CHAPTER II
LITERATURE REVIEW

2.1 Tire

A tire can be separated into six parts, which are tread, shoulder, sidewall, carcass, belt and bead are shown in Figure 2.1. Typically, the compositions of a tire are natural rubber (isoprene), synthetic rubber (butadiene and styrene butadiene rubber), sulfur and sulfur compounds, fabric (polyester, nylon, etc.), pigments (zinc oxide, titanium oxide, etc.), carbon black, and other additives. However, the compositions of tire depend on its applications.
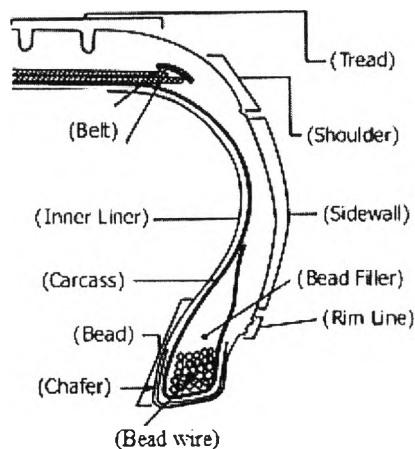

Figure 2.1 Private vehicle tire components
(http://www.bridgestone.co.th/th/tire_safety/).

Since a tire is chemically produced from a polymerization of low molecular weight hydrocarbons with vulcanization to the heavier and stronger material (Figure 2.2), the resulted tire thus has a possibility to thermally decompose to lighter hydrocarbons to be further used in some applications such as fuels, oils, and/or chemical feed stocks. The full range naphtha (30-200 °C) is an interesting product of pyrolysis due to its high value (containing BTX, and/or saturated hydrocarbon compounds). In addition, if the naphtha range contains a high amount of saturated hydrocarbons, it

can be used as chemical feed stocks in the process of olefins production because al-kanes are used as an olefins booster in the olefins production. On the other hand, if the naphtha range contains a high amount of single ring aromatics, namely Benzene, Toluene, and Xylenes (BTX), it can be used as chemical feedstocks in the aromatics extraction process. Owing to these needs, the pyrolysis process can be used because it has potential to produce both aromatics and saturated hydrocarbons from waste tire.
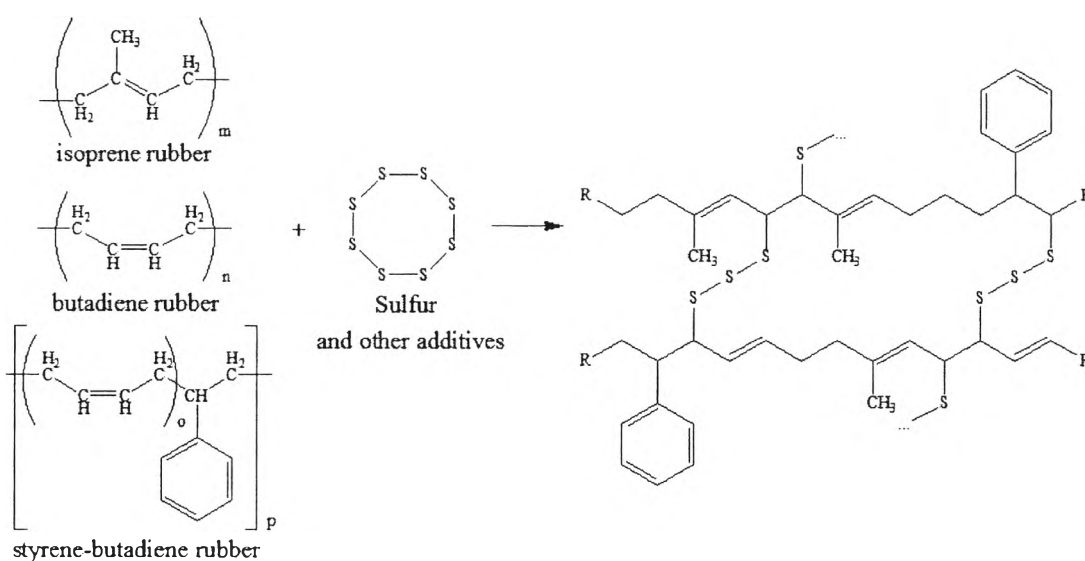

Figure 2.2 Compositions of tire and tire molecule (collected and redrawn from www.eng.buffalo.edu/.../FirestoneTiresReport.htm, http://en.wikipedia.org/wiki/Vulcanization, and Choosuton, 2007).

2.2 Pyrolysis of Waste Tire

The pyrolysis of waste tire, which is the thermal degradation of tire in an absence of oxygen, produces very low carbon-dioxide and carbon-monoxide emis-sions to the environment. Therefore, this process is friendly to the environment. In pyrolysis process, the high molecular weight compounds are heated and decomposed to the low molecular weight compounds. The obtained products are gaseous fraction, condensable oil, and char. Moreover, all of these products have potential to be uti-

lized; for examples, the gaseous fraction can be used to provide process energy, condensable oil can be used as a substitute fuel or a chemical feedstock, and the char can be used to produces a smokeless fuel, carbon black or low-grade activated carbon. However, the obtained pyrolytic products have low quality and quantity. Nevertheless, they depend on the conditions in the process.

Cunliffe and Williams (1998) studied the pyrolysis of tire in the static-bed reactor with varied temperatures in the range of 450-600 °C. They found that the oil yield decreased from 58.1 to 53.1 wt%, the gas yield increased from 4.5 to 8.9 wt%, and the char yield remained constant about 37.8 wt% with the increasing final pyrolysis temperature from 450 to 600 °C. The pyrolytic oil obtained from this process had similar properties to a light petroleum fuel oil, although it contains a wide range of hydrocarbons. Moreover, the increasing temperature resulted in an increase of aromatics content with a consequent decrease in aliphatics content because the Diels-Alder reactions can form polycyclic aromatic hydrocarbons at high pyrolysis temperatures. Diels-Alder mechanisms involve the dehydrogenation of alkane, followed by cyclization and aromatization reaction. Then, Murillo et al., (2006) studied the influence of operating conditions. They found that at 500 °C was the optimum temperature, since below 500 °C both conversion and oil yield decreased around 10 %, whereas at above 500 °C neither conversion nor oil yield increased. Similarly, Olazar et al., (2008) reported that the samples were not completely pyrolyzed at temperatures below 500 °C. Moreover, Chang (1996), who studied the degradation rate and product yields of the pyrolysis of waste tire, reported that both degradation rate and products yields varied with the temperature. The conversion was very sensitive to the temperature below 400 °C than above. The products distribution was also varied with temperature; for example, the residue oils and char yield decreased whereas the light oils and gases yield increased with an increasing temperature.

2.3 Catalytic Pyrolysis of Waste Tire

Catalysts are introduced in the pyrolysis process to increase the desired products. Because of theirs activity and selectivity, catalysts can modify the yield and composition of the products. Thus, several research outcomes of catalytic pyrolysis

have been reported. Li *et al.*, (2005) studied the influencing factors of the catalytic pyrolysis process and product distribution. They reported that several conditions affected to the product distribution, especially the feedstock properties and the type of catalysts.
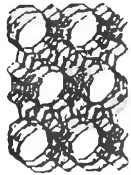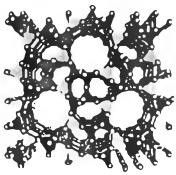
2.3.1 Acidic Zeolite Catalysts

Since the cracking reactions are the main reactions in the pyrolysis of waste tire, the acidic zeolite molecular sieve catalysts, whose the acidic sites can promote cracking reaction and the micro-pore site, can promote the selectivity of desired products, have become very interesting. The structures of three zeolites are shown in Table 2.1.

Table 2.1 Structure of zeolites used in this experiment
(http://tjchemist.en.ecplaza.net/product.asp, and
http://web.iyte.edu.tr/~selahattinyilmaz/Zeolites.htm)

Zeolite		Dimension	Si/Al ratio	Pore size (Å)
HBETA		3D	13.5	7.6 x 6.4
HY		3D	7.5	7.4
HZSM-5		3D	20	5.3 x 5.6

As a result of the potential of zeolites in the cracking activity, the several works thus have been done using zeolite catalysts to study the influence of many

factors such as the influence of catalyst bed temperature, the influence of catalyst to tire ratio, and the nature of the acidic zeolite catalysts affecting to pyrolysis products. The influence of catalyst bed temperature was studied by Williams and Brindle (2002) who varied the temperature between 430 and 600 °C in the fixed bed reactor. They found that the yield of oil decreased with a consequent increase in gas yield and coke formation on the catalysts, when the temperature was elevated. Also, the similar results were obtained with the presence of catalysts. Moreover, when catalysts were used in catalytic pyrolysis, the required pyrolysis temperature and reaction time reduced, whereas the yield of gases and light C_{10}- aromatics significantly increased in the expense of non C_{10}- aromatics (Olazar *et al.*, 2008). Moreover, the influence of catalyst to tire ratio on the product yields and the compositions of derived oil in a fixed bed reactor was studied by Boxiong *et al.*, (2007). Similar to the results obtained from increasing temperature, increasing the catalyst to tire ratio increased gas yield in the expense of oil yield, and increased the concentration of light fraction (<220 °C), which namely is the full range naphtha, because the increasing catalyst to tire ratio increased cracking activity in the catalytic pyrolysis of waste tire to lighter products. However, the increasing catalyst to tire ratio also resulted in a decrease of the oil yield; hence, both issues (the catalyst to tire ratio and oil yields) should be considered together.

The different properties of each zeolite such as micro-pore size, acidity, and hydrogen-transfer capacity result in the diverse influence to pyrolysis products. The three-dimensional microporous structure of HBETA zeolite consists of two channels of 7.6 x 6.4 Å and 5.6 x 5.6 Å with the opening intersection of 5.6 x 6.5 Å. This catalyst that has a high Si/Al ratio with high medium and strong acid sites has highly activity onto hydroisomerization, low hydrogen-transfer capacity, and low catalyst deactivation (Zhang *et al.*, 2010). In the work of Olazar *et al.*, (2008), the HBETA, which had the highest silica to alumina ratio when compared to HY and HZSM-5, gave the lowest activity on scrap tire pyrolysis since the maximum conversion (about 67 %conversion) was achieved in the longest reaction time. However, HBETA had higher transformation rate of liquid fraction to gases than HY and HZSM-5 because of its very strong acid sites. This transformation cannot be limited only to shape selectivity, which was able to alter single-ring aromatic C_{10}- molecules

to gas and non-aromatic C_5-C_{10}. Moreover, the higher external surface area of HBE-TA than HZSM-5 caused the first step decomposition of LDPE in the LDPE pyrolysis (Marcilla *et al.*, 2007). This result was attributed to the external acid sites of HBETA that was responsible for the pre-cracking step of polymer before passing through the internal pore system. Moreover, the larger pore size of HBETA produced higher concentration of C_4 and C_5 compounds and the higher ratios of isobutene/*n*-butane and paraffins/olefins.

HY zeolite has a cubic structure with the three-dimensional channels of 7.4 Å, which has "cages" intersection with a diameter of 12.4 Å. This catalyst has high acid density (low Si/Al ratio) resulting in the high hydrogen-transfer capacity which has excellent activity in cracking, isomerization, aromatization, and other reactions. Williams and Brindle (2002) used Y-type zeolite (CBV-400), which has the pore size and the Si/Al ratio of 7.8 and 5.4, respectively. They found that the larger pore size and higher surface area of Y-type zeolite, responsible for the selectivity of aromatic and catalytic activity, respectively, resulted in a higher concentration of aromatic compounds in the heavy naphtha range than those of ZSM-5 zeolite. In addition, Y-type zeolite also produced saturated hydrocarbon gases because of its high hydrogen-transfer capacity. Similarly, Olazar *et al.*, (2008) found that the higher hydrogen-transfer capacity of HY zeolite exhibited the formation of butane and paraffins in the liquid fraction. The acidity and micro-pore size of HY zeolite led to the formation of heavier products (tar and aromatics C_{10}- hydrocarbons). However, the HY zeolite has more deactivation than HBETA and HZSM-5 because of its large pore size and high acid density (Elordi *et al.*, 2011).

HZSM-5 zeolite has two different types of elliptic channels of 5.3 x 5.6 Å and 5.1 x 5.5 Å. ZSM-5 zeolite has efficiency for the catalytic degradation of polymer because of its strong acidity and unique pore structure. The small pore size of HZSM-5 produced a higher concentration of C_3 compounds with low paraffins/olefins ratio in the pyrolysis of LDPE (Marcilla *et al.*, 2007). Since ZSM-5 zeolite had very small porosity and low surface acidity, it produced a high amount of alkene gases but low single-ring aromatic compounds from the pyrolysis of waste tire. Although, ZSM-5 zeolite produced a lower concentration of aromatic compounds than Y-type zeolite, it had potential to produce a higher amount of mono-

aromatics in the heavy naphtha range than the thermal pyrolysis of waste tire (Williams and Brindle 2002). Olazar *et al.*, (2008) found that the HZSM-5 zeolite had the trend on monomolecular cracking, which increased the yield of gases because of its strong acidity. Moreover, using HZSM-5 also generated light aromatic C_{10}- hydrocarbons in the oil product by the condensation of light olefins. Qu *et al.*, (2006) studied the pyrolysis of waste tire and the combination with lubricant base oil by using the ZSM-5 catalyst. This catalytic process used the tire in the direct contact with the catalyst. They found that using ZSM-5 alone the pyrolytic rate was slightly increased, and the product yield and the product distribution were similar to those obtained from the process without ZSM-5. Likewise, using lubricant base oil alone, the pyrolytic rate was not enhanced. Whereas the combination of tire, ZSM-5, and lubricant base oil was used, the interactions between tire and catalyst were improved that led to the increment of catalytic activity. It can be observed that the heavy components were reduced and the light oils (n-C$\leq$12) were raised. From this experiment, it can be seen that the ZSM-5 zeolite was not suitable for the first pyrolysis step, but it may be suitable after it was used in the post catalytic process, which finally can increase the single-ring aromatics content (Williams and Brindle, 2002).

Elordi *et al.*, (2011) studied the pore structure in the deactivation of zeolites (HZSM-5, HBETA and HY) by coke formation on the pyrolysis of polyethylene in a conical spouted bed reactor. They found that the key factor for coke formation depended on the shape selectivity, physical properties, and acidity of catalyst. HZSM-5, which selectively produced light olefins, had an insignificant change in the products yield throughout the TOS of 15 h, resulting in the insignificant deactivation. For HBETA, the deactivation had a significant effect on which it increased the yield of waxes throughout the TOS of 15 h. Moreover, HY had the highest deactivation among the others. The coke deposition that had the greater effect on micro-porous than meso- and macro-porous resulted in the reduction of BET surface area and micro-pore area; however, the average pore diameter still increased.

Normally, the catalysts for fluid catalytic cracking (FCC) process consist of (i) active acid components that are zeolites, especially the large pore size such as HY or HX zeolites, (ii) additives such as HZSM-5 zeolite which is an octane booster, and (iii) other compositions. Therefore, the uses of mixed zeolites such as

binary zeolite or multiple zeolite have been reported in the process of FCC gasoline upgrading.

Y zeolite, which has an appropriate pore structure, acidity, thermal and hydrothermal stability, is wildly used in refineries. However, its high acid density facilitates the coke deposition which causes a blockage of the channels. On the other hand, the BETA zeolite, which has high Si/Al ratio (low acid density), exhibits low catalytic deactivation and high hydroisomerization activity. Hence, the composite binary microporous zeolites of Y-BETA were studied by Zhang *et al.*, (2010). The composite catalysts were the catalysts which consisted of two or more types of the aluminisilicate zeolite and/or alumino-phosphate, but they had some differences caused by from the physical mixing because of their chemical interaction. Y-BETA composite zeolites were prepared by the addition of BETA zeolite at 20, 40 and 60 wt%, respectively, and tested for hydrocracking performance. They observed that low BETA zeolite content (20 wt%) had the largest external surface area, pore volume and average pore size which favored the hydrocracking of bulky molecules. Furthermore, the ratio of BETA and Y zeolites had an influence on the acidity, so this implies that the acidity can be adjusted by controlling the amount of two zeolites. In the hydrocracking testing, they found that the BETA (both 20 and 40 wt%) mixed with Y zeolite had an excellent hydrocracking on heavy oil (vacuum gas oil), which can increase jet fuel and naphtha fractions, because these composite zeolites exhibited the weak acidity and low acid density, which favors the transformation of large molecule, and the modified pore structure (large pore volume and pore diameter), which prevents secondary cracking to smaller molecules.

Fajula *et al.*, (1990) synthesized the binary zeolite system comprising of offretite and omega zeolites as the additives for FCC process. Offretite zeolite formed a central core of catalyst which was surrounded by a crown of omega zeolite. These binary zeolites were synthesized by using sol-gel technique, which the aged offretite zeolite gel was firstly prepared and then an obtained gel was mixed with fresh omega zeolite gel. This binary system exhibited the chemical bond between them; thus, the distance between two structures was reduced and the mechanical properties were improved. They found that the addition of 5 wt% binary zeolite (containing 50 wt% of offretite and 50 wt% of omega zeolites), as an additive in Y zeolite

catalyst used in the conventional process of catalytic cracking, improved the selectivity of gasoline, and decreased coke content as compared to the conventional Y zeolite.

Tsang *et al.*, (1999a) studied the binary molecular sieve system which comprised of aluminosilicate zeolite (ZSM-5) and alumino phosphate molecular sieve (ALPO-5) in the propylene upgrading reaction and FCC processes. In this work, they studied both physical mixture and core-shell composite catalysts. The physical mixtures of ZSM-5 and ALPO-5 catalysts were prepared in the ratio of 0.25, 0.5 and 0.75, whereas the core-shell composite catalyst which had ZSM-5 as the core and ALPO-5 as the shell was prepared in the ratio of 0.5. The core-shell catalyst was synthesized by the addition of ZSM-5 powder into the aqueous slurry of ALPO-5, after that the mixture was kept at 200 °C in an oven for 5 days, and then it was dried and calcined at the end of the synthesis. For the testing of propylene upgrading, they used propylene mixed with propane as a feedstock in order to obtain the isobutylene for MTBE production. For the physical mixture catalysts, the results demonstrated that the yield of isobutylene rose to the highest value with using a low amount of ZSM-5 (at the ratio of 0.25) and further decreased with increasing the amount of ZSM-5; meanwhile, the core-shell composite catalyst represented the highest yield of isobutylene among all catalysts including physical mixture catalysts. For the FCC process, the binary zeolite catalysts (ZSM-5 mixed with ALPO-5) were used as an additive with the base catalyst (RE-USY zeolite). The results showed that the isobutylene yield increased with increasing the ratio; however, the gasoline yield decreased when the ratio was raised in the physical mixture catalysts. Moreover, the core-shell composite catalyst at the ratio of 0.5 had the similar activity in the FCC process to the physical mixture at the ratio of 0.25.

Fan *et al.*, (2004) used the binary, tertiary, and quadruple silicoaluminophosphate and aluminosilicate zeolites for upgrading gasoline to low olefins contents and high octane number. They found that the hydroisomerization reaction favored low operating temperatures, while the aromatization reaction favored high operating temperatures. For the binary system, the binary zeolites, HBETA (as a main catalyst) mixed with HZSM-5 (as an additive), exhibited stronger acidity than the other binary catalysts (HMOR/HZSM-5 and SAPO-11/HZSM-5). Moreover, an

Moreover, an HBETA/HZSM-5 catalyst represented the highest activity in hydroisomerization at low temperatures (<300 °C) and the highest aromatization activity at high temperatures (>300 °C) when compared to the other binary catalysts. However, the activity markedly decreased with increasing operating temperature, whereas the binary system of HMOR/HZSM-5 and SAPO-11/HZSM-5 which had weaker acidity, revealed the insensitivity to temperature. For the tertiary system of catalysts, the iso-paraffins content insignificantly changed from that obtained from binary catalysts, but they improved the sensitivity to temperature; meanwhile, the arene content markedly decreased as compared to that of binary catalysts. Hence, the octane number of gasolines obtained by using the tertiary system of catalysts was reduced because of the very low arene content. Moreover, the series of SAPO-11/HMOR/HBETA/HZSM-5 greatly increased the hydroisomerization activity, which resulted in a high content of iso-paraffins in the carbon range of C_5-C_6, and also greatly increased an aromatization activity, which gave the high arene content in the carbon range of C_8-C_{10}. Therefore, these quadruple catalysts gave higher liquid yield (low gasoline loss), improved the octane number (by balancing iso-paraffins and arene yields), and lower coke content.

2.3.2 Bifunctional Catalysts

The addition of noble metals onto the acidic zeolite catalysts has become a very useful technique since the noble metals can improve the hydrogenation, dehydrogenation, hydrogenolysis, heteroatom removal, and ring-opening reactions. Choosuton A., (2007) studied the effect of noble metals (Pt, Pd and Ru) and supports (HBETA, HMOR, USY, KL). He found that the HBETA increased total aromatics in gasoline fraction, and also reduced the total aromatics associated with increasing saturated hydrocarbons in the gas oil fraction. On the other hand, the USY zeolite increased the saturated hydrocarbons in conjunction with the reduction in the total aromatics in the kerosene fraction. After introducing the noble metals, the results represented that the Pt and Pd supported on zeolite catalyst, especially Pd/HBETA, gave the highest gasoline yield which had higher total aromatics and lower saturated hydrocarbon because the noble metals can enhance the activity on cracking heavier fractions. The kerosene yield was also increased because of the same reasons. He

concluded that the Pd/HBETA was the best catalyst for the gasoline production since this catalyst produced the highest quantity and quality of gasoline, and also it was suitably used for kerosene production because of high aromatics reduction. Moreover, Pd/HBETA catalyst selectively produced oil in the kerosene range which had a high amount of saturated hydrocarbons and low total aromatics contents because palladium can enhance hydrogenation and hydrogen transfer reaction on the heavy hydrocarbon; then, the obtained products were further cracked to lighter products or gases (Pintoo, 2008).

In addition, the reduction of poly- and polar-aromatic compounds, which are for examples heavy hydrocarbon compounds and very hazard components, initially requires the hydrogenation via the noble metal surface. Dũng et al., (2009) studied the polar-aromatic content in a tire-derived oil influenced by pyrolysis temperature and Pt-loaded on the zeolite (HBETA and HMOR) catalysts. They found that with the increasing pyrolysis temperature, the amount of polar aromatics increased in relation with the shift of peak to higher carbon numbers. With using only acidic zeolite catalysts, the results indicated that the HBETA had higher polar-aromatics reduction activity than the HMOR because of its higher surface area, higher medium and strong acid site, small crystal size, and 3D structure. Furthermore, the polar-aromatic improvement can be observed after loading Pt. Also, the Pt loaded on HBETA had higher activity than when loaded on HMOR because the dispersion of Pt over HBETA was higher than that over HMOR. Since Pt can promote hydrogenation reaction to form saturated hydrocarbons, the saturated hydrocarbons were then further cracked on the acidic sites.

Moreover, the catalyst preparation condition also affects to the catalytic activity. In 2010, Dũng et al. found that the heating rate (1, 5 and 10 °C/min) during calcination strongly affected to the activity of catalyst. With using the heating rate of 5 °C/min, Ru/SBA-1 gave the highest activity in terms of high sulfur tolerance and coke resistance, which were attributed to the smallest particle size and the strongest interaction between Ru and SBA-1. In 2008, Pintoo reported that the different amounts of metal loaded affected to the chemical composition; for example, the total aromatics increased with increasing metal loaded. He also found that with increasing catalytic temperature and residence time, the saturated hydrocarbons were

increased. Furthermore, the suitable technique for loading metal was impregnation technique because it resulted in the reduction of aromatics activity and increment of saturated hydrocarbons. Göhlich *et al.*, (2011) studied the dispersion of Pt/HZSM-5 on the hydrodearomatization of toluene to light alkanes. They used the different preparation techniques to obtain different Pt dispersion. The results showed that the increasing Pt dispersion led to the increase of the methane formation which was attributed to the increment of metal-support interaction. Furthermore, a high Pt dispersion enhanced the deactivation behavior. Similarly, Castaño *et al.*, (2006a), who studied the hydrodearomatization of pyrolysis gasoline by using the bifunctional catalysts, reported that the aromatic reduction consisted of two steps. The first one was hydrogenation taking place over the metallic surface, and the second step was isomerization, cracking reaction and/or coke formation. Thus, the highest metal dispersion gave the highest hydrogenation of aromatic compounds. They also reported that the total catalyst acidity was linearly affected to the C_2+ n-alkane formation (ring-opening reaction). Therefore, the influence of the catalytic activity and selectivity depended on the metal dispersion and the interaction between metal and support.

Recently, the palladium supported on the composite catalysts has been reported. He *et al.*, (2010) investigated the Pd/ZSM-5/MCM-48 composite catalysts which enhanced activity and stability for benzene oxidation. They prepared the composite catalysts ZSM-5/MCM-48 by using two-step crystallization with varying acidities (Si/Al molar ratio was varied at 20, 40, 80 and 160, respectively). They found that all of these composite catalysts, which had different acidity, showed the higher activity than the Pd/ZSM-5 and Pd/MCM-48 since the composite catalysts can improve Pd dispersion, CO_2 desorption capability, and acidity. High Pd dispersion can be described by the fact that the supporter had both more acid site, especially the strong acid sites, and a larger surface area (due to the combination with MCM-48) (He *et al.*, 2009).

HBETA has the pore openings of 7.6 x 6.4 Å and 5.6 x 5.6 Å. The cubic structure of HY has micro-pore size of 7.4 Å, while HZSM-5 has pore opening of 5.3 x 5.6 Å and 5.1 x 5.5 Å. From the several research works, it can be concluded that the quality and quantity of the desired products, especially the full range naphtha, can be improved by using the combination of two or more types of these zeolites

that have a different porosity, acidity, and selectivity. Moreover, since noble metals, especially platinum and palladium have potential to improve the quality and quantity of the products such as the reduction of poly- and polar-aromatics contents and prevention the undesired methane product from over-cracking. In addition, they can also improve the activity on cracking heavy fractions (vacuum gasoil) to the lighter fractions (full range naphtha, kerosene and/or gas fraction); thus, bifunctional catalysts with the addition of one or two additives at various catalyst to additive ratios will be used in this work for the catalytic pyrolysis of waste tire.

The objectives of this research work were to investigate the influence of two main cracking catalysts (Pd/HBETA and Pd/HY) on the products distributions, to investigate the addition of HBETA and HY zeolites as an additive into the catalysts affecting to pyrolysis products, and to observe the effect of the addition of HZSM-5 zeolite as the second additive into the catalysts on the pyrolysis products.

The scope of this research covers as follows: (1) the scrap tire pyrolysis was performed in a bench-scaled autoclave reactor, (2) the fixed parameters were 20-40 mesh of particle size, 30 g of sample, 7.5 g of catalyst, 500 °C for pyrolysis temperature, 350 °C for catalyst bed temperature, 90 min holding time, 10 °C/min of heating rate, and 30 ml/min of N_2 flow rate, (3) for bifunctional catalysts, the amount metal loaded was fixed at 1 wt%, (4) the introduction of an additive into the main cracking catalysts was investigated by varying the amount of additive at 10 wt% and 20 wt%, respectively.