CHAPTER I
INTRODUCTION

Nowadays, the world is running out of petroleum with the increase in the fuel consumption. Alternative energies such as biofuel, wind energy, and fuel from wastes are chosen to be the ones used to substitute the petroleum fuels. Oil from waste tires is one of an interesting fuel to be developed because there are a large number of waste tires in the world that are no longer used for vehicles. Waste tires are usually recycled for new shoes and basketball court (http://en.wikipedia.org/wiki/Tire_recycling), but they are required for only a small amount, and the rest is dumped into the landfills. These waste tires are one of wastes discharged in the largest amounts to the environment due to the large volume produced because waste tires need a long time for biological degradation, and these can make the environmental problems and health hazards. Pyrolysis is one of the suitable processes to utilize waste tires. Waste tires pyrolysis is the thermal degradation process in the absence of the oxygen for converting waste tires to hydrocarbons. Pyrolysis products consist of three phases, including gas, liquid, and solid residue (char) (Chang, 1996). Pyrolytic gas can be used as fuel, pyrolytic oil can be used as a chemical feedstock to substitute fuel oil, and solid char can be processed to carbon black and activated charcoal.

There were many researchers that used catalysts to improve the quality and quantity of the pyrolytic products. When the amount of catalyst increased, the gas yield increased while the oil yield decreased and also the light fraction in oil increased (Boxiong *et al.*, 2006). Bifunctional catalysts (metals supported on zeolites) become interesting to order to improve the efficiency of catalytic pyrolysis. Noble metals supported on acidic zeolite were used to optimize the high value products because noble metal can promote hydrogenation and ring opening (Du *et al.*, 2005). Dũng *et al.* (2009) used ruthenim on HBETA zeolite, and they found that using the bifunctional catalyst can improve the quality of the oil product by the reduction of poly- and polar-aromatics, leading to the yield of light oil, but the noble metal has low resistance to sulfur poisoning. Using zeolite catalysts give more selectivity toward the monoaromatic compounds in the pyrolytic product (Miguel *et al.*, 2006).

In the pyrolytic oil from waste tires, sulfur compounds are largely present in the form of polar-aromatics such as thiophene, benzothiophene, and dibenzothiophene, which can cause poisoning of the active sites in the catalyst. Moreover, if fuels contain sulfur, SO_2 that is a pollutant is produced during combustion. With this reason, many countries limit the amount of sulfur content in transportation fuels. Therefore, not only are the cracking of heavy hydrocarbons to light hydrocarbons as well as hydrogenation and ring-opening needed, but hydrodesulfurization is also important. Some noble metals on some acidic supports were found to increase hydrogenation and improve hydrodesulfurization. For examples, Pt/HBETA had high ability for polar-aromatic reduction, leading to a decreasing amount of sulfur in the pyrolytic oil (Dũng *et al.*, 2010). Tang *et al.* (2008) found that Pd/HBETA had higher desulfurization ability than Pd/Al-MCM-4 because of the difference in the acidity of supports; namely, HBETA zeolite exhibited higher acidic site and higher strong acidic than Al-MCM-41. Saeaeh *et al.* (2012) found that Ni loaded on HBETA zeolite increased the cracking ability of HBETA in tire pyrolysis because it increased the gas yield with a consequent decrease in the oil yield. They also found that the sulfur content in oil was further reduced by using Ni/HBETA catalyst. Pinket *et al.* (2011) used Co on KL zeolite in tire pyrolysis, and reported that it can further reduce the sulfur content in the pyrolytic oil. Ni and Co can promote hydrogenation (Villarroel *et al.* 2008), and they are active to the ring-opening of aromatics (Hernández-Huesca *et al.* 2001). Moreovers, bifunctional metals, such as NiMo, NiW, CoMo, and CoW (Mo and W as second metals to Ni and Co) on Al_2O_3 are normally used in hydrodesulfurization process (Torres-Mancera *et al.* 2005).

Due to the limit of sulfur in petroleum products and the high price of a noble metal, in this research, NiMo, NiW, CoMo and CoW were chosen as non-noble metals to be used in the pyrolysis of waste tire. The effects of non-noble metals (Ni and Co) modified with Mo and W as second metals and supported on HBETA zeolite for tire pyrolysis were investigated in this work on the quality and compositions of the pyrolytic oil products. Types and amounts of sulfur compounds in the oil were also studied. The purposes of this work were to study the cracking ability as well as the desulfurization ability of NiMo, NiW, CoMo and CoW loaded on HBETA in tire pyrolysis, and to study the change of sulfur compounds when the compositions of the bimetallic catalysts were varied.