



## CHAPTER I

### INTRODUCTION

The world production of waste tire is approximate  $6 \times 10^6$  tons/year, and nearly 70% of these wastes are simply dumped in an open or in the land fill (Galvagno *et al.*, 2002). This, together with the fact that tires are designed to be resistant to chemical, biological and physical degradation, has been causing serious environmental problems. Owing to the low bulk density, they occupy large volumes and, if buried, disrupt the integrity of landfill sites. Moreover, fires at tire deposits are very difficult to control, and generate high levels of pollution to the soil, atmosphere, and waters (San Miguel *et al.*, 2006).

In many countries, the environmental regulations concerning the waste tire are becoming more and more stringent. This waste hierarchy favors the valorization and recycling alternatives. Thus, over recent years, tire pyrolysis, a recycling process, has attracted renewed significant attention. It essentially involves decomposition of the tire components by exposure to high temperatures in the absence of oxygen. The result is a carbonized char, condensable oil, and a gas fraction. The char can be used as low-grade carbon black, as a solid fuel, or may be upgraded to activated carbon (Williams and Brindle, 2003), whereas the gas contains mainly hydrocarbons ( $C_1$ -  $C_5$ ), hydrogen with a relative high content (Barbooti *et al.*, 2004), and a low concentration of  $H_2S$  (Berrueco *et al.*, 2005). The tire-derived oil is a complex mixture of hydrocarbons with a high amount of aromatics (Cunliffe and Williams, 1998).

The tire-derived oil was reported to have a high calorific value of about 41-44 MJ/kg (Cunliffe and Williams, 1998). In addition, its property is similar, to a certain extent, to that of commercial petroleum naphtha (Benellal *et al.*, 1995). When it was used as a fuel by mixing with a reference fuel in a diesel engine, a reliable operation could be achieved up to 70% of this oil in the blend (Murugan *et al.*, 2009). However, higher smoke, hydrocarbon (HC) and CO emissions were recorded. Also, oil sticking was occasionally found on the nozzle stem and sac. These phenomena were believed to come from the high concentration of aromatics, especially the high concentration of polycyclic HCs (Murugan *et al.*, 2009). In addition, there are considerable amounts of sulfur-containing compounds such as thiophene, benzothio-

phene, and their derivatives found in the tire-derived oil (Williams and Bottrill, 1995; Pakdel *et al.*, 2001), then limiting its applications as a direct-usable fuel due to the serious problem of SO<sub>2</sub> emission and a decrease in the efficiency of the engine. Unfortunately, no study has been found so far on dealing with aromatic reduction, particularly poly- and polar-aromatics (PPAHs) in order to make the tire-derived oil applicable as a high quality fuel. Instead, the catalytic pyrolysis of waste tire has sometimes been focused on the possibility of aromatic production. Williams and Brindle (2002, 2003) investigated the pyrolysis of waste tire using ZSM-5 and Y zeolites with different Si:Al ratios and pore diameters to see the influences of zeolite structure, catalyst temperature, and catalyst-to-tire ratio on the yield and compositions of the tire-derived oil. Boxiong *et al.* (2007) studied the effects of USY and ZSM-5 on the compositions of the light fractions. Overall, higher aromatic concentrations could be obtained with using zeolites having higher acidity and larger pore diameter, and also with higher catalyst-to-tire ratios.

Bifunctional catalysts have been extensively studied for the reduction of aromatics in fuel (Lugstein *et al.*, 1999). Metals can catalyze the hydrogenation of the feedstock, making it more reactive for cracking and removing heteroatoms (sulfur, oxygen) (Ali *et al.*, 2002). And, a high level of aromatic hydrogenation at moderate hydrogen pressures can be achieved with noble metals catalysts (Eliche-Quesada *et al.*, 2006). This intrinsically-high hydrogenation activity might also help reducing steric effects that impede the direct elimination of the sulfur heteroatom (Pecoraro and Chianelli, 1981) in the hydrodesulfurization (HDS). However, noble metals display a low resistance to sulfur poisoning, thus limiting their applications. The sulfur tolerance of a noble metal-supported catalyst may be enhanced by (i) using acidic carriers (Barbier *et al.*, 1990), (ii) changing the metal particle size, or (iii) alloying with other metals (Lee and Rhee, 1998). Consequently, the activity of noble metal-supported catalysts depends strongly on the type of the support (Onyestyak *et al.*, 2002), the metal dispersion, and also the metallic nature (Castellon *et al.*, 2004).

The purpose of the present work is to investigate the influences of various noble metal supported catalysts on the yields and nature of the products obtained from waste tire pyrolysis. Particular focus is placed on the reduction of poly- and polar-aromatics for light oil production.