CHAPTER I
INTRODUCTION

Tires were discovered and first used in the 1880's. Since then, tires become popular have been used worldwide. Tires were used in several vehicles such as bicycle, car and aircraft for smooth, quiet, and safe ride. Tires consist of different materials such as rubber, fabric, carbon black, fillers, and additives which are not recycle easily. Moreover, tires are non-biodegradable material. When economy and population grow, people buy more cars or other vehicles. And, this leads to an increase in the production of tire. So, the amount of waste tires increases every day.

Waste tire causes many of the environmental, economical, and health problems. Tires take up large spaces of valuable landfill, and provide breeding sites for mosquitoes. Moreover, tire fire produces pollutants which are harmful to human health. For sustainable management of waste tires, incineration or landfill method shall be avoided. There are several methods for eliminating tires such as retreading (Purcell, 1978), grinding (Liang *et al.*, 2000) and reclaiming (De *et al.*, 2006). But, pyrolysis is the most interesting method because it can convert waste tires to fuels.

Pyrolysis is the thermal decomposition of organic materials to lower molecular weight compounds in the absence of oxygen. In addition, pyrolysis not only solves the disposal problems of waste tire, but also solves the shortage of fuels. The major pyrolysis products are gas, char, and oil. The gas has high calorific values around 30-40 MJ m^{-3}, and contains methane (CH_4), ethane (C_2H_4), ethene (C_2H_4), propane (C_3H_8) and other hydrocarbons. So, pyrolysis gas is used in a process plant (Laresgoiti *et al.*, 2000). The char is used as a low-grade activated carbon (Zabaniotou and Stavropoulos, 2003) and carbon black (Cunliffe and Williams, 1999), whereas the oil is used as a fuel substitute for combustion in a boiler (Williams and Brindle, 2003; Cunliffe and Williams, 1998).

Many researchers studied about tire derived oils, and they found that pyrolysis oil has a high concentration of valuable aromatics such as benzene and toluene used as petrochemical feedstock in chemical industry (Cunliffe and Williams, 1998; William *et al.*, 1998; Laresgoiti *et al.*, 2004). For the comparison between oil from tyre pyrolysis and petroleum naphtha, it was found that pyrolysis oil had higher octane number and levels of sulfur and nitrogen than petroleum naphtha. So, pyrolysis oil has to be hydrofined and reformed (Benallal *et al.*, 1995). Moreover, pyrolysis oil blended with petroleum diesel fuel at 5, 10, 25 and 35 % can be used in diesel engines without engine modification (Ilkilic and Aydin, 2011). Products from pyrolysis process without a catalyst such as oil still have complexity in composition, and contain high poly-aromatics hydrocarbons (PAHs). Because of these reasons, products from pyrolysis process have low cost and quality.

For improving pyrolysis products, a catalyst plays an important role. Catalytic pyrolysis of waste tires is an effective way to improve the product yields and reduce undesirable products. This technique depends on properties such as the pore size, selectivity and activity of catalyst. Elordi *et al.* (2009) studied the catalytic pyrolysis over zeolite catalysts (HZSM-5, HY and H-Beta), and found that small pore size such as HZSM-5 gave the highest yield of light olefins. Boxieng *et al.* (2007) found that USY gave higher total concentrations of single ring aromatics in oil due to its large pore size. Miguel *et al.* (2006) studied the pyrolysis of waste tire by using ZSM-5, Al-MCM-41 and Al-SBA-15. They found that mesostructured catalysts gave selectivity of single ring aromatic compounds due to their weaker Lewis acid and larger pore size. Fan *et.al.* (2005) studied an binary zeolite catalysts (HBETA/HZSM-5, HMOR/HZSM-5 and SAPO-11/HZSM-5), and they found that adding HBETA and HMOR with SAPO-11/HZSM-5 increased hydroisomerization and aromatization reactions, which led to an improvement in the quality and quantity of liquid yield.

Ingeneral, a bifunctional catalyst is composed of a metal supported on a zeolite. This type of catalysts is interesting because it takes the advantages from both metal and support. Noble metals such as Palladium (Pd), Platinum (Pt), and Ruthenium (Ru) have high activity in hydrogenation and ring opening reaction (Dung *et al.*, 2009). In 2007, Choosuton studied noble metals (Pt, Pd, and Ru) supported on zeolites (USY, Beta, MOR, and KL). The results showed that the products from bifunctional catalysts gave higher quality of gasoline, kerosene, and diesel due to the reduction of polyaromatics. Cobalt (Co) is a non-noble metal which can be used for catalytic pyrolysis process like noble metals. Moreover, Co has low cost availability, and also had high activity. In 2006, Pedrosa *et al.* studied about Co supported on HY zeolite. They concluded that Co gave higher activity and selectivity in the hydrogenation of paraffin isomerization than Nickel (Ni). In 2010, Pinket used Co supported on KL zeolite. She reported that 5 %Co/KL gave higher single-sing aromatics production than 1 %Rh/KL and 20 %Ni/KL.

The purpose of this research was to investigate Co supported on different zeolites (HY, HBETA, HMOR, HZSM-5 and SAPO-34) on the quality of tire pyrolysis products, especially on mono-aromatics production, and to investigate the effect of the addition of mesoporous SAPO-34 zeolite as an additive in pyrolysis of waste tire. Pyrolysis of scrap tire was performed in a bench-scaled autoclave reactor with a heating rate of 10 min/°C. The temperature in pyrolysis zone and catalytic zone were fixed at 500 °C, 350 °C. Particle size of tires, the ratio of tire per catalyst, holding time, and N_2 flow rate in this experiment were fixed at 25 %, 8-18 mesh, 30 min, 30 ml/min, respectively.