CHAPTER I
INTRODUCTION

Nowadays, the energy consumption continuously increases, and the fossil fuel is not a sustainable resource for production of fuel and petrochemical feedstock. Therefore, researchers attempted to seek for alternative fuels and petrochemical feedstock resources. Among all alternative resources, waste tire is much attractive because it mainly consists of hydrocarbons, which can be directly converted to useful products by pyrolysis. The products, which are obtained from pyrolysis of waste tire, are composed of gas, liquid oil and solid char. The liquid or tire-derived oil is much more interesting than the gas and char products since it contains valuable petrochemicals such as benzene, toluene, and xylenes, and could be used as a fuel that substitutes conventional fuels. However, a significantly-high amount of polycyclic aromatic, sulfur-containing and nitrogen-containing compounds limit the use of tire-derived oil as a fuel or petrochemical feedstock.

Consequently, several researchers focused on the enhancement of petrochemical production and reduction of the poly- and polar-aromatics in tire-derived oil. For instances, Boxiong *et al.* (2007a) reported that using ZSM-5 and USY zeolites selectively produced mono-aromatics, especially benzene, toluene, and xylenes. In addition, Choosuton (2007) also found that HMOR and HBETA zeolites increased the aromatic yields, especially the polar-aromatics yield. Muenpol (2014) stated that HBETA catalyst selectively produced benzene and ethylbenzene while HMOR catalyst significantly enhanced stylene production. Furthermore, HY catalyst selectively produced benzene and toluene as reported by Yuwapornpanit (2014). Among those zeolites, Y-zeolite enhanced saturated hydrocarbons and mono-aromatic production, and reduced the production of di-, poly- and polar-aromatics as reported by Manchantrarat (2011) ; Wehatornawee (2011).

However, a relatively-high concentration of poly- and polar aromatics still remains in the tired-derived oil. There are two possible reasons that can explain the high formation of bulky aromatic compounds. The first reason is that the formation of aromatics increases with the increase of acidity. The second reason is that the sizes of aromatics molecules are larger than the micropore of zeolites; then, large aromatic compounds are not cracked into smaller aromatics or light hydrocarbon products. As a result, mesoporous materials, which have a large pore size and low acidity, are attractive to the use as a catalyst in the pyrolysis of waste tire. Dũng (2009) reported that using MCM-41 as a catalyst caused a reduction in the concentration of poly- and polar- aromatics in the pyrolytic oil. A year later, Dũng (2010) informed that using SBA-1 did not alter the concentration of saturated hydrocarbon, mono-, di-, poly- and polar-aromatics in tire-derived oil. As a result, composite materials have been developed and used to overcome the drawbacks of zeolites and mesoporous materials. The so-called "core-shell" composites provided higher diffusion efficiency and more surface acidity distribution due to the good connection of their mesopores and micropores (Jia *et al.,* 2013). For example, MCM-41/FAU composite materials displayed higher conversion of vacuum gas oil than USY zeolite in cracking of vacuum gas oil (Kloestra *et al.,* 1996). MCM-41/ZSM-5 composite materials also showed the high catalytic performance in n-C12 cracking (Haung *et al.,* 2000). Similarly, MCM-41/ZSM-5 showed the higher catalytic performance in n-C12 cracking than fresh ZSM-5 and NaOH-treated ZSM-5 zeolites (Na *et al.*, 2013). MCM-41/BETA enhanced activity and selectivity of gasoline in the catalytic cracking of used palm oil (Ooi *et al.,* 2004). Therefore, it is evident that the composite of HY core and MCM-41 shell and the composite of HBETA core and MCM-41 shell can reduce large polycyclic aromatics, and increase valuable mono-aromatic production.

Furthermore, nickel-promoted catalysts play an important role in the enhanced production of valuable products and the reduction of sulfur content in tire-derived oil. For example, Pinket (2011) reported that Ni/KL increased light hydrocarbon production, and decreased the di- and poly-aromatic yields. It was reasonable to conclude that nickel provided high catalytic performance in hydrogenation and ring-opening reaction that converted multi-ring aromatics into mono-aromatics. Saeaeh (2012) also revealed that Ni/HMOR provided a high production of benzene, toluene and xylenes, and Ni/HBETA highly produced naphtha and saturated hydrocarbons. In addition, nickel supported on KL, HMOR and HBETA reduced the sulfur contents in tire-derived oil. However, the role of nickel supported on those zeolites on the species of mono-aromatics, poly- and polar-aromatics have not been clearly identified.

According to the above background, the core-shell composite of HY-zeolite and mesoporous MCM-41 and the core-shell composite of HBETA and MCM-41 are expected to be able to reduce large polycyclic aromatics and increase petrochemical products in tire-derived oil from pyrolysis of waste tire. Bulky hydrocarbons, which have larger sizes than the pore size of a zeolite, might be able to be cracked in MCM-41 shell. Smaller hydrocarbons, which are the cracking products of MCM-41 shell, later diffuse to the zeolite core to be further cracked to even much lighter hydrocarbons and valuable mono-aromatics. The types of mono-aromatic products are governed by the zeolite type. Likewise, HY and HBETA zeolites have the high potential to produce valuable mono-aromatics, and reduce sulfur contents in tire-derived oil. Therefore, using MCM-41 as a shell and HY as a core should be able to enhance the production of valuable mono-aromatics, especially benzene and ethylbenzene, and decrease bulky polycyclic aromatics in tire-derived oil. In addition, using MCM-41 as a shell and HBETA as a core might be able to enhance the production of value mono-aromatics, especially benzene and toluene, and also reduce heavy polycyclic aromatics in the tire-derived oil. The aims of this work were to investigate the effect of different zeolites (HY, HBETA) core of the core-shell composite materials on the species of waste tire pyrolysis products, and to investigate the effect of nickel supported on zeolites (HMOR, HBETA, KL, HY, HZSM-5) and mesoporous MCM-41 on the species of waste tire pyrolysis products.