CHAPTER II
LITERATURE REVIEW

In 2012, Freedonia group reported that the high production of 1.6 billion tires were accomplished. They are mainly supplied for transportation, especially personal car tires. On the other hand, tires are made from natural rubber, synthesis rubber, carbon black, accelerators, steel belt, steel-wire bead, etc. Tires are designed to resist extreme conditions through the vulcanization process. Crosslinking between sulfur and rubber molecular chain leads to formation of three dimensional network. Thus, tires have long-life and complication to recycle.

Pyrolysis of waste tires is a interesting technical way to treat and recover valuable products. Pyrolysis process is the thermal decomposition of substances at a high temperature in the absence of oxygen, involving breaking of large molecules into smaller molecules. The products of waste tire pyrolysis consist of carbonaceous materials and a mixture of hydrocarbons, which can be separated into gas and oil. These fractions can be used as valuable fuels and chemical feedstocks. Pyrolytic oils are important source of light mono-aromatics such as benzene, toluene, ethylbenzene, and xylenes.

2.1 Petrochemicals

2.1.1 Olefins

Olefins are hydrocarbons with a single double bond. Their demand is driven by petrochemicals prices, product yields and demand for consumer goods. They are mainly used to produce plastics and chemicals. Olefins, especially ethylene and propylene, are important petrochemicals. They are produced from fluid catalytic cracking unit in oil refineries and the steam cracking of natural gas. The double bond of olefins make the molecule easy for conversion to other products. Ethylene is conventionally produced by the thermal cracking of hydrocarbons ranging from ethane to heavy vacuum gas oils. It is the largest volume of olefins used in the manufacture of polymers such as polyethylene, polyester, polyvinyl chloride, and polystyrene. The intermediate chemicals produced from ethylene include ethylene oxide, ethylene glycol, and vinyl chloride monomer, etc. These products are used in a wide variety of industrial and consumer markets such as the packaging, and electronic industries. More than 60% of propylene is produced by thermal cracking as well as catalytic cracking technologies that will become more significant to produce propylene. It is dominated by production of polypropylene, which is about 60% of consumption. It can be made into fiber and film also. Other important derivatives of propylene are acrylonitrile, propylene oxide, cumene and acrylic acid. Butadiene is a versatile raw material used in the production of a wide variety of synthetic rubbers, elastomer, and polymer resins. A few chemical intermediates made from butadiene include adiponitrile and chloroprene, which are used in the manufacture of nylon and neoprene, respectively. The largest uses for butadiene are the productions of styrene butadiene rubber and polybutadiene rubber, which are used mainly in tires and other automotive products.

2.1.2 Aromatics

Petroleum is a fossil fuel, which concludes crude oil, natural gas. Aromatic hydrocarbons are important petrochemicals, which are derived from the catalytic reforming of naphtha. Aromatic hydrocarbons are used in wide range of materials. Benzene is a raw material for the production of dye, cumene, ethylbenzene and resin. Toluene is used in solvent and pesticide production. Xylenes have 3 isomers. Ortho-xylene is mainly used in the production of phthalic anhydride, para-xylene is used in the production of terephthalic acid, and meta-xylene is used to produce isophthalic acid. Therefore, light aromatics have many adventages. In contrast, heavy aromatics have serious drawbacks. Poly-aromatic hydrocarbons (PAH), which are identified as carcinogenics and mutagenic compounds, are extremely toxic to human health. Some reports demonstrated that PAH pollution during pregnancy caused low birth weight (Cunliffe and Williams, 1998; Williams *et al.*, 1998).

2.2 Sulfur Compounds and Sulfur Removal

Releasing of sulfur compounds in fuel oils result in environmental pollution. In addition, new environmental regulation of many countries impose a reduction of sulfur emission from fuel combustion. The species of sulfur in oils such as thioles, thiophenes, benzothiophenes, dibenzothiophenes and other derivatives need to be treated before using as fuels. There are many techniques to remove sulfur compounds such as hydrodesulfurization and adsorptive desulfurization. García-Cruz *et al.* (2008) reported that the activity of sulfur species towards hydrodesulfurization can be ranked as thiophenes > benzothiophenes > dibenzothiophenes > 4,6-dimethyldibenzothiophene. It is predicted that small sulfur compounds are easier to be desulfurized than larger sulfur compounds.

Zeolites have been paid the important role in the field of adsorptive desulfurization of transportation fuels, owing to the channel structure, high surface area and pore volume. Tian *et al.* (2012) reported that it was easy for thiophene molecules with a smaller diameter than benzothiophene and dibenzothiophene molecules to go inside the pore of HBeta and adsorb. Pore structure plays an important role in adsorptive desulfurization whereas the large pore of a zeolite is beneficial to great desulfurization.

2.3 Waste Tire Pyrolysis Products

Pyrolysis of waste tires is an interesting technical way to treat and recover valuable products such as light olefins, cooking gases, fuel oils and light mono-aromatics. Pyrolytic oil is an important source of light mono-aromatics such as benzene, toluene, xylenes, and styrene. Additionally, limonene is found in oil products, which plays an important precuser in solvent applications, resin production and substitutes for cholroflurocarbon solvent as an environmental solvent (Antoniou and Zabaniotou, 2013).

2.3.1 Non-catalytic Pyrolysis

There are a large number of research reports about the thermal pyrolysis of waste tire. In 2004, Laresgoiti *et al.* studied liquid products obtained from waste tire pyrolysis. They found that 500 °C was the optimum temperature for pyrolysis because over 500 °C had no influence on the product yield. The result showed that pyrolytic oil had-sulfur compounds around 1.0-1.4 wt.%, and it gave a high heating value for being used as fuel oils. Additionally, oils contained a large number of compounds, which were identified by using a GC/MS. The abundant species were toluene, ethylbenzene, xylene, styrene, dimethylcyclohexene and limonene. In addition, they reported that benzene, toluene, and xylenes were obtained high concentration at 500 °C. Polycyclic aromatics were increased at a higher temperature due to cyclation reaction in accordance with dehydrogenation of olefinic compounds. Islam *et al.* (2008) studied waste tire pyrolysis products, especially liquid products. They found that pyrolytic oils were complex mixtures, which consisted of aliphatic and aromatic compounds. The sulfur content in pyrolytic oils was 1.25%. Oils consisted of aliphatic and aromatic compounds around 49.54% and 16.65%, respectively. Limonene was the most abundant species in pyrolytic oils as well as benzene, toluene, and xylenes. These aromatic products were an important raw materials for chemical industries which had high market values. They found that pyrolytic oils can be directly used as fuels for furnace, power plant, and boilers. It can be used as diesel fuel after improving the quality such as desulfurization or blending with commercial fuels. Fernández *et al.* (2012) studied products from waste tire pyrolysis, particularly the liquid products. The result showed that 550 °C was optimum temperature which completed decomposition. Liquid products were analyzed, and they found that oils were the complex compounds containing ethylbenzene, xylene, styrene, and a high amount of limonene. They suggested that aromatics in oils were obtained from the decomposition of rubber via aromatization of alkene. Also, the gas products containing C_1-C_3 increased with temperature while C_4 reduced with temperature due to C_4 conversion to lighter hydrocarbon. Banar *et al.* (2012) studied pyrolytic oil from waste tire pyrolysis. The result showed that maximum oil yield was obtained at 400 °C, and the oil yield decreased with increasing heating rate from 5 °C/min (38.8%) to 35 °C/min (31.1%). They found that the fuel properties (H/C, HHVs and density) of pyrolytic oil was similar to those of the diesel and gasoline. Additionally, The oil mainly consisted of aliphatic and aromatic compounds such as *n*-undecane, *n*-tetradecane, naphthalenes and alkenes, particularly limonene. They suggested that the pyrolytic oil can be used as chemical feedstocks for aromatic production. As mentioned above, thermal pyrolysis is a good way to recover valuable products from waste tire, which causes environmental and health problems. However, thermal pyrolysis has some disadvantages; for example sulfur content in products is quite high as a consequence of high process purify cost.

2.3.2 Catalytic Pyrolysis

It is well-known that waste tire pyrolysis has some drawbacks. It requires high energy consumption in the process. The products consist of a high concentration of poly-aromatics and polar-aromatics as well as nitrogen and sulfur compounds, which make them have low quality and value. In order to increase the value of products, catalysts play an important role to enhance the quality and quantity of valuable products of waste tire pyrolysis. Many researchers used zeolites in waste tire pyrolysis.

Boxiong *et al.* (2007b) studied waste tire pyrolysis over USY catalyst. The result showed that the gas product was increased, and the oil product was decreased as compared to thermal pyrolysis. They found that the oil product consisted of a high concentration of single ring aromatics, which increased (62%) with using USY zeolite. The most abundant aromatic species were benzene, toluene, xylene and ethylbenzene. They also studied the catalytic pyrolysis of waste tire over USY and ZSM-5 zeolites. USY had larger pore size than ZSM-5, allowing more large molecules to be cracked inside the pore, and leading to a higher amount aromatic hydrocarbons. Lower Si/Al of USY was attributed a higher surface acidity of catalyst. The increasing concentration of aluminium on the catalyst surface caused an increase in aromatic yield. Additionally, USY gave a higher light yield of oil than ZSM-5. Using USY gave a higher concentration of benzene, toluene, and xylenes than ZSM-5. Moreover, the production of limonene was decreased with using both of zeolites due to the decomposition of limonene to form aromatic hydrocarbons (Boxiong *et al.*, 2007a). Olazar *et al.* (2008) studied the effect of using HY and HZSM-5 catalyst on waste tire pyrolysis. The gas product increased with using HZSM-5 due to cracking of heavy fractions, and it slightly decreased with using HY because HY favored the activation of olefin alkylation and condensation to form heavy products. Additionally, olefins which consisted of ethene and propene increased with the use of both catalysts. Poly-aromatics in oil products increased with using catalysts, especially HY. It was suggested that larger pore size and more hydrogen transfer capacity of HY thus caused more cyclization, aromatization, and condensation reactions occurred inside the pore to form aromatics. Moreover, single ring aromatics in the liquid product obtained from HZSM-5 was about 32.5 wt.% and 40.5 wt.% for HY. Also, limonene decreased with using all catalysts attributed to the catalysts that enhanced the cracking ability of limonene into other products. They also reported that the amount of sulfur in oils increased to 1.6 wt% for HZSM-5 and 1.8 % for HY. It was mentioned that sulfur compounds in oils were increased by the cracking of sulfur compounds in the solid products, which was the reason why sulfur compounds in the solid products were decreased. Dũng *et al.* (2009b) used HMOR zeolite in waste tire pyrolysis. The result showed that the presence of HMOR increased the light products, which caused the increment of gas yield and the reduction of oil yield. In addition, the introduction of HMOR led to the increasing amounts of gasoline and kerosene and the decreasing amounts of fuel oil and heavy vacuum gas oil due to the good cracking performance of catalyst. They mentioned that HMOR favored to produce gasoline, which was selective to pore size. The pyrolysis of waste tire with using HBeta, KL and HY zeolites were studied by Saeng-arayakul (2013). The comparison between acid and basic supports (HBeta and KL, respectively) was investigated. The results showed that using HBeta produced higher gas yield than using KL. Moreover, HBeta zeolite reduced the concentration of heavy liquid fractions (long residues and heavy gas oil) more greatly than KL zeolite. The results demonstrated that long-chain hydrocarbons were more easily cracked by HBeta.

2.4 Noble Metals in Catalytic Pyrolysis

Noble metals such as ruthenium (Ru), rhodium (Rh), platinum (Pt) have high activity in hydrogenation-dehydrogenation, and ring opening reactions. Many rechearchers used them in waste tire pyrolysis. Dũng *et al.* (2009b) investigated the effects of pyrolysis temperature and catalyst on polar-aromatics in oil by using platinum catalyst supported on HMOR and HBeta zeolites. They found that using HMOR and HBeta zeolites, polar-aromatic hydrocarbons were reduced. Loading Pt on zeolite supports caused polar-aromatics content further decreased. For the non-catalytic case, the distribution of polar-aromatics was in the range of gas oil and vacuum gas oil. The distribution of polar-aromatics shifted to lighter fractions in the catalytic case ascribed to Pt that enhanced hydrogenation reaction, which converted polar-aromatic hydrocarbons to saturated hydrocarbons. On the other hand, polar-aromatics increased with temperature. They suggested that more radicals generated at a high temperature led to the formation of polar-aromatic hydrocarbons by the combination of olefins and sulfur via Diel-Alders reactions.

Ruthenium on MCM-41 was studied in the pyrolysis of waste tire by Dũng *et al.* (2009a). The results showed that the presence of MCM-41 catalyst caused the increment of gas yield and the reduction of liquid yield. It was attributed to MCM-41 that enhanced cracking of the heavy products to lighter products. Using Ru supported on MCM-41 led to further increase in the gas yield due to the cracking of aromatics in the liquid as a result of the improved hydrogenation of aromatics by Ru. Moreover, Ru/MCM-41 highly increased the yield of light olefins. Moreover, the increment of single ring aromatics was observed with the introduction of catalyst, especially with using Ru/MCM-41. Also, polycyclic aromatics were reduced with using the catalyst. They stated that the hydrogenation of aromatic preferred polycyclic aromatics to single ring aromatics. Witpathomwong *et al.* (2011) studied waste tire pyrolysis with using Ru/MCM-48 catalyst. The results showed that with the catalyst, light olefins and saturated hydrocarbons were increased. Additionally, all aromatics species were reduced with the catalyst treatment due to cracking of aromatics into lighter products by MCM-48 and Ru. Moreover, sulfur compounds slightly reduced with using Ru/MCM-48, indicating the low activity of Ru in breaking C-S bond.

Rhodium catalyst supported on KL zeolite was used in waste tire pyrolysis by Pinket (2011). The result showed that Rh/KL promoted the gas production, and reduced the production of liquid compared to thermal pyrolysis and pyrolysis with pure KL zeolite. It was stated that Rh showed the activity in C-C bond breaking. In addition, Rh/KL catalyst resulted in a slight increase of saturated hydrocarbons, a high increase of mono-aromatics, and a decrease of multi-ring aromatics compared to using pure KL. Moreover, KL exhibited the ability in aromatization, and Rh showed high activity in hydrogenation and ring opening of poly-aromatic hydrocarbons to form light aromatics. Moreover, the high increase of mono-aromatics and decrease of poly-aromatics can be explained that the hydrogenation of multi-ring aromatics was easier to occur than that of mono-aromatics. Also, sulfur in oils was greatly reduced from 0.91 % to 0.35 % with the presence of Rh that exhibited a good ability in C-S bond breaking. Likewise, Rh metal in waste tire pyrolysis was studied by Saeng-arayakul (2013). The result showed that using zeolites (HY , HBeta, and KL) caused the reduction of liquid yield and the improved production of gas yield. Moreover, the introduction of Rh led to a further increase in the gas yield due to hydrogenolysis reaction on the metal. Moreover, using zeolites can reduce the concentration of heavy fractions in the liquid products due to cracking ability of zeolite. Introduction of Rh metals gave a slight increase in full range naphtha as well as a high increase of mono-aromatics in the liquid yield due to the hydrogenation ability of Rh. Furthermore, Rh supported on zeolites showed good performance in sulfur removal from oil. It was explained that hydrogenation on metal caused aromatics and hydrocarbon chains saturated before hydrogen sulfide was produced.

2.5 Non-noble Metal in Catalytic Pyrolysis

The use of zeolite catalyst is one of the directions to enhance the quality of waste tire pyrolysis products. Noble metals can promote the catalyst activity and selectivity for hydrogenation-dehydrogenation and ring opening reactions. However, high costs of noble metals are not effective for waste tire pyrolysis. Non-noble metals that have a good performance and low costs are interesting for waste tire pyrolysis. Therefore, the uses of non-noble metals rather than noble metals are preferred.

2.5.1 Cobalt Catalysts

Cobalt is a non-noble metal with a high availability. Many researchers studied about applications of Co, especially in catalytic fields such as hydrodesulfurization and Fischer-Tropsch synthesis. Metallic cobalt is a commonly-used catalyst selective to linear C_{5+} hydrocarbon. It has low activity for water-gas shift reaction and lower price as compared to a noble metal. Moreover supported Co catalysts gave a high yield of paraffinic hydrocarbons in Fischer-Tropsch synthesis

(Berge and Everson, 1997). Zennaro *et al.* (2000) mentioned that Co gave a lower olefin selectivity in Fischer-Tropsch synthesis attributed to a high hydrogen concentration on the catalyst surface and the re-adsorbtion of olefins on the surface that led to secondary hydrogenation. Likewise, Fischer *et al.* (2013) studied the effect of size of Co on the activity of Fischer-Tropsch synthesis. They found that a small size of Co showed the reduction of C_{5+} hydrocarbons and the increase of methane. They suggested that the decrease of surface activity was attributed to the decrease in crystallite sites. Teiseh *et al.* (2012) studied cobalt-based catalysts in Fischer-Tropsch synthesis by comparison between Co-SiO_2 and Co-SiO_2/Mo-Pd-Pt-ZSM-5 (a hybrid catalyst). They found that cobalt tended to produce high molecular weight hydrocarbons. Using Co/SiO_2, products obtained were in the range of gasoline, which were mainly in the range of C_9-C_{11}. Co/SiO_2 produced more olefins and isomers than the hybrid catalyst due to Co-SiO_2 that preferred isomerization to oligomerization. Comparison of the performance of Co/SBA-15 and Ru/Co/SBA-15 catalysts was investigated by Rodrigues *et al.* (2012). The results showed that Ru/Co/SBA-15 exhibited better performance than Co/SBA-15. It appeared to be more active and selective to C_{5+} than Co/SBA-15, which was attributed to the introduction of Ru that caused the high dispersion of Co. Additionally, cobalt promoted the re-adsorption of olefins and the conversion of light gases to heavy hydracarbons. Yang *et al.* (2007) studied Fischer-Tropsch catalysts. They compared the products obtained from Co/SiO_2, Co/SiO_2-ZSM-5(physical mixture), and a capsule catalyst of Co/SiO_2 covered by ZSM-5 zeolite. The result showed that Co/SiO_2-ZSM-5 appeared to give the narrower carbon number distribution in the range of C_3-C_7 compared to Co/SiO_2 because ZSM-5 zeolite helped to reduce heavy fractions to lighter ones by the enhancement of isomerization and the cracking ability of zeolite. The use of capsule catalyst caused the reduction of CO selectivity, which was attributed to the metal site that was reduced by the coverage of zeolite. Pedrosa *et al.* (2006a) studied Co supported on HY zeolite for *n*-hexane hydroconversion in order to produce branched hydrocarbons and to increase the octane number of gasoline. The temperature were varied between 300°C and 380°C. The results showed that the increment of *n*-hexane isomerization of Co/HY occurred with increasing reaction temperatures due to the activation of carbonium or carbenium ions that increased with temperature. However, iso-C_6 production decreased with temperature due to the reduction of metal-acid balance that caused the reduction of isomerization selectivity and the increment of cracking selectivity. The olefins formation was not observed. It indicated the good hydrogenation of Co on HY zeolite.

The use of a non-noble metal instead of a noble metal in waste tire pyrolysis was studied by Pinket (2011). She investigated the effects of the noble metal (Rh) and the non-noble metal (Co) supported on KL zeolite. The results showed that Rh had good ability in light mono-aromatics production and reduction in sulfur content in oil. In the case of using the cobalt catalyst, Co supported on KL exhibited good catalyst for light olefins and cooking gas production, especially 1%Co/KL that gave a higher amount of valuable gas production than the noble metal catalyst (1%Rh/KL). The Co catalyst also showed the high production of mono-aromatics and the low concentration of multi-ring aromatics. These result was attributed to Co that provided good performance in hydrogenation and ring opening reactions, leading to the conversion of multi-ring aromatics to mono-aromatics. 5%Co/KL yielded the highest production of light mono-aromatics (1.83 wt.%) among various Co loadings and higher than 1%Rh/KL (0.97 wt.%). Moreover, a high Co loading tended to improve the ability of sulfur removal from oil.

In 2012, Saparukpunya investigated catalytic waste tire pyrolysis using 5 wt.%Co supported on various supports, namely HY, HMOR, HBeta, HZSM-5 and SAPO-34. The results showed that the introduction of 5 wt.% Co on all of supports resulted in an increasing amount of gas fractions and a decreasing amount of liquid fractions compared to the non-catalytic pyrolysis due to the ability in breaking heavy to lighter products of acid supports. The presence of Co tended to increase ethylene and propane. Then, the hydrogenation reaction of ethylene and propylene was enhanced by Co catalyst. Co supported on HY and HZSM-5 gave the highest of light olefins and cooking gas, respectively. Also, mono-aromatic hydrocarbons were increased in all catalyst cases, and further increased with the increasing Co loading in the expense of poly-aromatics. Poly-aromatics conversion to mono-aromatics as a result of hydrogenation and ring opening reactions was enhanced by cobalt (Pinket, 2011). Moreover, the presence of Co on some supports

(HY, HMOR, and HBeta) caused the increase in heavy fractions (gas oil and long residue) by the transformation of light fractions (naphtha and kerosene). Additionally, the concentration of light mono-aromatic hydrocarbons (C_6-C_8) exhibited the highest value with using 5%Co/HMOR. Moreover, Co supported on HY, HMOR, and HZSM-5 showed the activity on reduction of sulfur in oil. Likewise, Piyawongpinyo (2013) studied modified Co supported on HBeta zeolite. He found that 5%Co/ HBeta catalyst had higher cracking ability than modified Co due to a higher gas/liquid ratio. Using 5%Co/ HBeta also gave the highest yield of cooking gas compared to the non-catalytic and modified Co cases. In addition, 5%Co/ HBeta can increase full range naphtha, and decreased heavy fractions. It can be concluded that Co catalyst can be used to produce the light fractions in oil with low contents of the heavy fractions. On the other hand, 5%Co/ HBeta catalyst had the good hydrodesulfurization ability since the sulfur content in oil was decreased from 1.36 wt.% for the in non-catalytic case to 1.06 wt.% for 5%Co/ HBeta.

2.5.2 Iron Catalysts

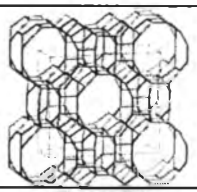
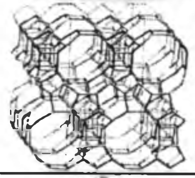
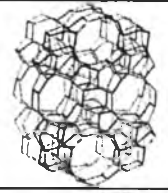
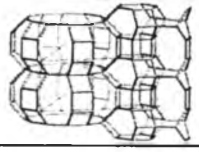
Iron catalysts are environment-friendly ones with low toxicity, and show significant activity in catalytic processes, combustion and emission control (Abbasi-Atibeh and Yozgatligil, 2013). The usage of iron catalysts are mainly in Fischer-Tropsch synthesis, and appear to be economically feasible in catalytic fields. Fischer-Tropsch synthesis using Fe and Co catalysts was investigated by O'Shea *et al.* (2007). They reported that the Fe catalyst exhibited high selectivity to lighter hydrocarbons compared to the Co catalyst. The Fe catalyst showed higher selectivity to alcohol than the Co catalyst. Increasing temperature resulted in longer chain hydrocarbons in the range of diesel and gasoline obtained from Fe catalyst, although the production of long chain hydrocarbons was lower than using Co catalyst. It was mentioned that the formation of light hydrocarbons was a behavior of Fe catalyst. Kang *et al.* (2010) studied Fe catalysts supported on ZSM-5 zeolite in Fischer-Tropsch process in order to produce light olefins. It was well-known that metallic iron and iron carbide (FeC_x) are active phase for Fischer-Tropsch reaction. They found that the Si/Al ratio of ZSM-5 played an important role on Fischer-Tropsch reaction; that is, iron carbide and metallic iron decreased with increasing Si/Al ratio, resulted in the reduction of activity and selectivity in Fischer-Tropsch reaction. In addition, the Si/Al ratio of 25 in ZSM-5 gave the highest selectivity to C_2-C_4 hydrocarbons and olefins productions among other Si/Al ratios of ZSM-5. Pour *et al.* (2008) studied Fischer-Tropsch synthesis catalyzed by pure Fe and Fe supported on ZSM-5. They indicated that the Fe/ZSM-5 catalyst gave a longer chain of hydrocarbons than the pure Fe catalyst because ZSM-5 promoted oligomerization activity, cracking activity, and shape selectivity, followed by aromatization that led to the reduction of light products. Moreover, ZSM-5 improved the quality of gasoline by increasing C_5-C_{11} hydrocarbons. Namely, Fe/ZSM-5 enhanced secondary chain growth. Kumabe *et al.* (2010) studied Fe-based catalysts for kerosene production in Fischer-Tropsch synthesis. They suggested that the reduced Fe favored to produce olefins rather than paraffins in C_6+ hydrocarbons range. It showed that low chain growth and low paraffins produced by the hydrogenation of olefins were attributed to the low surface area of reduced Fe. Yoneyama *et al.* (2005) studied a Fe-based catalyst over ZSM-5 zeolite in Fischer-Tropsch synthesis. They found that Fischer-Tropsch products catalyzed by the Fe catalyst consisted of *n*-paraffins and *α*-olefins. The distribution of hydrocarbons obtained from the Fe catalyst was in the range of C_1-C_{16} hydrocarbons. In the presence of ZSM-5, shorter chain hydrocarbons and isoparaffins were produced. The products consisted of C_4-C_6 branched hydrocarbons were increased and longer chain hydrocarbons were reduced. In addition, the hydrocarbons from using Fe/ZSM-5 were limited to C_{10} hydrocarbons. They suggested that the shape selectivity and cracking ability of ZSM-5 led to the production of branched light hydrocarbons. It can be concluded that Fe/ZSM-5 was selective for isoparaffins production.

Fe catalysts were investigated for selective catalytic reduction (SCR) by He *et al.* (2009). They studied the Fe catalyst supported on HBeta zeolite by varying iron loading from 0.5-7.0 wt.%, aiming reduce nitrogen oxide from the diesel engine. They found that iron loading at 2.5 wt.% gave the high conversion of NO about 97 %. Moreover, a higher iron loading than 2.5 wt.% gave the same conversion as 2.5wt.%. Additionally, they compared the activity of Fe/HBeta with Fe/ZSM-5. The result showed that Fe/HBeta gave higher activity of SCR than Fe/ZSM-5 due to higher surface area. Iron catalysts were also used in the hydrogenation of sulfur dioxide to hydrogen sulfide by Li and Hung (2003). They studied chromium-promoted Fe/SiO_2 catalyst, and found that the iron catalyst as a hydrogenation catalyst showed a high H_2S yield due to iron that adsorbed hydrogen. Addition of Cr and Si dramatically improved the SO_2 hydrogenation activity of the iron-based catalyst. The catalyst with a Fe/Si/Cr atomic ratio of 1/0.6/0.01 had the highest activity, which showed much better SO_2 hydrogenation activity than Fe/γ-Al_2O_3 catalyst of their previous work. The use of iron catalyst in waste tire pyrolysis was interesting. In 2012, Saeaeh studied a non-noble metal catalyst (Fe) as a substitute to a noble metal catalyst (Ru) in waste tire pyrolysis. The result showed that the increasing amount of Fe loading on HBeta and HMOR zeolites tended to enhance the cracking ability of liquid to gas products. For liquid products, it was reported that presence of Fe catalyst led to sharp increase in saturated hydrocarbons. Moreover, Fe catalyst decreased poly- and polar-aromatic hydrocarbons. It was attributed to Fe site that had an important role on promotion of hydrogenation and hydrodesulfurization reactions of poly- and polar aromatic hydrocarbons. Moreover, heavy fractions such as heavy gas oil and long residue increased with increasing Fe loading because the secondary reactions, which consist of oligimerization, aromatization and H-transfer, were enhanced on Fe. As observed above, the Fe catalyst had as high activity as the noble metal, Ru, which is costly.

According to the background and literature reviews, cobalt and iron are non-noble metals, which can be used as a catalyst in waste tire pyrolysis. These metals do not only play an important role as substitutes of noble metals, but also exhibit the good performance to produce high valuable products. From previous work, zeolites were selected in the pyrolysis in order to produce various kinds of products. However, the properties of zeolites which affected on products was not explained clearly.

The effects of zeolite supports (acidity-basicity of supports, channel structure, and pore size) on obtained products were investigated in this work. With the difference in channel structure of HMOR and HBeta, these two supports were investigated, and the results were compared. The straight pore of HMOR was expected to give higher light aromatics than HBeta, which has more intricate pore as compared to HMOR. The effects of pore size difference of HZSM-5 and HBeta were studied. HZSM-5 was expected to produce lesser coke than HBeta because the smaller pore size of HZSM-5 allow less number of molecules to crack inside the pore. The effects of acidity-basicity of supports (HMOR and KL) was also investigated. The acid support, HMOR, was expected to give higher light fractions than the basic support, KL. Furthermore, the performances of Co and Fe modified with zeolites on the catalytic pyrolysis of waste tire were investigated. The amount of Fe and Co loading was fixed at 5 wt.%.

Table 2.1 Properties of zeolites used in the experiments

Zeolite	Pore size (Å)	Channel structure	Channel system	Membered ring	Si/Al ratio
HMOR	6.5×7.0		1D	12	9.5
HBeta	6.4×7.6		3D	12	13.5
HZSM-5	5.3×5.6		3D	10	15
KL	7.1×7.1		1D	12	3

The objectives of this research work were thus to investigate the effect of pore structure of zeolites on species of pyrolysis products by using HMOR and HBeta zeolites, to investigate the effect of pore size of zeolites on species of pyrolysis products by using HZSM-5 and HBeta zeolites, to investigate the effect of acid and basic supports on species of pyrolysis products by using HMOR and KL zeolites, and to investigate the performance of different modified metals between Co and Fe on the quality and quantity waste tire pyrolysis products.

Table 2.2 Experimental design for effects of zeolite

Pore channel	HMOR
	HBeta
Pore size	HZSM-5
	HBeta
Acid and non-acid support	HMOR
	KL

The controlled parameters of this work are listed follows. Pyrolysis of scrap tire (Bridgestone TURANZA GR-80) was operated in a bench-scaled reactor. The fixed parameters were 20-40 mesh particle size of tire, 30 g of sample, 7.5 g of catalyst, 500 °C for pyrolysis temperature, 350 °C for catalytic temperature, 120 min holding time, 10 °C/min of heating rate, 30 ml/min of N_2 flow rate and atmospheric pressure. The catalysts were prepared by the incipient wetness impregnation method. The amount of Co and Fe was fixed at 5 wt.%. The zeolites used in this experiment were HMOR, HBeta, HZSM-5, and KL.

Table 2.3 Experimental design of metal-loaded part

Metal catalyst	**Zeolites**
5 wt.% Co	HBeta
	HMOR
	HZSM-5
	KL
5 wt.% Fe	HBeta
	HMOR
	HZSM-5
	KL