Techno-economic analysis of diethyl ether production via catalytic dehydration of ethanol

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การวิเคราะห์ทางด้านเทคนิค และเศรษฐศาสตร์ของกระบวนการผลิตไดเอทิลอีเทอร์ผ่านการดีไฮเดรชันด้วยตัวเร่งปฏิกิริยาของเอทานอล

น.ส.บุญรักษา ชัยอาภา

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บุญรักษา ชัยอาภา : การวิเคราะห์ทางด้านเทคนิค และเศรษฐศาสตร์ของกระบวนการผลิตไดเอทิลอีเทอร์ผ่านการดีไฮเดรชันด้วยตัวเร่งปฏิกิริยาของเอทานอล. (Techno-economic analysis of diethyl ether production via catalytic dehydration of ethanol) อ.ที่ปรึกษาหลัก : ศ. ดร.บรรเจิด จงสมจิตร, อ.ที่ปรึกษาร่วม : ดร.พงศ์ธร เจริญศุภนิมิตร

แหล่งพลังงานหลักที่สำคัญในปัจจุบันส่วนใหญ่มาจากพลังงานที่ไม่หมุนเวียน ซึ่งมีความไม่ยั่งยืน และมีผลกระทบด้านลบต่อสิ่งแวดล้อม ดังนั้นจึงมีการเปลี่ยนไปใช้พลังงานหมุนเวียนแทน เช่น ไบโอเอทานอล ซึ่งไดเอทิลอีเทอร์ (DEE) ก็เป็นสารเคมีที่ผลิตได้จากไบโอเอทานอล อย่างไรก็ตาม การเพิ่มขึ้นของรถยนต์ไฟฟ้า อาจลดความต้องการการใช้เอทานอลเพื่อเป็นเชื้อเพลิงชีวภาพในอนาคต ดังนั้นจึงสนใจที่จะเพิ่มมูลค่าให้กับเอทานอลผ่านการดีไฮเดรชันด้วยตัวเร่งปฏิกิริยา เพื่อผลิตไดเอทิลอีเทอร์ โดยทำการวิเคราะห์ทางด้านเทคนิค และเศรษฐศาสตร์ นอกจากนี้ ยังมีการเปรียบเทียบความเข้มข้นต่าง ๆ ของเอทานอล (เอทานอลที่มีความบริสุทธิ์ 93% และ 95%) ที่มีผลต่อการผลิตไดเอทิลอีเทอร์ ในส่วนของการออกแบบนั้น พบว่ากำลังการผลิตไดเอทิลอีเทอร์ที่ 3,600 ตันต่อปี เป็นกำลังการผลิตที่ทำกำไรได้มากที่สุด เนื่องจากมีอัตราการตอบแทนภายในสูงสุด และมีระยะเวลาคืนทุนที่สั้นกว่า นอกจากนี้ ที่กำลังการผลิตไดเอทิลอีเทอร์ 3,600 ตันต่อปี จะมีการใช้พลังงานสูงสุดทั้งในแง่ของสาธารณูปโภคทางความร้อน และสาธารณูปโภคทางไฟฟ้า เช่นเดียวกันกับการปล่อยก๊าซคาร์บอนไดออกไซด์ เนื่องจากต้องใช้สาธารณูปโภคขนาดใหญ่จึงปล่อยก๊าซคาร์บอนไดออกไซด์ออกมาในปริมาณมากขึ้น ในส่วนของการทดลองนั้น พบว่าปริมาณน้ำในสารละลายเอทานอลมีผลต่อตัวเร่งปฏิกิริยาที่มีการดัดแปลงของเบต้าซีโอไลท์ด้วยรูเทเนียมสำหรับร้อยละผลผลิตของเอทิลีนนั้น ปริมาณน้ำในสารละลายเอทานอลมีผลเล็กน้อยต่อตัวเร่งปฏิกิริยาที่อุณหภูมิ 400 องศาเซลเซียส ในทางกลับกันสำหรับร้อยละผลผลิตไดเอทิลอีเทอร์นั้นปริมาณน้ำในสารละลายเอทานอลมีผลต่อตัวเร่งปฏิกิริยาที่ 250 องศาเซลเซียสมากขึ้น เนื่องจากโมเลกุลของน้ำ ส่งผลให้ความเป็นกรดบรอนเสตดเพิ่มขึ้น และปิดกั้นตำแหน่งกรดลิวอิส ทำให้ความสามารถของตัวเร่งปฏิกิริยาลดลง ผลพลอยได้ในกระบวนการนี้คือ อะเซทัลดีไฮด์ เมื่อปริมาณน้ำเพิ่มขึ้น ร้อยละผลผลิตของอะเซทัลดีไฮด์จะเพิ่มขึ้น ตามลำดับ

สาขาวิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....
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The major source of energy comes from non-renewable fuels, which have a non-sustainability and negative impact on the environment. Thus, there is change to renewable fuels as bioethanol. Diethyl ether (DEE) is a part of bioethanol. However, the increase of electric vehicles (EV) may decrease ethanol demand for biofuel in the future. Thus, it will be interesting in adding value to ethanol via the catalytic dehydration to produce DEE by conduct techno-economic analysis. Further, there is comparison on different concentrations of ethanol (93% and 95% ethanol) that affect DEE production. For simulation part, the DEE capacity of 3,600 tons/year is the most profitable due to the highest %IRR and offers a shorter POP. The highest energy consumption of electricity and thermal duty is at the DEE capacity of 3,600 tons/year as well as the CO2 emission due to the large utility is required and larger CO2 content is released. For experiment part, the water content in the ethanol solution has effect on the Ru-HBZ catalyst. For ethylene yield, the water content has slight effect on the catalyst at 400°C. In contrast, for DEE yield, the water content has a greater effect on the catalyst at 250°C due to the water molecule resulted in an increase the Brønsted acidity and blocking of Lewis acid sites, to the lower activity of the catalyst. By-product is acetaldehyde when the water content increases, the acetaldehyde yield increases.

Field of Study:	Chemical Engineering	Student's Signature ....
Academic Year:	2020	Advisor's Signature ....
		Co-advisor's Signature ....

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Boonraksa Chaiapha

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CHAPTER 1

INTRODUCTION

1.1 Background

Currently, most of the energy used is from non-renewable energy sources. Most non-renewable energy sources are fossil fuels such as coal, petroleum, and natural gas. These natural resources are a major source of power for a vast amount of industries. However, there are numerous downsides to non-renewable energy, including it eventually will run out and their negative environmental impact because the combustion of fuel will generate toxic gas like carbon dioxide, carbon monoxide and sulfur dioxide, etc. [1]. People have begun to focus on renewable energy sources. Renewable energy is derived from natural processes such as heat generated from solar, wind, ocean, hydropower, biomass and biofuels [2]. In this area, the energy source that we are interested in using is the energy source of biomass to produce bioethanol.

Bioethanol is produced from ethanol process by biochemical processes and using agricultural materials such as sugar, flour and cellulose as raw materials or biomass fermentation. Bioethanol has properties like ethanol or ethyl alcohol. Ethanol is a high-octane fuel and has replaced lead as an octane enhancer in petrol. By blending ethanol with gasoline, we can also oxygenate the fuel mixture so it burns more completely and reduces polluting emissions [3]. In Thailand during the years 2015, 2016 and 2018, ethanol production is less than the demand for usage, which can be seen in Figure 1. However in 2017, the demand for ethanol is less than the production capacity. Although at present, domestic demand for ethanol is increased on the back of a general growth in demand for fuels and an expansion of the vehicle fleet is able to use higher ethanol mixes (e.g. E20 and E85), competition is likely to increase as a result of new production facilities being gradually introduced. The trend towards the market experiencing an over capacity will increase, with 2017 seeing an extra 1.22 million liters/day of capacity coming on-stream. This will give a total domestic installed production capacity of 5.66 million liters/day (at present there are 21 functioning ethanol production facilities in the country, which together have an installed capacity of 4.44 million liters/day) and will push the utilization rate down to around 68-70% [4].

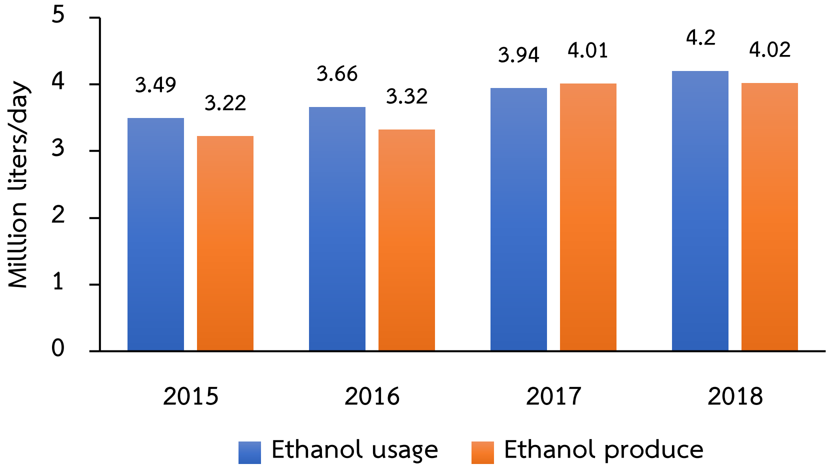


Figure 1 Domestic ethanol produce and usage

In addition, the development of technology for using electric vehicles (EV) begins to play a greater role due to 1) affordable electric power compared to fuel, because it can be recharged with normal home lighting. 2) cheaper maintenance fees due to the process of electric cars, no need for ignition like a fuel engine and still do not have to change the engine oil. 3) no fuel consumption and no burning occur pollution becomes zero, which will make the environment around us better. The electric car technology is expected to grow very rapidly in the near future due to the rapid production costs from advances in research and development especially the cost of battery production. It will result in price of EV cars narrowing down to make consumers more easily accessible. From the latest report of the International Energy Agency (IEA), it is found that the number of electric vehicles worldwide continues to increase steadily. In 2016, the globe has 2.01 million electric vehicles on the road, up 59.52% and new registrations (sales) of 7.53 hundred thousand electric vehicles, up 37.66%. The countries with the highest cumulative electric cars are China, USA, Japan, Norway and Netherlands [5].

While the current situation of electric vehicles in Thailand has become more clear that industrial development will rely on hybrid vehicles (HEV) to pass. The cooperation between various agencies associated became more clear as well reflected by the awareness of charging infrastructure or electric charging stations. The above guidelines are considered a good start for Thailand to develop the electric car industry to prepare for changing the structure of automobile production in the future [6]. From the above mentioned, it can result in decreased demand for ethanol usage in the future and ethanol oversupply. It is forecasted that the ethanol will become available as a used raw material to produce value-added chemical compounds. In this work, the purpose is increasing the value of ethanol by making it a precursor in diethyl ether production (DEE production).

DEE is selected in this study due to several reasons including 1) DEE is significantly more expensive than ethanol 2) Thailand wholly imports DEE from overseas. 3) DEE has a wide range of applications such as solvent in many industries. For fuel uses, it has a high cetane number and it is used as a starting fluid when used with petroleum distillates for gasoline and diesel engines because of it is good ignition and low flash point. For laboratory uses, it is a common laboratory aprotic solvent. In medical uses, it is used in pharmaceutical formulations such as anesthetic. For safety and stability, it has involved the explosive synthesis in some process [7]. Normally, the chemical reactions for DEE productions namely catalytic dehydration of ethanol.

In the present study, DEE production will be simulated using Aspen Plus in order to perform the process analysis and economic evaluation. The simulation and techno-economic results provided in this case are compared to choose the appropriate process for DEE production and to prove the possibility to use ethanol for DEE production which is one of the bio-refinery products gaining more attentions in the near future. Furthermore, we are interested in studying to compare various concentrations of ethanol that affect DEE production. In fact, industrial plants can produce ethanol with purity of 93% and 95% (the factory uses 93% ethanol mixed with absolute ethanol). Distillation more than 95% ethanol is difficult with a high investment cost due to ethanol/water azeotrope solution (ethanol : water = 95.63:4.37 by mass%) [8]. It is the concentration of ethanol that can actually be used in manufacturing.

1.2 Research objectives

The aim of this work is to conduct techno-economic analysis of diethyl ether production via catalytic dehydration of ethanol and to compare various concentrations of ethanol (93% and 95% ethanol) that affect DEE production during the catalytic dehydration of ethanol.

1.3 Research scopes

1.3.1 To simulate the catalytic dehydration process of ethanol by using Aspen Plus based on data from literatures including:

- 99.5% Ethanol is used as a reactant.
- The H-beta zeolite (HBZ) catalyst with ruthenium (Ru-HBZ) modification is used with the operating condition at atmospheric pressure and the reaction temperature of 250°C.
- The suitable condition was optimized by space velocity factor (WHSV=22.9 $(g_{ethanol}g_{cat}^{-1})\ h^{-1}$).
- The economic evaluation method was used to analyze the worthiness of the DEE production and the results of process were be compared to choose the appropriate process for the DEE production.

1.3.2 In laboratory, the effect of different concentrations (93% and 95% ethanol concentration) of ethanol on DEE production process over Ru-HBZ catalyst was investigated with the operating condition at atmospheric pressure and the reaction temperature ranging from 200-400°C (WHSV=22.9 $(g_{ethanol}g_{cat}^{-1})\ h^{-1}$).

1.4 Research benefits

1.4.1 Be able to improve and develop of the DEE production process.

1.4.2 Be able to adapt the lab scale to commercial scale.

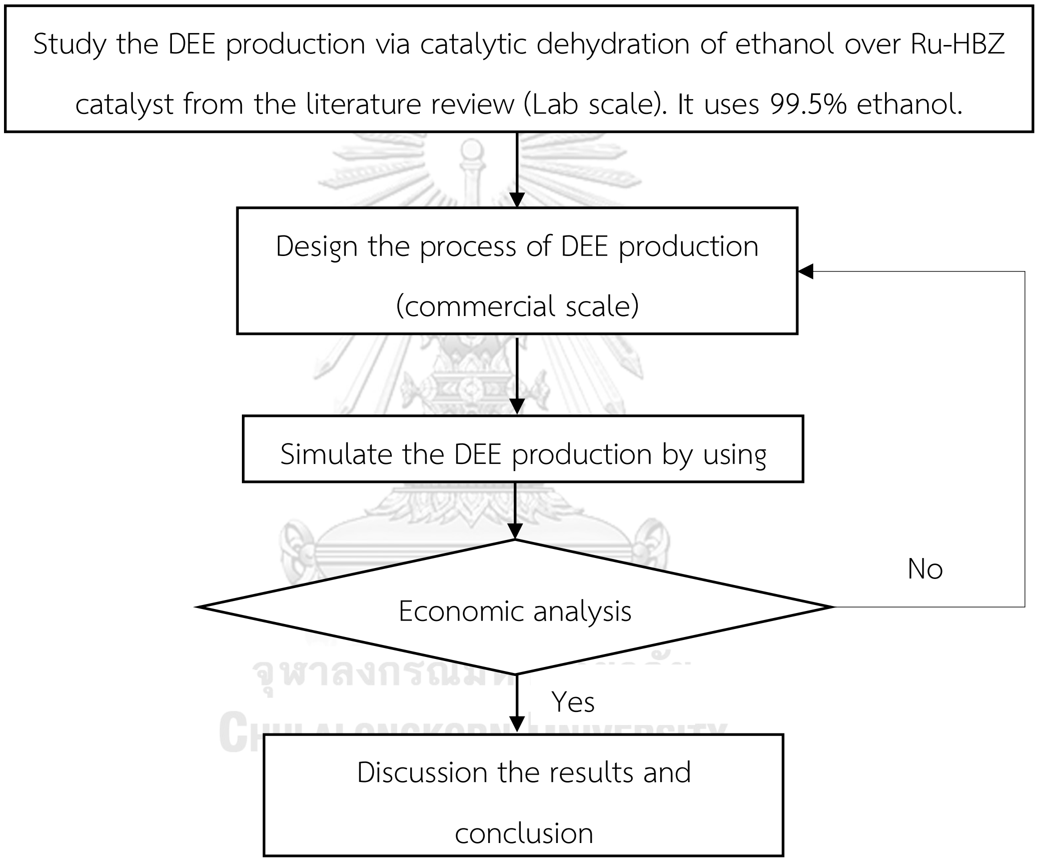
1.4.3 Can understand the procedure of manufacturing DEE from the combination of each unit as well as the effect of parameter on the process profitability, whether it be operating condition, raw material, product sale prices and energy consumption.

1.4.4 Can understand the factors that affect DEE production process at various concentrations of ethanol (93% and 95% ethanol concentration) such as water.

1.5 Research methodology

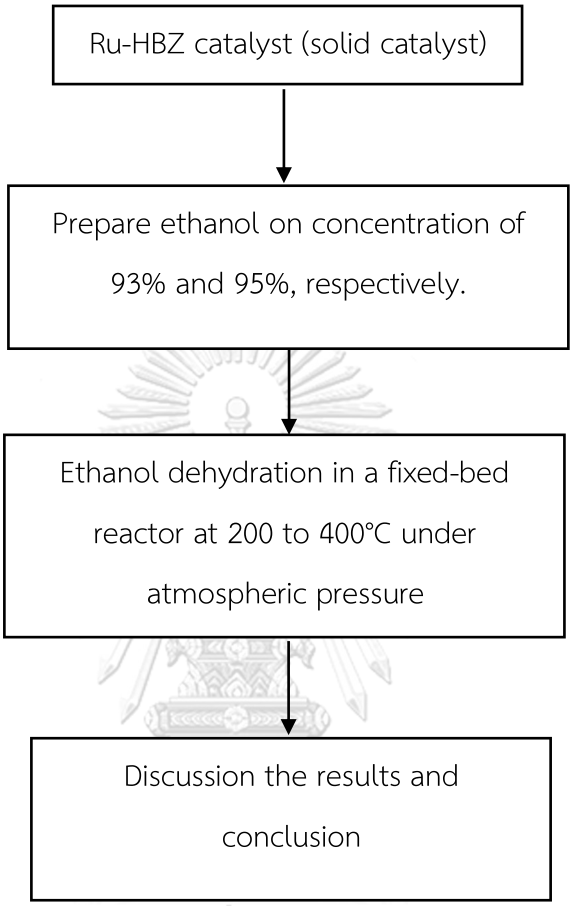
The research methodology is shown in this following diagram:

Part I: Simulation and economic evaluation of DEE production.



In this simulation part, it used 99.5% pure ethanol precursor, which was costly. In most industries, it used ethanol with purity 93% and 95%, which was cheaper. Therefore, it is interesting to study the effect of water in ethanol on conversion and selectivity, which leads to the next part.

Part II: Investigation of the different of various concentrations (93% and 95% ethanol concentration) of ethanol on DEE production process over Ru-HBZ catalyst.



CHAPTER 2

THEORIES AND LITERATURE REVIEW

This chapter explain the theoretical background and literature review that involves to this research like properties of chemical product (ethanol, and DEE), dehydration reaction, Ru-HBZ catalyst, input parameter and separation process used for simulating DEE production in this research follows in Chapter 2.

2.1 Theory

2.1.1 Physical and chemical properties of reactant (ethanol) and products (DEE) including their applications.

- Ethanol

The organic compound ethanol, also known as ethyl alcohol and grain alcohol, is produced from ethanol process by biochemical processes and using agricultural materials such as sugar, flour and cellulose as raw materials or biomass fermentation. Ethanol's chemical formula is C_2H_5OH ($CH_3–CH_2–OH$) that its molecular structure comprises of an ethyl group linked to a hydroxyl group. Ethanol is a flammable, volatile, low in toxicity, and colorless liquid with a pleasant odor. It is easily soluble in water [9]. For the specific physical and chemical properties of ethanol are listed below in Table 1.

Table 1 The specific physical and chemical properties of ethanol [10].

Properties	Information
Molar mass	46.07 $g·mol^{-1}$
Density	0.7893 g/cm^3
Normal boiling point	78.24 °C
Normal melting point	−114.14 °C
Vapor pressure	5.95 kPa

Ethanol is widely used as a solvent in the manufacture of perfumes, varnishes and scientific chemical testing. For medicine uses, a 70-85% of ethanol solution is commonly used as a disinfectant or antiseptic. It is effective against most bacteria and many viruses. In addition, it is a psychoactive substance and is the major type of alcohol found in alcoholic drinks. Ethanol is widely used as a solvent in the manufacture of perfumes, varnishes and scientific chemical testing. For medicine uses, a 70-85% of ethanol solution is commonly used as a disinfectant or antiseptic. It is effective against most bacteria and many viruses. In addition, it is a psychoactive substance and is the major type of alcohol found in alcoholic drinks. Ethanol is a high-octane fuel and has replaced lead as an octane enhancer in petrol. By blending ethanol with gasoline, we can also oxygenate the fuel mixture so it burns more completely and reduces polluting emissions due to ethanol as a clean-burning fuel source [9].

- Diethyl ether (DEE)

Diethyl ether or DEE also known as ethyl ether and anesthetic, is an organic compound in the ether class with the formula $C_4H_{10}O$. It is a colorless, highly volatile flammable liquid. For the specific physical and chemical properties of DEE are listed below in Table 2 [7].

Table 2 The specific physical and chemical properties of DEE.

Properties	Information
Molar mass	74.12 $g{\cdot}mol^{-1}$
Density	0.7134 g/cm^3
Normal boiling point	34.6 °C
Normal melting point	−116.3 °C
Vapor pressure	58.66 kPa

DEE is a high value chemical and there are many benefits. DEE is mostly used as a solvent in many industries. For fuel uses, it has a high cetane number and it is used as a starting fluid when used with petroleum distillates for gasoline and diesel engines because of it is good ignition and low flash point. For laboratory uses, it is a common laboratory aprotic solvent. In medical uses, it used in pharmaceutical formulations such as anesthetic. For safety and stability, it has involved the explosive synthesis in some process [7]. Thus, DEE is expensive and used in various applications as mentioned above.

Industrially, DEE can be produced by the distillation of ethanol with sulfuric acid (H_2SO_4) as called the acid ether synthesis, but the process is not flexible because concentration of catalyst becomes less with water produced through the reaction. But it can use the reactive distillation by separating the water leaves in the system to balance it to the right-hand side. The problems in the process are difficult to separate and eliminate the strong acid [7, 11]. In recent years, the ethanol dehydration reaction has been accepted to produce DEE. This is due to ethanol is the renewable sources. DEE is produced via dehydration of ethanol over solid acid catalyst which is occurring the removal of water molecule. It is shown in the reaction below that is exothermic reaction with low reaction temperatures [12, 13].

Acid ether synthesis [7]:

$$CH_3CH_2OH + H_3O^+ \longrightarrow CH_3CH_2OH_2^+ + H_2O \quad (2.1)$$

$$CH_3CH_2OH_2^+ + CH_3CH_2OH \longrightarrow H_2O + H^+ + CH_3CH_2OCH_2CH_3 \quad (2.2)$$

Ethanol dehydration reaction [12]:

$$C_2H_5OH \longrightarrow C_2H_5OC_2H_5 + H_2O \qquad \Delta H = -25.1 \text{ kJ/mol} \quad (2.3)$$

2.1.2 The information and mechanism of ethanol dehydration reaction

The ethanol dehydration reaction mostly consists of two competitive pathways as follows [14]:

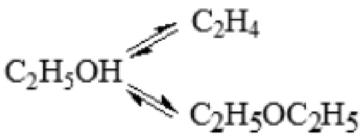
$$C_2H_5OH \longrightarrow C_2H_4 + H_2O \quad (2.4)$$

$$2C_2H_5OH \longrightarrow C_2H_5OC_2H_5 + H_2O \quad (2.5)$$

The first reaction (2.4) is endothermic reaction (+44.9 kJ/mol), which is the unimolecular mechanism producing ethylene formed by decomposition of ethoxide surface group and by-product is water. The second reaction (2.5) can be operated at lower temperature due to exothermic reaction (-25.1 kJ/mol) to obtain DEE and by-product is water. The DEE formation proceeds by either dissociative pathway or associative pathway. (It is reported that the associative pathway takes place from co-adsorption of two ethanol reacted and formed into DEE.) Thus, the ethylene will occur at high reaction temperature, whereas DEE will mainly occur at lower reaction temperature. Besides, it known that ethanol molecule can be dehydrated by using solid acid catalyst because it contains with hydroxyl group on surface, which can be converted into water molecule. Then, the water molecule is removed from ethanol molecule and the hydrocarbon forms into ethylene or DEE [15].

The mechanism research of ethanol dehydration reaction can be concluded as three type of routes including the parallel reactions, the series reactions and the parallel series reactions that is shown in Figure 2. In the parallel surface reactions, ethylene molecules and diethyl ether molecules were generated from ethanol molecules. In the series reaction, molecules of ethanol are converted to diethyl ether molecules after that changing to ethylene molecules. While in the parallel series reactions, the both routes are coexisted [16].

1) Parallel reactions



2) Series reactions

3) Parallel series reactions

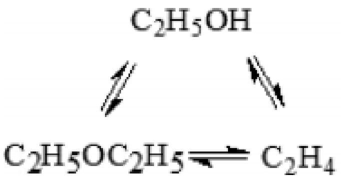


Figure 2 Mechanism of ethanol dehydration [16].

Ethanol dehydration to DEE requires weak acid site and low reaction temperature. It used two ethanol molecules, and no generation of carbocation taking place during the process to form DEE. The reaction start with the proton from acid catalyst protonates the hydroxyl group of the first ethanol molecule to electrophilic. Then, the lone pair electrons of second ethanol molecule attack the electrophilic of the first ethanol molecule before remove the leaving group [16, 17]. The formation of DEE may be occurred by two different pathways termed the associative pathway and the dissociative pathway. Both pathways are thought to take place at Brønsted acid sites [8] and the pathway of DEE is represented in Figure 3.

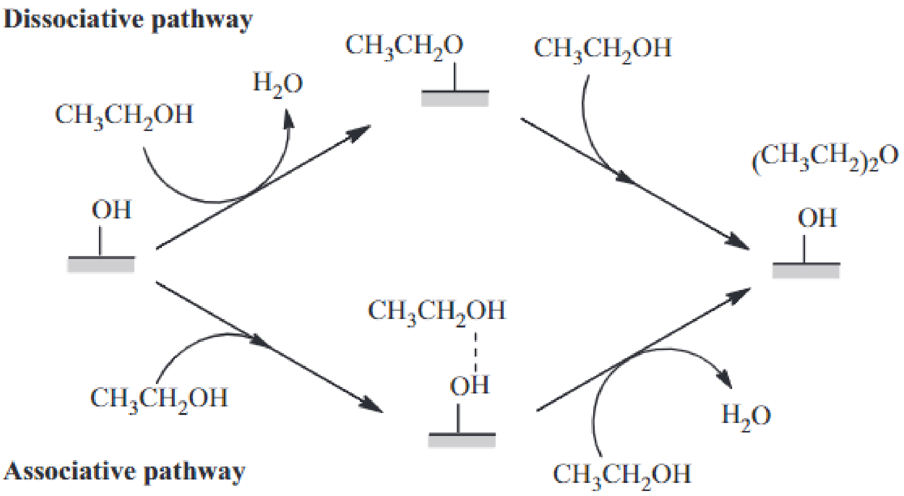


Figure 3 Mechanism of associative and dissociative pathways for ethanol dehydration of DEE [17].

2.2 Literature review

2.2.1 Catalyst involved in DEE production

In DEE production, various solid catalysts have been used in dehydration of ethanol such as metal oxides, alumina, silica-alumina, zeolites and supported phosphoric acid [18-23], which various catalyst types and operating conditions for DEE production are shown in Table 3.

According to the table, since the Ru-HBZ catalyst (H-beta zeolite support catalyst with Ru modification) is solid catalyst and gives the highest DEE yield more than other catalysts and the moderate ethanol conversion at low temperature

(250°C) at atmospheric pressure. In addition, the H-beta zeolite (HBZ) is a microporous zeolite. It is having high thermal stability, high surface area and high acidity (Brønsted acid sites; both in the internal and the external surface [24].) used in ethanol dehydration. Besides, HBZ exhibits larger pore size than H-ZSM-5. Thus, it is pleasing to produce hydrocarbon with less coke deposition due to higher diffusivity in the pore [25]. Ruthenium (Ru) promoter has been reported to exhibit high catalytic activity in a chemical reaction. In general, promoters have been studied in order to increase the activity of the catalyst and product selectivity [17, 25-27]. This is the reason for choosing Ru-HBZ catalyst. Therefore, set of experimental data obtained from catalytic dehydration of ethanol (namely, Ru-HBZ catalyst) are determined for process simulation and economic evaluation by using Aspen Plus in this work.

Table 3 Various catalyst types and operating conditions for DEE production.

Catalyst	Reaction temperature (°C)	Pressure (atm)	Ethanol conversion (%)	DEE selectivity (%)	DEE yield (%)	Ref.
HBZ	250	1	42	83.5	35	[14]
Ru-HBZ	250	1	54	86.7	47	[14]
Pt-HBZ	250	1	53	83.5	45	[14]
2%PHZSM-5	200-240	1	69-96	97.2-24.7	23-66	[28]
0.5%LaHZSM-5	200	1	86	34.3	29	[28]
TIO_2	300	1	36	2.1	1	[29]
WO_3/TiO_2	250	1	38	67.7	26	[29]

2.2.2 Separation of product in DEE production

Some products cause problem to the process particularly in the separation units. For example, azeotropic mixtures of ethanol/water is formed. Which the high purity ethanol product cannot be distilled by conventional distillation technique as the result of the azeotropic point. Therefore, there are several techniques to eliminate the azeotrope, which is described as follows:

- Azeotropic distillation

The azeotropic distillation refer to processes whereby a new component (called entrainer) is added to the original feed mixture to form an azeotrope which one or more of the feed components. The azeotrope then removed as either the distillate or the bottom of distillation. Usually refers to the specific technique of adding another component to generate a new, lower-boiling point azeotrope that is heterogeneous (e.g. producing two, immiscible liquid phases), such as the example below with the addition of benzene to water and ethanol [30]. The main disadvantage of the azeotropic distillation against the extractive distillation is the higher energy desire because of the vaporization of the entrainer [31].

- Pressure-swing distillation

In the literature pressure swing distillation (PSD) is often mentioned as an alternative process to the widely applied azeotropic distillation or extractive distillation. The PSD uses the dependency of azeotropic composition on the system pressure to break the azeotrope. If the pressure is increased, the azeotropic point shifts to lower concentrations of the low boiling component. So, a separation of the azeotropic mixture at different pressures is possible. The main advantages of these distillation compared to the other distillation, that no additional substances (entrainer) must be used. The PSD process can be operated in continuous mode, discontinuous mode and semi-continuous mode. For the continuous operation a heat compilation is possible which can save energy, but it has a greater require on automation. The discontinuous operation is much simple to control and operate. This PSD process is not widely used in industry, but it has a high potential because of the possible energy savings (continuous process) and the simple process structure (discontinuous process) [32]. The disadvantages of the process are a higher complexity of the process and a more complex automation therefore the development of applicable process control strategies is much more difficult [33].

- Vacuum distillation

The vacuum distillation can shift the azeotropic point with temperature change induced from a pressure change, a pressure reduction in the column can be used. The azeotropic point shifts to higher concentrations of the low boiling component and it is also possible to break the azeotrope. The disadvantages of the vacuum distillation are mainly the costs of the process and the complexity of the process because of the vacuum, so it is not often used [34].

- Pervaporation

The hybrid process means a combination of two different thermal unit operations, like a combination of distillation and a membrane process or pervaporation. It is used to separate azeotropic mixture. In pervaporation process, a binary liquid mixture is fed to contact with the active nonporous side of the membrane and a phase change of permeant take place in the membrane. The permeant diffuses through the membrane and desorbs on the permeate side of the membrane as vapor state. The main advantage is requiring the low separation energy and operate at room temperature. The disadvantage of these process is highest operating cost than other process [33, 35].

- Extractive distillation

The extractive distillation used to the separation of homogeneous close boiling or azeotropic mixtures. A low volatile liquid is added to the mixture as an entrainer to increase the volatility over the whole concentration region by decreasing the partial pressure or the volatility of one component. The main problem of the process is the choice of the right entrainer. The entrainer must fulfil many different properties. The boiling point of the entrainer must be much higher than the boiling points of the other components, it must be thermal stable, cheap, non-toxic and the entrainer must not be formed an azeotrope with any components in the original mixture [33]. The entrainer used for each binary system. is shown in Table 4.

Table 4 The entrainer used for each binary system [36].

Mixture	Solvent
Butadiene/Butene from C4 fractions	Furfural, Acetonitrile, NMP, DMF
Butane/Butene	Acetone
Butene/Isoprene	DMF
Acetone/Methanol	Water, Aniline, Ethylene glycol
Ethanol/Water	Ethylene glycol, Glycerine
Benzene/Cyclohexane	Aniline
Toluene/Heptane	Aniline, Phenol
Propylene/Propane	Acrylonitrile
HCl/Water, Nitric acid/Water	Sulfuric acid
Tetrahydrofuran/Water	DMF, Propylene glycol
Cumene/Phenol	Phosphates

From the table, the separating of ethanol/water or azeotropic mixtures is widely used the entrainer namely glycerine and ethylene glycol [36]. I.D.Gill *et al.* [37] studied the simulation of ethanol extractive distillation with mixed glycols as separating agent. It found that glycols have been shown to be the most effective solvents in extractive distillation, mainly ethylene glycol and glycerine. Glycerine achieving a higher purity product than ethylene glycol under the same operating conditions but required higher energy consumption. Because of glycerine higher boiling temperature (290°C). Thus in this work, it using ethylene glycol as a entrainer is proceed to break azeotrope. Ethylene glycol has the boiling temperature of 198°C and water has the boiling temperature of 100°C, which has the boiling temperature a distinctly different so ethylene glycol will extract water molecules depart of ethanol. It can be easily separation.

From the above several separation techniques, in this work focuses on the extractive distillation as follows:

William L. Luyben [38] had performed a comparison of extractive distillation and pressure-swing distillation for acetone-methanol separation. The main results represented that the extractive distillation has lower annual costs and equivalent dynamics compared to the pressure-swing distillation. However, it is more difficult to attain high product purities. Besides, the introduction of a third component (water) can lead to impurity issues in the products.

Xin-Yang Liu *et al.* [39] studied to comparison of extractive and pressure-swing distillation for separation of tetrahydrofuran-water mixture. It found that Aspen Plus simulator is used to simulate extractive distillation (ED) and pressure-swing distillation (PSD) process for separation of mixture of tetrahydrofuran-water (THF-water). Economic analysis is carried out by Aspen Process Economic Analyzer (APEA) found that the total annualized cost (TAC) of the extractive distillation is slightly lower than that of pressure-swing distillation. TAC costs can be calculated based on capital cost and utility cost (electricity and cooling water costs). The results obtained provide useful references for commercial separation of mixture of THF and water.

CHAPTER 3

METHODOLOGY

This chapter is divided into 2 parts including simulation and techno-economic analysis part by using Aspen Plus and experimental part. The first part describes in detail the research methodology for simulation and techno-economic analysis of DEE production from ethanol including Input parameter, process simulation, economic evaluation and CO_2 emission evaluation. The last part explains the information in experimental part including materials and reaction study in catalytic dehydration of ethanol.

3.1 Simulation and techno-economic analysis part

3.1.1 Input parameter

In this research, the suitable input data based on the literature is used to simulate the DEE production via catalytic dehydration of ethanol in accordance with Table 5 . Besides, DEE plant was designed with DEE production capacity of 1,800 tons/year, which is based on information of TKM Pharma private company limited [40]. Due to the high production rate, the production will be operated as a continuous process.

Table 5 Input data for DEE production by using Aspen Plus simulation [14].

	Operating conditions
Catalyst	Ru-HBZ
Temperature (°C)	250
Pressure (atm)	1
Ethanol conversion (%)	54
Selectivity (%)	86.7% of DEE 13.3% of ethylene

3.1.2 Process simulation

For process simulation, Aspen Plus is used to simulate the DEE production process from ethanol. As shown in Table 5, the operating conditions of the process for DEE synthesis is carried out at low pressure. Also, the process consists of polar molecules and azeotrope (i.e., ethanol-water mixture). Therefore, according to Eric Carlson's guideline [41], the activity coefficient model (NRTL) was selected to describe the DEE production by using Aspen plus.

3.1.2.1 Feedstock estimation

The feedstocks used for the DEE production is ethanol, the precursor involved in a chemical reaction. Ethanol with purity 99.5% is purchased from the external source. It is used in catalytic dehydration reaction. Furthermore, in order to determine the total amount of ethanol that must feed into the system, the DEE production capacity of 1,800 tons/year is used to determine the size of a process at the reactor outlet stream, which can be made this process economically possible. In addition, other three assumed capacities (900, 2,700 and 3,600 tons/year) will also be determined to view the trend of each capacity on process performance.

From stoichiometric ratio, if two moles of ethanol are utilized, 1 mole of DEE is then generated. Table 6 is shown the calculated results of 99.5% ethanol used to produce DEE, which is the entering the reactor. The calculation procedures for determining the amount of reactants are provided in Appendix A.

Table 6 The amount of ethanol necessary for DEE production.

Temperature (°C)	**250**			
DEE production capacity (tons/year)	900	1,800	2,700	3,600
Ethanol (tons/year)	2,242.21	4,484.43	6,726.64	8,968.85

3.1.2.2 Preliminary design

Figure 4 is the conceptual design to produce DEE from ethanol over Ru-HBZ catalysts, which can be divided into 5 systems including:

- Feed preparation system

Fresh ethanol feed in the process is stored in the storage tank at the temperature and pressure of 30°C and 1 atm. However, the suitable conditions for DEE production is 250°C at constant pressure of 1 atm as provided in Table 5. Thus, it is necessary to have the feed preparation system.

- Reactor system

After the preparation system, the reaction takes place in the reactor via two reactions which are main reaction and side reaction. All reactions react under the same temperature and pressure by using the isothermal reactor. The WHSV is used to determine the size of reactor for Ru-HBZ catalyst.

- Phase separation system

When the product stream leaves the reactor, the stream is full of the gas-liquid phase from the reactions. The liquid is DEE, water and unreacted ethanol remain from the reactions. The gaseous component is ethylene. Therefore, it is necessary to separate two phases by phase separation system.

- Separation system

The separation system is used to separate and purified the mixture components in order to gain the high purity products. The main equipment used in separation system is the distillation column. The design of the distillation column is proceeded by means of “DSTWU” model in Aspen Plus, to create a significant variable that is the number of stages, reflux ratio (RR), feed location, and distillate rate (kmol/h). Furthermore, the separation system will purify the DEE into desired purity by “RADFRAC” model in Aspen Plus. It is used for adjusting the RR or distillate rate values with Design Spec feature to obtain the desired purity.

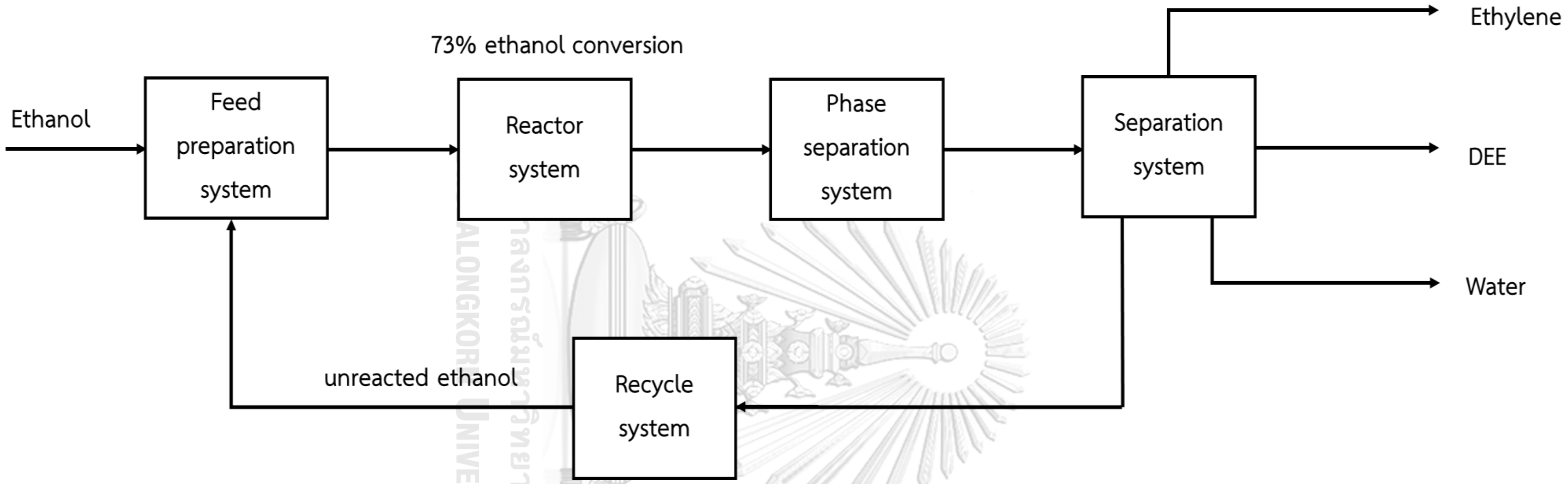


Figure 4 Block flow diagram of DEE production via catalytic dehydration of ethanol

- Recycle system

In the catalytic dehydration of ethanol over Ru-HBZ catalyst, ethanol conversion of 54% was obtained. Thus, there is ethanol remain from the reaction, the unconsumed ethanol must recycle back to conserve materials.

3.1.3 Process description

By using Aspen Plus Process Simulator, the process flow diagram of DEE production is shown in Figure 5 for the operating temperature of 250°C.

As look in Figure 5, fresh feed ethanol with purity 99.5% (FEED stream) and ethanol recycle (RETOH stream) are mixed in the mixer (M101). Then, the 1st mixed stream is discharged to a fired heater (H101). This equipment is increasing the temperature of ethanol (stream 1st) to 250°C, the desired temperature for DEE production. The stream 2nd outlet (H101) is then fed to a reactor (R201) for carried out the catalytic dehydration of ethanol. After the reaction, the stream 3rd is sent to the shell and tube heat exchangers viz H201, H202 and H203. With the first step, the hot stream 3rd is cooled from the temperature of 250 to 182°C (stream 4th) in primary heat exchanger (H201) to enter the secondary heat exchanger (H202). It will be decreased temperature to 45°C (stream 5th). After that, the temperature of stream 6th is decreased to 10°C in tertiary heat exchanger (H203) and then sent to a flash drum (F301) to separate the cooled stream 6th into two phases, including gas phase and liquid phase. The gaseous stream (ETHYLENE stream) component is ethylene. The liquid stream (stream 7st) from flash drum consists of DEE, water, and unreacted ethanol remain from the reactions is sent to the pump (P301) to raise the pressure from 1 to 2 bar (stream 8st) before entering the extractive distillation column (C401). This column is used to separate water from ethanol by using ethylene glycol (ethanol-water azeotropic mixture) and it has portion into three streams including 1) the gaseous stream (VAPOR stream) that component of the remaining gas, 2) the liquid stream (DEE+ETOH stream) that consists of DEE and unreacted ethanol fed into the distillation column (C402) to separate the DEE product with purity 99% (DEE stream) and unreacted ethanol recovery (ETOH stream), and 3) the liquid stream (WATER+EG stream) that contains water and ethylene glycol is fed into the

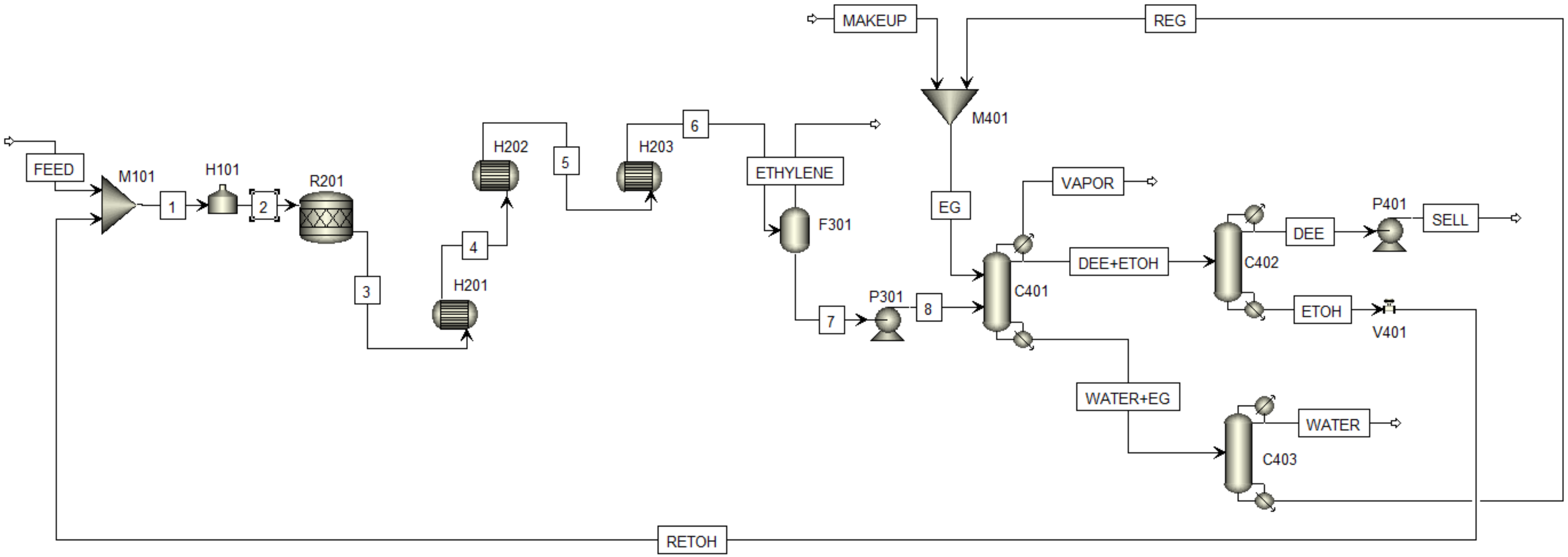


Figure 5 Process flow diagram of DEE production at 250°C.

distillation column (C403) to separate the water (WATER stream) and ethylene glycol recovery (REG stream). Finally, the product stream (DEE stream) at 1.4 bar is sent to pump (P401) for increasing the stream pressure to 1.6 bar, which is the storage condition for the obtained product.

3.1.4 Process performance evaluation

3.1.4.1 Energy utilization evaluation

Energy efficiency is an important factor to consider the process performance and economic results. In this research, it is referred to the specific energy consumption (SEC) which is calculated as following equation [42].

$$Specific\ Energy\ Consumption\ (SEC) = \frac{Energy\ used}{Product's\ amount} \tag{3.1}$$

In this work, thermal and electrical values are measured in term of energy used and then divided by the total amount of DEE produced. For the improvement of energy efficiency, it can be handled with heat exchanger network (HEN) to recover the energy of processes.

3.1.4.2 CO_2 emission evaluation

Climate change is one of the effects of human emissions of greenhouse gases like carbon dioxide (CO_2). For the plant design, the first thing that must be concerned is about the total amounts of CO_2 released from the process. The sources of CO_2 emission in this work is utilities usage which is the indirect CO_2 emissions. The net CO_2 emission can be calculated from Eq. 3.2

$$Net\ CO_2\ emission = \sum_{n}^{i} CO_{2_{Outlet}} - \sum_{n}^{i} CO_{2_{inlet}} \tag{3.2}$$

3.1.4.3 Economic evaluation

In this work, the ethanol and DEE prices are estimated to be about 0.49 \$/l and 5.61 \$/kg, respectively [43, 44]. It was used as a basis for economic evaluation of DEE production by using Aspen Plus (in part of Aspen Economic Evaluation). As for, the costs of utility are shown in Table 7.

Table 7 The costs of utility [45].

Utility	Price	Unit
Electricity	0.06	US$/kWh
Cooling water	0.067	US$/ton
Chilled water	0.185	US$/ton
Boiler feed water	2.45	US$/ton
Low pressure steam	12.68	US$/ton
Medium pressure steam	13.71	US$/ton
High pressure steam	16.64	US$/ton
Natural gas	6.0	US$/GJ

The economic performance indicator of the process is Profitability Index (PI) which can be calculated from the following equation.

$$Profitability\ Inde\ (PI) = \frac{Present\ Value\ of\ Future\ Cash\ Flows}{initial\ Investment} \qquad (3.3)$$

The rules of PI are that 1) If PI is greater than 1, the project should be accepted, and 2) If PI is less than 1, the project should be rejected. As such, the PI value only indicates the possible of the project, but incapable to set the period of returning the capital investment and profit rate. Thus, other parameters are required to meet these requirements including 1) Internal Rate of Return (IRR) is a financial indicator used to determine and evaluate the profitability of the project, and 2) Pay-out Period (POP) is how many years that this project will return the total investment costs. These three parameters can be defined using by the software in Aspen Plus.

3.2 Experimental part

3.2.1 Materials

The commercial HBZ was purchased from Tosoh Corporation. Ruthenium (III) nitrosyl nitrate solution (Ru 1.5% Sigma-Aldrich Chemical Company, Inc.) was used as Ru precursor. The chemicals and reagents that were used in dehydration of ethanol is shown in Table 8.

Table 8 The chemicals and reagents used in dehydration of ethanol

Chemical	Formula	Supplier
Ethanol (93% and 95%)	C_2H_5OH	Merck
Ultra-high purity nitrogen gas (99.99%)	-	Linde
High purity grade hydrogen (99.99%)	-	Linde
Air zero grade balance nitrogen available	-	Linde

Please note that the ethanol with the concentration of 93% and 95% used in this work is diluted from that of 99.99% and 99.99% ethanol is supplied by Merck.

3.2.1.1 Catalyst preparation

The Ru-HBZ catalyst was prepared from impregnation method and characterized as reported in another research [14].

3.2.2 Reaction study in catalytic dehydration of ethanol

The Schematic of the catalytic dehydration of ethanol is shown in Figure 6. In the experiment, the catalytic dehydration of ethanol was carried out in a fixed-bed continuous flow microreactor made from borosilicate glass (inside diameter = 0.7 cm, length = 33 cm). In the experiment, 0.05 g of catalyst and 0.01 g of packed quartz wool were loaded into the reactor. Then, the catalyst was in situ pretreated under gas flow (N_2) at 60 ml/min and 200°C for 1 h under atmospheric pressure to eliminate moisture on the surface of the catalyst. The liquid ethanol feed (various concentrations of ethanol are 93% and 95% respectively) was vaporized at 120°C in a flowing of nitrogen by controlling injection with a single syringe pump at a constant flow rate of 1.45 ml/h and fed into the reactor to obtain the weight hourly space velocity (WSHV) at 22.9 ($g_{ethanol}g_{cat}^{-1}$)h^{-1}. The ethanol dehydration reaction was tested at temperature ranging from 200 to 400°C by feeding the vaporized ethanol into the reactor. The products were analyzed with a gas chromatograph (GC) with flame ionization detector (FID) using capillary column (DB-5). Nitrogen was used as a carrier gas in GC. It was identified hydrocarbon product such as ethanol, DEE, ethylene and acetaldehyde. The operating condition in gas chromatograph (GC) is shown in Table 9.

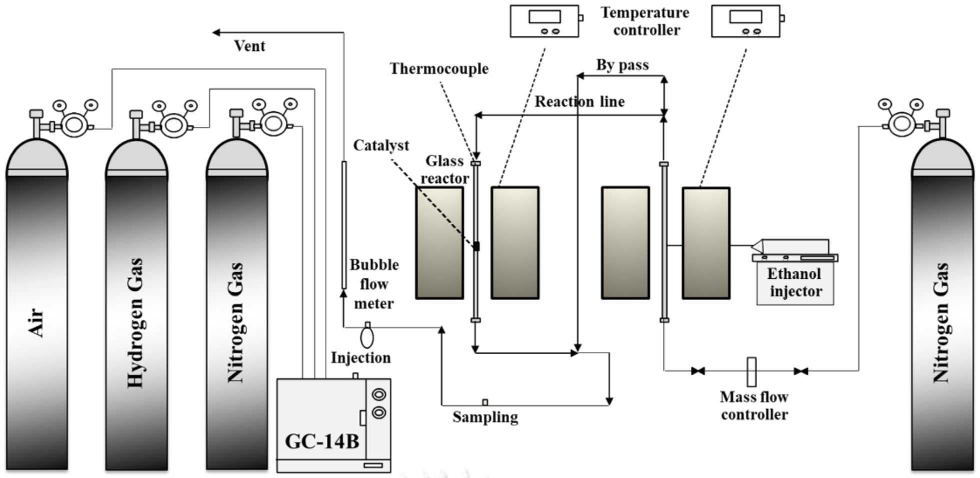


Figure 6 Schematic of the catalytic dehydration of ethanol

Table 9 The operating condition in gas chromatograph (GC)

Gas chromatograph (GC)	Shimadzu GC 14-A
Detector	FID
Capillary column	DB-5
Carrier gas	Nitrogen gas Hydrogen gas
Column temperature	Initial 40°C Final 40°C
Injector temperature	150°C
Detector temperature	150°C
Time analysis	8 min

CHAPTER 4

RESULTS AND DISCUSSION

This chapter is divided into 2 parts including simulation and techno-economic analysis part by using Aspen Plus and experimental part. The first part describes in detail the research methodology for simulation and techno-economic analysis of DEE production from ethanol including raw material utilization, the simulation results of DEE production process, energy utilization evaluation, CO_2 emission evaluation, heat recovery and economic evaluation. The last part explained the information in experimental part including reaction study in catalytic dehydration of ethanol and recommendation for future work.

4.1 Simulation and techno-economic analysis part

4.1.1 Raw material utilization

In catalytic dehydration of ethanol at 250°C, 54% ethanol conversion (a single-pass conversion) is achieved in the reactor. For this reason, ethanol fresh feed stream and ethanol recycle stream are proposed in this DEE production process. The ethanol feed rates and ethanol recycle rates for producing DEE at 250°C is shown in Table 10. These estimated values are calculated from the stoichiometric coefficients in the mass balance equations based on the assumption of perfect separations. This means that the ethanol content is not lost (e.g. in distillation columns involved in ethanol recovery) in the DEE production process.

Table 10 The ethanol feed rates and ethanol recycle rates obtained by stoichiometric calculation for producing DEE at 250°C

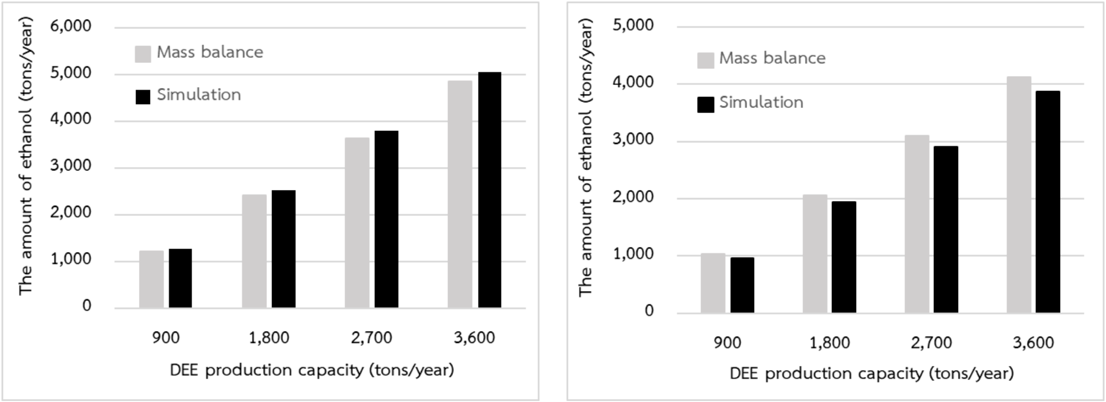
Ethanol flow rate (tons/year)	Stream name	DEE production capacity (tons/year)			
		900	1,800	2,700	3,600
Fresh feed	FEED	1,210.80	2,421.59	3,632.39	4,843.18
Recycle	RETOH	1,031.42	2,062.84	3,094.25	4,125.67

Table 11 The ethanol feed rates and ethanol recycle rates obtained by Aspen Plus simulation for producing DEE at 250°C

Ethanol flow rate (tons/year)	**Stream name**	**DEE production capacity (tons/year)**			
		900	**1,800**	**2,700**	**3,600**
Fresh feed	FEED	1,263.77	2,527.55	3,791.33	5,055.12
Recycle	RETOH	967.58	1,935.14	2,902.72	3,870.30

The ethanol feed rates and ethanol recycle rates obtained by Aspen Plus simulation for producing DEE at 250°C are shown in Table 11. As seen in the table, the simulated results show that the ethanol content in both streams is unequal to the values presented in Table 10, which is presented in Figure 7. As seen in Figure 7 (a), the fresh feed ethanol content obtained from mass balance calculation is less than the fresh feed ethanol content from simulation. On the other hand, the recycle ethanol content obtained from mass balance calculation is more than the recycle ethanol content from simulation (see in Figure 7 (b)). This is because the perfect separation would never be possible. Some ethanol has lost between the separation and purification process of DEE production. Thus, the ethanol content in recycle stream is less than the calculation. For this reason, the lost ethanol will be compensated by adding the ethanol to the fresh feed stream. Therefore, the ethanol content in fresh feed stream is more than the calculation as depicted in the figure.

According to Figure 8, the correlation between ethanol requirement and ethanol compensation for DEE production is illustrated. The compensation percentage is approximately 4.2% in all cases (for example, DEE production capacity of 1,800 tons/year case has approximately 4.2% ethanol compensation that is 2,527.55 tons/year for simulation). In other words, about 95.8% of the overall conversion of ethanol is accomplished when the process in Figure 5 is applied. In addition, the mass balance calculation for this research is exacted by confirmed with the compensation of ethanol increases linearly with the required amounts of ethanol.



(a) (b)

Figure 7 Comparison of mass balance and simulation between DEE production capacity at 250°C and (a) the amount of fresh feed ethanol (b) the amount of recycle ethanol

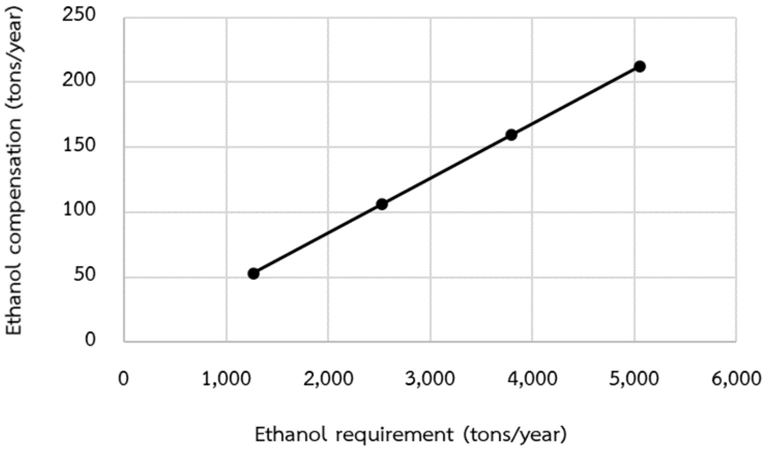


Figure 8 The correlation between ethanol requirement and ethanol compensation for DEE production at 250°C

4.1.2 The simulation results of DEE production process

According to the process flow diagrams represented in previous chapter, Section 3.1.3, stream results of DEE production from Aspen Plus Simulator are provided in Table 12. However, they only show the results of DEE production capacity at 1,800 tons/year in this part. The stream results for other capacities are provided in Appendix C.

Table 12 Stream results of DEE production at 250°C

Stream name	Unit	FEED	1	2	3	4	5	6
Temperature	°C	30	58.77	250	250	182.26	45	10
Pressure	bar	1	1	1	1	1	1	1
Molar Vapor Fraction	-	0	0	1	1	1	0.2667	0.0460
Mole Flows	kmol/hr	5.751	10.126	10.126	10.512	10.512	10.512	10.512
Mass Flows	tons/year	2540.25	4485.12	4485.12	4485.12	4485.12	4485.12	4485.12
Ethanol	tons/year	2527.55	4462.70	4462.70	2052.84	2052.84	2052.84	2052.84
Ethylene	tons/year	0	3.77E-08	3.77E-08	104.63	104.63	104.63	104.63
Water	tons/year	12.7013	16.05	16.05	520.83	520.83	520.83	520.83
Diethyl ether	tons/year	0	6.37	6.37	1806.82	1806.82	1806.82	1806.82
Ethylene glycol	tons/year	0	0.0059	0.0059	0.0059	0.0059	0.0059	0.0059

Table 12 Stream results of DEE production at 250℃ (Cont’d)

Stream name	Unit	7	8	ETHYLENE	EG	VAPOR	DEE+ETOH	WATER+EG
Temperature	℃	10	10.09	10	219.25	63.95	63.95	162.18
Pressure	bar	1	2	1	2	1.7	1.7	2
Molar Vapor Fraction	-	0	0	1	1.08E-06	1	0	0
Mole Flows	kmol/hr	10.028	10.03	0.48	9.00	0.70	6.32	12.02
Mass Flows	tons/year	4300.78	4300.78	184.34	5383.48	439.88	3324.38	5920.01
Ethanol	tons/year	2049.75	2049.75	3.09	0.0050	81.69	1947.26	20.80
Ethylene	tons/year	8.34	8.34	96.29	2.34E-09	7.42	0.92	2.55E-08
Water	tons/year	520.08	520.08	0.75	7.90	0.30	4.13	523.56
Diethyl ether	tons/year	1722.61	1722.61	84.21	5.24E-05	350.47	1372.06	0.08
Ethylene glycol	tons/year	0.0059	0.0059	1.72E-09	5375.57	1.45E-06	0.0058	5375.57

Table 12 Stream results of DEE production at 250℃ (Cont'd)

Stream name	Unit	DEE	ETOH	SELL	RETOH	WATER	REG	MAKEUP
Temperature	℃	34.27	91.71	34.31	77.62	110.56	219.24	221.34
Pressure	bar	1.4	1.7	1.6	1	1.7	2	2
Molar Vapor Fraction	-	0	0	0	0.0558	0	0	0
Mole Flows	kmol/hr	1.94	4.38	1.94	4.38	3.07	8.95	0.06
Mass Flows	tons/year	1379.48	1944.90	1379.48	1944.90	571.00	5349.01	34.47
Ethanol	tons/year	12.09	1935.17	12.09	1935.17	20.79	0.0050	0
Ethylene	tons/year	0.92	3.77E-08	0.92	3.77E-08	2.32E-08	2.34E-09	0
Water	tons/year	0.79	3.34	0.79	3.34	515.65	7.90	0
Diethyl ether	tons/year	1365.68	6.37	1365.68	6.37	0.08	5.24E-05	0
Ethylene glycol	tons/year	2.10E-25	0.0058	2.10E-25	0.0058	34.47	5341.10	34.47

4.1.3 Energy utilization evaluation

In this case, the energy in the process can be divided into two types viz electrical and thermal duties. The total amounts of electrical and thermal duties are presented in Table 13.

Table 13 Summary of total electricity and thermal duties in DEE production process at 250°C

DEE production capacity (tons/year)	Energy consumption (MW)	
	Thermal duty	Electrical duty
900	0.6211	2.77E-05
1,800	1.2427	5.54E-05
2,700	1.8637	8.31E-05
3,600	2.4857	1.11E-04

As shown in Table 13, the DEE production capacity at 3,600 tons/year will be used the electricity consumption more than other capacities, in which the total amount of electricity in this part is utilized by the pumps. Furthermore, energy efficiency is determining the process performance in this work that is defined by specific energy consumption (SEC) that has been calculated (See in Eq. 3.1). The specific energy consumption can be calculated by dividing the total electricity consumption by the total amount of DEE produced. The specific energy consumption for DEE production process is approximately around 0.00141 MJ/kg in all cases. This indicates that the process occurring uses electricity significantly. In respect of the thermal duty, the specific energy consumption for DEE production process is approximately around 31.65 MJ/kg in all cases.

The thermal duty in each units of DEE production process as illustrated in Figure 9. The highest use of thermal energy consumption is from the distillation units. The thermal energy consumption used in distillation column is about 72.9% of the total thermal requirement. In addition, the highest DEE production capacity (3,600 tons/year) is using the most energy as well. The 54% conversion of ethanol for DEE production is obtained at 250°C. Thus, it leads to the huge uses of the thermal energy quantity for internal circulation of the unreacted ethanol and ethylene glycol, which come from the combination of thermal utilities used in extractive distillation column (C401).

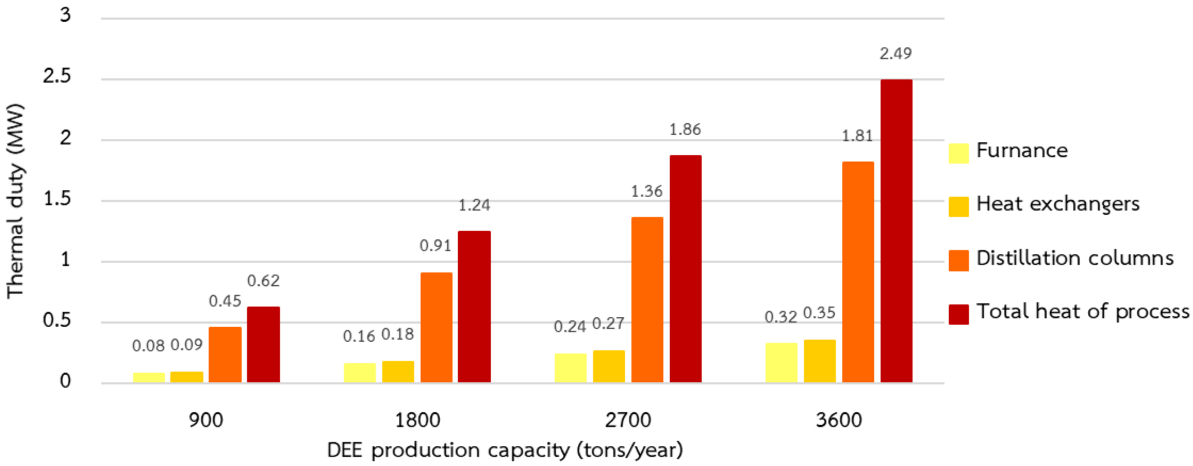


Figure 9 Thermal duty in each units of DEE production process at 250°C

4.1.4 CO_2 emission evaluation

As mentioned from previous chapter, the first thing that must be concerned for the plant design is about the total amounts of CO_2 released from the process that can cause a greenhouse gas. Thus, the net carbon dioxide emission of DEE production process will be according to Equation 3.2. Two possible sources of CO_2 emission include the utilities usage and chemical reaction which are indirect and direct CO_2 emissions, respectively. In this work, the sources of CO_2 emission are utilities usage as an indirect CO_2 emission only. However, the catalytic dehydration of ethanol reaction takes place without the utilization of CO_2. Therefore, the net CO_2 emission of this work is only calculated in term of CO_2 outlets. Net CO_2 emission in each production capacity of DEE is shown in Table 14.

The results on the Table 14 can be certain the amount of CO_2 emitted per 1 kilogram of producing DEE that is approximately 1.06 kg_{CO_2}/kg_{DEE} for DEE production process. The determinant that affected the large CO_2 emitted content in DEE production process was mainly from distillation column, which is exhibited in Figure 10.

Table 14 Summary of net CO_2 emission from the DEE production process at 250°C

DEE production capacity (tons/year)	Outlets CO_2	Net CO_2 emission (kg/hr)
	Indirect CO_2 (kg/hr)	
900	74.706	74.706
1,800	149.481	149.481
2,700	224.178	224.178
3,600	298.995	298.995

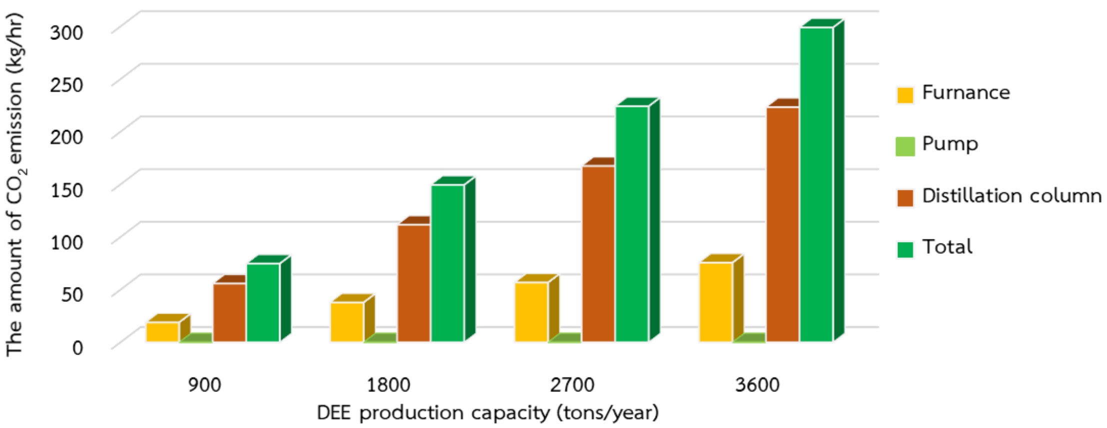


Figure 10 The amount of CO_2 emission from each unit for DEE production process

According to Figure 10 for dehydration of ethanol at 250°C, the amount of CO_2 emitted from the distillation column units is approximately 74.68% of the total CO_2 emission. The 3,600 tons/year of DEE production capacity has the highest amount of CO_2 emission. This is due to the enormous amount of process utility required. Thus, the larger the utility usage, the higher the amount of CO_2 emissions.

4.1.5 Heat recovery

Heat recovery has been used in this work also. Heat recovery system is conducted by using heat exchanger unit namely H201 in the DEE production process at 250°C. Besides, there is the utility involved in the heat recovery system that is boiler feed water (BFW), which is the water vaporized into the saturated steam.

The heat exchanger H201 of heat recovery system is used to exchange the heat during the process stream and boiler feed water by reducing the temperature from 250 to 182.26°C in stream 3rd. The boiler feed water at 172.26°C is used to absorb heat released from this process. After that, the boiler feed water can be used as utility for source of reboiler heat in the extractive distillation column C401. The heat utilities generated from the heat exchanger unit and applied in the distillation column unit can decrease the utility costs of the process.

4.1.6 Economic evaluation

In this work, the analysis tool using for the techno-economic analysis of DEE production processes is proceeded by Aspen Economic Analyzer program with a fixed 20-year project lifetime. The production capacity of DEE has been divided into two classifies viz 1,800 tons/year, which is a based case and 900, 2,700 and 3,600 tons/year are assumed cases. The economic evaluation of each DEE production capacity is based on fixed ethanol price to 0.49 US$ per liter that is a precursor and DEE price to 5.61 US$ per kilogram that is a product. The 1,800 tons/year of DEE production capacity is conventional process, which will be based on information of TKM Pharma private company limited (India) [40]. The process is expected to be began profitable and the other DEE capacity is designed to view trends in economic evaluation. Moreover, the catalytic dehydration of ethanol having a capacity of 1,800 tons of DEE per year is selected to determine the minimum DEE selling price that begins to turn a profit as well. After that, there will have the economic evaluation efficiency of DEE production processes to decide the optimum condition for DEE synthesis that uses ethanol as a starting material.

The economic analysis of DEE production process is proceeded by Economic Evaluator in Aspen Plus for the catalytic dehydration of ethanol with each production capacity. The selling price of DEE is 5.61 US$ per kilogram that is POP of about 6 years. In addition, the results of economic analysis of DEE production process is shown in Table 15 which have 20-year project lifetime.

Table 15 The results of economic evaluation of DEE production process at 250°C

Economic parameter	DEE production capacity (tons/year)			
	900	**1,800**	**2,700**	**3,600**
Total Capital Cost (USD)	6.96E+06	7.06E+06	7.17E+06	7.27E+06
Total Operating Cost (USD/Year)	2.53E+06	3.42E+06	4.31E+06	5.20E+06
Total Raw Materials Cost (USD/Year)	7.30E+05	1.46E+06	2.19E+06	2.92E+06
Total Product Sales (USD/Year)	3.51E+06	7.02E+06	1.05E+07	1.40E+07
Total Utilities Cost (USD/Year)	1.20E+05	2.12E+05	3.04E+05	3.96E+05
Equipment Cost (USD)	3.96E+05	4.33E+05	4.82E+05	5.34E+05
Total Installed Cost (USD)	1.84E+06	1.91E+06	2.01E+06	2.09E+06
Profitability index (PI)	0.83	1.13	1.29	1.39
POP (year)	-	5.78	3.57	2.77
%IRR	-	33.94	55.98	76.64

According to Table 15, the assumption of DEE production can be confirmed by the economic evaluation results. For, the DEE production capacity with a 900 tons/year, the result presents that profitability index (PI) of the process is less than 1. Therefore, the process this is not profitable. In respect of the DEE production capacity with an 1,800 tons/year, the process is profitable, but there is a POP more than 5 year, in which the selling price of DEE is about 5.61 US$/kg. However, it can be acceptable when the selling price of DEE will be higher. In part of the DEE production capacity with a 2,700 and 3,600 tons/year, the two process is profitable and there are a POP less than 5 year. In addition, based on the catalytic dehydration of ethanol with a production capacity of 1,800 tons/year, the minimum selling price of DEE that can return profit to the process is 4.55 US$ per kilogram having the PI of the process is 1, the IRR is 21.12% and POP of the process is about 10 years.

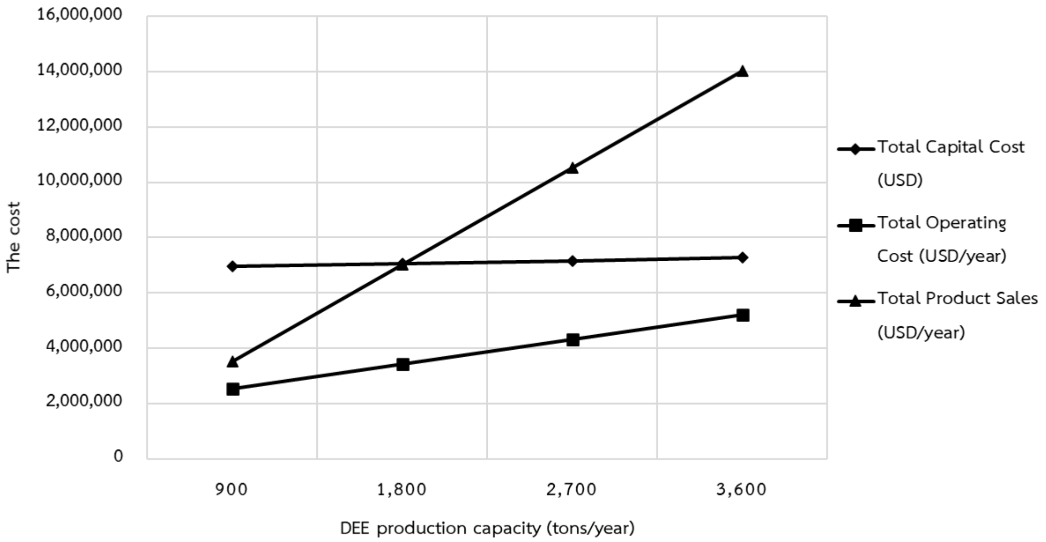


Figure 11 Trend of total capital cost, total operating cost, and total product sales for each DEE production capacity

According to Figure 11, the total product sales is higher than total capital cost and total operating cost for each DEE production capacity but except 900 tons/year of DEE production that is not profitability at project lifetime 20 years. Thus, the DEE production capacity with 1,800 tons/year begins to achieve the profit. The above results are corresponding with the results in Table 15 that the higher DEE production capacity has led to the process with higher profitability.

Furthermore, the economic evaluation results of DEE production process were found to have the highest internal rate of return (IRR), which is caused by the maximum production capacity used in this work. Thus, the optimum DEE production capacity is 3,600 tons/year, but the process that was chosen to mention in this work is 1,800 tons/year of DEE production process. Since this is a process with reference, profitable and this is the conventional process. The optimum operating condition for DEE synthesis will be mentioned the profitability only of the process, which did not include the amount of CO_2 emissions.

Figure 12 shows the selected condition for a flash drum of the DEE production capacity with 1,800 tons/year by using the sensitivity function in Aspen Plus. The optimum condition selected is at 10°C and 1 atm for the process operating at 250°C, which is the best condition to obtain the DEE recovery. The DEE recovery after leaving the flash drum is approximately 95.32%. This process does not require the installation of a compressor because there is already good separation of gas and liquid at flash drum and gas compressor is very expensive.

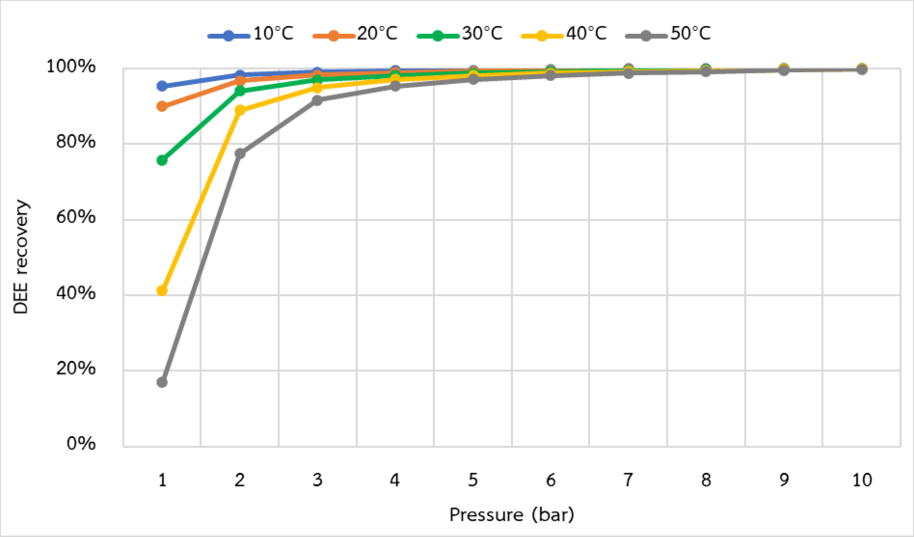


Figure 12 The various pressures and temperatures on the amount of DEE exiting the flash drum

Table 16 Total equipment cost for DEE production process at 250°C

DEE production capacity (tons/year)	Total Equipment Cost (USD)
900	395,500
1,800	433.300
2,700	482,100
3,600	534,400

Total equipment cost of each DEE production process is presented in Table 16. The results of economic evaluation show that the DEE production with 3,600 tons/year requires more cash in payment for the equipment than other production capacity. The equipment costs of each unit are represented in Figure 13.

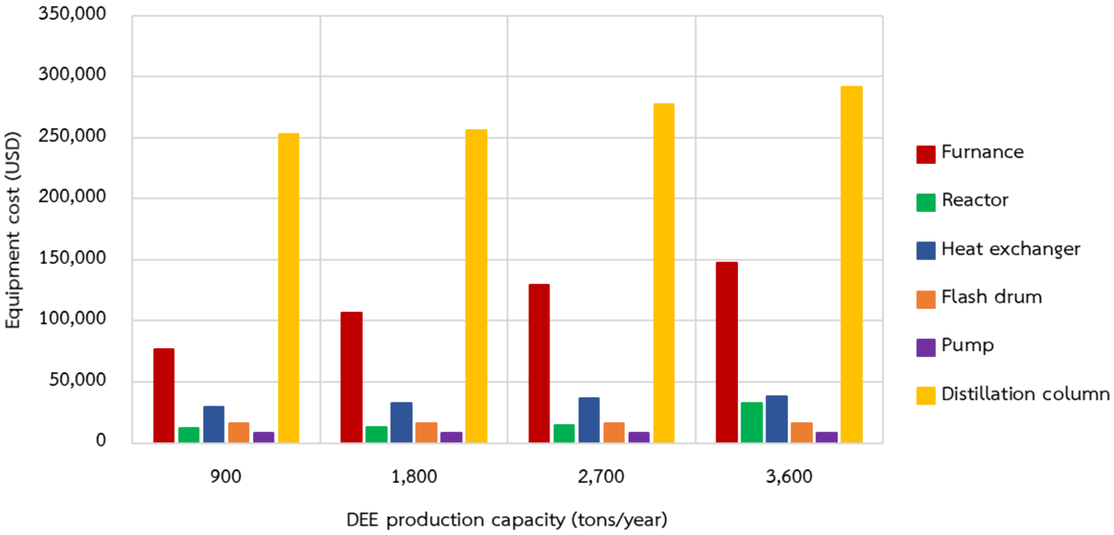


Figure 13 Equipment cost of each unit operation

As shown in Figure 13, it was found that the main equipment cost of DEE production process from the smallest to the largest capacities is the distillation column used to purify and separate chemical substances namely ethanol, DEE, ethylene, water and ethylene glycol The distillation column will more expensive than other unit operations.

In summary, the results of the economic evaluation relationship between economic parameters and DEE production capacity show that the optimum DEE production capacity is 3,600 tons/year because it has the highest internal rate of return (IRR) and it has a profitability index (PI) more than 1. This process will be more than other process profitable and desirable. In addition, the DEE production capacity of 1,800 tons/year is mentioned due to this is the process with reference and these are the conventional process. There are a number of reasons why this process is useful when compared the conventional process including 1) This process has achieved the profit because the process has a profitability index (PI) more than 1, Pay-out Period (POP) about 6 years, and good Internal Rate of Return (IRR). 2) The total equipment cost of this process is low when compared to the other capacities that is beginning to obtain the profit. 3) The process is environmentally friendly due to the Ru-HBZ catalyst is a heterogeneous catalyst, which is non-corrosive in unit operations of the process and different from the conventional process using sulfuric acid (Homogeneous catalyst) as a catalyst and 4) The Ru-HBZ catalyst can be easily separated from the DEE product since it is the solid catalyst.

In this simulation and techno-economic analysis part, it used 99.5% pure ethanol precursor in DEE production process, which is more expensive (Ethanol price is 0.49 US$/liter). In most industries, it used ethanol with purity 93% and 95%, which was cheaper (95% pure ethanol price is 0.0072 US$/liter [46]). Therefore, it is interesting to study the effect of water in ethanol on conversion and selectivity, which leads to the experimental part.

4.2 Experimental part

In this work, the catalytic dehydration of ethanol was studied over H-beta zeolite (HBZ) catalyst with ruthenium (Ru-HBZ) modification in the reaction temperature between 200 to 400°C under atmospheric pressure. There is a compare various concentration of ethanol including 93% and 95% of ethanol concentration that affect DEE production.

4.2.1 Reaction study in catalytic dehydration of ethanol

The various concentrations of ethanol over Ru-HBZ catalyst was tested in ethanol dehydration. In the experiment, 0.05 g of catalyst and 0.01 g of packed quartz wool were loaded into the fixed-bed continuous flow microreactor. Then, the gas phase of ethanol having a constant flow rate of 1.45 ml/h was fed into the reactor. The reaction was carried out in the temperature ranging from 200 to 400°C. The various concentrations for ethanol dehydration in terms of ethanol conversion is shown in Figure 14. It was found that the reaction temperature is increase resulted in an increase of ethanol conversion for both 93% and 95% ethanol concentrations. Thus, the various concentrations of ethanol exhibited the similar behavior over Ru-HBZ catalyst. The ethanol concentration of 95% with Ru-modified HBZ catalyst presented higher ethanol conversion than that the ethanol concentration of 93% for all reaction temperatures. However, the complete conversion can be achieved at 400°C.

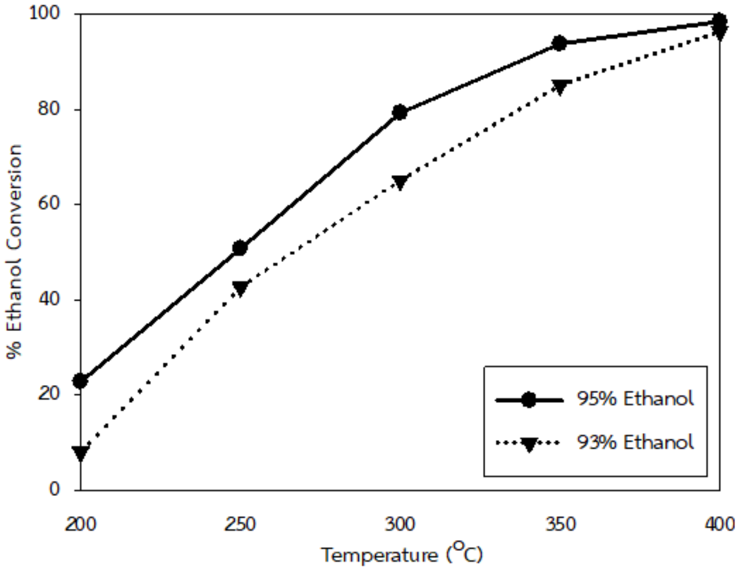


Figure 14 Ethanol conversion of different concentrations of ethanol at different temperatures.

Table 17 The selectivity of product and by-product in catalytic dehydration of ethanol over Ru-HBZ catalyst

Concentration of ethanol (%)	Product selectivity (%)	Temperature (°C)					Ref.
		200	250	300	350	400	
93	Ethylene	0.4	9.7	42.4	87.1	98.7	This work
	Acetaldehyde	1.2	2.4	1.8	0.9	0.7	
	DEE	98.6	87.2	56.3	11.9	0.6	
95	Ethylene	0.0	6.7	49.4	94.1	99.3	This work
	Acetaldehyde	1.0	3.1	1.3	1.0	0.7	
	DEE	98.8	90.9	48.7	5.1	0.0	
99.99	Ethylene	1.0	13.3	73.5	98.3	100.0	[14]
	Acetaldehyde	0.0	0.0	0.0	0.0	0.0	
	DEE	99.0	86.7	26.5	1.7	0.0	

According to Table 17, that is presented the selectivity of product for different concentrations of ethanol over Ru-HBZ catalyst. For the ethylene selectivity, when the reaction temperature is increased, it resulted in an increase of the ethylene selectivity. The ethanol concentration of 93% and 95% obviously resulted in decreased ethylene selectivity between the reaction temperatures of 300 to 400°C. At the same time, the results of DEE selectivity for different concentrations of ethanol displayed that they apparently decreased with increased reaction temperature. Although DEE selectivity with ethanol concentrations of 93% and 95% at 200°C is the highest, ethanol conversion at this temperature is very low. Therefore, in this work, it is interesting to study the DEE yield achieved (product of DEE selectivity and ethanol conversion) in each temperature. This result corresponds to thermodynamic properties, in catalytic dehydration of ethanol to ethylene is endothermic reaction, which requires the high temperature. In contrast, in catalytic dehydration of ethanol to DEE, it is exothermic reaction, which is favor at the low temperature. Furthermore, the by-product is acetaldehyde when reducing the concentration of ethanol (the high-water content). However, acetaldehyde selectivity was very much lower than other products due to different concentrations of ethanol.

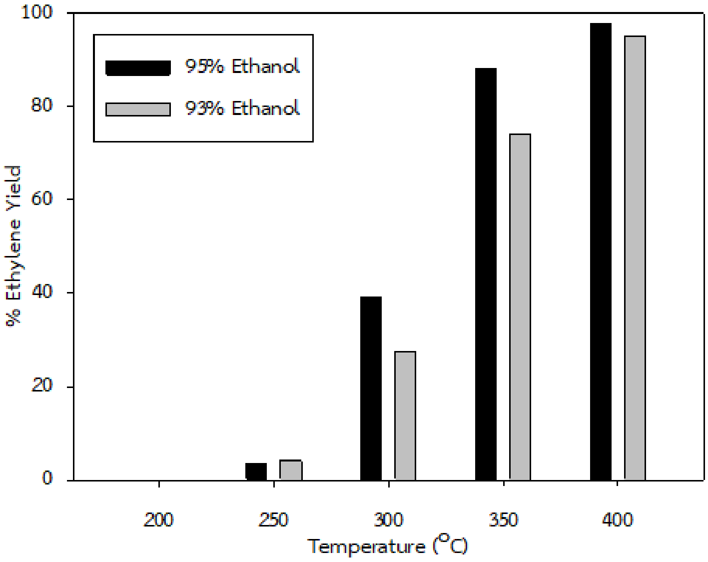


Figure 15 Ethylene yield of different concentrations of ethanol at different temperatures

As shown in Figure 15 , it was found that the highest ethylene yields for different concentrations were achieved at 400°C pointed out the high catalytic activity and ethanol conversion is the highest compared to the low temperature reaction. Thus, increasing of the ethanol conversion will result in increased ethylene as well. At this temperature, the ethanol concentration of 93% and 95% represented the highest ethylene yield reaching to 95% and 98%, respectively. In another research [14], the ethanol concentration of 99.99% represented 99% of ethylene yield. It was denoted that the water in the ethanol solution had only slight effect on the catalyst. The DEE yield is illustrated in Figure 16. It reveals that the highest DEE yields for various concentrations were achieved at 250°C.

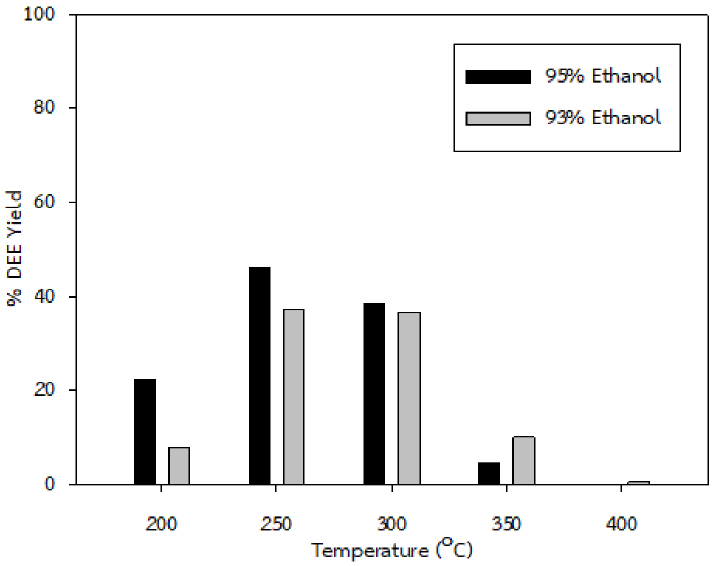


Figure 16 DEE yield of various concentrations of ethanol at different temperatures

Moreover, the increasing of reaction temperature resulted in decrease of DEE yield. It can be concluded that at lower temperature, alkoxy- groups coexist with gas phase ethanol and participate in the reaction producing DEE, while ethylene is not observed. In contrast, the gas phase ethanol is no more available and at higher temperature, ethoxy- groups crack to ethylene [12]. In addition, the low DEE yield is caused by low ethanol conversion observed from the ethanol conversion at 200°C, that is very low. Hence, the DEE yield was quite low. Thus, the most appropriate temperature for DEE production is 250°C. At this temperature, the ethanol concentrations of 93% and 95% have 37% and 46% of DEE yield, respectively. In another research [14], the ethanol concentration of 99.99% displayed 47% of DEE yield. It was denoted that the water in the ethanol solution has a greater effect on the catalyst.

Previously, González et al. indicated that the appearance of water increases the formation of direct ethanol dehydration products. A possible explanation for this behavior could be that the increase in Brønsted acidity of the catalyst possibly by transformation of some of the Lewis acid sites into Brønsted acid sites with water chemisorption. This transformation could also the blocking of Lewis acid sites, to the lower activity of the catalyst in the attendance of water [47]. Therefore, it can be explained that the water molecule may be able to block the surface of the catalyst, which would provide a straightforward explanation for the significant reduction in the active sites, as well as the catalytic performance for ethanol dehydration.

Table 18 Comparison of various concentrations of ethanol for DEE yield and ethylene yield

Concentration of ethanol (%)	Reaction at 250 °C		Reaction at 400 °C		Ref.
	Ethanol conversion (%)	DEE yield (%)	Ethanol conversion (%)	Ethylene yield (%)	
93	43	37	96	95	This work
95	51	46	98	98	This work
99.99	54	47	99	99	[14]

The DEE yield and ethylene yield at reaction temperatures of 250°C and 400°C respectively, with different concentrations of ethanol are summarized in Table 18. At reaction temperature of 400°C, it is illustrated that when concentration of ethanol decreased from 95% to 93%, it resulted in decreased ethylene yield ca. 3.06%. At reaction temperature of 250°C, it indicated that when concentration of ethanol decreased from 95% to 93%, it led to decrease DEE yield ca. 19.57%. From these results, it revealed that water in ethanol solution has a greater impact on DEE production than ethylene production.

4.2.2 Recommendation for future work

In this work, a simulation of the DEE production process over a Ru-HBZ catalyst at 250°C was studied by using 99.5% pure ethanol as a precursor only. In addition, the experiment of catalytic dehydration of ethanol to produce DEE over a Ru-HBZ catalyst by using ethanol with purity 93% and 95% was studied. It was found that water had an effect on ethanol conversion and selectivity. Moreover, there is a by-product as acetaldehyde, in which the acetaldehyde is an azeotrope with DEE. It is difficult to separate acetaldehyde from DEE product. So, I would like to recommend to demonstrate a simulation of the DEE production process over a Ru-HBZ catalyst at 250°C by using 93% and 95% pure ethanol as a precursor. The Aspen Plus program was used to simulate this process. It should be noted that the reaction temperature and the operating pressure were assumed to be unchanged. For the ethanol concentration, ethanol conversion, product selectivity and structure of distillation units of DEE production, they will change. After that, it was performed the economic evaluation by using an Aspen Economic Analyzer program to check that this process will be profitable or not.

CHAPTER 5

CONCLUSION

Currently, the major source of the energy used is from non-renewable fuel, which has many disadvantages of non-renewable energy including the non-sustainability and its negative impact on the environments. Thus, attempts have been made to replace the non-renewable with the renewable one such as bioethanol. DEE is a part of bioethanol. However, the involvement of electric vehicles (EV) may decrease ethanol demand for gasohol in the future. Accordingly, in this work, it will apply ethanol to produce DEE via the catalytic dehydration of ethanol reaction to add value offer ethanol. In addition, there is a comparative study on different concentrations of ethanol (93% and 95% ethanol) that affects DEE production during the catalytic dehydration of ethanol to view how the water effects on ethanol conversion and selectivity.

For simulation and techno-economic analysis part, the process simulation and economic evaluation of the DEE production process is proceeded by Aspen Plus program. The operating conditions were obtained from literatures. The catalytic dehydration of ethanol over a Ru-HBZ catalyst at 250°C under atmospheric pressure was used as input data to simulate the DEE production process. The production capacity of DEE has divided into four capacities viz 900, 1,800, 2,700 and 3,600 tons/year.

First, the results of raw material utilization indicated that the ethanol content utilization, which is calculated from the stoichiometric coefficients in the mass balance equations based on the assumption of perfect separations unequal to the ethanol content utilization, which is calculated from Aspen Plus program. Since the perfect separation would never be possible because some ethanol has lost between the separation and purification process of DEE production. The overall conversion of ethanol achieved from DEE production is about 95.8%.

Second, the energy utilization evaluation of the DEE production process is defined by specific energy consumption (SEC). In terms of electricity duty, the SEC for DEE production process is approximately 0.00141 MJ/kg in all capacities and the energy consumption comes from pump unit. In terms of thermal duty, the SEC for DEE production process is approximately 31.65 MJ/kg in all capacities. Moreover, the highest use of thermal energy consumption comes from the distillation units, which is about 72.9% of the total thermal requirement. In addition, the DEE production capacity of 3,600 tons/year will the most energy consumption too.

Third, the results of the amount of CO_2 emitted per 1 kilogram of producing DEE are approximately 1.06 kg_{CO2}/kg_{DEE}, which is the indirect CO_2 emission from utility utilization. Mainly the CO_2 emission from the distillation column units is about 74.68% of the total CO_2 emission. Apart from that, the DEE production capacity of 3,600 tons/year has the highest amounts of CO_2 emitted because the large utility is required. It should be noted that if the larger utility is used, the high level of CO_2 emissions is obtained.

Lastly, the optimum capacity of DEE production at 250°C for economic evaluation results is 3,600 tons/year due to the highest %IRR about 76.64%. This process can make a profit returning within 3 years. In contrast, the 900 tons/year of DEE production is impossible for profitability at project lifetime 20 years. Furthermore, the main equipment cost of the DEE production process of each capacity is the distillation column units that are more expensive than other unit operations. In addition, there is considering the DEE production capacity of 1,800 ton/year due to its initial the initial production capacity will be profitable. It has a reference, and these are the conventional process. There are a number of reasons, why the process is appropriate for DEE synthesis from dehydration of ethanol when compare the conventional process including 1) This process has achieved the profit because the process has PI more than 1, pretty Internal Rate of Return (IRR) and this process can make a profit returning within 6 years. 2) The total equipment cost of this process is lower. 3) The process is environmentally friendly and 4) The Ru-HBZ catalyst can be easily separated from the DEE product. Moreover, the heat recovery will be used in this work by the heat utilities generated from the heat exchanger unit that can be applied to the distillation column unit, which can decrease the utility costs of the process.

For the experimental part, it can be summarized that the water content in the ethanol solution has an effect on the Ru-modified HBZ catalyst. In case of ethylene yield, the water content in the ethanol solution has a slight effect on the catalyst at temperature of 400°C. At this temperature, the 93% and 95% of ethanol concentration represented the highest ethylene yield approximately 95% and 98%, respectively. On the other hand, for DEE yield, the water content in the ethanol solution has a greater effect of the catalyst at a temperature of 250°C (The catalytic dehydration of ethanol must be operated at low reaction temperature to maintain high selectivity of DEE). At this temperature, the 93% and 95% of ethanol concentration represented the DEE yield about 37% and 46%, respectively. Owing to the water molecule resulted in an increase the Brønsted acidity and blocking of Lewis acid sites, to the lower activity of the catalyst. By-product is acetaldehyde, in which acetaldehyde yield apparently increases with a water content.

For the future work, the alternative way to a simulation of the DEE production process over Ru-modified HBZ catalyst at 250°C by using 93% and 95% pure ethanol as a feedstock. This process will decrease the cost of feedstock, which can prove that the process is actually profitable in the future.

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APPENDIX

APPENDIX A
CALCULATION FOR MASS BALANCE

For the simulation of DEE production process, we must firstly determine the amounts of reactants fed into the system. In this work, DEE is produced by dehydration of ethanol using Ru-HBZ catalyst at 250°C under atmospheric pressure. The obtained results are represented in accordance with Table A1.

Table 19 Conversion and selectivity in dehydration of ethanol using Ru-HBZ catalyst at 250°C

T (°C)	P (atm)	Ethanol conversion (%)	Selectivity (%)	
			DEE	Ethylene
250	1	54	86.7	13.3

Moreover, the experimental results such as conversion and selectivity are used to calculate the value of the mass flow rate of 99.5 wt% ethanol based on the fixed DEE production capacity of 1,800 tons/year at reactor outlet stream. The calculation procedure is shown as the following steps:

1. Unit conversion: tons/year of DEE to mol/year.

   At reactor outlet stream: 1,800 tons/year of DEE production is determined.

$$\frac{1{,}800\ \frac{\text{tons}}{\text{year}} \times \frac{10^{6}}{1}\ \frac{\text{g}}{\text{tons}}}{74\ \frac{\text{g}}{\text{mol}}} = 24.32\times10^{6}\ \frac{\text{mol}}{\text{year}}$$

2. Finding the amount of ethanol used for producing DEE via catalytic dehydration.

   Basis: overall product = 100 $\frac{\text{mol}}{\text{year}}$

- Ethanol to DEE (86.7% selectivity of DEE)

	$2C_2H_5OH$	$\longrightarrow$	$C_2H_5OC_2H_5$	+	H_2O	
Molecular weight	46		74		18	$\frac{g}{mol}$
Basis (Mole basis)	173.4		86.7		86.7	$\frac{mol}{year}$
(Mass basis)	7,976.40		6,415.80		1,560.60	$\times 10^{-6}\ \frac{tons}{year}$
This work (Mole)	48.64		24.32		24.32	$\times 10^{6}\ \frac{mol}{year}$

Rule of three:

$$\text{Basis DEE} = 86.7\ \frac{mol}{year} \longrightarrow \text{DEE in this work} = 24.32 \times 10^{6}\ \frac{mol}{year}$$

$$\text{Basis ethylene} = 13.3\ \frac{mol}{year} \longrightarrow \text{Ethylene in this work}$$

$$= \frac{24.32 \times 10^{6} \times 13.3}{86.7} = 3.73 \times 10^{6}\ \frac{mol}{year}$$

- Ethanol to ethylene (13.3% selectivity of ethylene)

	C_2H_5OH	$\longrightarrow$	C_2H_4	+	H_2O	
Molecular weight	46		28		18	$\frac{g}{mol}$
Basis (Mole basis)	13.3		13.3		13.3	$\frac{mol}{year}$
(Mass basis)	611.80		372.40		239.40	$\times 10^{-6}\ \frac{tons}{year}$
This work (Mole)	3.73		3.73		3.73	$\times 10^{6}\ \frac{mol}{year}$

On a mass basis, the DEE is produced approximately 6,415.80 x 10^{-6} tons/year. In this work, the DEE has increased production to 1,800 tons/year. Therefore, the total mass of ethanol, ethylene and water is used can be calculated as follows.

$$\text{Ethanol} = (\text{Ethanol})_{\text{DEE}} + (\text{Ethanol})_{\text{Ethylene}}$$

$$= \frac{(7{,}976.40 + 611.80) \times 10^{-6} \times 1800}{6{,}415.80 \times 10^{-6}} \frac{\text{tons}}{\text{year}}$$

$$= 2{,}409.48 \frac{\text{tons}}{\text{year}}$$

$$\text{Ethylene} = \frac{372.4 \times 10^{-6} \times 1800}{6{,}415.80 \times 10^{-6}} \frac{\text{tons}}{\text{year}}$$

$$= 104.48 \frac{\text{tons}}{\text{year}}$$

$$\text{Water} = \frac{(1{,}560.60 + 239.40) \times 10^{-6} \times 1800}{6{,}415.80 \times 10^{-6}} \frac{\text{tons}}{\text{year}}$$

$$= 505 \frac{\text{tons}}{\text{year}}$$

For ethanol, the total mass flow rate of ethanol consumed in reactions as mentioned above = $(48.64 + 3.73) \times 10^6 = 52.37 \times 10^6$ mol/year or 2,409.48 tons/year at 54% conversion of ethanol. Therefore, the actual feed of ethanol can be calculated as follows.

Rule of three:

$$\text{Conversion 54\%} \longrightarrow \text{Ethanol} = 52.37 \times 10^6 \frac{\text{mol}}{\text{year}}$$

$$\text{Conversion 100\%} \longrightarrow \text{Ethanol} = \frac{52.37 \times 10^6 \times 100}{54} = 97 \times 10^6 \frac{\text{mol}}{\text{year}}$$

Thus, the actual feed of ethanol = $97 \times 10^6 \frac{\text{mol}}{\text{year}} \times 46 \frac{\text{g}}{\text{mol}} \times \frac{1}{10^6} \frac{\text{tons}}{\text{g}} =$ 4,462.01 tons/year at 100% conversion of ethanol. The total mass flow rate of recycle ethanol can be calculated as follows.

$$\text{Ethanol recycle} = (97 - 52.37) \times 10^6 \frac{\text{mol}}{\text{year}}$$

$$= 44.61 \times 10^6 \frac{\text{mol}}{\text{year}} \times 46 \frac{\text{g}}{\text{mol}} \times \frac{1}{10^6} \frac{\text{tons}}{\text{g}}$$

$$= 2{,}052.52 \frac{\text{tons}}{\text{year}}$$

However, in this work uses a 99.5 wt% grade ethanol. Then, the actual feed of ethanol = 4,462.01 / $\frac{99.5}{100}$ = 4,484.43 tons/year at 100% conversion of ethanol, the total mass flow rate of ethanol = 2,409.48 / $\frac{99.5}{100}$ = 2,421.59 tons/year at 54% conversion of ethanol and total mass flow rate of ethanol recycle = 2,052.52 / $\frac{99.5}{100}$ = 2,062.84 tons/year.

3. Finding the fractional conversion of ethanol in reactor unit

- First reaction (ethanol to DEE)

$$\text{Fractional conversion} = \frac{48.64 \times 10^6}{97 \times 10^6} = 0.5015$$

- Second reaction (ethanol to ethylene)

$$\text{Fractional conversion} = \frac{3.73 \times 10^6}{97 \times 10^6} = 0.0385$$

APPENDIX B
REACTOR SIZING

In this work, the catalytic dehydration of ethanol to DEE using Ru-HBZ catalyst will used the packed bed reactor. Thereby, the parameter related to reactor sizing to economic evaluation can be calculated as follows and the DEE production capacity for example in the calculation is 1,800 tons/year.

1. Finding the reactor diameter (D)

The reactor diameter can be computed using equation given below:

$$G = \frac{4\dot{m}}{\pi D^2}$$

Where G = mass velocity (kg/m^2·s)

$\dot{m}$ = mass flow rate (kg/h)

D = vessel diameter (m)

For the catalytic dehydration of ethanol at 250°C to DEE production capacity with 1,800 tons/year, the ethanol flow rate is approximately 461.84 kg/h and mass velocity (G) is about 1.35 kg/m^2·s due to the reaction is carried out in a vapor-phase packed bed reactor.

$$\text{Diameter (D)} = \left(\frac{4 \times 461.84\ \frac{\text{kg}}{\text{h}} \times \frac{1}{3600}\ \frac{\text{h}}{\text{s}}}{1.35\ \frac{\text{kg}}{\text{m}^2\cdot\text{s}} \times \pi}\right)^{\frac{1}{2}}$$

$$= 0.3478\ \text{m}$$

2. Finding the catalyst weight (W_{cat})

Weight hourly space velocity (WHSV) of this work is 22.9 ($g_{ethanol}g_{cat}^{-1}$) h^{-1}. The catalyst weight can be computed using equation given below:

$$\text{WSHV} = \frac{\dot{m}}{W_{cat}}$$

$$\text{Catalyst weight } (W_{cat}) = \frac{461.84 \frac{kg}{h}}{22.9 \frac{kg_{ethanol}}{kg_{cat} \cdot h}} = 20.17 \ kg_{cat}$$

3. Finding the volume of catalyst bed (V_{bed})

In this work, the Ru-modified HBZ catalyst was prepared from impregnation method and it has a bulk density (ρ_b) of about 0.50 g/cm^3 or 500 kg/m^3. The volume of catalyst bed can be computed using equation given below:

$$V_{bed} = \frac{W_{cat}}{\rho_b}$$

$$\text{Volume of catalyst bed } (V_{bed}) = \frac{20.17 \ kg_{cat}}{500 \frac{kg}{m^3}} = 0.0403 \ m^3$$

4. Finding the length of the reactor (L_{react}) and length of the catalyst bed (L_{bed})

The length of the catalyst bed can be computed using equation given below:

$$V_{bed} = \frac{\pi D^2 L_{bed}}{4}$$

$$\text{The length of the catalyst bed } (L_{bed}) = \frac{4 \times 0.0403 \ m^3}{\pi \times (0.3478 \ m)^2} = 0.4245 \ m$$

$$\text{The length of the reactor } (L_{react}) = L_{bed} + 0.942 = 0.4245 + 0.942 = 1.3664 \ m$$

The parameter related to reactor sizing to economic evaluation for each production capacity at 250°C is shown in Table B1.

Table 20 Summary of the parameter related to reactor sizing to economic evaluation for each production capacity at 250°C

DEE production capacity (tons/year)	D (m)	W_{cat} (kg)	V_{bed} (m^3)	L_{bed} (m)	L_{react} (m)
900	0.2460	10.08	0.0202	0.4245	1.3664
1,800	0.3478	20.17	0.0403		
2,700	0.4260	30.25	0.0605		
3,600	0.4919	40.34	0.0807		

APPENDIX C

STREAM RESULTS OF DEE PRODUCTION PROCESS

Table 21 Stream results of DEE production capacity of 900 tons/year at 250°C

Stream name	**Unit**	**FEED**	**1**	**2**	**3**	**4**	**5**	**6**
Temperature	°C	30	58.77	250	250	182.26	45	10
Pressure	bar	1	1	1	1	1	1	1
Molar Vapor Fraction	-	0	0	1	1	1	0.2667	0.0460
Mole Flows	kmol/hr	2.875	5.063	5.063	5.256	5.256	5.256	5.256
Mass Flows	tons/year	1270.12	2242.55	2242.55	2242.55	2242.55	2242.55	2242.55
Ethanol	tons/year	1263.77	2231.34	2231.34	1026.41	1026.41	1026.41	1026.41
Ethylene	tons/year	0	1.88E-08	1.88E-08	52.31	52.31	52.31	52.31
Water	tons/year	6.35	8.03	8.03	260.41	260.41	260.41	260.41
Diethyl ether	tons/year	0	3.18	3.18	903.41	903.41	903.41	903.41
Ethylene glycol	tons/year	0	0.0029	0.0029	0.0029	0.0029	0.0029	0.0029

Table C1. Stream results of DEE production capacity of 900 tons/year at 250°C (Cont'd)

Stream name	Unit	7	8	ETHYLENE	EG	VAPOR	DEE+ETOH	WATER+EG
Temperature	°C	10	10.09	10	219.25	63.95	63.95	162.18
Pressure	bar	1	2	1	2	1.7	1.7	2
Molar Vapor Fraction	-	0	0	1	1.09E-06	1	0	0
Mole Flows	kmol/hr	5.013	5.014	0.24	4.50	0.35	3.16	6.01
Mass Flows	tons/year	2150.38	2150.38	92.17	2691.83	219.94	1662.18	2960.09
Ethanol	tons/year	1024.87	1024.87	1.55	0.0025	40.85	973.62	10.40
Ethylene	tons/year	4.17	4.17	48.14	1.17E-09	3.71	0.46	1.28E-08
Water	tons/year	260.04	260.04	0.37	3.95	0.15	2.07	261.78
Diethyl ether	tons/year	861.30	861.30	42.10	2.63E-05	175.23	686.03	0.04
Ethylene glycol	tons/year	0.0029	0.0029	8.57E-10	2687.88	7.28E-07	0.0029	2687.88

Table C1. Stream results of DEE production capacity of 900 tons/year at 250°C (Cont'd)

Stream name	Unit	DEE	ETOH	SELL	RETOH	WATER	REG	MAKEUP
Temperature	°C	34.27	91.71	34.31	77.62	110.55	219.24	221.34
Pressure	bar	1.4	1.7	1.6	1	1.7	2	2
Molar Vapor Fraction	-	0	0	0	0.0558	0	0	0
Mole Flows	kmol/hr	0.97	2.19	0.97	2.19	1.53	4.48	0.029
Mass Flows	tons/year	689.74	972.44	689.74	972.44	285.52	2674.58	17.26
Ethanol	tons/year	6.04	967.58	6.04	967.58	10.40	0.0025	0
Ethylene	tons/year	0.46	1.89E-08	0.46	1.89E-08	1.16E-08	1.17E-09	0
Water	tons/year	0.39	1.67	0.39	1.67	257.82	3.95	0
Diethyl ether	tons/year	682.84	3.19	682.84	3.19	0.04	2.63E-05	0
Ethylene glycol	tons/year	1.05E-25	0.0029	1.05E-25	0.0029	17.25	2670.62	17.26

Table 22 Stream results of DEE production capacity of 2,700 tons/year at 250°C

Stream name	Unit	FEED	1	2	3	4	5	6
Temperature	°C	30	58.77	250	250	182.26	45	10
Pressure	bar	1	1	1	1	1	1	1
Molar Vapor Fraction	-	0	0	1	1	1	0.2667	0.0460
Mole Flows	kmol/hr	8.626	15.189	15.189	15.768	15.768	15.768	15.768
Mass Flows	tons/year	3810.39	6727.69	6727.69	4485.12	4485.12	4485.12	4485.12
Ethanol	tons/year	3791.33	6694.05	3079.27	2052.84	2052.84	2052.84	2052.84
Ethylene	tons/year	0	5.65E-08	156.94	104.63	104.63	104.63	104.63
Water	tons/year	19.0519	24.08	781.25	520.83	520.83	520.83	520.83
Diethyl ether	tons/year	0	9.55	2710.23	1806.82	1806.82	1806.82	1806.82
Ethylene glycol	tons/year	0	0.0088	0.0088	0.0088	0.0088	0.0088	0.0088

Table C2. Stream results of DEE production capacity of 2,700 tons/year at 250°C (Cont'd)

Stream name	Unit	7	8	ETHYLENE	EG	VAPOR	DEE+ETOH	WATER+EG
Temperature	°C	10	10.09	10	219.25	63.95	63.95	162.18
Pressure	bar	1	2	1	2	1.7	1.7	2
Molar Vapor Fraction	-	0	0	1	1.09E-06	1	0	0
Mole Flows	kmol/hr	15.042	15.042	0.73	13.51	1.05	9.48	18.03
Mass Flows	tons/year	6451.18	6451.18	276.51	8075.38	659.82	4986.57	8880.18
Ethanol	tons/year	3074.63	3074.63	4.64	0.0074	122.54	2920.89	31.20
Ethylene	tons/year	12.51	12.51	144.43	3.52E-09	11.13	1.38	3.83E-08
Water	tons/year	780.123	780.123	1.12	11.86	0.44	6.20	785.34
Diethyl ether	tons/year	2583.92	2583.92	126.31	7.88E-05	525.70	2058.09	0.12
Ethylene glycol	tons/year	0.0088	0.0088	2.57E-09	8063.51	2.18E-06	0.0088	8063.51

Table C2. Stream results of DEE production capacity of 2,700 tons/year at 250°C (Cont'd)

Stream name	Unit	DEE	ETOH	SELL	RETOH	WATER	REG	MAKEUP
Temperature	°C	34.27	91.71	34.31	77.62	110.56	219.24	221.34
Pressure	bar	1.4	1.7	1.6	1	1.7	2	2
Molar Vapor Fraction	-	0	0	0	0.0558	0	0	0
Mole Flows	kmol/hr	2.91	6.56	2.91	6.56	4.60	13.43	0.09
Mass Flows	tons/year	2069.22	2917.35	2069.22	2917.35	856.48	8023.70	51.70
Ethanol	tons/year	18.13	2902.76	18.13	2902.76	31.19	0.0075	0
Ethylene	tons/year	1.38	5.66E-08	1.38	5.66E-08	3.48E-08	3.51E-09	0
Water	tons/year	1.18	5.01	1.18	5.01	773.48	11.86	0
Diethyl ether	tons/year	2048.53	9.56	2048.53	9.56	0.12	7.88E-05	0
Ethylene glycol	tons/year	3.16E-25	0.0088	3.16E-25	0.0088	51.68	8011.83	51.70

Table 23 Stream results of DEE production capacity of 3,600 tons/year at 250°C

Stream name	Unit	FEED	1	2	3	4	5	6
Temperature	°C	30	58.77	250	250	182.26	45	10
Pressure	bar	1	1	1	1	1	1	1
Molar Vapor Fraction	-	0	0	1	1	1	0.2667	0.0460
Mole Flows	kmol/hr	11.502	20.252	20.252	21.024	21.024	21.024	21.024
Mass Flows	tons/year	5080.52	8970.27	8970.27	8970.27	8970.27	8970.27	8970.27
Ethanol	tons/year	5055.12	8925.42	8925.42	4105.69	4105.69	4105.69	4105.69
Ethylene	tons/year	0	7.54E-08	7.54E-08	209.25	209.25	209.25	209.25
Water	tons/year	25.4026	32.10	32.10	1041.67	1041.67	1041.67	1041.67
Diethyl ether	tons/year	0	12.74	12.74	3613.65	3613.65	3613.65	3613.65
Ethylene glycol	tons/year	0	0.0117	0.0117	0.0117	0.0117	0.0117	0.0117

Table C3. Stream results of DEE production capacity of 3,600 tons/year at 250°C (Cont'd)

Stream name	Unit	7	8	ETHYLENE	EG	VAPOR	DEE+ETOH	WATER+EG
Temperature	°C	10	10.09	10	219.25	63.95	63.95	162.18
Pressure	bar	1	2	1	2	1.7	1.7	2
Molar Vapor Fraction	-	0	0	1	1.08E-06	1	0	0
Mole Flows	kmol/hr	20.056	20.056	0.97	18.02	1.40	12.63	24.03
Mass Flows	tons/year	8601.59	8601.59	368.68	10766.95	879.76	6648.78	11840.01
Ethanol	tons/year	4099.51	4099.51	6.19	0.0099	163.39	3894.53	41.60
Ethylene	tons/year	16.67	16.67	192.58	4.67E-09	14.84	1.84	5.09E-08
Water	tons/year	1040.17	1040.17	1.50	15.81	0.59	8.27	1047.12
Diethyl ether	tons/year	3445.23	3445.23	168.42	10.5E-05	700.94	2744.13	0.16
Ethylene glycol	tons/year	0.0117	0.0117	3.43E-09	10751.13	2.91E-06	0.0116	10751.13

Table C3. Stream results of DEE production capacity of 3,600 tons/year at 250°C (Cont'd)

Stream name	Unit	DEE	ETOH	SELL	RETOH	WATER	REG	MAKEUP
Temperature	°C	34.27	91.71	34.31	77.62	110.56	219.24	221.34
Pressure	bar	1.4	1.7	1.6	1	1.7	2	2
Molar Vapor Fraction	-	0	0	0	0.0558	0	0	0
Mole Flows	kmol/hr	3.88	8.75	3.88	8.75	6.13	17.90	0.11
Mass Flows	tons/year	2758.97	3889.81	2758.97	3889.81	1141.97	10698.05	68.91
Ethanol	tons/year	24.17	3870.36	24.17	3870.36	41.59	0.0099	0
Ethylene	tons/year	1.84	7.54E-08	1.84	7.54E-08	4.63E-08	4.67E-09	0
Water	tons/year	1.58	6.69	1.58	6.69	1031.31	15.81	0
Diethyl ether	tons/year	2731.38	12.75	2731.38	12.75	0.16	10.5E-05	0
Ethylene glycol	tons/year	4.21E-25	0.0116	4.21E-25	0.0116	68.91	10682.23	68.91

APPENDIX D
CALIBRATION CURVE

Calibration curve is used to calculation mole of ethanol, DEE, ethylene, and acetaldehyde as presented in Figure D1.-D4. The products were analyzed with a gas chromatograph (GC) with flame ionization detector (FID) using capillary column (DB-5).

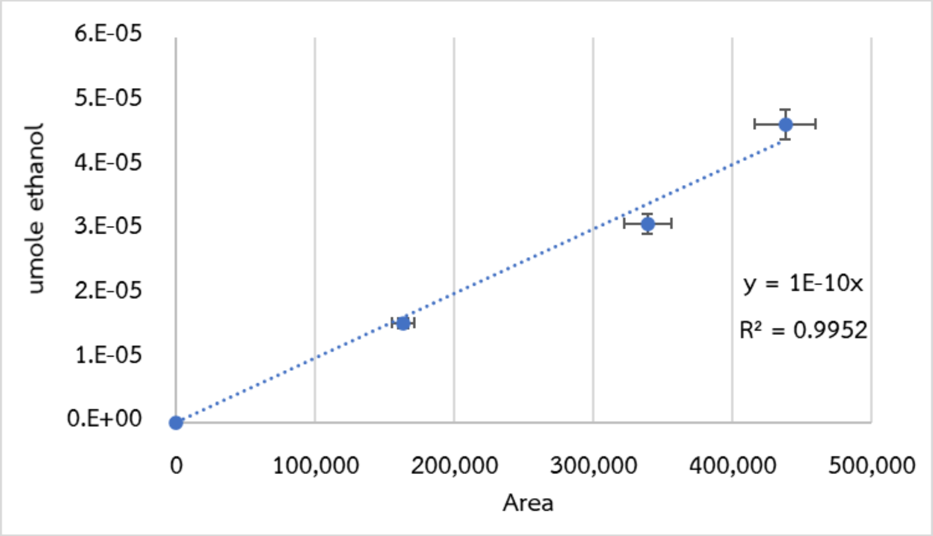

Figure 17 The calibration curve of ethanol

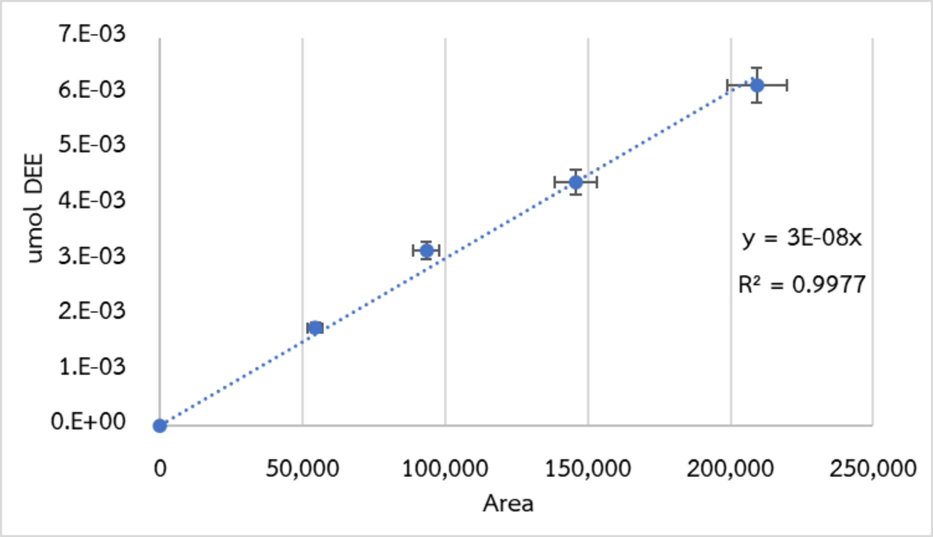

Figure 18 The calibration curve of DEE

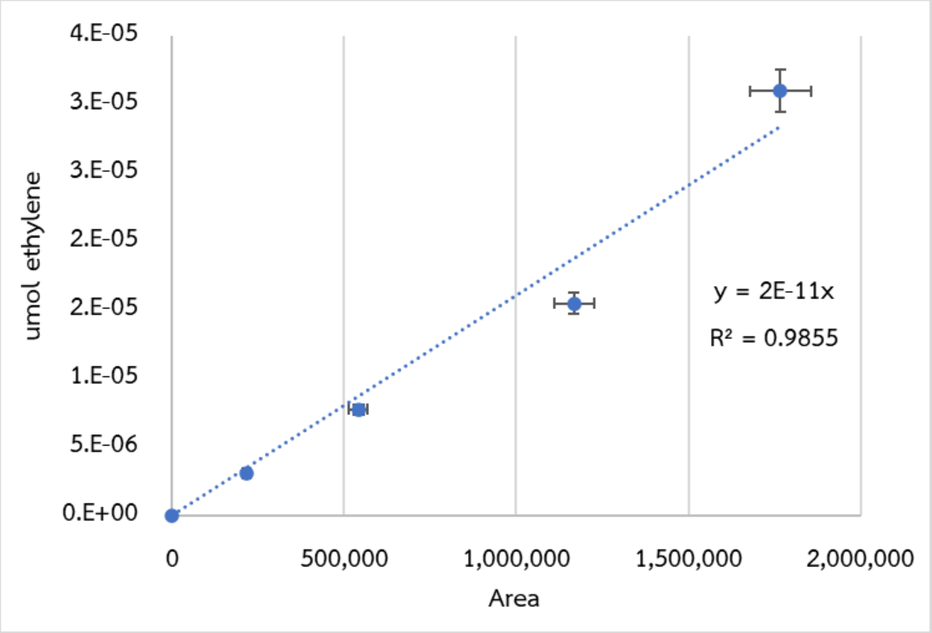

Figure 19 The calibration curve of ethylene

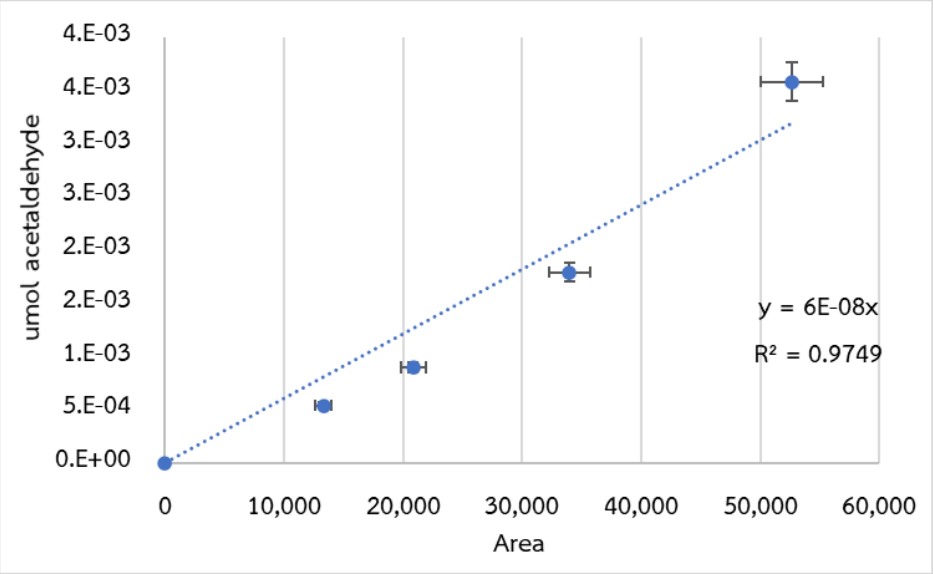

Figure 20 The calibration curve of acetaldehyde

APPENDIX E
CONVERSION, SELECTIVITY AND YIELD

1. Ethanol conversion

$$\text{Ethanol conversion (\%)} = \frac{(\text{mole of ethanol in feed - mole of ethanol in product}) \times 100}{\text{mole of ethanol in feed}}$$

2. Selectivity of product

The selectivity of products is defined as a mole of product convert to non-reactive product. The mole of total products are DEE, ethylene and acetaldehyde.

$$\text{DEE selectivity (\%)} = \frac{\text{mole of DEE in product} \times 100}{\text{mole of total product}}$$

$$\text{Ethylene selectivity (\%)} = \frac{\text{mole of ethylene in product} \times 100}{\text{mole of total product}}$$

$$\text{Acetaldehyde selectivity (\%)} = \frac{\text{mole of acetaldehyde in product} \times 100}{\text{mole of total product}}$$

3. Yield of product

The yield of products is evaluated in term of ethanol conversion and selectivity of product.

$$\text{DEE yield (\%)} = \frac{\text{DEE selectivity} \times \text{ethanol conversion}}{100}$$

$$\text{Ethylene yield (\%)} = \frac{\text{ethylene selectivity} \times \text{ethanol conversion}}{100}$$

$$\text{Acetaldehyde yield (\%)} = \frac{\text{acetaldehyde selectivity} \times \text{ethanol conversion}}{100}$$

Example of determining the mole of each products

From calibration curve in APPENDIX D

Mole of ethanol = $(1 \times 10^{-10}) \times$ area

Mole of DEE = $(3 \times 10^{-8}) \times$ area

Mole of ethylene = $(2 \times 10^{-11}) \times$ area

Mole of acetaldehyde = $(6 \times 10^{-8}) \times$ area

The area of reactant and product in above equation can be detected by the gas chromatography.

VITA

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