# CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Theoretical Background

A passenger tire is mainly composed of rubbers which are polyisoprene, polybutadiene and polystyrene-butadiene. Tire is commonly produced via vulcanization process which causes a chemically cross-linked polymer. The result network contains sulfur atoms or carbon to carbon bonds resulting in durable rubber and more resistance to heat and chemical attack (http://en.wikipedia.org/wiki/). Due to the complexity of tire components, the tire is non-biodegradable and consequently difficult to degrade. There are many ways to recycle the used tire such as landfilling, open dumping, ultrasound recycling, grinding, retreading and incineration. However, some of them have some disadvantages in the view of environmental problems (Jang *et al.*, 1998).

Pyrolysis has been proposed as an effective way to recycle waste tire because of mild environmental concern. It involves a thermal decomposition of large molecule toward small molecule in the absence of oxygen. The operating conditions in the process such as temperature, heating rate, tire composition and catalyst can significantly affect the process resulting in several reactions which lead to the formation of various pyrolytic products. The main products of pyrolytic process are classified into gaseous, liquid and solid fractions whose components are complex mixtures (Chen *et al.*, 2003). The liquid product consists of valuable chemical substance such as benzene, toluene, and xylene. The gas product contains methane, ethane, butadiene and others having high enough calorific value which can be used as a fuel in a process plant. The solid product can be used as a smokeless fuel and carbon black (Williams *et al.*, 1998).

Many types of reactions occur in the pyrolysis. Elimination and rearrangement are the main reactions. The elimination associates with a free radical mechanism resulting in the formation of molecular fragments and then the conversion to a new molecule. For the rearrangement, it involves the movement of

one atom to another in the same molecule. Moreover, other reactions such as oxidation, reduction, substitutions, or additions may take place during the process depending on operating control (Moldoveanu, 2005).

(a)

(b)

Polyisoprene   **Polybutadiene**

Styrene-butadiene

(c)
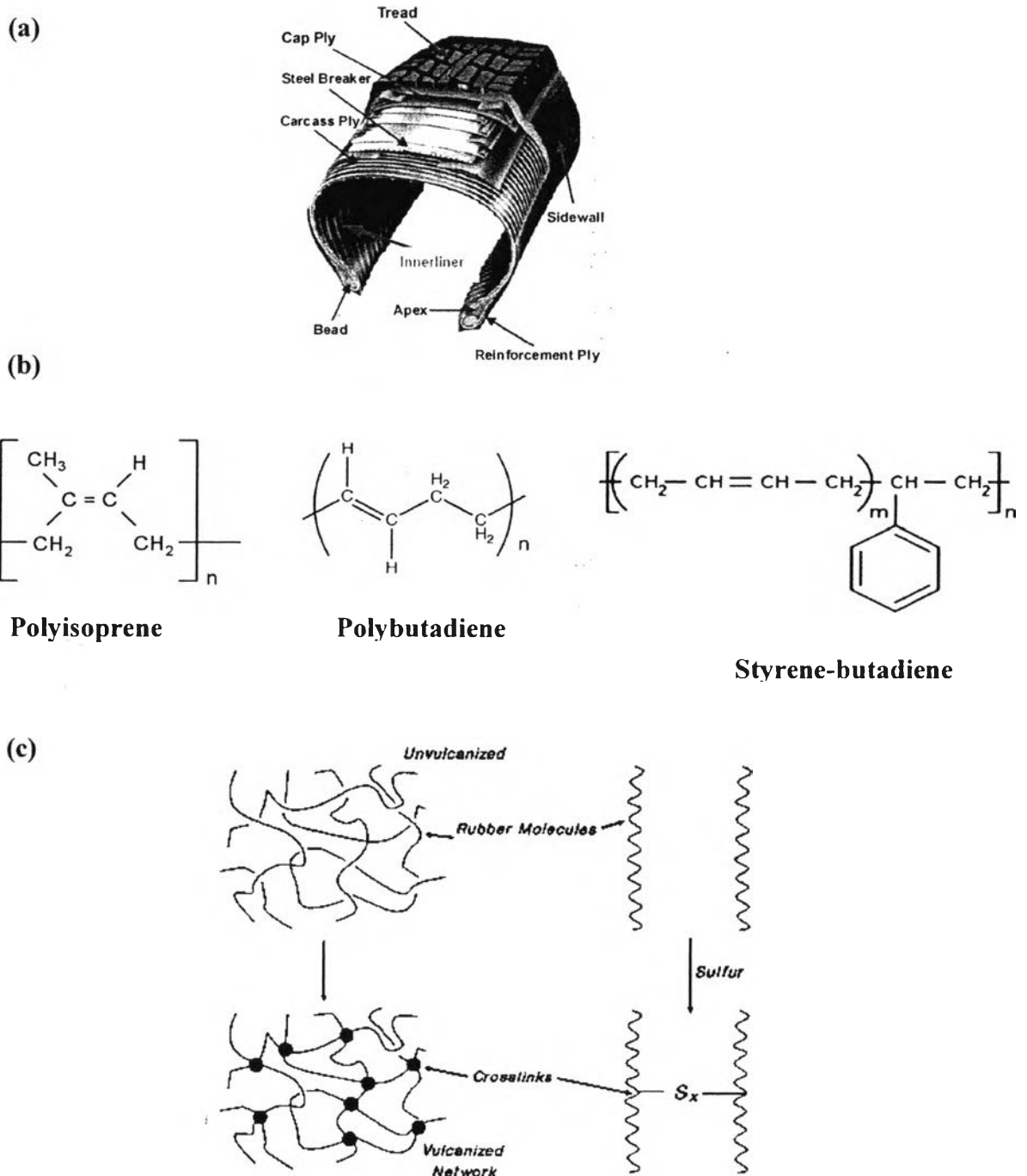
Figure 2.1   (a) Tire structure (www.mindfully.org), (b) Rubbers composition (http://en.wikipedia.org/wiki/Styrene-butadiene), and (c) Vulcanization (www.eng-forum.com/articles/tires...res2.htm).

2.2 Literature Review

2.2.1 Pyrolysis

According to the marked advantages in the pyrolysis of waste tire, the researchers in this field have paid high attention so far. Chen *et al.* (2000) studied on the thermal degradation of polybutadiene, which is the raw material of butadiene rubber and used for a passenger tire. They found that cyclization was the main reaction at 390°C, and the temperature range of 450°C was suitable range to obtain a lot of xylene since the depolymerization occurred. Over 600 °C the lower –molecular weight products occurred because of deep decomposition. Likewise in 2003, a waste rubber composed of natural rubber, butadiene rubber carbon black and other additives was investigated. It was suggested by Chen *et al.* (2003) that pyrolysis process involved isomerization and dehydrogenation explained by the radical mechanism which was bond scission mainly at the β position. Seidelt *et al.* (2006) investigated three types of rubber in pyrolysis which were natural rubber, styrene-butadiene rubber and butadiene rubber. They reported that no effect of used tire additives was found on thermal degradation. Williams *et al.* (1998) studied the composition of oils derived from batch pyrolysis, and found that the concentration of light aromatic hydrocarbon, such as benzene, toluene, xylene and styrene, and polycyclic aromatics hydrocarbons increased with increasing temperature from 450 to 600°C. They reported that the formation of polyaromatic hydrocarbons was accompanied by Diels-Alder mechanism for alkane dehydrogenation to alkene followed by cyclization and aromatization.

Laresgoiti *et al.* (2000) used an autoclave reactor in pyrolysis at 400, 500, 600 and 700°C. At temperatures over 500°C, no effect on product yields was found, and light hydrocarbons in the gaseous fraction had high calorific value providing the energy requirement of the process plant. Furthermore, they observed that the amount of valuable aromatics increased with temperatures up to 500°C. The same trend was found by Rodrigues *et al.* (2001), who operated the pyrolysis of scrap tires under nitrogen in an autoclave at 300-700°C. They indicated that the temperatures over 500°C did not affect the pyrolysis products, and 500°C was the

suitable temperature because of the complete decomposition of rubber and less required energy. Berrueco *et al.* (2005) conducted an atmospheric static-bed batch reactor to study the influence of temperature ranging from 400 to 700°C. They found that the liquid yield increased with temperatures from 400-500°C and remained almost constant at temperatures over 500°C. Moreover, higher temperatures resulted in the increase of gas fractions, which were H_2, CO, CO_2 and light hydrocarbons. Likewise, a decrease in oils and an increase in gases with increasing temperature were observed by Dai *et al.* (2001) who used a circulating fluidized-bed reactor in pyrolysis. They suggested that long residence time can promote secondary reactions leading to the reduction of oil yield. Galvagno *et al.* (2002) operated tire pyrolysis process with varying the temperature from 550-680°C. They found that increasing temperature promoted the secondary reactions of volatile fraction resulting in an increase of gaseous fraction. In 2002, Leung *et al.* studied the pyrolysis of tire powder with temperatures in the range of 500-1,000°C. They observed that gas yield increased with temperature and long residence time because of the further cracking of gaseous fraction leading to a decrease in the heating value of gas. Mastral *et al.* (2000) studied the influence of parameters such as temperature, heating rate, reaction time, carrier gas velocity, and hydrogen pressure on the oil product. They mentioned that 500°C tended to be the optimum temperature because at higher temperatures, the total conversion and oil yield remained almost constant resulting from the complete reaction of tire pyrolysis. They also found that the reaction time in the range of 15-60 min and the heating rate from 25-300°C/min showed no significant effect on the product yields. Additionally, light products were observed at a high hydrogen pressure.

The effect of final temperature on the calorific value of liquid product was investigated in 2004 by Diez *et al.* They found that the liquid product had high calorific value as temperature increased. In addition, the amount of sulfur increased with temperature, and sulfur remained in liquid and gas products because at a high temperature the breaking of C-S bond occurred whereas the amount of chloride still remained in the solid fraction. Tang *et al.* (2004) studied sulfur distribution during the thermal plasma pyrolysis of used tires. They mentioned that more than 90% of total sulfur remained in the solid fraction, and the gaseous fraction contained sulfur

compounds in hydrogen sulfide form. Moreover, the effect of different types of used tires in pyrolysis was studied by Ucar *et al.* (2005). It was observed that the gas yield of two types of used tires were similar, but the pyrolysis of a passenger car tire gave a higher amount of gasoline, aromatics and sulfur than that of a truck tire.
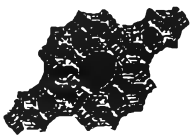
2.2.2 Catalytic Pyrolysis

The catalytic pyrolysis of waste tire is one of the alternative ways that can be carried out to have high product yield and also decrease undesirable products. This technique can provide lower operating temperature than the process without catalysts, and consequently reduce energy consumption. Many kinds of catalysts have been used in the pyrolysis such as zeolite catalysts and bifunctional catalysts. Li *et al.* (2005) investigated the effect of parameters such as feedstock properties, catalytic types, pyrolysis equipment, and operating conditions in catalytic pyrolysis in order to produce light olefins. They found that the keys having significant effect were feedstock properties and catalysts. Moreover, for the different cracking feedstocks, the production of light olefins can be increased over the same type of catalysts. Bonetto *et al.* (1992) found a high yield of iso-butane in gas oil cracking process by using beta zeolite. Moreover, wood can be also used as a raw material in pyrolysis to produce valuable products which was found by Vitolo *et al.* (1999). They tried to upgrade wood pyrolysis oils to fuel over different zeolites, HZSM-5 and HY, in a fixed-bed reactor. They concluded that the strong acid sites and shape selectivity of HZSM-5 zeolites promoted a highly deoxgenated oil with a raised heating value and good combustibility. For the H-Y catalysts, the liquid obtained showed a suspension of oil in water. Marcilla *et al.* (2007) used H-beta and HZSM-5 zeolites in the catalytic pyrolysis of LDPE. They reported that H-beta exhibited higher catalytic activity than HZSM-5 with varying temperature, which was due to the different pore structure. Likewise, Marcilla *et al.* (2006) studied the influence of various acid catalysts in the pyrolysis of different polymers. They conducted the pyrolysis of LDPE, PP, PE and EVA copolymer over HZSM-5 and two different Al contents of MCM-41. It was found that the characteristics of catalysts and structure of polymers played an important role in pyrolysis process. The catalytic activity depended on the pore size and acid site of catalysts which affected on the

crossectional area of the polymers. The same result was found by Miguel *et al.* (2006) who investigated the influence of five catalysts in thermal and catalytic conversion of used tires toward hydrocarbon products. It was suggested that ZSM-5 promoted the aromatization capacity to produce single ring aromatics which can be explained by the strong acid properties. For the mesostructure catalysts, Al-MCM-41 and Al-SBA-15 showed both a strong aromatization capacity and alkylation effect on the aromatic ring products providing the formation of larger molecular size because they had weaker Lewis type acid centers and also larger pore sizes.

Williams *et al.* (2002) investigated two types of zeolites, Y and ZSM-5, in the pyrolysis of tires. It was observed that the larger pore and higher surface acidity of the Y zeolites provided the higher concentration of aromatic compounds than that of the ZSM-5 zeolite. And, they found that increasing catalytic temperature showed a decrease in the concentration of the alkyl substituted aromatic compound. In 2003, they further studied three types of zeolites with different pore sizes and Si/Al ratio. The results exhibited that ZSM-5 provided the lower yield of single ring aromatic compounds than the two of Y-zeolites because of lower pore size and surface acidity. They suggested that the zeolite needed to have enough pore size for hydrocarbon to enter the pore. The pyrolysis of waste tires by using USY zeolite was studied by Shen *et al.* (2006). They reported that an increase in catalytic temperature and catalyst/tire ratio increased the gas yield and consequently decreased the oil yield. Moreover, the pyrolysis with USY displayed a higher total concentration of single aromatics compared with the use of ZSM-5 and Y zeolite in the pyrolysis studied by Williams *et al.* (2002).

2.2.3 KL Zeolite

KL zeolite, whose formula is $K_9Al_9Si_{27}O_{27,}$ has basic properties and one dimensional channel of 12 membered rings with a pore size of 0.71 nm. (Sato *et al.*, 1999). KL zeolite can act as an electron donor and stabilize electron rich metal particles inside the zeolite framework (Alvavarez-Rodriguez *et al.*, 2008). It has been used as a support in several studies to improve catalytic activity and selectivity.

Zeolite	Dimension	Si/Al	Pore size (Å)
KL	1 D	6	7.1

Figure 2.2 The structure of KL. (www.chemistry.nus.edu.sg).

A highly selective catalyst in the aromatization of n-hexane was found by Barrer and Villiger (1969), who used the platinum catalyst supported on KL zeolite. The influence of different alkali catalysts on the aromatization selectivity was investigated by Becue *et al.* (1999). The highest selectivity on Pt/KL catalyst was found, and it should promote an increase in octane number. The application of KL catalyst selective hydrogenation reaction has been studied in several researchers. Jacobs *et al.*, 2001 studied the different preparations of Pt/KL catalyst for n-hexane aromatization. They explained that the different methods affected the various results of platinum cluster distribution on the KL support. They also suggested that the vapor phase impregnation was an effective method on KL powder, but not on the extrudates whose efficiency decreased in the presence of the binder material. In 2008, Kumar *et al.*, studied the role of pore size on the aromatization activity of Pt/KL catalyst, which light naphtha was used as a feedstock. It was noted that the pore volume and dispersion was decreased at high metal loading above 0.4wt% because of the Pt agglomeration. No loss in pore volume and surface area was found at low metal loading. In addition, they suggested that the catalyst prepared by incipient wetness impregnation can be an active and stable catalyst for aromatization. The selective hydrogenation was studied by Alvavarez-Rodriguez *et al.* (2005). They found selectivity and activity on the hydrogenation of unsaturated aldehyde by using ruthenium supported on KL zeolite. Later, they further studied the effect of various preparation methods of catalysts. They reported that the Ru/KL catalyst prepared by incipient wetness impregnation showed less reactive but more selective to unsaturated alcohol than catalyst prepared by treating with $RuCl_3 \cdot xH_2O$. These

results related to the size and location of particles in the zeolite framework. In the other study, Alvavarez-Rodriguez *et al.* (2008) reported that nickel supported on KL catalyst showed the positive relationship of catalytic activity. However, the addition of copper on Ni/KL catalysts inhibited the hydrogenation of nickel.

2.2.4 Supported Rhodium Catalysts

Rhodium, a noble metal, provides catalytic activity and selectivity in many reactions. It has been reported in several catalytic applications. In 2000, Teschner *et al.* studied the hydrogenolytic ring opening of methylcyclopentane on Rh/Al_2O_3 with different metal loading (0.3, 3 and 10%). It was observed that different H_2 pressure and temperatures could affect selectivity to ring opening products and consequently towards fragmentation products ($<C_6$) resulting from multiple C-C bond ruptures. Likewise in 2002, they suggested that the hydrogenolytic cleavage of hydrocarbon C-C bonds was found as a main reaction in the conversion of C_6 alkanes and methyl cyclopentane while C_5-cyclization was a minor reaction. Jacquin *et al.* (2003) investigated novel supported Rh, Pt, Ir and Ru mesoporous aluminosilicates as catalysts in the hydrogenation of naphthalene. They reported that at 300°C and atmospheric pressure, rhodium exhibited higher selectivity to hydrogenolysis and/or ring-opening products than platinum-containing catalysts. Moreover, at 6 MPa supported rhodium catalyst promoted the high amount of high-molecular weight and fully hydrogenated products from naphthalene. Similarly, Albertazzi *et al.* (2003) also found an increase in catalytic activity of rhodium supported on MCM-41 catalyst in the hydrogenation of naphthalene at 6 MPa. However, low thio-tolerance resulting in catalyst deactivation in the dry reforming of methane was found on the catalysts. In 2009, Barama *et al.* found the most active catalyst for the dry reforming of methane was the Rh/Al-PILC catalyst among Pd, Ni and Ce catalysts. It was suggested that rhodium catalyst can be used in many reactions as an effective catalyst.

2.2.5 Nickel And Cobalt Catalysts

A non-noble metal such as Co and Ni is an alternative catalyst to be used as attractive materials because of metal availability, low cost, and high activity.

The nickel catalysts have been used in widely reactions such as hydrogenation and dehydrogenation. Jovanovic *et al.* (1998) studied nickel catalyst for the selective hydrogenation of sunflower seed oil and soybean oil. They used 0.33wt% Ni content supported on silicate. It was found that Ni catalyst had good activity in hydrogenation resulting in a decrease in iodine value to 0.1-0.5. In addition, the Ni catalyst showed high selective hydrogenation of sunflower and soybean oils. In 2008, Yolcular *et al.* investigated Ni/Al_2O_3 catalysts in the dehydrogenation of methylcyclohexane for hydrogen production. The Ni/Al_2O_3 with various contents, 5, 10, 15 and 20%, were used to study the reaction temperature in the range of 653-713K. They found that the conversion of H_2 increased with the reaction temperature but decreased when calcination temperature increased. The catalysts activated at 723 K with H_2 and air flow exhibited higher dehydrogenation activity than other catalysts with higher activated temperature. Moreover, 20%wt Ni content gave better conversion than other contents. Zhao *et al.* (2009) studied the influence of supported Ni catalysts on the product gas distribution and H_2 yield in the pyrolysis of cellulose. $Ni/\gamma-Al_2O_3$ and Ni/MCM-41 prepared by incipient wetness impregnation were used. They found that 15% $Ni/\gamma-Al_2O_3$ and 5% Ni/MCM-41 showed a high yield of H_2 and total gaseous products both under Ar and with water vapor injection. They suggested that Ni catalysts were expected to affect gas product quantity and composition in three ways:

1) Improving tar cracking reaction by catalyzing C-C bond breaking,

2) Enhancing the reforming of light gas molecules such as breaking C-H bond, and

3) Enhancing the water-gas shift reaction towards maximizing the consumption of CO.

For the cobalt catalysts, they have been investigated in various applications. Nitta *et al.* (1999) investigated the selective catalysts in the hydrogenation of unsaturated aldehyde. It was found that supported cobalt catalysts gave higher selectivity than noble metals (Pt, Rh and Ru). Bifunctional zeolites supported cobalt for Fischer-Tropsch catalysts were studied by Bessell *et al.* (1995). It was noted that the channel size of zeolites played an important role in hydrocarbon products more than the acid site of the zeolites. Lighter hydrocarbon products and

less n-alkanes were observed on a larger channel of zeolites which promoted the high dispersion of cobalt particles and the restructuring reactions of the primary products inside the pore. Likewise, Yin *et al.* (2001) investigated the cobalt supported on mesoporous catalysts in the Fischer-Tropsch reaction. High activity and C_5^+ selectivity were observed. Khemthong *et al.* (2010) investigated cobalt and cobalt-platinum supported on NaY zeolites in butane hydrogenolysis. They found that Co loading of 6%wt and 10%wt produced only methane because of multiple hydrogenolysis involving more than one C-C bond breaking. The presence of a small amount of platinum affected selectivities and increased n-butane conversion in the hydrogenolysis reaction.

The comparison between cobalt and nickel supported on HY zeolites in the hydroconversion of n-hexane was studied by Pedrosa *et al.* (2006). They found that cobalt supported on HY zeolite exhibited the higher selectivity of paraffin isomerization than Ni/HY while Ni/HY gave more cracking selectivity explained by the differences in acidity and micropore area. Chica *et al.* (2009) investigated catalysts based on nickel and cobalt supported on all silica delaminated ITQ-2 zeolite, the absence of acid site, in bioethanol steam reforming. It was concluded that Ni/ITQ-2 was the most active catalyst whereas Co/ITQ-2 showed the highest H_2 selectivity and the lowest CO selectivity.

2.2.6 Bimetallic Catalysts

The addition of a second metal is another choice to improve the catalytic performance such as activity, selectivity, and stability. Akhmedov *et al.* (2000) studied the hydroconversion of alkanes (n-pentane, n-hexane, n-heptane and 2-methylpentane) and cycloalkane (cyclopentane, cyclohexane and methylcyclopentane) over Ru-containing supported catalysts. It was found that the presence of rhodium in the bimetallic Ru-Rh/ZSM-5 catalyst could change the catalytic properties, and affected the rate of hydrogenolysis of hydrocarbons, which gave the most reactivity of cyclopentane conversion. Furthermore, they also suggested that rhodium had an active site promoting a marked selectivity toward terminal C-C bond splitting. In 2007, an unsupported Pt-Rh catalyst for methylcyclopentane hydrogenative ring-opening reaction was studied by Paal *et al.*

They concluded that a small amount of rhodium on Pt-Rh catalyst behaved as a bimetallic giving activity and selectivity value between the single Pt and Rh catalyst. Jacquin *et al.* (2008) tried to upgrade diesel oil by adopting the hydrogenation of naphalene and tetralin model and using bimetallic PdRh supported on a mesoporous aluminosilicate catalyst with different preparation methods. Very small particle size and well dispersion were observed on the impregnation of PdRh catalyst. They concluded that the catalyst showed higher activity at a lower temperature compared with a reference catalyst used in the industrial condition. Moreover, the increase in cetane number and the decrease in non-selective cracking products were found.

The noble metal modified with non-noble metal has gained attention in terms of cost reduction and catalytic improvement. Zhao *et al.* (2008) investigated a nano-nickel catalyst modified by ruthenium for hydrogenation and hydrodechlorination. They reported that higher selectivity, activity and stability was found on NiRu catalyst than Ni catalyst. Likewise, Miyata *et al.* (2006) studied the effect of the addition of noble metals on Ni/Mg(Al)O in methane steam reforming. It was observed that the noble-Ni supported catalysts decreased the reduction temperature of Ni^{2+}, and increased the amount of H_2 uptake on the Ni^0 over the Ni/Mg(Al)O catalyst. Additionally, only 0.05% of Rh loading was able to suppress the deactivation during the operation. The same trend was found by Nurunnabi *et al.* (2006). 0.035% Rh on NiO-MgO was the most effective catalyst to improve catalytic activity and inhibit carbon deposition.

As stated above, the rhodium supported on KL zeolite has not been investigated in the catalytic pyrolysis of waste tire before. The combination of basic properties and shape selectivity in KL zeolite with the ring-opening, hydrogenation and hydrogenolysis properties of rhodium catalyst in the hydrocarbons C-C bonds breaking is expected to promote pyrolytic process with the inhibition of non-selective cracking products, and then to enhance the quality and quantity of the pyrolytic products. Furthermore, non-noble metals, Ni and Co, supported on KL zeolite and the effect of bimetallic NiRh and CoRh catalysts were investigated in this process as a competitor of the supported monometallic rhodium catalyst in terms of cost reduction and metal availability in order to improve catalytic activity in waste tire pyrolysis.

The objectives of this research work were to investigate the quality and quantity of oils and others products by using noble metal (Rh) and non-noble metals (Ni and Co) on KL catalyst, and to study the effect of the noble metal modified by non-noble metals as catalysts on the quantitative and qualitative pyrolysis products.

The scope of this research covers as follows: (1) the pyrolysis of scrap tire was operated in a bench-scaled autoclave reactor, (2) N_2 flow rate, heating rate, the amount of sample and the amount of catalysts were fixed at, 30 ml/min, 10°C min, 30 g and 7.5 g, respectively, (3) the monometallic catalysts (1%wt Rh and 1, 5, 10, 15, 20%wt of Ni and Co) supported on KL zeolite were investigated by incipient wetness impregnation technique, and (4) the bimetallic catalysts supported on KL zeolite (RhNi/KL and RhCo/KL) were prepared by co-impregnation technique with a total metal content of 1 %wt with the varied amount of Rh from 0.05 to 0.75 %wt according to the following Table 2.1

Table 2.1 The amount of metal loading on the bimetallic catalysts

Sample catalysts	$wt_{metals} = wt_{Rh} + wt_{Ni\ or\ Co}$		
	$wt_{metals}(\%)$	$wt_{Rh}(\%)$	$wt_{Ni\ or\ Co}(\%)$
Rh-Ni/KL	1	0.05	0.95
		0.25	0.75
		0.50	0.50
		0.75	0.25
Rh-Co/KL	1	0.05	0.95
		0.25	0.75
		0.50	0.50
		0.75	0.25