CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

Pyrolysis is an effective process for eliminating a large number of waste tires that have caused environmental problems for several years. Furthermore, the pyrolysis process can produce higher value products that all of the products can be used in several applications. Proper product uses can be considered from the results in terms of the amounts of sulfur, saturated hydrocarbons, total aromatics, etc. in the liquid product, the amounts of cooking gas, light olefins, mixed-C_4, etc. in the gas products, and heating value, sulfur content, etc. in the solid product by using several high performance instruments. Furthermore, the uses of catalysts in pyrolysis process, called catalytic pyrolysis, play an important role for upgrading quality and quantity of desired products. Especially, zeolites that have shape selectivity properties can highly affect the quality of desired products. Moreover, metals that can do cracking, hydrogenation, dehydrogenation, hydrogenolysis and ring-opening activities can reduce heavy fractions in oils and increase lighter products, resulting in an increased value of pyrolysis products as well. So, metal loading on each zeolite can exhibit synergism effects, resulting in an increased performance of catalysts. However, even though metal-loaded catalysts have high performance for producing high quality and yields of desired products, the almost ever used metals are noble metals that have high prices; so, the uses of noble metals in pyrolysis catalysts are improper in terms of economy. Non-noble metals are a choice for increasing the possibility of uses of the catalysts in waste tire pyrolysis process. Details of all mentioned issues are discussed below.

2.1 Waste Tire Pyrolysis Products

Pyrolysis can convert tires into three types of products that are gas, liquid and solid, which has a higher value than other recycle tire methods because all of the products can be used in several applications such as fuels, chemicals, etc. Generally, waste tire pyrolysis produces gas, liquid and solid products in the range of 0.4-26.7 wt%, 18.1-55.6 wt% and 36.7-81.5 wt%, respectively (González *et al.*, 2001). The important and interested species are H_2, CH_4, light alkanes (C_{2-5}), light olefins (ethylene and propylene) in gas products that can be used as fuels (high enough heating value for uses as pyrolysis heat source reported by Aylón *et al.* (2007)) or chemicals while benzene, toluene, mixed-xylenes, isoprene, limonene and styrene are the species in liquid products that can be used as petrochemicals (Williams and Besler, 1995; Mastral *et al.*, 2000; Kaminsky and Mennerich, 2001). Furthermore, the liquid products that can be used as fuels have the properties similar to those of light gas oil the most in terms of heating value and amount of sulfur and nitrogen as reported by Cunliffe and Williams (1998). They can be separated into several fractions for uses in proper applications according to their boiling points in two different methods of cutting system: (1) gasoline, kerosene, gas oil, light vacuum gas oil, heavy vacuum gas oil, and long residue, and (2) full range naphtha, kerosene, light gas oil, heavy gas oil and long residue. The solid product can be further processed and then used as, for examples, activated carbons (Cunliffe and Williams, 1999; Zabaniotou and Stavropoulos, 2003), solid fuels (Chaala and Roy, 1996), and adsorbents (Murillo *et al.*, 2006).

The species, yield, and quality of products obtained from waste tire pyrolysis process can be analyzed by using several instruments. The product is analyzed for the properties in terms of elemental composition, specific surface area, %acetone extract, %inorganic compounds and sulfur content for the further use as an additive in tire rubber manufacture, like carbon black (Kaminsky and Mennerich, 2001). The gas product is generally analyzed by using a gas chromatograph (GC) equipped with either on TCD or FID. Each technique can report accuracy of product yields and qualities in a satisfied level. However, the accuracy of identification of chemical species is limited by the complexity of analysis, analysis time, and resolution. For example, Šebor *et al.* (1999) separated the pyrolysis products of high boiling point fraction into saturated hydrocarbons, mono-, di-, poly-aromatics, and polar-aromatic compounds by using column chromatography. Several solvents were used as mobile phases for eluting each oil fraction out of a glass column earlier packed with a consecutive layer of silica and alumina. So, this method is a time-consuming process. Even though this method can classify the oil into several fractions, it cannot identify particular species in each fraction at all. HPLC technique is a choice for analyzing oils, which gives more details than column chromatography and spends less analysis time. HPLC and column chromatography can be used in association with other instruments such as GC/MS, GC×GC and GC-TOF that can help further identifying specific species in oils. For examples, Qiang and Lu (1999) used an HPLC technique to separate lube base oil and high boiling point distillates (350-500 °C) into the fractions of saturates, mono-, di-, poly-aromatics and resin (more than six-ring aromatics and polar-aromatics). Likely, Satou *et al.* (1989) separated coal-derived oils into alkanes, mono-, di-, tri-, and tetra-, and poly-aromatics, and polar-aromatics by using HPLC, and further analyzed for aromatic hydrocarbons in each fraction by using a GC/MS. Furthermore, other techniques can be used to separate oils into fractions, and can also identify specific species, for examples, 2D GC×GC, quadrupole GC-MS, fast GC-TOF/MS, GC×GC-TOF/MS, etc. Nowadays, GC×GC-TOF/MS is the best technique for analyzing oils due to short analysis time, high accuracy, and high precision (Shelli *et al.*, 2001), which can solve the disadvantages of each techniques, such as GC×GC, quadrupole GC-MS and fast GC-TOF/MS (Hamilton and Lewis, 2003).

2.2 Sulfur Species in Tire-derived Products and Sulfur Distribution

The species of sulfur compounds can be identified by using many instruments such as GC×GC, GC/MS, GC-TOF/MS and GC×GC-TOF/MS (Satou *et al.*, 1989; Shelli *et al.*, 2001; Hamilton and Lewis, 2003). Furthermore, an elemental analyzer can also report sulfur content in solid products while a wavelength dispersive X-ray (WDX) technique can report sulfur species (Olazar *et al.*, 2008).

Sulfur in a whole tire (1.4 wt%) can distribute in each part of tire-derived products in different amounts: 10.6 wt% S in gas, 48.8 wt% S in oil, and 40.6 wt% S in carbon black (Kaminsky and Mennerich, 2001). Likely, sulfur in a whole tire (1.5 wt%) distributes in tire-derived products in different amounts: 2.5-5.1 vol% H_2S in gas, while 1.0-1.4 wt% S in oil, and 2.3-2.6 wt% S in char as reported by de Marco Rodriguez *et al.* (2001).

Generally, sulfur species in gas products consist of H_2S, SO_2, COS and CS_2 and H_2S, which are the main sulfur species (Teng *et al.*, 1995; Zhang *et al.*, 2008).

Liquid products contain many types of sulfur containing compounds that the main groups were thiophenes, benzothiazoles, benzothiophenes, dibenzothiophenes, and their alkylated derivatives while minor groups were also found such as naphthothiophenes, benzonaphthothiophenes, and their alkylated derivatives (Williams and Besler, 1995; Mastral *et al.*, 2000; Kaminsky and Mennerich, 2001; Unapumnuk *et al.*, 2008). In the main groups of sulfur containing compounds, main species found in the reports as mentioned above were 2-methylthiophene, 3-methylthiophene, 2,3-dimethylthiophene, 2,5-dimethylthiophene, 2-ethylthiophene, dibenzothiophene, methyldibenzothiophenes, dimethyldibenzothiophenes and trimethyldibenzothiophenes. For the solid product, sulfur species are in forms of sulfur atom and/or ZnS, depending on pyrolysis conditions as reported by Olazar *et al.* (2008). When the pyrolysis reaction was operated below 700 °C, the form of sulfur and zinc in carbon black was only sulfur element and ZnO, and no ZnS form appeared. However, above 700 °C α-ZnS (sphalerite) and β-ZnS (wurtzite) crystals were formed.

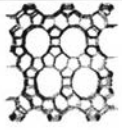
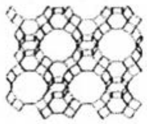
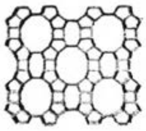
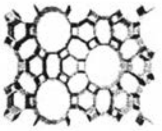
Furthermore, the pyrolysis conditions can affect the sulfur distribution in each part of waste tire pyrolysis products as well. Susa and Haydary (2012) reported that the residence time (73.9-88.6 s) insignificantly affected the sulfur distribution while the operating temperature (600-800 °C) significantly affected the sulfur distribution because the cracking activity of tire molecules increased with temperature. At the end of the pyrolysis process, all products (gas, liquid and solid) contained sulfur varied in the range of 11.31-29.73 wt%, 10.32-20.12 wt% and 59.29-70.47 wt%, respectively. Additionally, Susa and coworker also reported that a higher temperature increased gas yield and sulfur content in gas products while liquid and solid products had lower amounts of sulfur and lower yields. The heating rate (1, 5 and 10 °C/min) did not affect the sulfur content in oils and solid product while temperatures in the range of 350-400 °C can reduce sulfur content, and then the sulfur content was constant at higher temperatures (400-800 °C) in liquid and solid products. Unapumnuk *et al.* (2008) reported the effect of heating rate (1-10 °C/min) and pyrolysis temperature (325-1,000 °C) on sulfur content in the pyrolysis oils and solid char obtained from waste tire pyrolysis. The results showed that the heating rate insignificantly affected overall desulfurization (sulfur content in oils and char). The increasing temperature from 350 to 400 °C can increase overall desulfurization, and the temperature higher than 400 °C did not affect the change of the overall desulfurization as compared with at 400 °C. About 50 % of sulfur in waste tire (2.5 wt%) remained in solid char after the pyrolysis in the temperature range of 350-850 °C. Likely, the report of Williams and Bottrill (1995) showed that the increasing heating rate (from 5 to 60 K/min) in the bench-scale batch reactor insignificantly increased total sulfur-polycyclic aromatic hydrocarbons (PASH) contents (from 297 to 337 ppm). In the bench-scale fluidized bed reactor, the increasing temperature from 400 °C to 550 °C significantly increased PASH concentration in the oils (from 659 to 1,223 ppm) because higher temperature increased the formation of PASH like a Diels-Alder type reaction for polycyclic aromatic hydrocarbons (PAHs). Dũng (2009) reported the effect of pyrolysis temperature (500 °C, 600 °C and 700 °C) on the amount of polar-aromatics in waste tire pyrolysis oils. He found that the increasing pyrolysis temperature can cause the increment of polar-aromatic content in oils because more free-radicals (active species for generating polar-aromatic hydrocarbons) were higher generated at a higher temperature.

2.3 Effects of Zeolites on Waste Tire Pyrolysis Products

Both quality and quantity of waste tire pyrolysis products can be enhanced by using catalysts. Due to their acid/basic properties and shape selectivity, zeolites were selected to be catalysts for enhancing the products. The difference of zeolite structures and properties caused getting different desired products as discussed later.

MOR catalyst (Si/Al=9.5) was used in the work of Choosuton (2007) and Dũng (2009). As compared with the non-catalytic case, it can enhance the gas production, especially propane production, and reduce the liquid yield while the solid yield was constant. Furthermore, the support enhanced kerosene and gasoline production, and reduced asphaltene and poly-aromatic contents in oils and the production of heavy fractions (light and heavy vacuum gas oil). Similar to the work of Wehatoranawee (2011), the MOR support (Si/Al=9.5) enhanced full range naphtha production and reduce heavy fractions (light and heavy gas oil fractions and long residue). As mentioned above, the MOR support had high cracking ability.

Table 2.1 Structure and physical properties of zeolites (Tosoh Company, Singapore)

Zeolite	**Dimension**	**Membered Ring**	**Pore size (Å)**
BETA 	3D	12	7.6 × 6.4
Y 	3D	12	7.4
MOR 	1D	12	7 × 6.5
KL 	1D	12	7.1

Additionally, Choosuton reported that the MOR catalyst can improve the quality of kerosene and gas oil fractions due to the high saturated hydrocarbon content in each fraction, while total aromatics were highly produced in gasoline fraction as compared with the non-catalytic case. As compared with the non-catalytic case, Choosuton and Wehatoranawee reported that the MOR catalyst increased polar-aromatics in oils due to high acid strength of the catalyst.

KL catalyst (Si/Al=3) can enhance the gas production and reduce the liquid yield while the solid yield was constant as compared with the non-catalytic case (Choosuton, 2007). It did not significantly affect the gas compositions. Heavy fractions (gas oil, light and heavy gas oil fractions) were highly cracked into lighter fractions, especially kerosene fraction. Due to its low acid strength, saturated hydrocarbons in oils were highly produced, especially in gasoline fraction. Furthermore, the basic property of KL catalyst affected total aromatic production as well, while asphaltene and polar-aromatic contents in oils were reduced. However, Wehatoranawee (2011) showed that KL increased the amount of polar-aromatics in oils as compared with the non-catalytic case due to the basic property promoting aromatization reaction to polar-aromatics as well.

Williams and Brindle (2003) revealed that Y catalysts (Si/Al=5.4 and 40) enhanced the gas production, and reduced the liquid production while the solid yield was constant. Furthermore, the production of mono-aromatics was enhanced as compared with the non-catalytic case. Additionally, Wehatoranawee (2011) used Y catalyst (Si/Al=7.5) in the catalytic pyrolysis of waste tire as well. The results showed that the Y catalyst enhanced light olefins (ethylene and propylene) production due to its high pore volume, resulting in the cracking of heavy primary products into light olefins occurred in the pores. It can slightly promote full range naphtha production. Moreover, the catalyst can enhance saturated hydrocarbons content in oils, and reduce di- and polar-aromatic contents in oils as well.

Choosuton (2007) studied the effect of BETA catalyst (Si/Al=13.5) on the catalytic pyrolysis of waste tire. He stated that the catalyst promoted the gas production while the liquid and solid yields were reduced and constant, respectively, as compared with the non-catalytic case. Mixed C_4 and mixed C_5 were highly produced when the catalyst was present. It can be explained that BETA catalyst cracked heavy primary products into monomers, and did not further cracked into lighter products. In the liquid product, di- and poly-aromatics were highly produced due to the high acid strength and cracking ability of the catalyst, resulting in aromatic formation via carbocation active species. Furthermore, the high acid strength of BETA catalyst caused a high amount of total aromatics in gasoline while that of saturated hydrocarbons were highly produced in the kerosene range. Polar-aromatics in the catalytic case were higher produced than those in the non-catalytic case.

2.4 Copper

Copper is a transition metal that is widely used in electronic applications because it has high mechanical strength, and good electrical conductivity, like silver and gold that are in the same group of periodic table while copper has a highly lower price. The other properties of copper that are similar to silver and gold are half fill electron configuration and oxidation states (+1 and +2, except Au (+1 and +3)). For other applications, copper is used in agricultural ways such as pesticides in the form of $CuSO_4.5H_2O$, and in many industrial ways such as batteries and electroplating, wiring, and piping due to its good conductivity and high malleability (Patel *et al.*, 2010). For catalysis applications, copper catalysts are widely used to catalyze the selective hydrogenation of organic compounds, similar to nickel (Ni), ruthenium (Ru), palladium (Pd), palladium-silver (Pd-Ag), and palladium-gold (Pd-Au) catalysts in the refining and petroleum industries (Marcilly, 2003). Furthermore, copper based adsorbents can be used in sulfur removal applications from liquid fuels since it has the performance similar to silver and nickel adsorbents as discussed below.

2.4.1 Utilization of Copper as Selective Hydrogenation Catalysts

Setiawan and Cavell (1995) reported the removal of unsaturated hydrocarbons, alkynes and butadiene, in an industrial C_4-stream by using highly selective hydrogenation catalyst, Cu/SiO_2, prepared by ion exchanged method and used in the form of metallic copper. The results showed that the catalysts selectively hydrogenated the unsaturated hydrocarbons to butenes, and a very small amount of C_4 feed was converted into butanes at reaction temperature of 320 °C. Similarly, Moyes *et al.* (2002) studied the electronic effects of various transition metal catalysts in butadiene hydrogenation. At the operating temperature of 383 K, 42.0 mg of Cu metal film catalyst was selective to hydrogenate butadiene to butenes, but the author suggested that it could have higher activities at higher operating temperature. The author also reported that butadiene was hydrogenated over copper catalyst via state of σ-bonded half hydrogenation producing 1-butene by an 1,2-addition process, or via states of $\pi\sigma$-bonded half hydrogenation and π-allylic transition states producing 1-butene and 2-butene by 1,2- and 1,4- addition processes. For the electronic effect of metals, Pauling electronegativity is an important parameter for indicating the product selectivity of butadiene hydrogenation and governing the extent of overall 1,2-addition process. Copper has Pauling electronegativity of 1.9 that is high as compared with the almost transition metals in the same period of periodic table, resulting in a high percentage of 1-butene yield produced. Bridier *et al.* (2010) studied the gas-phase hydrogenation reaction of propyne over 15 wt%Cu-based hydrotalcite and malachite catalysts prepared by coprecipitation method, over 15 wt% Cu/SiO_2 and 15 wt% Cu/Al_2O_3 prepared by incipient wetness impregnation method. The results showed that all catalysts can partially hydrogenate propyne at a high reaction temperature (523 K), and give a high selectivity of propylene (60-80 %) as a product. The authors revealed that Cu-based hydrotalcite was the best catalyst because it showed the highest propyne conversion (100 %) and propylene selectivity (~75 %). Furthermore, it gave the low amount of oligomerized products as well.

2.4.2 Utilization of Copper in Sulfur Removal Applications

For sulfur reduction applications by using adsorbents in the forms of exchanged ion, Khan and Jhung (2012) studied benzothiophene (BT) removal using Cu^+/MOFs prepared by wet ion exchange method. The BT in *n*-octane was used as a feed in various concentrations (5,000-50 μg/g solution). They found that Cu^+/MOFs can be an efficient adsorbent of BT for liquid-phase adsorption at a medium copper loading amount (Cu/Fe (wt./wt.) ratio = 0.07) and an adsorption temperature of 25 °C. Tang and Shi (2011) studied the performance of adsorption desulfurization of $Cu^+/HY\text{-}Al_2O_3$, prepared by kneading method, and investigated the adsorption mechanism of thiophene on $Cu^+/HY\text{-}Al_2O_3$. The feed of this experiment was thiophene in *n*-octane with the thiophene concentration of 500 ppmw. The results showed that the best adsorbents for sulfur removal at room temperature was at 12 wt% of copper loaded on $HY\text{-}Al_2O_3$ because it had highest the number of weak Lewis acid sites that were used to generate S-M (σ) bonds between sulfur atom in thiophene and a Cu^+ site. For sulfur removal on this adsorbent, not only S-M (σ) bond occurred but also π-complexation between thiophene molecules and Cu^+ sites, and the intermolecular interaction between thiophene molecules can occur. Hernández-Maldonado *et al.* (2005) studied the performance of π-complexation-based sorbents for desulfurization of diesel, gasoline, and jet fuels. The sorbents were Cu^+, Ni^{2+} and Zn^{2+} cations over faujasite zeolites (Y zeolite) prepared by different techniques consisting of vapor phase, solid-state, and liquid phase ion exchange techniques. They found that Cu^+/Y prepared by vapor phase ion exchange method was the best sorbent because it had the highest strength of π-complexation interaction between sulfur atom in sulfur heterocycles and transition metal cations. Similarly, Gong *et al.* (2009) studied the deep desulfurization of thiophene in gasoline by using Cu(I)- and Ag(I)-BETA prepared via solid state ion exchange method. They found that the presence of the copper or silver ions on BETA surface can enhance thiophene adsorption because they increased the number of Lewis acid sites on the surface. Moreover, 15 wt% of Cu^+ or Ag^+ on Beta zeolites were the best loading amount of ions, and they gave the highest activity to remove sulfur in the model gasoline at ambient condition. Both adsorbents similarly exhibited sulfur removal capacity. The adsorbents had high thermal stability and similar adsorption capacity as well. Furthermore, copper was used as a promoter in hydrodesulfurization process. Villarroel *et al.* (2008) used the first row transition metals (Mn, Fe, Co, Ni, Cu and Zn) to promote Mo and W sulfides for sulfur removal of gas-oil containing 2700 ppm in sulfur compounds. They found that at an operating temperature of 325 °C the metal sulfides can generate spillover hydrogen on their surfaces, and then transfer hydrogen atoms to the surface of molybdenum or tungsten sulfides that can enhance hydrodesulfurization activity.

2.4.3 Utilization of Copper in another Applications

Moreover, copper-based catalysts have been used in other reactions as well, for examples, hydrogenolysis and ring-opening reactions. Chen *et al.* (2009) studied the performance of Cu/SBA-15 catalysts prepared by several methods (incipient wetness impregnation (IWI), deposition precipitation (DP), grafting method, and homogeneous deposition precipitation (HDP)) in the hydrogenolysis of dimethyl maleate (DMM). The results showed that all Cu/SBA-15 (~9 wt% Cu) gave a high conversion of DMM, and selectivity of 1,4-butanediol at the operating temperature and pressure of 473 K and 5 MPa, respectively. Furthermore, the authors revealed that metallic copper was only active sites in the hydrogenation of the ester while Cu^+ exchanged form could play a necessary role in DMM hydrogenolysis. Similarly, Vasiliadou *et al.* (2013) studied the performance of 18 wt% Cu/SiO_2 catalyst prepared by impregnation method for glycerol hydrogenolysis to produce propylene glycol. They found that the catalyst gave glycerol conversion in the range of 20-50 %, and gave the high selectivity of propylene glycol (>90 %) at the reaction temperature of 240 °C, H_2 pressure of 7 MPa and reaction time of 5 hours. A ring-opening reaction was studied by Fási *et al.* (1999). The report showed that Cu/ZSM-

5 catalysts prepared by wet ion exchange (2.3 wt% Cu^{2+}) and solid state ion exchange (2.7 wt% Cu^{2+}) methods were used to be not only $deNO_x$ materials but also ring-opening catalysts. Methyloxirane and 2,3-dimethyloxirane can be mainly ring-opened and dimerized over the catalysts in hydrogen atmosphere at temperature of 363 K. The ring-opening reaction occurred via cationic ring-opening mechanism on Lewis acid and Brønsted acid sites of the catalysts.

2.5 Zinc

Zinc is a transition metal in the IIB group in periodic table. This metal group enormously differs from other metal groups due to their properties. Zinc (Zn) is in the same group of cadmium (Cd) and mercury (Hg) in the periodic table. They have several similar properties such as low melting point, low boiling point, fully fill electron configuration, and a principal oxidation state (+2, except Hg (+1 and +2)), but some properties are different; for examples, Hg is in a liquid state while Zn and Cd are in a solid state at ambient temperature, Zn is fairly toxic while Cd and Hg are very toxic. For zinc applications in industries, Zn metal is mainly used to produce galvanized nails, coating (protect iron or steel from corrosion), and dry cell batteries. Some applications highly use zinc combining with other metals, forming alloys (such as Zn-Cu, Zn-Ag and Zn-Au) that are used in as joined electrical components (such as pipes and other metals). Zinc oxide is used in several industries, for examples, paints, rubber, cosmetics, plastics, etc. while zinc sulfide is used to produce luminous dials, fluorescent light, and television screens (Schnelker, 2010). For catalysis applications, Zn/ZSM-5catalysts are widely used to catalyze the aromatization of light alkanes in the refining and petroleum industries as similar as Ga/ZSM-5 and Pt/KL catalysts (Marcilly, 2003).

2.5.1 Utilization of Zinc as Aromatization Catalysts

Berndt *et al.* (1996a) studied the influence of preparation method by changing the zinc species location on the structural properties and catalytic activity of Zn/ZSM-5 to convert propane into aromatics at the temperature range of 723-823 K in part I of the studies. They found that the 1.6 wt% Zn/ZSM-5 catalyst prepared by ion-exchange method gave more activity than 1.5 wt% Zn/ZSM-5 catalyst prepared by incipient wetness impregnation method because the catalyst prepared by ion-exchange method higher promoted the formation of Lewis sites that are strongly acidic and very active. Additionally, at 778 K zinc loading amounts for the catalysts prepared by impregnation method gave the maximum propane conversion and aromatics selectivity at about 1 wt% while the increment of zinc loading amounts for the catalysts prepared by ion-exchanged method increased propane conversion, but aromatics selectivity was maximized at about 1 wt%. The propane conversion increased with temperatures. Furthermore, the conversion and reaction activity were promoted by increasing zinc content, but these were limited by partial pore blocking with the over increment of zinc content. In part II of the studies (Berndt *et al.*, 1996b), they studied the nature of the activation procedures and active sites of Zn/ZSM-5 catalysts. They found that ZnO reducibility was very low in Zn/ZSM-5 catalysts, and the reacting species of the catalysts were $Zn[(OH)]^+$-ions located on a Brønsted sites. The propane conversion depended on the amount of the active species in the channel of the zeolite. Moreover, the treatment with hydrogen can activate HZSM-5 impregnated by $Zn(NO_3)_2.6H_2O$ solution or physically mixed ZnO because the active Lewis acid sites were generated after hydrogen treatment that increased the amount of $Zn[(OH)]^+$-ions in the zeolite channels. Fu *et al.* (1995) studied Zn/ZSM-5 (0, 0.4, 1.5, 2.0 and 2.4 wt% of Zn) preparation by using two different methods; that are, wet ion-exchanged and solid state reaction methods. The report showed that 2.0 wt% Zn/ZSM-5 synthesized in the experiment gave the highest activity for propane conversion and high yields of BTX at reaction temperature of 773 K under helium atmosphere. Zinc ion can enhance the dehydrogenation rate of propane and intermediate transformations into aromatics. Moreover, the authors revealed that both catalyst preparation methods can give the same activity for propane aromatization. For the solid-exchange reaction of between ZnO and HZSM-5, to generate active sites of the catalyst under helium atmosphere at 853 K, ZnO was decomposed first to zinc atom and oxygen molecule, and zinc atoms then lost two electrons to form zinc ions, followed by the introduction of zinc ions into the zeolite channels. Then, the zinc ions occupied the strong acid sites of HZSM-5 by exchanging the strongly acidic H^+. Viswanadham *et al.* (1996) studied the reaction pathways for *n*-heptene and Bombay High light naphtha aromatization over HZSM-5 and Zn/HZSM-5 at 500 °C and nitrogen atmosphere. They found that 1 wt% ZnO/HZSM-5 (or 0.1 g zinc metal) prepared by impregnation method increased the aromatic yields by paraffin dehydrogenation, and enhanced the production of olefins by zinc species on the catalyst. The olefins subsequently further converted into aromatic compounds by oligomerization reaction at the acid sites of the zeolite and aromatization at the active sites of ZnO/HZSM-5, respectively. Similarly, Biscardi and Iglesia (1996) reported the function and structure of metal cations and of Brønsted acid sites in propane reaction over modified HZSM-5 catalysts at a reaction temperature of 773 K. The addition of exchanged Ga (2.1 wt%) or Zn cation species (1.3 wt% exchanged zinc and 2.8 wt% impregnated zinc) into HZSM-5 affected the increment of propane consumption rate, hydrogen disposal rate, propylene formation rate and aromatic selectivity. The propylene obtained after the dehydrogenation reaction would rapidly oligomerize, and after that the intermediate further reacted by cyclization and aromatization into stable C_{6+} aromatics on HZSM-5. Liu *et al.* (2004) studied the aromatization of FCC naphtha as a feed over Zn/ZSM-5 catalysts at 500 °C. They reported that ZSM-5 zeolite was very active for cracking all components in the gasoline range, except aromatics. The use of a higher Si/Al ratio of zeolite reduced olefin cracking rate, resulting in a high amount of *i*-paraffins and a low amount of aromatics than the use of a lower Si/Al ratio. Thus, the addition of zinc decreased the cracking ability of ZSM-5 because it decreased the number of Brønsted acid sites but it increased the number of Lewis acid sites; so, dehydrogenation reaction was enhanced. The dehydrogenation properties of zinc-loaded catalysts were also reported in the work of Du *et al.* (2005). They studied the catalytic dehydrogenation and cracking of dipentene at 673 K by using Zn/SBA-15 as a catalyst compared with Al/SBA-15 catalyst. They reported that Al/SBA-15 had weak Brønsted and strong Lewis acid sites, resulting in a higher production of toluene as a cracking product than Zn/SBA-15 that had only moderate Lewis acid sites. Therefore, Zn/SBA-15 can rather produce dehydrogenation products consisting of *p*-cumene as a major product.

2.5.2 Utilization of Zinc in Sulfur Removal Applications

Applications of zinc species (ion exchanged forms) in sulfur removal were studied by many researchers. For examples, Villarroel *et al.* (2008) used the first row of transition metals (Mn, Fe, Co, Ni, Cu and Zn) to promote molybdenum and tungsten sulfides. They found that zinc sulfide increased hydrodesulfurization activities of MoS_2 and WS_2 because it can enhance hydrogen spillover content in the system. Aboul-Gheit *et al.* (2011) studied the effect of substituting half loading amount of molybdenum with copper or zinc for catalyzing natural gas conversion into petrochemicals at ambient pressure and a temperature of 700 °C. The result showed that 3 wt% Mo + 3 wt% Zn/HZSM-5 increased benzene selectivity and yield, and further reduced coke formation on the catalysts as compared with 6 wt% Mo/HZSM-5. Oliveira *et al.* (2009) used NaY zeolite exchanged with 5 wt% of transition metals (Ag(I), Ni(II) and Zn(II)) for studying the adsorption of thiophene at 30 and 60 °C. The result showed that all the transition metals can enhance thiophene removal from *i*so-octane as an inert solvent because the metal loaded Y zeolite can interact with thiophene by σ-donation and d-π^* back-donation while NaY can interact with thiophene by σ-donation only. Furthermore, zinc might be used in oxide form for removing H_2S from coal-derived gas. Shangguan *et al.* (2013) revealed that the addition of alumina can improve pore structure of zinc oxide and desulfurization performance at an operating temperature and a pressure of 300 °C and 1 atm, respectively. The pore structure of modified ZnO sorbent had bigger surface area and micro pore than original ZnO, which can improve the H_2S diffusion and sorption rate from gas to the surface of ZnO based sorbent. Furthermore, the modified ZnO sorbent also improved the diffusion rate of formed COS, difficult to removal from ZnO surface than H_2S.

2.6 Research Motivation

Similar to the silver-loaded catalysts in the previous work reported by Wehatoranawee and Jitkarnka (2010), copper metal catalysts have hydrogenation activity to hydrogenate unsaturated hydrocarbons (Setiawan and Cavell, 1995; Moyes *et al.*, 2002; Bridier *et al.*, 2010). Therefore, they might enhance the gas production, and increase the amount of cooking gas, and the amount of saturated hydrocarbons in oil obtained waste tire pyrolysis. Furthermore, Cu was used in the adsorbent application for sulfur removal; so, copper-loaded catalysts might also reduce sulfur content in oils. Moreover, Cu catalysts have lower prices than silver ones. Thus, Cu may be used to substitute Ag in an Ag-loaded catalyst or other catalysts for waste tire pyrolysis. Similarly, zinc-loaded catalysts might be used to substitute Ru in a Ru-loaded catalyst, Rh in a Rh-loaded catalyst, or other catalysts in the previous works. Since zinc species in bifunctional catalysts exhibit dehydrogenation activity for producing olefins as intermediates of aromatic formations (Fu *et al.*, 1995; Berndt *et al.*, 1996a; Biscardi and Iglesia, 1996; Viswanadham *et al.*, 1996; Liu *et al.*, 2004; Du *et al.*, 2005). So, zinc-loaded catalysts might enhance light olefin production similar to 0.7 wt% Ru/HMOR and/or other catalysts, or mono-aromatic production similar to 1 wt% Rh/HMOR, and/or other catalysts as reported by Dũng *et al.* (2009). Furthermore, the zinc-loaded catalysts might also reduce sulfur compounds in pyrolysis oils because zinc has sulfur removal ability as well.

In this work, the effects of Cu- and Zn-promoted catalysts on the products of waste tire pyrolysis were investigated. In the first part, the copper loading on each zeolite was fixed at 5 wt% for studying the effect of the presence of copper. In the second part, the zinc loading on each zeolite was fixed at 5 wt% for studying the effect of the presence of zinc.

2.7 Objectives

The objectives of this work were to study the effects of Cu- and Zn-promoted catalysts on waste tire pyrolysis products.

2.8 Scope of Research

The scope of this research covered as follows:

a. The tire pyrolysis was conducted in a bench-scale autoclave reactor. For reaction condition, N_2 flow rate, particle size of catalysts and shredded tire, heating rate holding time and tire to catalyst ration were fixed at 30 ml/min, 40-60 mesh (250-424 µm), 20-40 mesh (425-850 µm), 10 °C/min, and 35 g: 7.5 g, respectively.

b. For the first part, the copper loading on zeolites (KL, MOR, Y and BETA) was fixed at 5wt%.

c. For the second part, the zinc loading on zeolites (KL, MOR, Y and BETA) was also fixed at 5 wt%.