



## CHAPTER II

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Bio-ethanol

Bio-ethanol or fermentative ethanol is derived from renewable feedstocks as a resource through biological fermentation process. Resources that contain sugars can be used as a feedstock for fermentation. Many resources that can be used to produce ethanol by fermentation can be divided into three main raw materials (Sanchez and Cardona, 2008) – starch, sugar, and lignocellulosic biomass materials:

1. *Sugar materials.* These materials mainly include sugarcanes and sugar beets.

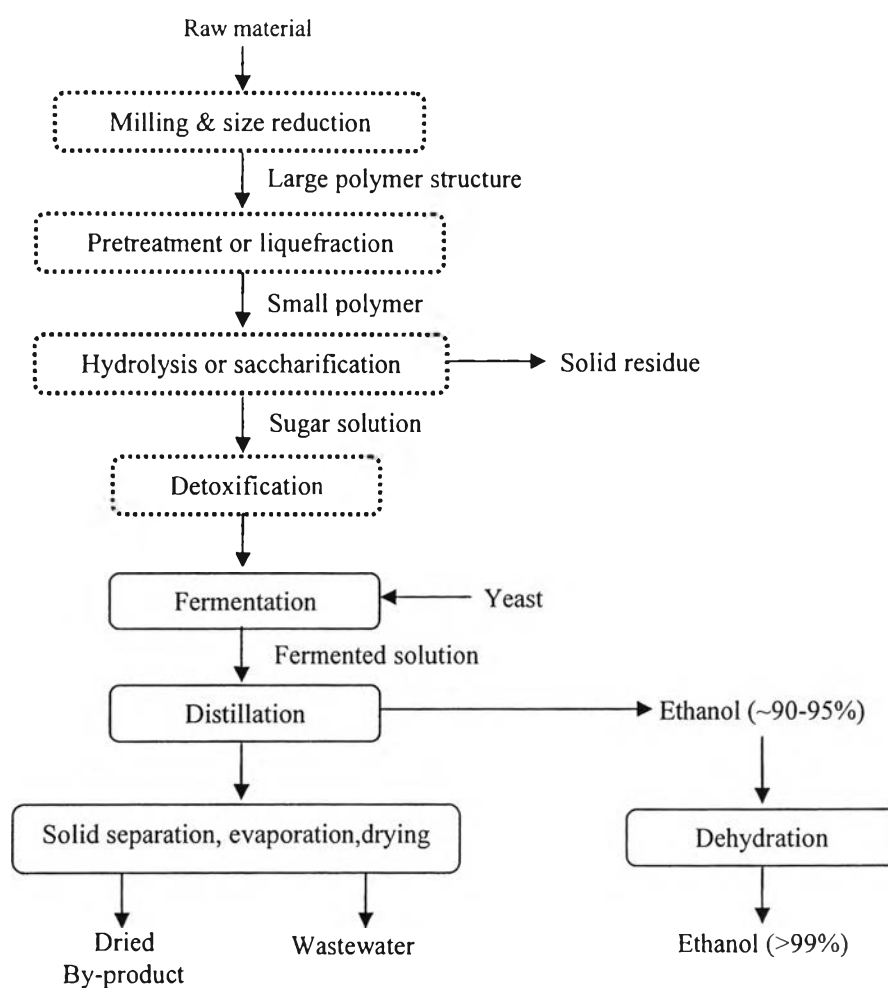
2. *Starch materials.* These materials are the most important raw materials, which can be used for the production of ethanol by microbial strains. Cassava, corn, barley, rice, and sorghum belong to the group of starch materials.

3. *Lignocellulosic biomass materials.* These materials are a promising raw materials for ethanol production. Corn stover, crop stalks, cane bagasse, wood and forestry wastes, wheat straws, paper mill, and sugar-containing-cellulose wastes belong to the group of lignocellulosic biomass materials.

For the process of ethanol production, it depends on raw materials used. A general simplified process is shown in Figure 2.1. If sugar materials such as sugarcane juice and molasses are used as raw materials, the milling, pretreatment, hydrolysis and detoxification are not necessary. Milling, liquefaction, and saccharification processes are necessary for the production of fermentable sugar from starch materials while milling, pretreatment and hydrolysis are typically used for ethanol production from lignocellulosic biomass materials. Furthermore, a detoxification is not always used, except for the case that a toxic substance is fed to the fermentation reactors (Ahindra, 2008).

There are many different fermentation processes applicable for ethanol production. Fermentation processes as well as biological processes can be classified into batch, fed-batch (semi-continuous), and continuous processes (Ahindra, 2008).

These methods are applicable in the fermentation of sugar and starch materials. For the fermentation process of lignocellulosic biomass materials, it is more complex



**Figure 2.1** A general process scheme for ethanol production from different raw materials (Ahindra, 2008).

than other materials (sugar and starch materials) because the hydrolysate of lignocellulosic biomass material is toxic to the fermenting organism, and there is more xylose in the hydrolysate (Huang, 2010). Therefore, it is still a challenge to utilize the xylose in glucose fermentation process.

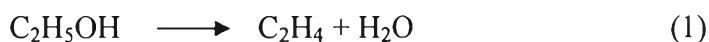
After fermentation processes, a fermented solution typically contains 8-12% ethanol that has to recovery and purification. Distillation is typically used for the separation of ethanol from water. When the ethanol concentration in the mixture reaches 95.57%, the mixture cannot be further purified because ethanol and water

form an azeotrope at 95.57% ethanol (Ahindra, 2008). When ethanol is used to blend with gasoline, the water content of ethanol must be reduced to less than 1% usually by dehydration processes (Molecular sieve drying or membrane technology) to obtain 99.5% ethanol.

## 2.2 Catalytic Dehydration of Bio-ethanol to Ethylene

### 2.2.1 Reaction Mechanism of Catalytic Dehydration of Ethanol

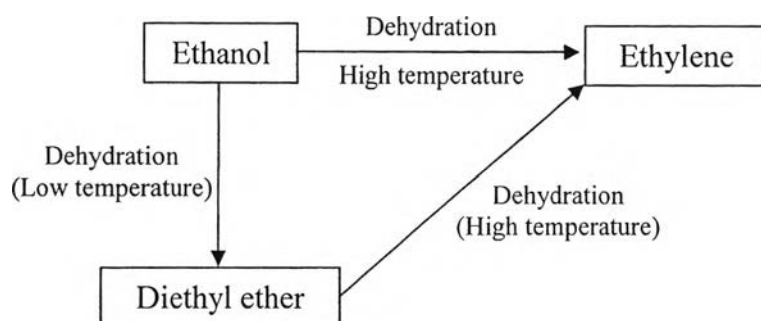
The reaction mechanism for the catalytic dehydration of ethanol to ethylene is generally considered as parallel reactions to produce C<sub>2</sub>H<sub>4</sub> through Reaction (1) and C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub> through Reaction (2) (Chen *et al.*, 2007).



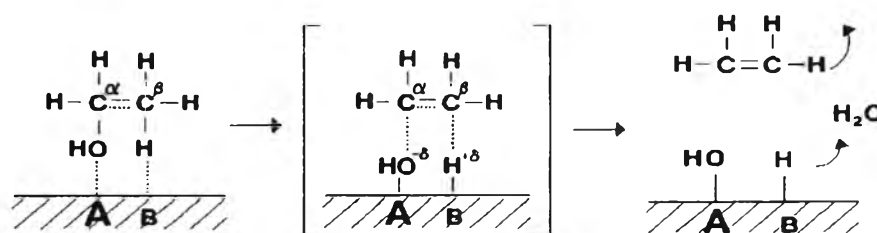
At the high temperature range between 320 °C and 500 °C (Morschbacker, 2009), the direct formation of ethylene occurs by the intra-molecular dehydration of ethanol. However, diethyl-ether is produced by the inter-molecular dehydration of ethanol at low temperatures between 150 °C and 300 °C. And, it appears that diethyl-ether can be further dehydrated to ethylene at high temperatures (Philips and Datta, 1997; Inaba *et al.*, 2005; Gayubo *et al.*, 2010) as shown in Figure 2.2. Other by-products formed by side reactions or obtained from ethanol contaminants are acetic acid, ethyl acetate, acetone, methanol, methane, ethane, propane, propylene, butane, butylenes isomers, hydrocarbons with 5 carbons or more, carbon monoxide, and carbon dioxide (Morschbacker, 2009).

Cosimo *et al.*, (1998) suggested the mechanism of ethanol dehydration to ethylene catalyzed by activated alumina. The mechanism is a concerted single-step mechanism, which involves Lewis acidic and basic sites of balanced strength as shown in Figure 2.3. Furthermore, Kondo *et al.*, (2005) studied the mechanism of ethanol dehydration on the surface of zeolites, and also compared with the conventional cationic intermediate in acid solutions. They suggested that acid-catalyzed ethanol dehydration on zeolites was shown to proceed through a covalent

ethoxy group ( $C_2H_5O$ ) as a stable intermediate, and it was directly observed by IR spectroscopy as shown in Figure 2.4. However, the operation conditions and catalysts would influence the reaction mechanism (Philips and Datta, 1997).

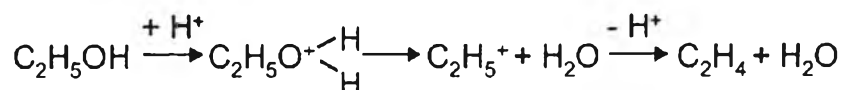


**Figure 2.2** A scheme of reaction pathway for the catalytic dehydration of ethanol to ethylene.

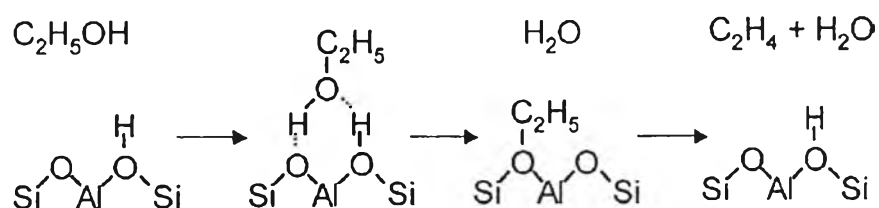


**Figure 2.3** Mechanism for the catalytic dehydration of ethanol to ethylene on  $Al_2O_3$  (Cosimo *et al.*, 1998).

(a) Conventional mechanism through cationic intermediate



(b) Mechanism on zeolite through covalent intermediate



**Figure 2.4** Comparison of two mechanisms for the catalytic dehydration of ethanol to ethylene: (a) in acidic solution, and (b) on zeolite (Kondo *et al.*, 2005).

### 2.2.2 Catalysts for Catalytic Dehydration of Ethanol

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; Arenamarta and Trakarnpruk, 2006). Especially, catalysts based on activated alumina are the most efficient catalysts for bio-ethanol dehydration, and are mostly used in industrial production (Teng *et al.*, 2009).

Kojima *et al.*, (1981) reported that an activated alumina catalyst, which has a purity of 99.6% or more and contains alkali metal, sulfur, iron and silicon in amount of 0.04, trace, 0.002 and 0.03 wt% or less respectively, showed the high conversion of ethanol (94 mol%) as well as the high yield of ethylene (90 mol%) when used in the dehydration reaction of ethanol to ethylene. They concluded that the presence of exceeding alkali metal decreased the conversion of ethanol, and the presence of exceeding sulfur, iron, and silicon decreased the yield of ethylene. Furthermore, they also studied the effect of adding a small amount of metal phosphate into high purity activated alumina catalyst. The magnesium, calcium, and zinc phosphate were used. And, these metal phosphate were added to alumina in the amounts in the range of 0.1 to 1.0 wt% based on the weight of alumina. They found that the addition of various kinds of phosphate to alumina could improve both the conversion of ethanol and the yield of ethylene. Especially, the magnesium phosphate could be used effectively for their purpose with the optimum amount of 0.5 wt% (the conversion of ethanol and yield of ethylene increased to 96 mol% and 94 mol%, respectively). Moreover, the alumina catalyst having 0.5 wt% of magnesium phosphate exhibited a higher catalytic stability after being conducted for 1,500 hours for the production of ethylene when compared with alumina catalyst.

The effect of Na<sub>2</sub>O treatment of the Mn<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> on the catalytic conversion of ethanol was studied by Doheim *et al.* (2002). They found that the

increasing addition amounts of Na<sub>2</sub>O (0.75-6 mol%) to 0.1 Mn<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> solids resulted in an effective increase in their catalytic dehydration of ethanol activities. The addition of 3 mol% Na<sub>2</sub>O could increase in the percentage conversion of ethanol, measured at 300°C, from 22% to 97%. From this result, they concluded that the addition amount of Na<sub>2</sub>O to 0.1 Mn<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> increased the concentration of OH groups on the surface which acted as active sites for the dehydration of ethanol reaction.

In addition to metal phosphate and Na<sub>2</sub>O doped on alumina catalyst, the TiO<sub>2</sub> was also studied by Chen *et al.* (2007). In their work, they purposed to investigate the modification effects of TiO<sub>2</sub>-doped on alumina catalysts packed in microreactors. For the effects of reaction temperature, they found that at the same conversion, the reaction temperature of 10% Ti/γ-Al<sub>2</sub>O<sub>3</sub> was lowered by 50 °C as compared with pure γ-Al<sub>2</sub>O<sub>3</sub>. They also found that the catalysts doped with 10% TiO<sub>2</sub> had the high ethanol conversion of 99.7% and the ethylene selectivity of 98.6% when 93.8 wt% ethanol was used as a feedstock. Furthermore, the effects of ethanol concentration on conversion and selectivity were also investigated. They found that at the reaction temperature of 440 °C, the ethanol conversion and the ethylene selectivity increased with decreasing ethanol concentrations (99.9% conversion and 99.3% ethylene selectivity). Moreover, the selectivities of C<sub>3</sub> and C<sub>4</sub> decreased with decreasing ethanol concentration, and they concluded that the optimum ethanol concentration in feed was 30-50% ethanol.

The most representative of catalysts based on activated alumina is **SYNDOL** with a main composition of MgO–Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>, 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<sup>-1</sup> (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).

However, catalysts based on activated alumina still have some disadvantages, such as low activity, low LHSV of the feedstock, high reaction temperature, and high energy consumption.

The zeolite catalysts have been paid more attention for ethanol dehydration to ethylene in the recent years. The researcher discovered that zeolite catalysts in ethanol dehydration were better than oxide catalysts owing to the lower reaction temperature (Le Van Mao, 1989; Ouyang *et al.*, 2009). These zeolite catalysts included HZSM-5, H-mordenite SAPO-34 and SAPO-34 (Le Van Mao and Dao, 1987; Aguayo *et al.*, 2002; Takahara *et al.*, 2005; Zhang *et al.*, 2008b; Chen *et al.*, 2010). Zeolite catalysts have a higher ethanol conversion rate, higher ethylene selectivity, and allow a lower concentration of ethanol raw materials (Le Van Mao and Dao, 1987). Among these zeolite catalysts, HZSM-5 is most popular used for ethylene production from dehydration of ethanol. This is the most promising catalyst for a commercial use (Huang, 2010). However, the HZSM-5 catalysts have poor hydrothermal stability and resistance to coke formation. In order to improve the catalyst activity and stability, HZSM-5 catalysts have to be modified.

The HZSM-5 doped with Zn and Mn was reported by Le Van Mao and Dao (1987). They found that the ethylene yield of the ZSM-5/Zn-Mn was very high (higher than 90 wt%), and did not change when ethanol concentration was varied. Zhang *et al.*, (2008a) reported on the effect of the phosphorus content on the catalytic performance of phosphorus modified HZSM-5 catalysts in the dehydration of ethanol to ethylene. They found that the main product was ethylene at 300–440 °C, and the coke resistance of the catalysts modified by phosphorus of 3.4 wt% was improved, owing to the presence of weak acid sites after phosphorus modification. Similarly, Ouyang *et al.*, (2009) studied the lanthanum modified HZSM-5. They found that 3 wt% La-modified HZSM-5 catalyst displayed high reaction activity. 98.5% ethanol conversion and 99.5% selectivity could be achieved at 260 °C, LHSV  $1.1 \text{ h}^{-1}$ , and 50% ethanol concentration. Under this condition, they also found that the ethanol conversion and selectivity over this catalyst could be maintained above 98% for more than 950 h.

### 2.2.3 The Process for Catalytic Dehydration of Ethanol

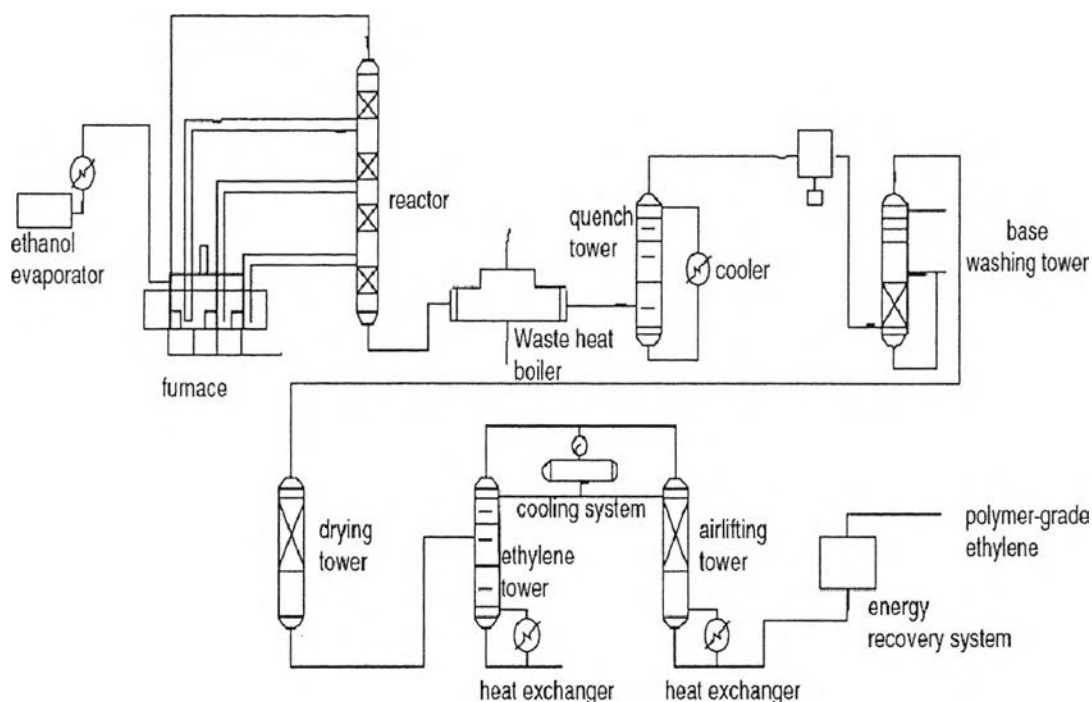
The catalytic dehydration of ethanol is carried out in the vapor phase reaction through fixed bed or fluidized bed reactors (Pearson, 1983). For fixed bed reactors, the operation can be isothermal or adiabatic. An isothermal fixed bed reactor usually consists of multitubular arrangement where the catalyst is placed inside the tube, and the heating fluid circulates externally to the tubes to heat endothermic reaction and maintain temperature. However, the use of multitubular reactor presents technical and economical disadvantages. For examples, it is necessary to work at a low LHSV in order to obtain enough heat for ethanol dehydration reaction, and there is still a problem with the sizing and engineering design (Barrocas *et al.*, 1980). Therefore, adiabatic fixed bed reactors were developed for ethanol dehydration.

The adiabatic fixed bed reactors used for ethanol dehydration reaction were reported by Barrocas *et al.*, (1980). The adiabatic fixed bed reactors may be used in parallel, or be disposed in series, or arranged in parallel series assemblies, or only a single reactor, and the heat carrying fluid introduced into reactor with the feed can supply the heat necessary for the reaction. For a fluidized-bed reactor, Tsao and Zasloff (1979) reported about the fluidized-bed reactor for ethanol dehydration. It was operated with the temperatures at least 399 °C (700 °F). The ethanol conversion was 99.6%, and the selectivity to ethylene was 99.9%. The endothermic heat requirements for the reaction can be provided by the hot feed and circulating catalyst from the regenerator. Similarly to the adiabatic process, there is no need of external heating for the reactor (Morschbacker, 2009). Different catalytic dehydration of ethanol to ethylene technologies have been developed by many companies as shown in Table 2.1 (Tsao and Zasloff,1979; Barrocas and Junior, 1983; Koh, 1993).

**Table 2.1** Different technologies for the catalytic dehydration of ethanol to ethylene

Technology	Halcon/SD technology	Lummus technology	Petrobras technology
Development company	Halcon/SD company, USA	Lummus company, USA	Petrobras company, Brazil





**Figure 2.5** Halcon Scientific Design’s process diagram of ethanol dehydration to ethylene (Huang, 2010).

Figure 2.5 illustrates the polymer grade ethylene production which is designed by Halcon Scientific Design company in 1980, currently owned by Chematur Engineering AB. The production process includes two parts (reaction and separation). The ethanol is vaporized, then the vaporized ethanol is preheated in the furnace, and passed to the first coil where its temperature is raised to 425 °C. The superheated ethanol then flows to the first catalyst bed reactor of the multibed adiabatic reactor. In the first reactor bed, about 30% of the ethanol is converted to ethylene, then the partially converted gases are fed to the furnace where they are reheated to 425 °C and passed to the second bed reactor. In the second bed, the conversion raises to 60%. A similar succession of reheat and reaction in three and four bed reactors increases the conversion to 86% and finally 99% conversion (Koh, 1993). Gas leaving the catalyst bed reactors contains crude ethanol, that did not react, as well as ether, acetaldehyde, methane, carbon dioxide, etc.. After recovery heat by waste heat boilers, the raw ethylene is sent into the quench tower where water and condensable polar substances such as non-reacted ethanol and small amounts of

acetaldehyde and acetic acid are removed. The crude ethylene leaving the top of quench tower is compressed, and passed through a caustic scrubbing tower and then a fixed bed gas drying tower to reduce the concentrations of carbon dioxide and water to specification levels. At this time, the ethylene purity is greater than 99% (Morschbacker, 2009). When polymer grade ethylene is required, ethylene will be sent to an ethylene tower and a stripping tower where heavy and light contaminants are removed. Finally, the ethylene product meets all polymer grade specifications.

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>). However, there is no information about the process data of the process. Furthermore, Dow Chemical plans to build the plant for PE production based on ethanol produced from sugarcane in Brazil (<http://www.icis.com>).

As mentioned above, catalysts based on alumina are the most efficient type of catalysts for ethanol dehydration, and are used the most in industrial production. Moreover, the modification of an alumina catalyst with magnesium phosphate can improve both the ethanol conversion and the yield of ethylene. However, the operating conditions (reaction temperature and ethanol concentration in feed) have an effect to catalytic activity. Therefore, the operating conditions were expected to improve the ethanol conversion and ethylene selectivity. Furthermore, there are only two processes providing some process data which are Chematur Engineering AB and Petrobras (may be related with Braskem process) designed with capacity 33,000 tons of ethylene per year, and 200,000 tons per year of ethylene, respectively. For pre-feasibility study, the two commercial processes have to compare in term of economic feasibility.

The objectives of this research work were to investigate and verify the  $\text{MgHPO}_4/\text{Al}_2\text{O}_3$  catalysts 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.

The scope of this research covers as follows: (1) the two commercial plants of ethylene production from bio-ethanol (Chematur Engineering AB and Petrobras) were performed and investigated for the economic viability determined by using Payback period (PB), Net present value (NPV), Internal Rate of Return (IRR), and Profitability index (PI), (2) the catalytic dehydration of bio-ethanol to ethylene was performed in an isothermal fixed-bed reactor and atmospheric pressure, (3) the effects of reaction temperature (370-460 °C) and ethanol concentration (40-50%, 95%, and 99.5%) over 0.5 wt% MgHPO<sub>4</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst was investigated at LHSV= 1.0 h<sup>-1</sup> according to following Table 2.2.

**Table 2.2** The effects of reaction temperature and ethanol concentration over 0.5 wt% MgHPO<sub>4</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst at LHSV= 1.0 h<sup>-1</sup>

Catalyst	Temperature (°C)	Ethanol Concentration (%)
0.5 wt% MgHPO <sub>4</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	370	40-50
		95
		99.5
	400	40-50
		95
		99.5
	430	40-50
		95
		99.5
	460	40-50
		95