CHAPTER I
INTRODUCTION

In the past decade, a numerous number of tires are produced to supply the growth of transportation industries, especially in the industry of private vehicles. After their life time, waste tires mainly from passenger cars are dumped in the landfills. Some of them can be reused into some applications such as those used in the playgrounds, pet toys or a habitat of frogs, but they are used in a very low amount. The waste tires that are dumped in the landfills create many problems, and affect to the environment. One of the most commonly found problems of waste tire is the non-biodegradability of tires, since tires consist of natural rubber (poly-isoprene), synthetic rubber (butadiene rubber and styrene-butadiene-rubber), carbon black and other additives, and become a thermosetting material by vulcanization with sulfur.

As a result, waste tires which consist of heavy hydrocarbon compounds may possibly be processed to lighter products used in some applications. One of the methods for dealing with the tire's problems is pyrolysis process. Pyrolysis is the thermal degradation in the absence of oxygen that generates gas, oil, and char from waste tires. Pyrolytic gases can be used to provide process energy. Pyrolytic oils can be used as a fuel substitute or chemical feed stock, whereas char can be used as a smokeless fuel or low-grade activated carbon.

Moreover, catalysts were introduced into the process to increase the quality and quantity of the desired products. In refineries, acidic zeolite catalysts are widely used in the fluid catalytic cracking unit because they have potential to convert heavy feed into lighter products by cracking reactions on the acidic sites. Hence, the several works that studied the effect of zeolites on the catalytic pyrolysis of waste tire have been reported. For example, Williams and Brindle (2002) studied the influence of catalyst bed temperature by using two types of micro-porous zeolite catalysts (Y-type and zeolite ZSM-5) with different pore sizes and surface acidity. They reported that the presence of catalysts increased the yield of gas and coke formation on the catalyst with a consequently reduced yield of oil, whereas the yield of char remained constant. The concentrations of mono-aromatics were also increased. These results were similarly reported in other works. Furthermore, the binary and multi systems of molecular sieve have potential for FCC gasoline upgrading (Fan *et al.*, 2005). They succeeded in using a quadruple composite catalyst composed of SAPO-11/HMOR/HBETA/HZSM-5, which can increase the liquid yield and lower the coke content. In addition, aromatization activities were increased, when HZSM-5 was used as an additive for HBETA at high temperatures. Meanwhile, the Y-BETA binary zeolites, which Y zeolite was the main zeolite whereas BETA zeolite was the additive in this binary zeolite, had a suitable potential for the hydrocracking of vacuum gas oil which can increase the heavy naphtha and jet fuel yields (Zhang *et al.*, 2010).

Bifunctional catalysts have become interesting in the pyrolysis of tires with the fact that the noble metals, especially Pt and Pd can promote hydrogenation, dehydrogenation, heteroatom removal, and ring-opening reactions. In addition, they also reduce the catalyst deactivation. Pt/HBETA has high polar-aromatic reduction activity because Pt metal sites promote hydrogenation reaction which the polar-aromatics are converted to saturated hydrocarbons, and then, the saturated products are further cracked on the acidic sites (Dũng *et al.*, 2009). Moreover, Pintoo (2008) showed that the Pd/HBETA can reduce heavy fractions to lighter fractions, which produced a high amount of saturated hydrocarbons, suitable for kerosene production.

In this work, the different micro-porosity and shape selectivity of each zeolites (HBETA, HY, and HZSM-5) were focused. With the combination of two or more types of zeolites, the different hierarchical structures of zeolites may have possibilities to increase the yield of full range naphtha or improve the quality of oil. Furthermore, noble metals, especially Pt and Pd have potential to improve the quality and quantity of the products such as the reduction of poly- and polar-aromatics contents, prevent the undesired methane product from over cracking, and increase on the cracking activity of heavy fraction (vacuum gasoil) to the lighter fractions (full range naphtha, kerosene and/or gas fraction); thus, bifunctional catalysts were used in this experiment.

The purpose of this research was to investigate the addition of a second microporous zeolite with different pore sizes (HBETA, HY, and HZSM-5) as an additive into the main catalysts (Pd/HBETA, and Pd/HY), expectedly influencing to the pyrolyzed products, especially full range naphtha. The waste tire pyrolysis was carried out in the bench-scale autoclave reactor at the atmospheric pressure. The temperature was risen with the heating rate of 10 °C from room temperature to the final temperature of 500 °C. In addition, the other parameters such as 20-40 mesh particle size, 30 g of sample, 7.5 g of catalyst, 90 min holding time, and 30 ml/min nitrogen flow rate were fixed in every test.