Co-Mo-S and Co-W-S depended on the difference in the bond energy of W-S bond and Mo-S bond. Torres-Mancera *et al.* (2005) studied the hydrodesulfurization of 4-6 dimethyl dibenzothiophene (4-6DMDBT) on NiMo and CoMo catalysts supported on B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>. 4-6DMDBT (500 ppm sulfur) in n-hexadecane was the feed in this work. They found that the boron-modified catalyst could generate intermediates, which make the feed easy to desulfurize and also prevent deactivation of catalysts. The result showed that the acidity of CoMo/B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> was higher than NiMo/B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>; therefore, the CoMo catalyst gave higher conversion of 4-6DMDBT and isomerization products than the NiMo catalyst. However, it was easy for the CoMo catalyst to be deactivated by coke due to its strong acidity whereas the NiMo catalyst was more resistant to poisoning, and showed the higher hydrodesulfurization activity than the CoMo catalyst.

From the previous background and literature review, in most of the works regarding to pyrolysis, noble-metals supported on acidic zeolites were to increase the quality and quantity of the pyrolytic products. However, due to the limit of sulfur contents in petroleum products and the high prices of some noble metals, in this work, non-noble metals (Ni and Co) with Mo or W as a second metal supported on HBETA zeolite were chosen for pyrolysis process. Bimetallic catalysts (NiMo, NiW, CoMo and CoW) over acidic zeolites have been proven to be very active catalysts for hydrogenation, ring-opening and hydrocracking, and can also enhance the deep hydrodesulfurization. The purposes of this work were to investigate the performance of NiMo, NiW, CoMo and CoW on HBETA zeolite in pyrolysis process for pyrolysis of waste tires as well as the simultaneous reduction of sulfur contents in the pyrolytic oil, and to study the types and amount of sulfur compounds when the composition of bifunctional metals changes. In particular, the aims of this work were to inves-

investigate the influence of the addition of Mo or W as a second metal into the Ni and Co catalysts on the quality and quantity of the pyrolytic oil, specially on the reduction of polar-aromatic and sulfur compound, and to study the types and amounts of sulfur compounds in pyrolytic products. The percentage of Ni and Co loaded on HBETA was fixed at 5%wt, and the amount of a second metal on the main catalyst was varied as 10%wt and 20%wt of Mo or W. The NiMo, NiW, CoMo, and CoW catalysts were prepared by co-impregnation on HBTEA zeolite using the incipient wetness method.