CHAPTER I

INTRODUCTION

A number of sulfur compounds in petroleum crude oil and other oil-derived feedstock are not only problem with oil product properties but also environmental regulations and they also have caused oil products to lose their price. Moreover, sulfur in oil can reduce the efficiency of catalysts that are used to convert any reactant into other valuable products by poisoning the catalysts (Sidhpuria *et al.*, 2008-2009) that is similar to the pyrolysis of waste tire. Waste tire comprises of various sulfur molecules that are obtained from large network between sulfidic crosslinks and rubber chains on account of vulcanization process (Bilgili *et al.*, 2001). This reason leads to the development of strategies for main cracking process together with sulfur content reduction. The combination of pyrolysis process and desulfurization at the same time are required in order to obtain pyrolysis oil with the lowest sulfur levels.

The investigation of sulfur species in products and reactants is extremely necessary because it may reveal new alternative ways to eliminate and handle a great number of sulfur compounds that are not desired products. It is clearly found that sulfur compounds with large structure would be obstacles because their structures keep distance between sulfur atoms in the structure and the active sites of a catalyst (García-Cruz *et al.*, 2008). Therefore, they might be minimized by hydrogenation or cracking before desulfurization in order to drive away hindering structures. The combination of both hydrogenation and desulfurization ability is named hydrodesulfurization

Hydrodesulfurization is one of the most important steps that is extensively used for removing sulfur compounds such as thiols, thiophenes, alkylthiophenes and other derivatives under severe conditions by adding hydrogen to form hydrogen sulfide. As commercial hydrotreating catalysts, nickel- or cobalt-promoted molybdenum or tungsten are widely used in hydrodesulfurization for refinery. Ni and Co as promoters that are usually supported on Al_2O_3 gave the highest activity in hydrodesulfurization because of the maximum hydrogen spillover (Villarroel *et al.*, 2008), but the Ni promoter had more hydrodesulfurization activity than the Co one

(Rodríguez-Castellón *et al.*, 2008). NiMo was found to have a little bit higher hydrodesulfurization conversion of dibensothiophene than NiW (Ding *et al.*, 2009).

In the catalytic pyrolysis of waste tire, the high levels of sulfur contamination of about 1.4-1.5 wt% in the oil products (Cunliffe and Williams, 1998) can be diminished by the collaboration of cracking and desulfurizing catalysts. It has been well-known that noble metals present a very high performance in hydrogenation reaction, and they can be used in forms of transition metal sulfides for hydrogenation. The very small amount of Rh in the conversion of sulfur compound groups indicates that Rh has a high performance in hydrodesulfurization (Ishihara *et al.*, 2005). Rh-containing catalysts yield highly-hydrogenated products (Jacquin *et al.*, 2003). Pinket and Jitkarnka (2011) reported that the sulfur contents in pyrolysis oil could be reduced from 1.40 to 0.91 wt% by Rh loading on KL zeolite, meaning that Rh supported on non-acidic KL zeolite has ability in the desulfurization of effluent from the pyrolysis of waste tire. For acid catalysts, Rh/HBETA performed good activity for toluene hydrogenation (Sidhpuria *et al.*, 2008). Dũng *et al.* (2009) mentioned that HBETA with their large pore size showed the high ability in reduction of polar-aromatics in tire-derived oil. Sugioka *et al.* (1996a) reported that USY gave the highest cracking of thiophene among H-zeolites, and showed high thiophene hydrodesulfurization activities when doped with Pt or Rh metal. Therefore, Rh-loaded acidic supports (HY and HBETA) were expected to be high effective catalysts because the combination between the high hydrogenation ability of Rh and the cracking ability of HY and HBETA with large pore sizes. The cracking ability of acid catalysts combined with the hydrogenation and desulfurization activities of a noble metal are a good approach to obtain high-value lighter products along with low sulfur in oil from waste tire pyrolysis.

For this study, Rh-loaded HY and HBETA catalysts were investigated and compared with Rh/KL catalyst in terms of cracking ability and sulfur reduction in waste tire pyrolysis. Moreover, the commercial catalysts, regenerated $NiMoS/Al_2O_3$ and fresh $CoMoS/Al_2O_3$ were also investigated for their potentials as a catalyst for waste tire pyrolysis with sulfur reduction ability.