CHAPTER I
INTRODUCTION

Ethylene is widely used in petrochemical industries. It is a major chemical intermediate used in the production of polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS), polyethylene terephthalate (PET), ethylene oxide, ethylene dichloride, etc. Generally, more than 98% ethylene is mainly produced (Morschbacker, 2009) by the steam cracking of the petroleum liquids (naphtha, condensate and gas oils) and natural gas (ethane, propane and butane) feedstocks. Furthermore, it can be produced from the fluid catalytic cracking of heavier oils, heavy gas oil or vacuum gas oil. However, crude oil and natural gas used as raw materials for both petroleum and petrochemical industries have been more scarce and have high price; therefore, alternative sources for the production of ethylene become more interesting.

The catalytic dehydration of bio-ethanol has become more and more competitive and attractive route to produce ethylene because of some advantages, such as the reduction of CO_2 emission (Takahara *et al.*, 2005), low production cost and energy consumption when compared with the traditional routes. Bio-ethanol can be obtained easily by the fermentation of a sugar source, mainly sugarcane juice, molasses, cassava, and starch from corn grain or renewable biomass. Bio-ethanol is catalytically dehydrated to ethylene. Two reactions can occur in parallel during catalytic dehydration of bio-ethanol to ethylene (Chen *et al.*, 2007): $C_2H_5OH \rightarrow C_2H_4 + H_2O$ (intra-molecular dehydration), and $2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O$ (inter-molecular dehydration). The main reaction and side reaction are endothermic and exothermic, respectively. At low temperatures, diethyl-ether is produced by the inter-molecular dehydration of bio-ethanol; however, high temperatures favor the intra-molecular dehydration of bio-ethanol to ethylene.

An efficient catalyst is an important key for the catalytic dehydration of bio-ethanol to ethylene process. Many catalysts have been studied for the catalytic dehydration of bio-ethanol to ethylene. These catalysts are phosphoric acid (Pearson, 1983), activated alumina (Wu and Marwil, 1980; Kojima *et al.*, 1981; Doheim *et al.*, 2002; Chen *et al.*, 2007), transition metal oxide (Zaki, 2005), heteropolyacid

(Vazquez *et al.*, 2000; Varisli *et al.*, 2007; Potter *et al.*, 2010; Bokade and Yadav, 2011) and zeolites such as H-Mordenites, H-ZSM-5, H-beta (Oudejans *et al.*, 1982; Aguayo *et al.*, 2002; Takahara *et al.*, 2005; Arenamnarta and Trakarnpruk, 2006). Especially, the catalysts based on alumina are the most efficient catalysts for bio-ethanol dehydration, and are used the most in industrial production (Teng *et al.*, 2009). Kojima *et al.*, (1981) reported that an alumina catalyst modified with magnesium phosphate can improve both the conversion of ethanol and the yield of ethylene (96 mol% and 94 mol%, respectively). Moreover, the alumina catalyst having magnesium phosphate exhibited a higher catalytic stability after being conducted for 1,500 hours for the production of ethylene. The most well-known representative of catalysts based on activated alumina is **SYNDOL** with a main composition of $MgO–Al_2O_3/SiO_2$, developed by Halcon Scientific Design Company. This catalyst has been applied commercially for ethanol dehydration to ethylene, and carried out at 340–450 °C with a LHSV (liquid hourly space velocity) of 0.7 h^{-1} (Huang, 2010). At start of run, the conversion of ethanol and the selectivity of ethylene are typically about 99% and 97%, respectively (http://www.chematur.se). The lifetime of Syndol is predicted to about 2 years (Koh, 1993).

For the commercial processes and plants, Halcon Scientific Design Company designed ethanol dehydration technology to produce ethylene in the 1980s, currently owned by Chematur Engineering AB. Recently, Braskem has introduced a new ethylene plant that uses ethanol produced from sugarcane as the feedstock. It is the first large-scale ethylene project to use 100% renewable raw materials with the capacity 200,000 tons per year, and it is also the first commercial-scale green ethylene plant in the world. Braskem invested approximately $278 million on the plant (http://www.chemical–technology.com).

The purposes of this work were to investigate and verify the catalysts based on alumina in terms of conversion, selectivity, feed flexibility and operating conditions, to perform the economic evaluation of two commercial plants for ethylene production via catalytic dehydration from bio-ethanol, and to analyze and compare the two commercial plants in terms of advantages/disadvantages of process, investment, and economic viability.