CHAPTER I
INTRODUCTION

From the past to the present, waste tire elimination has been an important problem because the tires are highly stable in chemicals and environments. Pyrolysis is a thermal degradation method of waste tires that is a more effective process than other waste tire elimination methods because it can not only eliminate the waste tire but also recover usable products; so, waste tire pyrolysis is widely used in nowadays. The waste tire pyrolysis can produce three parts of products consisting of gases, oils and char. The interested product is pyrolysis oil that can be fractionated according to boiling points into gasoline, kerosene, gas oil, heavy gas oil, light vacuum gas oil, and heavy vacuum gas oil. Furthermore, some components in gas and oil can be used as chemicals such as methane, light olefins (ethylene and propylene), mixed-C_4, BTX, styrene, limonene, etc. Two noticeable compositions are propane and butane that can be used to be LPG fuels. Solid product or char can be directly used as fuels, or also used to be additive or adsorbent application.

Noble metal-loaded catalysts can play an important role for upgrading waste tire pyrolysis products, resulting in a high quality and quantity of desired products. Generally, noble metals have high ability for hydrogenation, dehydrogenation, hydrogenolysis, cracking, ring-opening, etc., depending on the nature of each metal, resulting in a high gas production. For examples, Dũng (2009) revealed that platinum-loaded catalysts were selective to produce kerosene fraction in oils. Furthermore, platinum-loaded catalysts can also increase polar-aromatic reduction due to low light olefins production that olefins were intermediates for aromatic formation. Pintoo (2008) revealed that palladium-loaded catalysts can highly produce saturated hydrocarbons and slightly produce aromatics in oils. Palladium-loaded catalysts were selective to produce kerosene fraction in oils. Furthermore, methane, ethylene, ethane and C_{5+} yields were also increased. Choosuton (2007) and Dũng (2009) revealed that ruthenium-loaded catalysts were highly selective to produce light olefins in the gas products, and gasoline and kerosene fractions in oils. Furthermore, poly- and polar-aromatics were enormously reduced. For rhodium-loaded catalysts, Pinket (2011) revealed that rhodium was selective to produce methane, ethane and propane in gas products and mono-aromatics in oils. Moreover, di- and poly-aromatics in oils were also reduced. Wehatoranawee and Jitkarnka (2010) found that silver-loaded catalysts were selective to produce cooking gas and saturated hydrocarbons in oils and non-selective to produce aromatic hydrocarbons in oils. Additionally, the catalysts can also reduce polar-aromatic and asphaltene contents in oils. Dũng (2009) and Mahanin (2011) showed that rhenium-loaded catalysts were selective to produce aromatics in oils, especially mono-aromatics, by reducing di- and poly-aromatics in oils, and asphaltene content as well. Rhenium-loaded catalysts can also enhance sulfur reduction in oils.

For catalysis applications, copper catalysts are widely used to catalyze the selective hydrogenation of organic compounds, which are similar to nickel (Ni), ruthenium (Ru), palladium (Pd), palladium-silver (Pd-Ag), and palladium-gold (Pd-Au) catalysts used in the refining and petroleum industries (Marcilly, 2003). For example, Cu catalysts were used to hydrogenate unsaturated hydrocarbons into mono-ene hydrocarbons as reported by Setiawan and Cavell (1995), Moyes *et al.* (2002), and Bridier *et al.* (2010). Furthermore, copper based adsorbents can be also used in sulfur removal applications of liquid fuels.

Similar to Ga/ZSM-5 and Pt/KL catalysts in the refining and petroleum industries (Marcilly, 2003), Zn/ZSM-5 catalysts are widely used to catalyze the aromatization of light alkanes. For examples, Zn/ZSM-5 catalysts were found to produce aromatics (BTX) from propane (Fu *et al.*, 1995; Berndt *et al.*, 1996a). The catalysts gave a high conversion of propane and a high selectivity of BTX. Du *et al.* (2005) revealed that zinc species in Zn/SBA-15 catalyst had dehydrogenation properties that can generate olefins as intermediates of aromatic formation, like a Diels-Alder type reaction. Furthermore, zinc species were used for sulfur removal applications as well.

As mentioned above, copper has hydrogenation properties; so, if the copper-loaded catalysts are used in waste tire pyrolysis, the catalysts might increase the yields of cooking gas and light oil fractions. On the other hand, zinc has dehydrogenation properties; so, similar to some noble metals, zinc-loaded catalysts might promote light olefin production and/or mono-aromatic production. Furthermore, copper- and zinc-loaded catalysts might reduce sulfur content in oils because both copper and zinc are widely used as adsorbents in sulfur removal applications. In this study, the objectives were therefore to investigate the effects of copper and zinc over supports (KL, MOR, BETA and Y) on waste tire pyrolysis products.