CHAPTER I
INTRODUCTION

Recently, global energy consumption grew by 2.5% in 2011. Especially, Asia economy and energy consumption are grown up rapidly. In addition, crude oil prices have been increased continuously, which was over 100$/bbl. in 2010. The most anxious problem that crude oil from petroleum is a nonrenewable energy should be realized. Hence, alternative energies like biomass energy, wind energy, solar energy, geothermal energy and hydroelectric energy are alternatives to fossil fuel. Biomass is an attractive new sustainable energy. In 2011, 10,000 b/doe (barrels per day oil equivalent) biofuels were produced, which was grown up 0.7% from 2010 (BP, 2012).

In 1970's, ExxonMobil Research and Engineering Company had developed the methanol-to-gasoline process in a commercial scale (ExxonMobil, 2005). Not only is methanol converted to hydrocarbons, but ethanol can also be possibly used. Thailand is an agricultural country that has a lot of raw materials, which is used to produce bio-ethanol by fermentation process. Many researches succeed to produce light olefins and aromatics from bioethanol. Ethanol dehydration over Al_2O_3, H-ZSM-5, or SAPO-34 can produce light olefins, like ethylene (Zhang *et al.*, 2008; Kagyrmanova *et al.*, 2011). Propylene yield from bio-ethanol dehydration was promoted by using modified SAPO-34 physically mixed with metal oxides, or by using ZSM-5 treated with KOH 0.1 M (Wongwanichsin, 2013). Aromatic hydrocarbons can be produced by using medium or large pore zeolite catalysts such as H-ZSM-5, H-Y, H-Beta, etc. (Freeman *et al.*, 2002; Viswanadham *et al.*, 2012; Pasomsub, 2013). However, a few research studies have been made on ethanol-to-gasoline process. Derouane *et al.* (1978) studied the ethanol to hydrocarbons process. Ethanol was converted to ethylene and heavier hydrocarbons products. Liquid hydrocarbons products were mainly comprised of C_5-C_6 hydrocarbons.

The zeolite activity was affected by Si/Al ratio (related to acid strength and acid density), the type and amount of metal in zeolite, catalyst topology, crystal size, and processing conditions, etc. (Niaei *et al.*, 2013). Talukdar *et al.* (1997) studied the effect of SiO_2/Al_2O_3 ratios on the conversion of ethanol. They found a high amount of Bronsted acid sites on the zeolites with low SiO_2/Al_2O_3 ratios tended to convert ethanol to aromatics and paraffins.

Pasomsub (2013) studied two consecutive layers of catalysts for the dehydration of bio-ethanol. The first layer was comprised of 2% Ga_2O_3/HZSM-5. The addition of 2% Ga_2O_3 improved the yield of gas oil, light vacuum gas, and heavy vacuum gas. The second layer consisted of either H-X, H-Y, or H-Beta that promoted the formation of heavy aromatic hydrocarbons, like C_9 and C_{10}^+ aromatics, and the selectivity of p-xylene. The effect of various metal loading was investigated by Wongwanichsin (2013). 5% loading of Ga_2O_3 over SAPO-34 significantly improved the extracted oil yield. The result from 5% loading of GeO_2 over SAPO-34 showed the increasing kerosene and gas oil yields.

Hence, this research work desired to study the effect of Si/Al ratio on bio-ethanol to hydrocarbons reactions. The acid density and the acid strength were adjusted by using zeolites with Si/Al_2 ratio of 27, 37 and 300. The low acid density was expanded to produce heavy hydrocarbons products. The mass transfer and yield of bulky hydrocarbons can be improved in a micro/mesoporous composite. So, the second scope of studies was on the bio-ethanol to heavy hydrocabons conversion over the different pore structures of MSU-S (a type of micro/mesoporous composites). Hexagonal pore structure was formed by cetyltrimethyl ammonium bromide template (CTAB).