



CHAPTER I

INTRODUCTION

Pyrolysis gasoline or pygas is an intermediate boiling-point byproduct of olefin production by naphtha steam cracking. Generally, pygas composes of 70–80 wt% aromatics and is subjected to solvent extraction to separate aromatics from the balanced non-aromatic hydrocarbons. The aromatic compounds obtained from pygas by using extractive distillation are separated as benzene, toluene, xylenes, and heavy C_9^+ aromatics according to their boiling points (Choi *et al.*, 2006). Particularly, a C_9^+ aromatics fraction possesses less industrial values, thus, it is usually being blended into gasoline pool to enhance its octane number. However, recent specifications for gasoline drastically limited its aromatics content resulting in increasing aromatics available for BTX production. Due to the increasing BTX demand C_9^+ aromatics become the new source of BTX. Recently, there have been commercial technologies to add more value of C_9^+ aromatics by converting them into xylenes via dealkylation (complete or partial removal of alkyl groups), transalkylation (transfer of alkyl groups between different molecules), and disproportionation (re-arrangement of alkyl groups between two identical molecules, such as toluene) reactions which have been developed by many companies such as UOP (TAC 9TM), ExxonMobil (TransPlusSM), SK Corporation (APUSM), etc. In order to develop a new technology to upgrade C_9^+ aromatics, hydrogenolysis is an attractive route. Hydrogenolysis is the catalytic chemical reaction whereby the molecule of H_2 is added over a C-C bond or C-hetero atom bond, effectively causing a lysis of a bond.

The purpose of this work is to study the hydrogenolysis of *para*-methylethylbenzene (*p*-MEB) to *p*-xylene. First of all, ethylbenzene was used as a model feed to investigate the hydrogenolysis reaction over Pt/SiO₂ catalyst. However, the literature revealed that catalysts containing molybdenum oxide (Covini *et al.*, 1965), nickel oxide (Van *et al.*, 1987), and nickel-molybdenum oxide (Jik *et al.*, 1978) are also sufficiently active for this purpose. Therefore, the hydrogenolysis reaction was also studied over Ni/Al₂O₃, Mo/Al₂O₃, and NiMo/Al₂O₃ catalysts under various conditions.

The activity and selectivity of the catalysts were tested in a continuous flow fixed-bed reactor. Many effects such as reaction temperature (350–500°C), liquid hourly space velocity (2–4 h⁻¹), and H₂ to feed molar ratio (4–10) were investigated over the commercial NiMo/Al₂O₃ catalyst. Moreover, the synthesized Ni/Al₂O₃, Mo/Al₂O₃, and NiMo/Al₂O₃ catalysts were also studied in order to compare the catalytic activity with the commercial one. The optimum condition from hydrogenolysis of ethylbenzene was then applied for the study of hydrogenolysis of *p*-MEB.