CHAPTER I
INTRODUCTION

Due to the growth of population and development of transportation in Thailand, a large number of cars have been increased rapidly resulting in a lot of tires consumed in every year. Waste tire become more serious environmental problem because of its non-biodegradable properties. Thus, the waste tire management needs to be concerned. There are many ways to recycle the waste tire for example landfilling, but it requires a large amount of space and emits hazardous gases when contacting with fire. It can be used in the cement industry as a substitute of fossil fuel (Seidelt *et al.*, 2006). Moreover, retreading, reclaiming and grinding are also the waste tire recycling methods, but they all have some disadvantages (Rodrigues *et al.*, 2001).

Tire is commonly composed of different components such as several rubbers, carbon black, steel cord and other additives. The rubber which is a chemically cross-linked polymer is the main component of it (Rodrigues *et al.*, 2001). Owing to the complexity of the tire components, it is difficult to recycle and degrade.

Pyrolysis has been introduced in this decade as a renewable waste tire recycling technology in Thailand. The pyrolysis, an oxygen-free thermal degradation, decomposes high molecular weight materials into low molecular weight products, which are typically classified into liquid, gas and solid residual. The liquid product can be used as a fuel and chemical feed stock in industrial processes (Ucar *et al.*, 2005). The pyrolysis gases can be used as fuels because they have high enough calorific value. And, char which remains as solid fraction is also used as a smokeless fuel and a low grade activated carbon or carbon black (Williams *et al.*, 1998).

Liquid fraction consists of oil and valuable chemical substances such as benzene, toluene, xylene, lemonene, and other aromatics, which have ability to compete with the products from refining industry. The gas product is also useful since it is full of methane, ethane, butadiene and others which may provide high energy required for the process plant. As mentioned, several techniques have been proposed in order to improve products and reduce undesired products.

Catalytic pyrolysis of waste tire is one of the effective ways that the process can be carried out to have high product yield and also decrease undesirable products such as polyaromatics and solid residual. Taking advantages of catalyst properties such as pore size, activity and selectivity, catalysts play an important role on the pyrolysis process.

Bifunctonal catalysts associated with the influence of support with one or two metals can provide the high activity and selectivity of hydrogenation and the ring opening of hydrocarbons. Noble metals (Pt, Ir, Rh, Ru) supported on zeolites have been widely used in hydrogenation and the ring opening reaction. Rhodium was found to be one of the most active noble that showed higher yield in hydrogenation and the ring opening of naphthalene than Pt and Ir for diesel upgrading (Jacqiun *et al.*, 2003). Choosuton (2007) used noble metals supported on a zeolite. It was suggested that the catalysts can reduce polyaromatic hydrocarbons in the oil because of its high activity and selectivity for hydrogenation and ring opening of aromatic hydrocarbons.

Non-noble metals such as Co and Ni are alternative catalysts to be used as attractive materials. They can compete with noble metals in terms of metal availability, low cost, and high activity. It was found that supported cobalt catalysts gave higher selectivity than noble metals (Pt, Rh and Ru) in the hydrogenation of unsaturated aldehyde (Nitta *et al.*, 1999). Pedrosa *et al.* (2006) found that cobalt supported on HY zeolite exhibited the higher selectivity of paraffin isomerization than Ni/HY, while Ni/HY gave more cracking selectivity in the hydroconversion of hexane.

The addition of second metal can influence the activity and selectivity. In 2008, Jacquin *et al.* found that bimetallic PdRh showed activity and selectivity in hydrogenation and the ring opening of polyaromatic compound. Additionally, the noble metal modified with a non-noble metal seem to be the effective way in order to improve catalytic activity. Nurunnabi *et al.* (2006) reported that the addition of 0.035% Rh on NiO-MgO made it the most effective catalyst to improve catalytic activity and inhibit carbon deposition in methane steam reforming.

A support can also promote those previously-mentioned reactions due to its pore size and acidic properties. On the other hand, the high acidity of a zeolite can cause excessive cracking, and consequently an undesirable non-selective reaction can occur. KL zeolite has basic property and one dimensional channel of 12 membered rings with a pore size of 0.71 nm. (Sato *et al*., 1999). There have been less number of reports of this catalyst compared with other acidic zeolites which can be related to catalytic pyrolysis. Azzam *et al.* (2010) studied the aromatization of hexane over Pt/KL catalyst, and they found that L-zeolite channels inhibited the coke formation and catalyst deactivation. Álvarez-Rodríquez *et al.* (2009) reported selectivities and activities on the hydrogenation of unsaturated aldehyde over Ru/KL catalyst.

As mentioned above, the utilization of a rhodium supported on KL zeolite catalyst has not been found in the catalytic pyrolysis of waste tire. However, its abilities could make it an effective catalyst in this process. Non-noble metals also were investigated and compared with noble metals. The aims of this research were to investigate the bifunctional catalysts: rhodium, nickel, and cobalt supported on KL zeolite in waste tire pyrolysis, and the effect of the noble metal modified by non-noble metal catalysts on qualitative and quantitative pyrolytic products was also investigated.