CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Theoretical Background

2.1.1 Chemistry and Anatomy of Tires

Tire is a polymer of rubber. The major compositions of tire are natural rubber and styrene butadiene rubber. The properties of tire can be improved by adding the other chemicals. Table 2.1 below shows the typical types of materials used in tire manufacture.

The processes in tire production and physical compositions in tire are shown in Figure 2.1. The first step in tire manufacturing process is the mixing of raw materials such as rubber, carbon black, sulfur, and other materials to form a rubber compound. After the rubber is prepared, it is sent to a tire-building machine, where a worker builds up the rubber layers to form the tire.
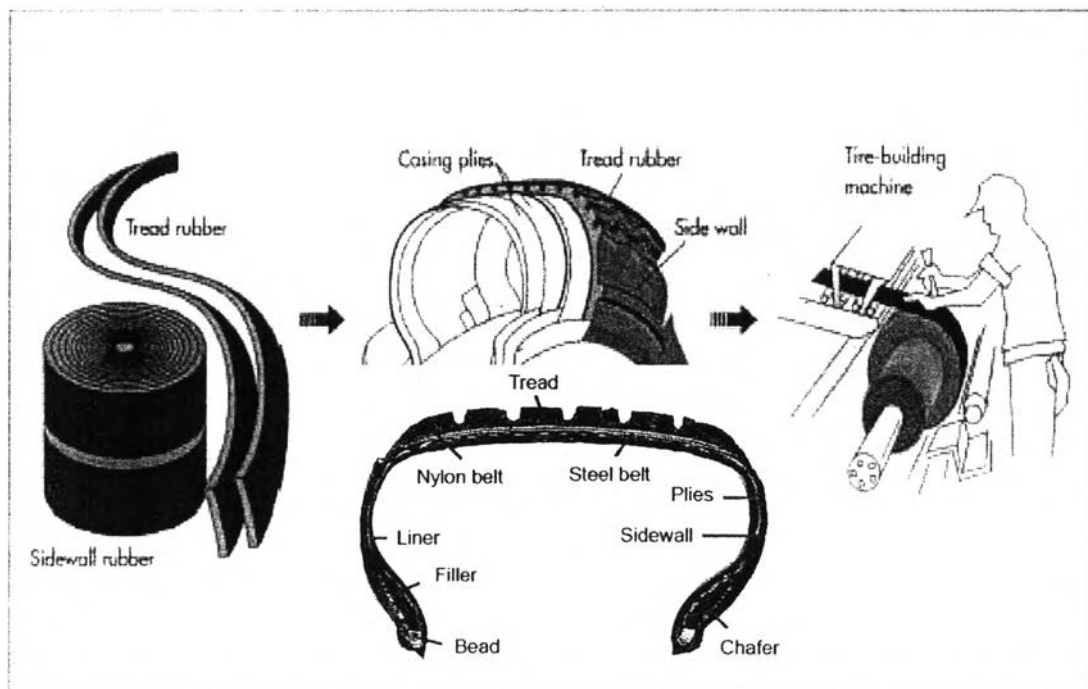

Figure 2.1 Physical composition and building machine
http://www.swicofil.com/images/tire_construction.jpg.

Table 2.1 Chemical compositions and function in tire manufacture

Material	Function
Natural rubber or polyisoprene	The basic elastomer in tire making
Styrene-butadiene co-polymer (SBR)	For substitution in the part of natural rubber base on the comparative of materials cost
Polybutadiene	For combination with other rubbers due to its low heat-build up properties
Halobutyl rubber	For the tubeless inner liner compounds
Carbon Black	For reinforcement and abrasion resistance.
Silica	For high performance tire
Sulphur	For cross-linking the rubber molecules in the vulcanization process
Vulcanizing Accelerators	Speed up the vulcanization
Activators	An assister for the vulcanization, such as zinc oxide
Antioxidants and antiozonants	A preventer of sidewall cracking due to the action of sunlight and ozone

With the higher demand of automobiles, waste tire is rapidly increased. The management of waste tire is difficult because of tire compositions. For example, sulfur and halogen atoms are hazardous materials that make the environmental problems. Waste tire is hard to degrade because it is non biodegradable. There are several technologies to eliminate waste tire such as landfill, incineration, and recycle. The waste tires recycle technologies become interesting because they can produce high energy and high value products from wastes. The selectivity of recycling technology is necessary for the elimination of waste tire. There are several recycling technologies such as Tire-Derived Fuel (TFD), retread, rubber modified asphalt, and pyrolysis. Pyrolysis technology becomes interesting because of low emissions to the environment. The pyrolysis theory is described in the next section.

2.1.2 Waste Tire Pyrolysis

The waste tire pyrolysis process is the thermal decomposition of large molecules to lower molecular-weight molecules in the absence of oxygen. The pyrolysis processes involve several steps of polymer cracking such as initiation, propagation, and termination. The advantage of this application is the conversion of waste tire into higher value products such as olefins, chemicals, and surface-activated carbon. Pyrolysis becomes interesting and profitable alternatives for waste tire recycling because of low emissions to the environment. The main products of waste tire pyrolysis consist of gas product, liquid oil, and char. The properties of these products are shown in Table 2.2.

Table 2.2 The properties of main products obtained from tire pyrolysis (http://www.ciwmb.ca.gov/Publications/Tires/43296029.doc)

Product	Composition	Properties
Gas (10-30%)	Hydrocarbon mixture, low sulfur content	Calorific value of 19-45 MJ m^{-3} (500-1,200 Btu ft^{-3})
Oil (38-55%)	Contains less than 1% sulfur	Calorific value of 42 MJ kg^{-3} (18,000 Btu lb^{-3})
Char (33-38%)	Contains 2-3% sulfur and approx. 4-5% zinc	Calorific value of 28-33 MJ kg^{-3} (12,000-14,000 Btu lb^{-3})

The high molecular-weight compounds are limitation in the value of pyrolysis products. A catalyst is introduced to waste tire pyrolysis for obtaining higher value products from waste tire pyrolysis. Nowadays, there are many reports that have been investigated the effect of catalyst for the improvement of quality and quantity of products obtained from waste pyrolysis.

2.1.3 Zeolites

In petrochemical industry, catalysts have been introduced for reaction improvement and value-added products. Catalysts are used to improve the condition

of reaction such as temperature and holding time. Catalysts can reduce the activated energy of reaction. There are many types of catalysts used in petrochemical industry. The properties of catalysts play an important role in the selectivity of products. A zeolite is a commercial catalyst used in petrochemical industry. It is a crystalline material with cross-linked structure of SiO_4 and AlO_4. The crystalline faulting in zeolite structures affects both the catalytic and sorption properties. Using zeolites as catalysts gives many advantages since they can be recovered. The advantages of zeolite catalysts are low cost and higher activity. The zeolite applications are important in cracking refinery process. So, zeolites are commonly used in catalytic operations.

There are several types of zeolites used in cracking reaction due to the difference in the properties of zeolites. The next section introduces the characteristics of four commercial zeolites that will be used in this study.

(a) BETA zeolite

BETA zeolite is considered as a kind of high silica zeolite with the Si/Al ratio of 13.5. The channel system of BETA zeolite is straight. The pore size of BETA zeolite has three-dimension and has a cross section of 0.76 x 0.64 nm. And, it has an intersecting channel system with 12-membered rings. The structure and channel systems of BETA zeolite are presented in Figure 2.2.

The introduction of BETA zeolite in petrochemical or petroleum refinery industry is to be used as a catalyst in aromatic alkylation, isomerization, hydrocracking, catalytic cracking, and so on BETA zeolite has a good selectivity on chain hydrocarbon cracking.
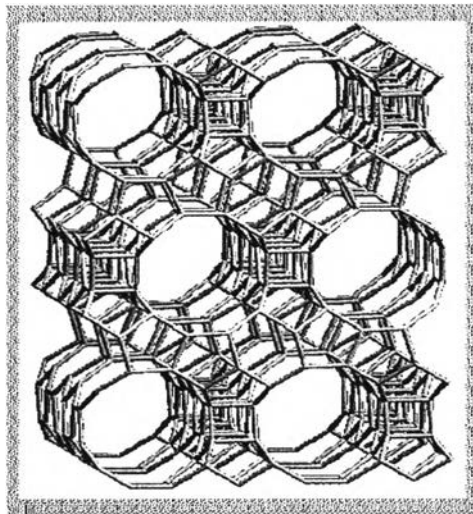
Figure 2.2 BETA zeolite structure (www.chemistry.nus.edu.sg).

(b) Y zeolite

Y zeolite is an intermediate silica zeolite with the Si/Al ratio of 7.5. Y zeolite has the structure as FAU (faujasite). It is considered as three-dimensional pore structure. The pore diameter is 7.4 Å with 12 membered rings. And, this zeolite has surface area approximately 600 m^2/g. The structure and channel system of Y zeolite are presented in Figure 2.3.
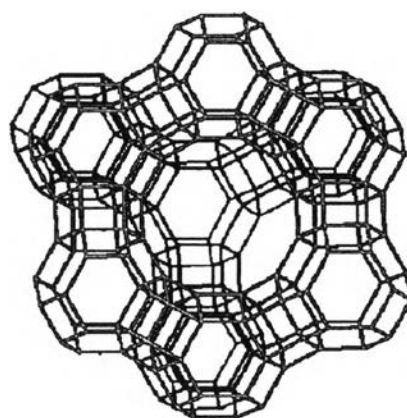

Figure 2.3 Y zeolite structure (www.chemistry.nus.edu.sg).

Normally, the application of Y zeolite is used in catalytic cracking. The most importance of this zeolite is used in the acidic form for petroleum refinery catalytic cracking units. The advantage of acidic form can

increase the yield of gasoline and diesel fuel from crude oil feedstock by cracking heavy paraffins into gasoline.

(c) KL zeolite

KL zeolite is considered as a basic zeolite with the Si/Al ratio of 3.0. It has one-dimension with the straight channel structure of 12-membered rings. The channel of KL zeolite has unique framework topology with an opening of 0.71 nm in diameter. The structure and channel system of KL zeolite are presented in Figure 2.4.
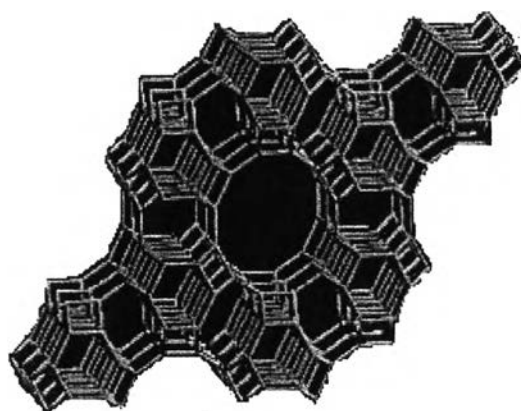

Figure 2.4 KL zeolite structure (www.chemistry.nus.edu.sg).

KL zeolite is a basic catalyst. It acts like an electron donor. This property of KL zeolite can increase the electron density on the metal clusters. There are several researchers who studied the effect of metal loaded on KL zeolite. They reported that KL zeolite was often used as a support for highly dispersed Pt. The Pt/KL was a selective catalyst to produce benzene in the aromatization of n-hexane. The high aromatization activity of the Pt/KL zeolites resulted from the electronic property. Furthermore, the octane number of gasoline fraction can be improved by the basicity of catalyst due to aromatization ability.

(d) HMOR zeolite

HMOR zeolite is a moderate acidic zeolite with the Si/Al ratio of 9.5. It has large pore size with an opening of 6.5 Å x 7.0 Å. HMOR zeolite is considered as one-dimensional straight channel structure with 12-membered rings, and it has surface area approximately 380 m^2/g. The structure and channel system of HMOR zeolite are presented in Figure 2.5.
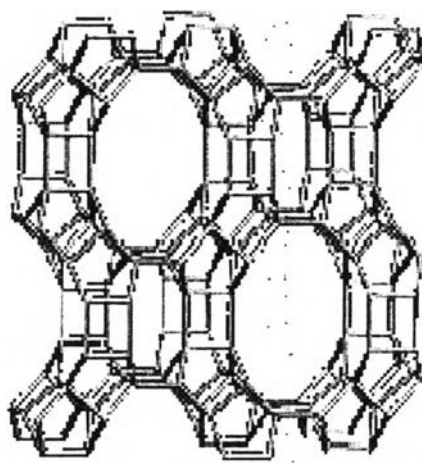

Figure 2.5 HMOR zeolite structure (www.chemistry.nus.edu.sg).

HMOR zeolites is used as solid acid catalyst and widely used in hydrocracking and hydroisomerization process.

2.2 Literature Reviews

2.2.1 Waste Tire Pyrolysis

Many researchers have studied the pyrolysis of waste tire. The major compositions of tire are natural rubber (NR), butadiene rubber (BR), and styrene-butadiene rubber (SBR). Waste tire has higher energy than bituminous coal (subbituminous: 24,428 kJ/kg, tire: 33,035 kJ/kg), so energy recovery could be a recycling strategy. Pyrolysis is one of the interesting alternatives to deal with rubbers and polymers by converting them to energy and fine chemicals. There are many factors affecting the waste tire pyrolysis such as residence time, lamping rate, pyrolysis temperature, and carrier gas flow rate. Many researchers have tried to find

the optimum conditions for complete pyrolysis. Juan *et al.* (2004) studied the different conditions in scrap tire pyrolysis. They compared the experiments at 450, 750, and 1000°C both in nitrogen and 10% of oxygen atmospheres. The production yield of the different conditions showed that at 1,000°C there was no formation of a liquid fraction both in nitrogen and 10% of oxygen. They found that liquid fraction decreased when increasing temperature both in the presence and absence of oxygen, whereas the solid fraction increased. Likewise, Diez *et al.* (2004) studied the influence of the final temperature on waste tire pyrolysis. They used the derived thermogravimetry (DTG) to analyze the scrap tire pyrolysis process. The results showed that there were three stages observed: 200-350, 350-450, and 450-550°C. It was concluded that after 550°C the waste tire pyrolysis process was complete. The production of oils and gases increased to the maximum at 550°C. The increase in temperature affected an increase in gases production and a decrease in oils production, whereas solid fraction remained constant. The authors explained that the secondary cracking reactions caused the over cracking reactions of pyrolysis products. Mastral *et al.* (2000) studied the influence of process variables on waste tire pyrolysis. They found that at 500°C was an optimum temperature. It was explained that at a higher temperature both the total conversion and oil yield were not increased further. The results also showed that below 500°C both the total conversion and oil yield decreased around 10%. Also, Rodriguez *et al.* (2001) pyrolyzed the used tire without catalysts. They studied the final pyrolysis temperature of the reactor. They found that no significant influence of temperature on the amount of pyrolysis products was observed over 500°C. The authors concluded that 500 ^{0}C was the optimum temperature for tire pyrolysis process. The decomposition of rubber was complete, and less energy was required than at higher temperatures.

In 2002, Leung *et al.* studied the pyrolysis of tire powder at high heating rates. They found that the gas yield increased with increasing gas residence time when the temperature was higher than 700 °C. At high temperatures, heavy hydrocarbon gases were cracked into low hydrocarbon gases. The effect of increasing residence time on secondary reactions was little at high temperatures. And, Xianwen *et al.* (2001) reported that at high temperatures the residence time had

the strong effect on the oil and gas productivity. They explained that the longer residence time contributed to secondary reactions which led to less oil and more gas production. Barbooti *et al.* (2004) studied the effect of nitrogen flow rate in scrap tire pyrolysis. They found that at high gas flow rates (0.45–0.5 m^3 h^{-1}), oil products increased when increasing the N_2 flow rate. Contrariwise, the yield of oils sharply decreased with nitrogen flow rate increased up to 0.35 m^3 h^{-1}. The authors explained that it was due to the efficiency of condensation stage. Murillo *et al.* (2006) studied the influence of the heating rate on waste tire pyrolysis. They reported that the heating rate showed no influence on the total conversion of waste tire. The heating rate affected on product distribution and characteristics. And, Mastral *et al.* (2000) reported that carrier gas velocity was directly related to vapor residence time. The carrier gas velocity affected on both product distributions and compositions. The results showed that the type of carrier gas was not important in the conversion and distribution of products. Furthermore, the authors found that the conversions and yields of oil were low with increasing gas velocity. In case of oil compositions, the saturated and aromatic hydrocarbon concentrations increased with increasing gas velocity.

2.2.2 Catalytic Pyrolysis

The limitation of waste tire pyrolysis is low value products obtained. There are several researchers who have tried to use catalysts in waste tire pyrolysis for value-added products. A zeolite is a commercial catalyst used in the petrochemical field. The efficiency of zeolites in cracking reaction is due to their properties such as pore structure and acidity. The pore structure of zeolite has the effect on shape selectivity in cracking reactions. For the acidity, it has the effect to the carbon-carbon bond scission due to the acid strength of each zeolite. The effects of zeolite properties on waste tire pyrolysis have been investigated by several researchers such as Miguel *et al.* (2006). They used three different zeolites (ZSM-5, nanocrystalline n-ZSM-5, and Beta) to investigate the effect of various acid catalysts on the conversion of tire. The results showed that the larger crystal size of ZSM-5 and weaker acidity of beta catalyst gave lower aromatics capacity, whereas the nanocrystalline n-ZSM-5 gave higher aromatics production. The authors explained

that the higher aromatics production was due to the strong acid properties and the accessible improvement of n-ZSM-5 molecules. In case of Beta zeolite, the results showed that Beta zeolite produced high single aromatic content in oil product, but gave lower aromatic capacity. The lower aromatic capacity resulted from weaker acid site of Beta zeolite. In 2007, Shen *et al.* studied the effect of the pore size and Si/Al ratio of zeolites in waste tire pyrolysis. They reported that the large pore size promoted hydrocarbons to enter the pore which led to the formation of aromatic hydrocarbons from catalytic cracking reaction. For the effect of Si/Al ratio, they reported that lower Si/Al ratio resulted in high activity.

There are many types of commercial zeolites used as catalysts in cracking reaction. The selectivity of zeolite is due to the individual properties of each zeolite type. In 1997, Zhu *et al.* compared the catalytic activity of KNO_3 loaded on zeolites (KL, NaY, Kβ, KZSM-5, KY, and KX) in cis-2-butene isomerization. The results showed that KNO_3 loaded on the five zeolites (NaY, Kβ, KZSM-5, KY, and KX) were inactive in the isomerization of cis-2-butene. The authors explained that cis-2-butene directly isomerized to trans-2-butene. The cis-trans isomerization of butane directly isomerized on the strong basic site of catalyst. All of the tested zeolites had the difference in basic strength, but the basic strength cannot be attributed to Si/Al ratio. The authors said that X zeolite had lower Si/Al ratio than L zeolite, but KNO_3 loaded on X zeolite gave lower basic strength than KNO_3 loaded on L zeolite. The authors also referred that L zeolite had the special structure that should be considered as a factor for the high basic strength. Arandes *et al.* (2008) used two different catalysts as CAT-1 and CAT-2 represented to commercial HY zeolites in order to study the effect of catalyst properties on the cracking of polypropylene. They found that CAT-2 gave the high yield of coke, whereas the yield of gasoline and LPG were not affected by the acidity of catalyst. CAT-2 had the higher acid site density which led to higher activation for hydrogen transfer reaction. The different hydrogen transfer capacity of two catalysts influenced the difference of gasoline compositions. So, CAT-2 exhibited the higher concentration of aromatics and paraffins, whereas gas olefinicity decreased. And, Aguado *et al.* (2009) studied the catalytic cracking of polyethylene over mordenite zeolite with the different textural properties. They added the amount of organosilane in mordenite

zeolite from 0 to 15 mol% (mor-0 (traditional mordenite zeolite), mor-8, and mor-15). All of three catalysts have the difference on textural properties such as micropore, BET, and external surface area. The authors found that the use of mor-0, mor-8, and mor-15 increased the conversion of LDPE from 40% to 57%. The results also showed that the large proportion of heavy hydrocarbons in the range of C_{13}-C_{35} was formed over the traditional mordenite with lower external surface area. The authors explained that the primary products may undergo cracking reaction over the high proportion of acid sites on mordenite zeolite with higher external surface area. The activities increased with increasing the amount of organosilane in mordenite zeolite. And, Kumar *et al.* (2008) studied the effect of preparation variables on the aromatization activity over Pt/KL catalysts. The results indicated that the performance of catalysts was affected by the change in porosity. The acidity or basicity of the support caused the porosity changing. The changes of porosity made the metal–support interaction occur, and Pt atoms prefered to agglomerate on the support. The agglomeration greatly influenced to the pore volume patterns and the aromatization activity of the catalysts.

2.2.3 Silver-Loading Catalysts

Metal-exchanged zeolites can serve as oxidation or reduction catalysts, e. g. Ti-ZSM-5 in the production of caprolactam, and Cu-zeolites in NO_x decomposition. Moreover, noble metals are often used in catalytic cracking reaction because they have high activity for hydrogenation reaction. The metal clusters of noble metals supported on zeolites are formed by the reduction reaction of balancing charge. The formations of metal cluster are usually stable and well-dispersed. Furthermore, the hydrogenation reaction can be carried out mostly using Group VIII metals. There were several reports demonstrating that Ag-modified zeolites showed high activity in many catalytic processes. In 2008, Ausavasukhi *et al.* studied the reversible interconversion behavior of Ag species in AgHZSM-5. They tested the catalytic activity of ethanol aromatization. For the catalytic view, they found that the AgHZSM-5 with Si/Al ratio of 28 showed activity and BTX selectivity lower than HZSM-5 with the same Si/Al ratio. They explained that the Brønsted acid sites cannot be recovered in the AgHZSM-5 due to the reversible interconversion of Ag

species. The decrease of acid sites resulted in the complete conversion of ethanol to ethylene.

Moreover, the effects of acidity and the pore size of support are the important factors. In 2008, Wong *et al.* reported that Y zeolite had larger pore size than ZSM-5; therefore, AgY exhibited good performance in the catalytic oxidation of butyl acetate more than AgZSM-5. They explained that the AgY had the larger pores which had less resistance for the diffusion of reactants and products. They also found that at low temperatures, there was no conversion of butyl acetate when using AgZSM-5 as a catalyst. They explained that water vapor formation could block the micropores of Ag/zeolite, and consequently prevent the oxidation reaction at low temperatures. Furthermore, the authors compared their work with the other work reported, and they found that silver-loaded zeolites were better in oxidation performance than the other work. They concluded that silver-loaded zeolites had the potential to be used as effective oxidation catalysts like noble metals over butyl acetate. And, Ding *et al.* (2008) studied the methane activation over Ag-modified ZSM-5 zeolite. The results showed that the isolated Ag^+ cations exhibited a positive effect to methane activation. The amount of charge transfer when methane interacted with Ag-ZSM-5 was much higher than it interacted with H-ZSM-5. Furthermore, the barrier of C-H bond breaking over H-ZSM-5 was higher than over Ag-ZSM-5 zeolite. The authors explained that the interaction between methane and Ag-ZSM-5 was stronger than between methane and H-ZSM-5. The effect of silver structure was studied by Shibata *et al.* (2004). They studied the active Ag clusters in Ag zeolites for SCR of NO and the activity of silver loaded on two types of zeolites as H-MFI and Na-MOR. The results showed that Ag clusters were formed in the Ag-MFI zeolite by the H_2 reduction. Contrariwise, the Ag clusters did not form on Ag-MOR under the same conditions. The results suggested that the $Ag_n^{\delta+}$ clusters occurring on Ag-MFI zeolite were probably those of Ag_4^{2+}. The Ag_4^{2+} clusters were predominant on Ag-MFI zeolite in the reaction. The authors concluded that the activity correlated well with the amount of Ag_4^{2+} clusters. The Ag-MFI catalyst was responsible for the selective catalytic reduction of NO. And, Baba *et al.* (2007) studied the catalytic properties of silver-exchanged zeolites for propene production by the conversion of methane in the presence of ethane. They found that the Ag_n^+ was regenerated by the

reaction of Ag_n-H with acidic protons, which were formed simultaneously accompanying the formation of propene. These acidic protons were essential for maintaining the catalytic reaction of methane with ethane. The small pore size of Ag-A zeolite promoted the selective formation of propene in comparison with Ag-Y. The acidity of protons in Ag-A was not sufficient to convert lower alkenes to higher alkene and aromatic hydrocarbons.

The amount of silver loading was investigated by Kumar *et al.* (2007). They studied the catalytic decomposition of ozone by Ag-modified H-Beta, H-MCM-41, and SiO_2. They varied the amount of Ag loaded on each support between 2wt% and 5wt%. The authors found that the activity of catalysts increased with increasing the amount of silver loaded. The content of Ag was essential for ozone decomposition. The results showed that at 5wt% silver loaded on both-MCM-41 and SiO_2 exhibited higher activity than 2wt% silver loading. The authors explained that silver was presented on the carrier surface in the form of isolated ions and clusters. In the case of low metals content, isolated silver ions were presented, which were less active in ozone decomposition. The active clusters formation resulted from the carrier surface saturated with silver ions. The higher surface area of support promoted more clusters formation. In 2009, Stanković *et al.* studied the effect of silver modification on the structure and catalytic performance of Ni-Mg/diatomite catalysts for edible oil hydrogenation. The results showed that the silver presence was beneficial in limiting *cis–trans* isomerization. The metallic silver retarded the access hydrogen to Ni^{2+} species system. The coverage and blocking affected on the Ni^{2+} species, and caused the decreasing in hydrogenation activity which limited the *cis–trans* isomerization on the silver-modified catalysts. The authors also stated that catalysts with higher silver content were selective catalysts for the edible oil hydrogenation. The increase of the silver loading resulted in the development of porosity.

Furthermore, Ag modified zeolites have been well studied in desulfurization reaction as Oliveira *et al.* (2009) studied the adsorption desulfurization of model gasoline on NaY zeolites exchanged with Ag(I), Ni(II) and Zn(II). They found that the adsorption capacity for thiophene in the studied samples followed the order: AgY > NiY > ZnY > NaY. The AgY showed the highest

adsorption capacity for thiophene (60 - 90% more than the starting material NaY). In the same year Gong *et al.* studied the deep-desulfurization of gasoline using Ag/BETA. They found that the case of using BETA zeolite alone, it is very inefficient with only 20% sulfur removal, while Ag/BETA can remove 87% sulfur for model gasoline. For actual gasoline, the desulfurization capacity was reduced by about 30%, as compared to the model gasoline

As mentioned above, silver supported on zeolites showed high activity in many catalytic processes. Generally, zeolites have been used to improve the quantity and quality of waste tire pyrolysis products. Silver modified zeolites affect both on structure and acidity of zeolites in several reactions. They are promising to improve the pyrorysis products and reduce sulfur content in pylolytic oils.

Therefore, this work investigated both the amount of silver loading and the effect of silver loaded on the different zeolites in waste tire pyrolysis. Moreover, this work also investigated the effect of addition of second metal (Pd) on Ag-modified zeolite on the pyrolysis products.

The scope of this research covered the followings:

1. Pyrolysis of scrap tire was performed in a bench-scaled autoclave reactor.

2. Particle size of tires, holding time, N_2 flow rate, heating rate, temperature in pyrolysis zone, temperature in catalytic zone and the ratio of tire per catalyst were fixed to 8-18 mesh, 30 min, 30 ml/min, 10 min/°C, 500°C, 350°C and 25% (tire:30 g per catalyst: 7.5 g), respectively.

3. The percentage of silver loading on Y zeolite was varied to 1, 2, and 3% by weight.

4. The commercial zeolites were used in this experiment, namely BETA, KL, HMOR, and Y zeolites. For Beta, KL, and HMOR zeolites, the amount of silver loading will be fixed to 1% by weight.

5. The amounts of Ag and Pd metals supported on zeolite were varied from 0.2, 0.4, 0.6, and 0.8 % by weight.