CHAPTER I
INTRODUCTION

Waste tires, indegradable materials, are difficult to manage. The lifetime of waste tires in a landfill span in the period of 80 -100 years (Martínez *et al.*, 2013). Therefore, pyrolysis of waste tires is an interesting process to transform waste tires to valuable products, such as gas and oil. Tire-derived oil is remarkable product in the process. It is an aromatic-based hydrocarbon mixture. However, tire-derived oil usually consists of some large aromatic hydrocarbons, sulfur compounds and small amounts of petrochemicals. The presence of large aromatic hydrocarbons and sulfur compounds in fuels not only destroys the engines, but also increases the high amount of toxicity in the environment due to the incomplete combustion and SO_x emission. Moreover, petrochemicals such as benzene, toluene, xylenes, ethylbenzene, and cumene in tire-derived oil are interesting products because they are widely used as raw materials in petrochemical industry. For examples, benzene and xylenes are used for coating, printing and extracting. Furthermore, they are used as raw materials for production of plastics. Toluene is used as an octane booster to improve the performance of engines. Ethylbenzene is primarily used in the manufacture of styrene. Normally, styrene is used to make plastic materials via polymerization reaction. Cumene is mainly used as a raw material in the manufacture of phenol and acetone. Therefore, catalysts are necessary in process to improve the quality of tire-derived oil.

To decrease large molecules in tire-derived oil, a catalyst with a large pore size is needed. Previously, researchers studied the performance of mesoporous molecular sieves, MCM-48 and MCM-41, as a catalyst in waste tire pyrolysis. Dũng *et al.* (2009a) observed that MCM-41 catalyst decreased the carbon number distribution in tire-derived oil from C5-C50 for the non-catalytic case to C10-C20. The result from column chromatography shows that MCM-41 can reduce the contents of poly- and polar-aromatics, with the increasing mono-aromatic hydrocarbons in the oil. In addition, the activity of mesoporous MCM-48 catalyst in waste tire pyrolysis was studied by Witpathomwong *et al.* (2011). Similarly, it was found that the concentration of poly- and polar-aromatic hydrocarbons slightly decreased, indicating that the elimination of large molecules in tire-derived oil was successful using mesoporous catalysts because of their large pore sizes that can handle the large molecules.

Furthermore, many researchers studied the desulfurization in oils. Unapumnuk *et al.* (2008) investigated two parameters; temperature and heating rate, affecting the sulfur removal from tire-derived oil. They observed that the heating rates did not affect on sulfur content whereas desulfurization increased with increasing the temperature from 350 to 400 °C. Furthermore, the zeolites (HMOR, HZSM-5, and HBETA) can reduce sulfur content in tire-derived oil, reported by Muenpol and Jitkarnka (2015). The authors found that the straight channel of HMOR can remove sulfur from tire-derived oil better than the zigzag channel of HBeta. Additionally, the medium pore of HZSM-5 gave a high sulfur removal than the larger pore of HBETA. Moreover, mesoporous molecular sieves, Al-MCM-41 with various Si/Al ratios, were used as adsorbents to desulfurize the commercial diesel fuel (Liu *et al.*, 2007). The authors observed that sulfur removal can be ranked in the order: Al-MCM-41(50) > Al-MCM-41(30) > Al-MCM-41(100), indicating that the adsorption capacity of sulfur-containing compounds depends on the amount of Lewis acidic sites. A strong interaction between sulfur-containing compounds with Lewis acidic sites helped to increase the adsorption capacity over Al-MCM-41. Therefore, there are many factors that affect to the ability of sulfur removal. The acid properties of catalysts are very interesting effects that help to remove sulfur in tire-derived oil.

On the other hand, zeolites were used as the catalyst in waste tire pyrolysis to improve the valuable of oils. Olazar *et al.* (2008) studied acid catalysts (HZSM-5 and HY) on pyrolysis of scrap tire. The authors found that HZSM-5 had a medium pore size and a fraction of strong acid sites. It was able to crack mono-aromatic hydrocarbons (C_{10}^-). Moreover, it can enhance the BTX production, resulting from olefins condensation in pores by Diel-Alder reaction; however, heavier aromatic hydrocarbons cannot be formed due to the limitation of pore size, whereas HY that has a larger pore size enhanced the formation of heavier aromatic hydrocarbons due to high hydrogen transfer capacity in pores. Muenpol and Jitkarnka (2015) have studied the effect of pore size catalyst (HZSM-5 and HBETA) in waste tire pyrolysis. They found that HBETA gave about 61 % petrochemicals in gasoline, which was more greatly than HZSM-5, indicating that the large pore size of HBETA was more suitable to produce petrochemicals in tire-derived oil than the medium pore size of HZSM-5. The purpose of this work was therefore to investigate the potential effect of acid density of mesoporous MCM-48 catalysts in waste tire pyrolysis on removal of large aromatic and sulfur compounds. Moreover, to improve the quality of tire-derived oils by decreasing large molecules and increasing petrochemicals, the double beds of mesoporous Si-MCM-48 and microporous (HBETA, HY, and HZSM-5) as catalysts were used by placing Si-MCM-48 as the lower bed, aiming to firstly decrease large aromatic hydrocarbons in tire-derived oil, and a zeolite was placed consecutively as the upper bed to investigate whether or not petrochemical productions and desulfurization in tire-derived oil can be enhanced.