



CHAPTER I INTRODUCTION

The combination of less available petroleum reserves, increased oil price, and increased awareness of environmental impact has drawn the attention to renewable energy sources as replacements of conventional petroleum-derived fuels. Fatty acid methyl esters (FAMES), known as biodiesel, which is produced through trans-esterification of triglyceride with methanol is one of the most attractive renewable fuel resources (Lopez *et al.*, 2007; Martyanov and Sayari, 2008). Although the biodiesel exhibits a very high cetane number, low sulfur content, high flash point, and the cleanness of the exhaust emissions, its oxidative and thermal instabilities due to the presence of oxygen is a major technical concern (Knothe, 2005; Knothe *et al.*, 2003). Elimination of the oxygen content in the biodiesel would readily improve the fuel stability and enhance its utilization potential. Several processes for deoxygenation, including hydrogenolysis (Brands, 1999), decarbonylation (Kubickova *et al.*, 2005), and decarboxylation (Maki-Arvela *et al.*, 2007) of FAMES have been proposed to transform the biodiesel into the hydrocarbon base fuel.

Generally, the deoxygenation has been carried out on the noble metal catalysts. It has been reported that Pd/C, and CoMo-, and NiMo- supported on Al₂O₃ catalysts are effective catalysts for the deoxygenation of oxygenates compounds (Maki-Arvela *et al.*, 2007; Senol *et al.*, 2007). However, the operating total pressure is generally high, to facilitate the interaction between the oxygenates and the metals, and to achieve a high activity of deoxygenation. To reduce the severity of the operation, several attempts have been made to utilize the zeolites to transform the oxygen-containing molecules under atmospheric pressure.

Extensive studies have shown that the ZSM5 zeolite catalyst is a selective catalyst for the transformation of a variety of raw materials, for instance alcohol, acid, ketone, and aldehyde to hydrocarbons. The hydrocarbons obtained from the reactions are paraffins and olefins, with substantial amounts of aromatics. The different reactivities of the oxygenate compounds on the H-ZSM5 catalyst has been investigated. It was reported that acids are more significantly reactive than aldehydes

and ketones (Gayubo *et al.*, 2004). The hydrocarbons are mainly formed through decarboxylation and dehydration. While the deoxygenation of alcohol, acid, aldehyde and ketone is fully studied and understood, but the studies with biodiesel (methylesters) is limited.

Therefore, in this work, the conversion of methyl octanoate, a model of biodiesel fuel over the H-ZSM5 zeolite was investigated for the production of hydrocarbon base fuels. The study of the methyl ester was carried out in the gas phase at 773 K under atmospheric pressure and was discussed in Chapter IV. The reaction pathways also were clarified. Also, the product distribution from the methyl octanoate ester was compared to that from an alkane with the same chain length (n-octane). The interesting correlations between non-aromatic yields and aromatic yields were observed when the different feed was used. As reported by others (Biscadi and Iglesia, 1999) that the addition of zinc cation would facilitate the aromatic formation, the deoxygenation of the methyl octanoate over the Zn/H-ZSM5 catalyst was investigated in Chapter V.

Although the H-ZSM5 showed the excellent activity on the aromatization of the methyl octanoate, the yields of cracking products was still high due to its high acid strength. Therefore, the second part of this project would be discussed about the deoxygenation of the methyl octanoate over CsNaX zeolite catalysts, a basic catalyst. As summarized in Chapter VI, the detailed study of the deoxygenation of the methyl ester included the effects of solvent and carrier gas. The role of cesium was also discussed. Several characterization techniques; such as temperature programmed techniques (TPD, TPR_x, TPR, and TPO), were carried out to investigate the reaction pathways and surface chemistry.

To sum up, the overall conclusions from the study of the methyl octanoate conversion and some recommendations are summarized in Chapter VII.