CHAPTER I
INTRODUCTION

According to the transportation in Thailand has been more convenient nowadays, many roads have been constructed, which lead to the change in major types of transportation in Thailand. People tend to travel by cars, buses, etc. That is why there are a large number of cars having been produced. Consequently, the materials which are soon to become some parts of cars have been launched to the market increasingly as well.

One of the main parts of vehicles is tire. Tire is a double bond-containing polymer which can be chemically cross-linked by vulcanization process. The main compositions of passenger tire are natural rubber, synthetic rubber, carbon black, steel, fabric, and some chemical substances. The average weight of used tires is about 20 lbs. In 2005, Pollution Control Department reported that there were about 1.7 million ton per year of tires produced in Thailand. (http://ptech.pcd.go.th/p2/ waste-util-article-view.php?aid=49). These tires become one of the most serious problems because they are non-biodegradable.

However, there are several ways to dispose and eliminate these used tires such as landfilling, tire recycling; including re-treading, reclaiming, incineration, and grinding, all of which have significant drawbacks and/or limitations (Rodriquez *et al.*, 2001).

Pyrolysis is an innovative method, which usually means the chemical decomposition of organic materials by heating in the absence of oxygen or any other reagents. In terms of the pyrolysis of tire, the tire is primarily decomposed into the lower molecular weight products. Liquid fractions can be used as fuels or as a source of chemicals since they contain various aromatic and polyaromatic compounds such as benzene, toluene, xylene and limonene. Gaseous fractions are essentially composed of methane, ethane, butadiene and other hydrocarbon gases (Rodriquez *et al.*, 2001). Char may be used as a precursor for the manufacture of low-grade activated carbon, carbon black, and smokeless fuel. In 1999, Roy *et al.* found that another potentially important end-use of the pyrolytic carbon black may be as an additive for road bitumen.

There have been many technologies being developed such as microwave pyrolysis, ultrasonic devulcanization, and supercritical fluid depolymerization, which intend to improve organic vapor residence time in the reactor and also to reduce the occurrence and intensity of secondary reactions by using the various pyrolysis-assisting techniques. Besides, improving the product prices are also desired because the primary products contain a low amount of low molecular weight olefins and char which have low prices. The other attempt is to reduce the process cost in the removal of high molecular weight substances.

The catalytic pyrolysis of waste tire process is one of the most well-known techniques that a catalyst plays an important role on modifying the product yields and the compositions of hydrocarbon products. There are many series of catalysts used in the catalytic pyrolysis process, depending on their properties such as activity, pore size and selectivity. One of the most interesting series of catalysts used in catalytic pyrolysis is bifunctional catalysts because they can reduce polyaromatic hydrocarbon in the oil due to its high activity and selectivity for hydrogenation and ring opening of aromatic hydrocarbons (Choosuton, 2007), and they can decrease poly- aromatics, resulting in the increase of the cetane number of diesel.

KL zeolite, a basic zeolite, has one dimensional channel of 12 membered rings with a channel opening of 0.71 nm in diameter, and its nominal composition is $K_9Al_9Si_{27}O_{27}$ (Sato *et al.*, 1999). It has good properties, but there have been a few researches that supported the use of this zeolite in the catalytic pyrolysis of tire. In 1999, Bécue *et al.* investigated the behavior of the different alkali catalysts on the aromatization selectivity. They found that Pt/KL has the highest aromatization selectivity. Therefore, the octane number of gasoline should be increased by using Pt/KL. In 1969, Barrer and Villiger found that the platinum catalyst supported by KL zeolite had a high selectivity for the aromatization of n-hexane. And In 2005, Álvarez-Rodríquez *et al.* found that the ruthenium supported on KL zeolites showed selectivities and activities on the hydrogenation of unsaturated aldehyde.

Moreover, Santikunaporn *et al.* (2004) studied the ring opening of decalin and tetralin on HY and Pt/HY zelolite catalysts. They investigated that the production of ring opening products was greatly enhanced by the presence of platinum. In 2002, William and Brindle studied the influence of the temperature in the catalytic pyrolysis

with the two zeolites of different pore sizes, Y-type zeolite and ZSM-5. They found that the Y-type zeolite, which has larger pore size and higher surface acidity, yielded higher aromatic compounds but lower liquid yields than the ZSM-5 catalyst. Furthermore, Park and Ihm (2000) investigated the effect of bifunctional platinum catalysts containing ZSM-5, ZSM-22, SAPO-11, Al-MCM-41, H-Y, and H-β on the hydroisomerization of n-hexadecane under the reaction condition of 350°C and 103 bar. They reported that Pt/ZSM-5, Pt/ZSM-22, and Pt/H-β catalysts with strong acid sites showed a high hydrocracking activity whereas Pt/SAPO-11, Pt/Al-MCM-41, and Pt/H-Y catalysts showed better isomerization selectivity due to their moderate acid strength.

According to the above researches, the influence of the catalyst mixing between acid (Y zeolite) and basic (KL zeolite) catalyst and the order of mixing in the reactor was studied because the high isomerization activity (KL), aromatization activity (KL) and ring opening activity of heavy pyrolytic products (Pt/Y) in order to produce molecules of higher valuable products.

The purposes of this research were to study the effect of catalyst mixing (Y and KL zeolite), the order of catalyst mixing in the reactor, and catalyst mixing ratio in order to improve the quality and quantity of oils and others pyrolysis products. Moreover, the bifunctional catalysts, platinum supported on the mixed catalysts, were investigated for their effects on the quality and quantity of pyrolysis products.