CHAPTER I
INTRODUCTION

One of the biggest problems of the world is the energy crisis. Fossil fuels have been used from the past to now. Thus, the amounts of fossil fuels have decreased simultaneously. Not only have the amounts of the fuels decreased but also pollutions have occurred from using them. There are many renewable resources such as biomass, wind power, solar energy. Ethanol is the one key product from the fermentation of a biomass such as sugar or cellulosic materials that can be produced abundantly. In Thailand, the main usage of ethanol is to blend with gasoline to produce E10, E20 and E85. The ethanol for blending with gasoline has to be refined to reach the purity of 99.5%.

The major problem of ethanol nowadays is the surplus of production. The new ways to utilize ethanol are to convert ethanol to hydrocarbons. There are many research reports in this area. Heterogeneous catalyst is the major catalyst to convert ethanol to gaseous and liquid hydrocarbons. H-ZSM-5 was a widely-used zeolite for the dehydration of ethanol. Talukdar et al. (1997) doped the various noble metals to H-ZSM-5 in order to study the effects of temperature, SiO_2/Al_2O_3 ratio, percentage of Al_2O_3 binder and the percentage of ethanol feed. They found that the high percentage of Al_2O_3 binder (80%) and high temperature (723 K) yielded the light olefin products. The propylene production from bio-ethanol conversion was investigated by Furumoto et al. (2011). They introduced Ga and Fe in the framework of HZSM-5. The (Ga) HZSM-5 gave a high selectivity to propylene, but (Fe) HZSM-5 gave a high selectivity to ethylene. Some researchers can convert ethanol to heavy hydrocarbons such as aromatic products. Inaba et al. (2006) revealed that Ga and Au can improve xylene and benzene production, respectively. Viswanadham et al. (2012) studied the effects of particle size and Si/Al ratio of HZSM-5. They revealed that the aromatic selectivity was increased on the nano-sized particle of HZSM-5. Most liquid products contained aromatics such as benzene, toluene, and xylene (BTX). The heavy product and coke formation were limited by a medium pore size of HZSM-5. HFAU and HBEA dehydrated the ethanol to C12+ hydrocarbons at the time on stream of 0.8 h. But, at 10 h time on stream, the C12+ hydrocarbons were absent, and the catalysts yielded almost ethylene (Madeira et al., 2009). Moreover, Gu et al. (2012) have investigated the different effects of HZSM-5, H-Beta, HY, nano HZSM-5, HZSM-11 and nano HZSM-11 on glycerol dehydration to acrolein reaction. They found that nano HZSM-11 showed the best performance in glycerol dehydration (81.6% conversion) to acrolein (79.4% selectivity). In the same way as Zhang et al. (2010), the aromatic product was obtained the most when the aromatization and isomerization of 1-hexene occurred on HZSM-11.

Doping metals, semi-metals and non-metals to a zeolite to improve the activity of the reaction has been investigated. The doped elements can be divided into many forms; however, the oxide form is one of useful forms. The 5A oxides (P_2O_5, Sb_2O_5 and Bi_2O_5) are acidic oxide. H-ZSM-5 doped with these oxides showed the improvement of C10+ aromatic products (Pasomsub, 2013). Doping Bi_2O_5 on H-ZSM-5 showed the highest selectivity of C10+ aromatics (45%) compared with the pure H-ZSM-5 (12%). Moreover, Wongwanichsin (2013) also revealed that the dehydration of ethanol on antimony oxide-doped SAPO-34 showed a great yield of C10+ aromatics as well.

From the aforementioned, the acidic oxides of group 5A, which are P_2O_5, Sb_2O_5 and Bi_2O_5, doped on H-ZSM-5 can help to improve the C10+ aromatic products. However, the moderate and small pore sizes of zeolite such as HZSM-5 and SAPO-34 can limit the formation of large molecules of products. So, the zeolites, which are HBEA and HY, with large pore sizes were aimed to enhance the production of longer chain hydrocarbons such as those in gas oil range. Moreover, the sinusoidal channel of HZSM-5 affected the product distribution as well. So, the influence of straight channel structure of HZSM-11 was investigated to compare with that of sinusoidal channel structure of HZSM-5.