CHAPTER I
INTRODUCTION

Aromatics, including benzene, toluene, ethylbenzene, and xylene are widespread used as feedstocks for numerous chemical industrial processes. Normally the catalytic reforming of heavy naphtha and aromatization of light paraffins are the main routes for producing aromatics (Ransley *et al.*, 1978). Nevertheless, both processes relied on the nonrenewable resources of crude petroleum oil and coal. Due to the depletion of fossil fuel resources and the rising of environmental concern, the possibility to use sustainable sources has gained more attention. There are various alternative sources, reported as feedstock for producing aromatics, including but not limited to methanol (Niu *et al.*, 2014), ethanol derived from biomass (Borght *et al.*, 2015), and isobutyl alcohol (Yu *et al.*, 2012). However the possibility to economically apply these processes is still a matter of dispute.

During the last 10 years, many research attempts have been devoted to the production of biofuels. Among them, biodiesel from transesterification of vegetable oil is one of the most preferred alternative fuels and the consumption rate has been increased significantly (Chew *et al.*, 2008). As a consequence, the finding solution to eliminate the upcoming increase in waste by–products has also been a top priority in biodiesel industry. In order to make the biodiesel competed economically with petroleum diesel; the by–product from the biodiesel production has been interested as an alternative feedstock for producing chemicals. In this work, we focus on two types of biodiesel by–product; palm fatty acid distillate (PFAD) and glycerol. Palm fatty acid distillate (PFAD) is a by–product from the steam distillation of crude palm oil while glycerol is a by–product from the transesterification to produce biodiesel.

Herein, we reported the conversion of palm fatty acid distillate (PFAD) and glycerol to aromatics. Due to its shape selectivity and suitable acid properties, HZSM–5 catalysts showed the superior catalytic performance in converting biomass derived feedstock to aromatics (Yu *et al.*, 2012). Broadly speaking, the incorporation of Zn on HZSM–5 catalyst significant improves aromatics yield by promoting the dehydrogenation activity. The presence of different Zn species on Zn/HZSM–5 catalysts was proved to strongly depend on the preparation methods (Berndt *et al.*, 1996). The aqueous phase ion–exchange of solution zinc salt with HZSM–5 catalysts would lead to two types of zinc at exchange sites: $ZnOH^+$ at isolated Al center and at two closely located Al centers. Under high reaction temperature the dehydroxylation over later species resulted in the exchangeable Zn^{2+} species (Biscardi *et al.*, 1998). In addition, by using incipient wetness impregnation method not only zinc at exchange site but also ZnO was found (Almutairi *et al.*, 2012). Many researchers have summarized that in contrast with ZnO, Zn at exchange site cannot be completely reduced even at 900 °C. Despite that, Triwahyono and co–workers showed that the thermal treatment of Zn/HZSM–5 under hydrogen atmosphere resulted in the recovery of protonic acid site, enhancing the isomerization of *n*–pentane (Triwahyono *et al.*, 2011). For a decade that many researchers have attempted to identify which types of Zn species that enhanced the aromatization reaction. However, the understanding is still under controversy.

On the whole, this research was divided into four parts. Part I and II have been devoted to investigate the effect of the conventional Zn species, $(ZnOH)^+$ and ZnO species, in the transformation of glycerol and palm fatty acid distillate (PFAD) to aromatics. The evolution of the conventional Zn species, $(ZnOH)^+$ to the new active Zn species, was studied by pre–treating Zn/HZSM–5 catalysts under high temperature of inert and hydrogen atmosphere. The generation of the new Zn species was also tested for its activity in the conversion of *n*–pentane to aromatics, illustrated in part III. Even though the purpose of this research is to enhance the aromatics yield, among the aromatics compound, *p*–xylene is very considerable because of its increase in demand for producing terephthalic acid, feedstock for producing polyester fibers and plastic bottles. Thus the designing of catalyst that provides the highly selective of *p*–xylene formation was also studied in this work. In the final part (part IV), the understanding from the previous parts was applied to design the Zn promoted HZSM–5 catalysts that exhibited the highly selectivity in the transformation of *n*–pentane to *p*–xylene. EXAFS, XANES, and XPS were used to investigate the formation of different Zn species.