CHAPTER I
INTRODUCTION

Aromatic hydrocarbons, in particular BTX (Benzene, Toluene, and Xylenes), are important starting raw materials for a wide range of consumer products and commercially valuable products in the petrochemical industry. Not only can they perform as octane boosters to enhance the performance of gasoline, but also they can be used as a feedstock for plastics manufacture or as commodity chemicals. At present, the basic commercial processes for aromatic hydrocarbon production are solid-fuel (coal and shale oil) process, pyrolysis, and catalytic reforming (Ni *et al.,* 2010), of which the feedstock is derived from petroleum. However, the petroleum resources are limited, and also their combustion increases CO_2 emission into the atmosphere. Therefore, great attention has been paid to biomass as an alternative resource instead of petroleum because it is a renewable resource and more environmentally friendly.

Bioethanol is the ethanol directly obtained by biomass fermentation. It can be converted to more valuable hydrocarbon compounds like ethylene, C_{3+} olefins, and aromatics. The catalytic transformation of bioethanol to aromatics is one of the routes for upgrading cheaper raw materials (low molecular weight alcohol, bioethanol) to more expensive products (specifically aromatic hydrocarbons). In recent years, many researches related to the aromatization of ethanol using the H-ZSM-5 as a catalyst have been investigated, and it was found that the formation of aromatics was greatly occurred when the H-ZSM-5 zeolites with low Si/Al_2 ratio were used, and operated under high temperature condition (Inaba *et al.,* 2005; Brathos *et al.,* 2006; Makarfi *et al.,* 2009). However, further studies mentioned that the modification of H-ZSM-5 zeolite by the incorporation of metal, metal oxides, and metal carbide such as Ga, Zn, and Mo_2C, etc, can increase the rate and selectivity of aromatization reaction as well as can enhance the lifetime of catalysts (Saha and Sivasanker, 1992). For example, Saha and Sivasanker reported that the use of a ZSM-5 (SiO_2/Al_2O_3 = 82) doped by Zn and Ga can increase the yield of liquid products, the aromatic content, and also the lifetime of Zn- and Ga-catalysts. In addition, the enhancement of aromatic formation using two beds of catalysts was investigated

(Brathos *et al.,* 2006). The researchers mentioned that it was a very effective procedure, especially using the pure ZSM-5 as a catalyst in the first bed and the ZSM-5 combined with 2% Ga_2O_3/ZSM-5 as a catalyst in the second bed.

Moreover, the associated reactions with bioethanol conversion to aromatic hydrocarbons are very complicated because dehydration, cracking, oligomerization, cyclization, hydrogen-transfer, and aromatization can be simultaneously occurred. According to a theory, bioethanol is firstly converted to ether, ethylene, and/or some light olefins. The main products depend on the catalysts used and operating conditions. Subsequently, ethylene and some olefins formed are finally converted to aromatics. Therefore, ethylene is one of the essential intermediates for the aromatics formation in the dehydration process of ethanol. In the previous work, the deposition of different additives, such as ZnO, Ga_2O_3, and Mo_2C, over ZSM-5 markedly promoted the ethylene aromatization from ethanol (Brathos *et al.,* 2006). Besides aforementioned, the several factors affecting to catalyst stability were also considered. A hybrid catalyst was responsible for significantly higher aromatization activity when compared to the mono-component of parent H-ZSM-5 zeolite. The results of Le Van Mao *et al.,* (1997) confirmed that the hybrid catalysts containing Zn or Ga species supported co-catalysts led to more activity, selectivity, and stable catalysts than the parent ZSM-5 zeolite.

The aim of this research was to study the transformation of bioethanol to aromatics using sets of two consecutive beds of catalysts. The dehydration of bioethanol to olefins such as ethylene was expected to occur at Bed #1 of $MgHPO_4$-doped activated alumina, which was used as a catalyst for all of experiments. The aromatization of olefins to aromatics (especially, BTX) was expected to take place at Bed #2 of modified H-ZSM-5 catalysts. The aromatization activity and the aromatics selectivity of catalysts, modified H-ZSM-5 zeolite (ZnO- and Ga_2O_3- supported H-ZSM-5) and hybrid catalysts (zinc oxide/aluminum oxide co-precipitate mixed with H-ZSM-5 zeolite), was investigated. Finally, the economics of a proper process designed for bioethanol conversion to aromatics using a set of double bed catalysts was evaluated.