



CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Monoaromatics

Valuable aromatics (benzene, toluene, and xylenes or BTX) play important roles in petrochemical and chemical industry. Aromatics are used as a chemical feedstock and starting materials to produce other compounds. Aromatics have a lot of applications; for example, benzene is used in the production of cumene, ethylbenzene, and cyclohexane. Moreover, benzene is used in the manufacture of dyes and pharmaceuticals. Toluene can be used as a solvent and used in the production of benzene, toluene diisocyanate, and benzoic acid. Xylenes have three isomers (ortho-xylene, meta-xylene, and para-xylene), and each isomer has a different placement of the two methyl groups. Ortho-xylene is a raw material for the production of phthalic anhydride, dyes and pigments. Meta-xylene is used to produce isophthalic acid. Moreover, meta-xylene is used in the plastic, dye, and fiber industries. Para-xylene is used in the production of dimethyl terephthalate and polyester fibres. The structure of benzene, toluene, and xylenes are shown in Figure 2.1.

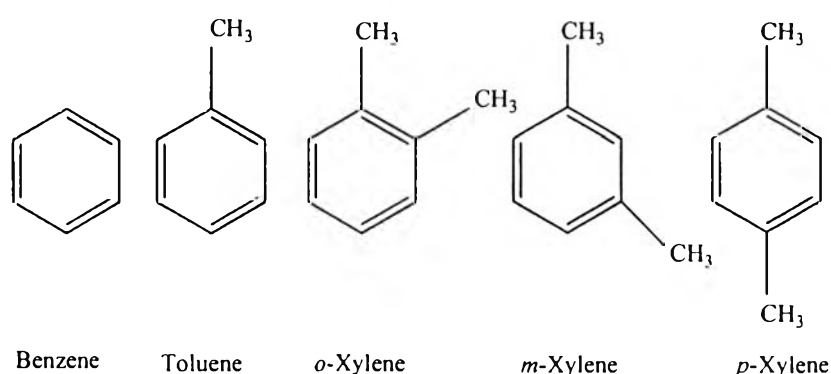


Figure 2.1 Structure of benzene, toluene, and xylenes.

The main sources of aromatics (BTX) are from catalytic reforming, pyrolysis gasoline from stream-cracker, and coke oven light oil from coke oven plants. Catalytic reforming is the process which converts low octane naphtha to high

octane liquid product called reformates. There are many reactions which occur in this process such as dehydrogenation, isomerization, aromatization, and hydrocracking. Catalytic reforming accounts for 68 % of the world's aromatics production. Pyrolysis gasoline is another source of produce aromatics, and it accounts for 29 % of the world's aromatics production. This process uses natural gas, naphtha, or other hydrocarbons to produce hydrogen, ammonia, and methanol. Coke oven light oil accounts for 3 % of the world's aromatics production. This process is used for recover benzene, toluene, and xylene by using hydrofining, stabilizer, deheptaniser, and distillation (<http://www.uhde.eu>).

The world's demand for aromatics (BTX) is about 110 million tons per year. In 2009, the demand of benzene increased almost 4 % due to the growing market of polystyrene, polycarbonate, and nylon. The demand xylenes are determined by para-xylene due to many applications of para-xylene. The demand of xylenes in 2009 increased 5 %. The overall consumption of toluene is less than 3 % because toluene is converted into benzene and xylene (<http://www.uhde.eu>). Many researchers studied about the comparison between the market demand and the amounts of BTX. They found that the amounts of BTX produced from catalytic reforming and naphtha pyrolysis processes were different from the market demand. And, toluene had the lowest market demand (Roldán *et al.*, 2004). However, the demand of BTX is still higher than the production rate. So, the production of BTX is important. Also, the price of BTX has high cost compared to other products from refinery process.

2.2 Waste Tire Pyrolysis

Pyrolysis is thermal decomposition of large molecules of organic materials to shorter molecular weight compounds in the absence of oxygen. Tire pyrolysis is for disposal of waste tires with recovery of valuable aromatics-range hydrocarbons. The pyrolytic products are gas, oil, and char. There are many reports that the products of pyrolysis have been investigated. In 2002, Leung *et al.* studied tire pyrolysis in a special reactor at a high heating rate of 1,200 °C/min and temperatures between 500 °C to 1,000 °C. They found that the gas products had high heating values in the range of 20 to 37 MJ/Nm³, and consisted of H₂, CO, CO₂, H₂S and

hydrocarbons. Zabaniotou and Stavropoulos (2003) studied the use of char from the pyrolysis of tires. The result showed that tire chars with steam had higher reactivity than the one with CO₂. In addition, the possess surface areas of active carbons produced from tire char can be comparable with those of commercially available active carbons. Cunliffe *et al.* (1999) studied tire chars, and found that they can be used as carbon black. In 1998, Cunliffe and Williams studied the composition of oils derived from the batch pyrolysis of tires, and they found that tire derived oils had fuel properties similar to a light petroleum fuel oil. Pyrolysis oil had high concentrations of benzene, toluene, xylenes, and styrene. The combustion of pyrolysis was studied by William *et al.* (1998). The result showed that pyrolysis oil had compositions similar to petroleum oil. Similarly, Benallal *et al.*, (1995) concluded that pyrolysis oil has higher octane number, and levels of sulfur and nitrogen than petroleum naphtha, so pyrolysis oil must be hydrofined and reformed. Pyrolysis oil has an advantage of being used in diesel engines and gas turbines. Ilkilic and Aydin, (2011) studied pyrolysis oil blended with petroleum diesel fuel, and they concluded that pyrolysis oil at 5, 10, 25 and 35 % blending can be used in diesel engines without any engine modifications.

Different processes and conditions such as pyrolysis, gasification and incineration give different products as shown in Figure 2.2. The main difference between pyrolysis, gasification, and incineration is the amount of oxygen supplied to the reactor. Pyrolysis needs an absence of oxygen to produce gas, oil and char. Gasification needs a limit of oxygen from air, steam or pure oxygen to produce carbon monoxide and hydrogen (syngas). Incineration requires an excessive supply of oxygen for combusting organic materials. The products from incineration are carbon dioxide, water, ash, and other products (Williams, 2005).

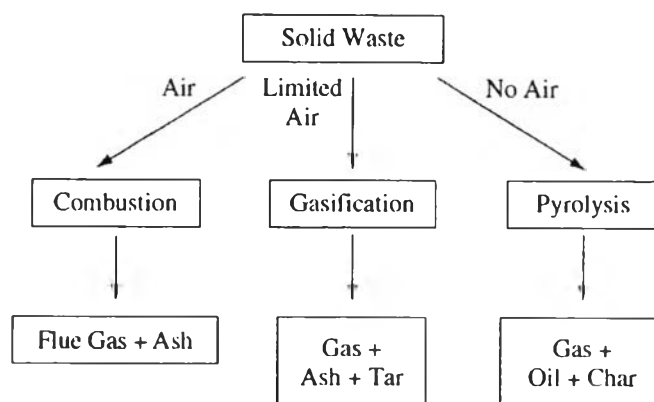


Figure 2.2 Process characterisation of incineration, gasification, and pyrolysis (Williams, 2005).


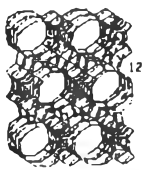
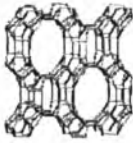
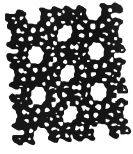
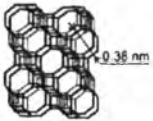
2.3 Zeolite

Products from tire pyrolysis such as oil has complexity in chemical composition, and contain a high content of poly-aromatic compound. Catalytic pyrolysis is the way to improve the products quality and increase the yield of products. Several researchers studied the effect of zeolite in pyrolysis of waste tires. Miguel *et al.* (2006) investigated the effect of catalysts on tire products. Three zeolites (standard ZSM-5, monocrystalline n-ZSM-5 and BETA zeolite) and two mesostructured materials (Al-MCM-41 and Al-SBA-15) were used in this work. They found that all zeolites gave selectivity toward mono-aromatic compounds. Mesostructured catalysts (Al-MCM-41 and Al-SBA-15) gave a wide range of aromatic products, and exhibited stronger aromatization and benzene alkylation because of their weaker Lewis acid and larger pore size. In 2006, Boxieng *et al.* studied the effect of USY zeolite on the yield and composition of products from pyrolysis process. They found that the USY zeolite reduced the yield of oil, but increased the gas yield. Moreover, rising temperature and catalyst/tire ratio led to high gas yield and coke formation. Additionally, the authors reported that USY zeolite gave a high total concentration of benzene, toluene and xylenes. In 2007, they studied the influence of USY catalyst/tyre ratio on the products. They concluded that the highest concentration of benzene and toluene occurred at the catalyst/tyre ratio of 0.5. And, the concentration of xylenes rose with increasing the catalyst/tyre ratio.

Moreover, they also studied the concentrations of single ring-aromatic compounds by using USY and ZSM-5 zeolites. The result showed that USY gave higher total concentrations of single ring-aromatics in oil than ZSM-5 because USY had larger pore size and lower Si/Al ratio.

From several research works, the acidity and pore size of a zeolite are the important factors for increasing the concentration of valuable aromatics (BTX). Zeolites that have large pore size and lower Si/Al ratio promote a high concentration of single ring-aromatics. In addition, mesoporous catalysts have efficiency for the production of single ring aromatic compounds. The zeolites studied in this research work are shown in Table 2.1.

Table 2.1 Structure of zeolites

Zeolite	Pore size (Å ^o)	Si/Al
Y 	7.4	7.5
BETA 	7.6 x 6.4	13.5
HMOR 	7 x 6.5	9.5
ZSM-5 	5.3 x 5.6	20
SAPO-34 	4.3	0.44

2.3.1 Y Zeolite

Y zeolite has three dimensional straight channel structures with 12-membered rings. The pore size of Y zeolite is 7.4 Å. It is used in hydrocracking and fluid catalytic cracking (FCC) catalysts. The structure of Y zeolite is shown in Figure 2.3.

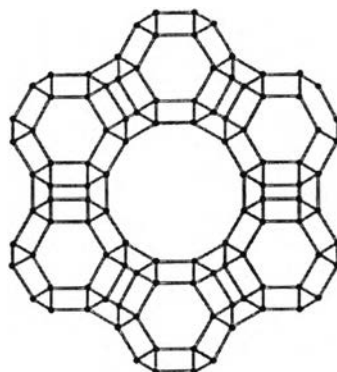


Figure 2.3 Y zeolite structure (<http://en.wikipedia.org/wiki/Faujasite>).

Many research results on using HY zeolite in tyre pyrolysis were reported. In 2008, Olazar *et al.* studied HY and HZSM-5 zeolite catalysts in a conical spouted bed reactor for tyre pyrolysis. They found that HZSM-5 produced high yields of olefins, and decreased the molecular weight of the liquid fraction and the tar. Furthermore, HY and HZSM-5 increased the yield of the aromatic fraction, but HY produced more concentration of single ring-aromatics than HZSM-5. William and Brindle (2003) studied tyres pyrolysis by using three types of catalysts (ZSM-5, Y-zeolite (CBV-780 and CBV-400)). They found that CBV-400 provided higher yield of single ring-aromatics than CBV-780 and ZSM-5 because CBV-400 had higher pore size and lower Si/Al ratio. They explained that the large pore size promoted the hydrocarbons entering the pore structure of catalyst more than small pore size. In addition, they found that the amount of oil yields decreased when a higher catalyst/feed ratio was applied.

2.3.2 BETA Zeolite

BETA zeolite has three-dimension, 12-membered rings and the cross section of 0.76 x 0.64 nm. It is used for aromatic alkylation, isomerization, hydrocracking, catalytic cracking in petrochemical or petroleum refinery industry. Moreover, it has a good selectivity on chain hydrocarbon cracking. The structure of BETA zeolite is shown in Figure 2.4.

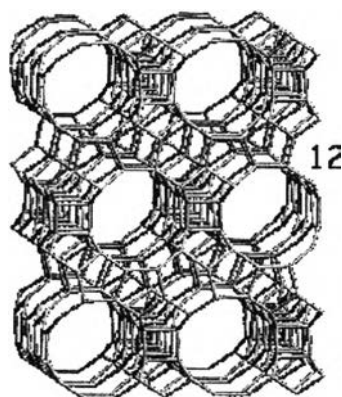


Figure 2.4 BETA zeolite structure (www.chemistry.nus.edu.sg).

The BETA zeolite was studied by several researchers. In 1999, Halgeri and Jagannath studied BETA zeolite for some of the important industrial alkyl aromatics transformation, and they found that the xylene yields of large pore zeolite were better than medium pore zeolites. Moreover, the cumene selectivity on BETA zeolite was higher than ZSM-5 zeolite due to the high acidity and large pore size of BETA zeolite. Marcilla *et al.* (2007) studied the catalytic pyrolysis of LDPE over H- BETA and HZSM-5 zeolites. They found that BETA zeolite gave higher selectivity to C4 and C5 compounds, while HZSM-5 zeolite produces a gas richer in C3 compounds than H- BETA zeolite. Moreover, BETA zeolite gave higher isobutane/n-butane ratio than HZSM-5 due to a large pore of BETA.

2.3.3 HMOR Zeolite

The chemical formula of HMOR zeolite is $(Ca, Na_2, K_2)Al_2Si_{10}O_{24} \cdot 7H_2O$. HMOR zeolite has one-dimensional straight channel structure with 12-membered rings. It has the surface area of $380 \text{ m}^2/\text{g}$ and the pore opening of $6.5 \text{ \AA} \times 7.0 \text{ \AA}$. HMOR zeolite is a moderate acidic zeolite with the Si/Al ratio of 9.5. HMOR zeolite is widely used in hydrocracking and hydroisomerization process. The structure of HMOR zeolite is shown in Figure 2.5.

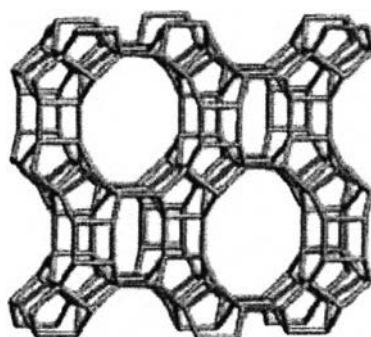


Figure 2.5 Mordenite zeolite structure (<http://www.xextex.com>).

In 1998, Lin and Sharratt studied the catalytic pyrolysis of polymers over catalysts. The result showed that HZSM-5, HMOR, and HUSY were more effective in converting polyolefins to volatile hydrocarbons than the amorphous catalysts (SAHA and MCM-41). Moreover, HZSM-5 produced olefins in the range C3-C5 over 80 wt%, while HMOR promoted the highest yield of C4 paraffins in all catalysts studied. Additionally, HUSY and HMOR which had larger-pore showed rapid deactivation. Choosuton (2007) studied the effect of zeolites on pyrolysis products, and they found that Beta, MOR and KL zeolites were selective catalysts for gasoline production. Moreover, HMOR and Beta produced high saturated hydrocarbon contents.

2.3.4 ZSM-5 Zeolite

ZSM-5 zeolite is an aluminosilicate zeolite, and its chemical formula is $\text{Na}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192}\cdot 16\text{H}_2\text{O}$ ($0 < n < 27$). ZSM-5 zeolite has a three-dimensional straight channel structure with 10-membered rings. It has the surface area of $360 \text{ m}^2/\text{g}$ and the pore opening of $5.3 \times 5.6 \text{ \AA}$. It is used as a catalyst for isomerization and cracking processes in the petroleum industry. The structure of ZSM-5 zeolite is shown in Figure 2.6.

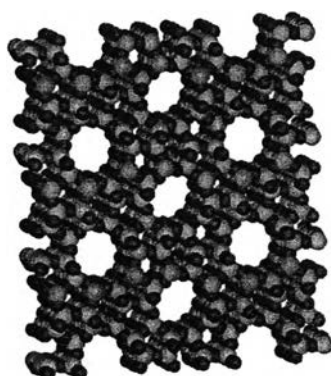


Figure 2.6 ZSM-5 zeolite structure (<http://en.wikipedia.org>).

In 2006, Qu *et al.* studied the pyrolysis of waste tire on ZSM-5 zeolite. They found that with using ZSM-5 or lubricant oil (LBO) alone, the pyrolytic rate was slightly increased. Moreover, the pyrolysis of waste tire using ZSM-5 and LBO increased the yields, and decreased the heavy components. Olazar *et al.* (2008) studied HY and HZSM-5 zeolite catalysts for tire pyrolysis. They found that HY produced higher concentration of single ring-aromatics than HZSM-5, but HZSM-5 produced high yields of olefins. In addition, HY had more deactivation than HZSM-5 because of its structure. Elordi *et al.* (2009) studied catalytic pyrolysis of HDPE in a continuous mode over zeolite catalysts (HZSM-5, HY and H-Beta) in a conical spouted bed reactor. They found that HZSM-5 gave the highest yield of light olefins. The catalyst with the largest pore size had the highest amount of butenes, while propylene is the product given by the catalyst with the smallest pores. Moreover, the yield of single-ring aromatics increased with acid strength, so HZSM-5 catalyst gave higher yield of single ring-aromatics than HY and H-Beta.

2.3.5 SAPO-34 Zeolite

SAPO-34 is a silicoaluminophosphate microporous zeolite, and its chemical formula is $(\text{Si}_{0.09}\text{Al}_{0.50}\text{P}_{0.41})\text{O}_2$. It has 8-membered ring and the pore opening of 0.43 nm. SAPO-34 is used as a catalyst for methanol conversion to olefins (MTO) and the conversion of light alkenes. The structure of SAPO-34 zeolite is shown in Figure 2.7.

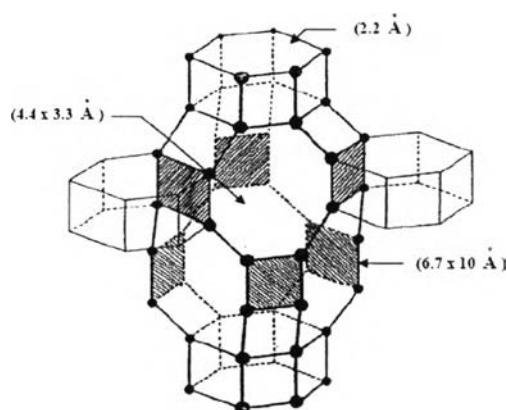


Figure 2.7 SAPO-34 zeolite structure (<http://www.sciencedirect.com>).

Normally, SAPO-34 is used in methanol to olefin (MTO) process and selective adsorption/separation. Recently, SAPO-34 is used in catalytic cracking in petrochemical industry. In 2007, Zhao *et al.* studied the catalytic cracking of C₄ to olefins by using HZSM-5, HMOR, and SAPO-34. They found that all catalyst produced propylene, C₅+ products, and other products. Moreover, H-ZSM-5 and H-mordenite zeolites showed a high conversion of C₄ to olefins. Although, H-SAPO-34 showed low conversion of C₄ to olefin during an initial time, the stability of HZSM-5 and SAPO-34 was not significantly different. In 2009, Nawaz *et al.* studied the catalytic cracking of 1-hexene to propylene by using SAPO-34. The result showed that SAPO-34 had high activity to cracking propylene because of its acid sites and structure. Moreover, they studied SAPO-34 mixed with kaolin and silicon solution for high conversion and high selectivity. However, they found that adding kaolin and silicon solution had no significant effect on the conversion of 1-hexane. Moreover, it showed low selectivity due to limited acid sites and pore exposure.

In 2005, Fan *et al.* studied binary zeolite catalysts (HBETA/HZSM-5, HMOR/HZSM-5 and SAPO-11/HZSM-5) in order to improve the performance of FCC gasoline. They found that HMOR, HBETA and SAPO-11 had efficiency in hydroisomerization, and HZSM-5 has efficiency in aromatization. Moreover, they concluded that hydroisomerization activity increased at low temperatures, but aromatization activity rose with increasing temperature. For binary systems, HBETA/HZSM-5 showed high aromatization activity and high coke content. For multiple zeolite system, adding HMOR into SAPO-34/HZSM-5 increased RON of the products; on the contrary, adding HBETA decreased RON of the products. Moreover, SAPO-34/HMOR/HBETA/HZSM-5 improved the highest liquid yield with the lowest the content of coke.

Chae *et al.* (2010) studied ZSM-5/SAPO-34 for MTO reaction. They reported that the combination of ZSM-5 and SAPO-34 showed slightly higher acidity and increased selectivity to ethylene. They found that ZSM-5 had the lowest acidity and pore size, and SAPO-34 had high mesoporous structure, which increased surface area for catalytic cracking in MTO reaction.

2.4 Bifunctional Catalysts

It had been known that the products from pyrolysis process contain undesirable components. Using zeolites catalyst is the way to improve the quality of products. Moreover, using metals help to improve catalyst activity and selectivity for the hydrogenation and ring opening of aromatic hydrocarbons. A bifunctional catalyst takes the combined advantages of the metal and the support. Noble metals such as Pt, Pd, and Ru can be used to prepare bifunctional catalysts for tire pyrolysis. Dung *et al.* (2009) studied the effect of Pt-loaded catalysts on polar-aromatic content in tire-derived oil, and they found that Pt-supported catalysts showed better polar-aromatic reduction activity than using zeolites alone. Furthermore, Pt showed high hydrogenation activity. Choosuton (2007) studied noble metals (Pt, Pd and Ru) supported on zeolites (USY, BETA, MOR and KL), and he found that bifunctional catalysts can reduce polyaromatics by 50-70 wt%. Moreover, bifunctional catalysts produced a greater quality of gasoline and kerosene.

2.5 Supported Cobalt Catalysts

Cobalt (Co) is a non-noble metal which can be used in pyrolysis process like noble metals. Co has low cost, high availability, and high activity. Co catalysts were studied for several applications in many reports. Yin *et al.* (2001) studied Co supported on mesoporous materials such as hexagonal mesoporous silica (HMS), Al-HMS, and MCM-41. They found that Co catalyst had C_5^+ selectivity, especially Co supported on HMS, because it had smaller domain size, shorter channels, and textural mesoporosity. Moreover, they found that using ZrO_2 and MnO_2 as a promoter improved the dispersion of Co metal on the surface of HMS. Concepcion *et al.* (2004) studied Co supported on all-silica delaminated ITQ-2 and ITQ-6 zeolites, and they found that Co/ITQ-6 had good dispersion and high reducibility of the supported Co_3O_4 particles. Moreover, Co/ITQ-6 and Co/ITQ-2 presented a higher selectivity toward the formation of C_5^+ hydrocarbons than Co/ SiO_2 and Co/MCM-41. Kaliya and Kogan (2005) studied Co-N on alumina catalyst, and they concluded that Co had high performance in the oxidative cracking of n-butane to ethylene and propylene. The performance of Co-N on alumina catalyst was determined by three factors. First, Co catalyst was used for cracking hydrocarbons. Second, γ -alumina showed significantly affected catalyst performance. Last, nitrogen led to an enrichment of mobile oxygen species that improved the cracking activity and the formation of lower olefins. Pedrosa *et al.* (2006^a) studied cobalt and nickel supported on HY zeolite. They found that when Co was supported on HY zeolite, it gave catalytic activity in the hydroconversion of n-hexane. Furthermore, they also studied the catalytic properties of Co/HZSM-12 and Ni/HZSM-12, and they found that these catalysts were active for n-hexane isomerization and selectivity to C_6 isomers products. Although the Co/HZSM-12 catalyst had smaller micropore area than Ni/HZSM-12, Co-catalyst had higher density than Ni-catalyst. So, Co/HZSM-12 catalyst had higher selectivity to n-hexane than Ni/HZSM-12 catalyst. Bessell (1995) investigated ZSM-5, ZSM-11, ZSM-12 and ZSM-34 supported cobalt for Fischer-Tropsch reaction. They reported that the products became lighter, and contained less n-alkanes with decreasing the acidity of the zeolite and increasing the channel size of the zeolite. So, they concluded that ZSM-12 was the most active catalyst, followed

by ZSM-5, ZSM-11, and ZSM-34. Ngamcharussrivichai *et al.* (2007) studied Co catalysts supported various zeolites (USY, ZSM-5 and MCM-22) for a slurry-phase Fischer–Tropsch synthesis. They found that carbon number distribution shifted to the gasoline range (C₄–C₁₂) with using acidic supports. Moreover, Co supported on MCM-22 had high activity, high C₄⁺ isoparaffins product, and the selective production of gasoline-range hydrocarbons because MCM-22 had a unique channel structure that gave highly active and selective bifunctional Co catalyst for the CO hydrogenation to gasoline products.

The Co particle size was investigated by Espinosa *et al.* (2011). They studied Co supported on beta catalyst for Fischer–Tropsch reactions, and reported that Co dispersion depended on the influence on Co particles and surface acidity. Catalysts that had smaller cobalt oxide particles had higher amount of surface metallic sites and higher conversion of syngas. Zola *et al.* (2007) studied Co supported on different zeolites for Fischer-Tropsch synthesis. They reported that catalysts activities for Fischer-Tropsch synthesis decreased with increasing average crystallite size. Moreover, the average Co particle size increased in the following sequence: Co/H-Beta < Co/H-USY < Co/HMordenite < Co/H-ZSM-5.

The amount of Co loading was investigated by Khemthong *et al.* (2010). They found that the amount of metal loading defined the reducibility of Co species. And, the catalyst had low catalytic activity when cobalt oxides was not fully reduced. At 1 wt%, Co was not reducible, but the degree of reduction increased with metal loading between 6 and 10 wt% Co. Furthermore, the addition of Pt improved n-butane conversion, and enhanced the reducibility of the 6 and 10 wt% Co loading.

The use of non-noble metals in tire pyrolysis was studied by Pinket (2010). She used Co, Ni and Rh supported on KL zeolite for the pyrolysis of tire, and she reported that 5 %Co/KL gave higher single ring-aromatics production than 1 %Rh/KL and 20 %Ni/KL due to the high activity in hydrogenation and activity in C-C bond breaking. Moreover, she found that 0.05 %Rh modified with 0.95 %Co gave the highest concentration of saturated hydrocarbons. Additionally, Co loaded on support KL had an effect on polar-aromatics and sulfur reduction in oil.

As mentioned above, the production of single ring-aromatics depends on the structure of zeolite. There have been a few research works that used HY in catalytic

pyrolysis of tire for the production of single-ring aromatics, and Boxiong *et al.* (2007) found that HY produced high concentration of single ring-aromatics because HY has large pore size and low Si/Al. Moreover, HY, HBETA, HMOR and HZSM-5 are advantageous in isomerization and aromatization. SAPO-34 is advantageous in cracking large molecular reactants due to its pores, so combining SAPO-34 with HY, HBETA, HMOR, and HZSM-5, respectively, can be considered beneficial for the catalytic pyrolysis of waste tire.

Co supported on zeolites has high activity in many applications. It has high activity in hydrogenation, and also high activity in C-C bond breaking, which help to increase single-ring aromatics. Moreover, Co supported on zeolites (HY, HBETA, HMOR, HZSM-5 and SAPO-34) has not been investigated in the catalytic pyrolysis of waste tire before. So, this work studies about the effect of Co loaded on the different zeolites in waste tire pyrolysis and using SAPO-34 as a binary support.