Process analysis and economic evaluation of acetaldehyde production from ethanol via non-oxidative dehydrogenation

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Chemical Engineering
Department of Chemical Engineering
FACULTY OF ENGINEERING
Chulalongkorn University
Academic Year 2020

การวิเคราะห์กระบวนการ และการประเมินทางเศรษฐศาสตร์ของกระบวนการผลิตอะเซทัลดีไฮด์จากเอทานอลผ่านปฏิกิริยาดีไฮโดรจิเนชันแบบไร้ออกซิเจน

นายธนกาญจณ์ สุทธิโรจน์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2563

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ในปัจจุบัน ได้มีการตระหนักถึงภาวะโลกร้อน การใช้เชื้อเพลิงเผาไหม้ในรถยนต์ก็เป็นอีกสาเหตุที่มีการปล่อยก๊าซคาร์บอนไดออกไซด์ซึ่งก่อให้เกิดภาวะโลกร้อน จึงทำให้รถยนต์ไฟฟ้ามีบทบาทมากขึ้นในทั่วโลกรวมไปถึงประเทศไทย ส่งผลให้การใช้เชื้อเพลิงมีลดลง ด้วยเหตุนี้ความต้องการใช้เอทานอลจึงลดลงไปด้วย ดังนั้นการหาทางเลือกอื่น ๆ ในการเปลี่ยนเอทานอลไปเป็นอะเซทัลดีไฮด์จึงน่าสนใจสำหรับงานชิ้นนี้ เนื่องด้วยราคาที่สูงกว่า รวมไปถึงการนำไปใช้ประโยชน์ได้อย่างหลากหลาย

งานวิจัยนี้เป็นการออกแบบกระบวนการ และวิเคราะห์กระบวนการสองกระบวนการ โดยเปรียบเทียบกระบวนการที่มีค่าเปอร์เซ็นการเปลี่ยนไปเป็นผลิตภัณฑ์ของสารตั้งต้นที่สูง แต่มีค่าการเปลี่ยนแปลงไปเป็นผลิตภัณฑ์ที่ต่ำกับกระบวนการที่มีค่าเปอร์เซ็นการเปลี่ยนไปเป็นผลิตภัณฑ์ของสารตั้งต้นที่ต่ำ แต่มีค่าการเปลี่ยนแปลงไปเป็นผลิตภัณฑ์ที่สูง และมีการประเมินทางเศรษฐศาสตร์ผ่านโปรแกรมที่มีชื่อว่า แอสเพน พลัส การวิเคราะห์ทางเศรษฐศาสตร์ของกระบวนผลิตอะเซทัลดีไฮด์เริ่มต้นที่กระบวนการผลิต 120,000 ตันต่อปี ซึ่งเป็นกำลังการผลิตที่สูงที่สุดของทั้งสองกระบวนการ จากผลการวิเคราะห์พบว่ากระบวนการผลิตอะเซทัลดีไฮด์ที่กำลังการผลิตสูงสุดสามารถให้อัตราผลตอบแทนที่มากที่สุด รวมไปถึงระยะเวลาการคืนทุนให้กับกระบวนการผลิตในระยะเวลาที่สั้นที่สุด โดยกระบวนการที่ค่าเปอร์เซ็นการเปลี่ยนไปเป็นผลิตภัณฑ์ของสารตั้งต้นให้ผลลัพธ์ออกมามีดีที่สุด และเหมาะสมกับการนำไปใช้ออกแบบกระบวนการผลิตอะเซทัลดีไฮด์ เนื่องจากค่าการใช้พลังงาน และค่าอุปกรณ์ที่ต่ำกว่าเป็นผลมาจากไม่มีการใช้คอมเพรสเซอร์ในกระบวนการนี้

สาขาวิชา วิศวกรรมเคมี
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ลายมือชื่อนิสิต ....
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6170178321 : MAJOR CHEMICAL ENGINEERING

KEYWORD: Acetaldehyde production, Non-oxidative dehydrogenation, Economic evaluation, Aspen plus

Thanakarn Suthirojn : Process analysis and economic evaluation of acetaldehyde production from ethanol via non-oxidative dehydrogenation. Advisor: PONGTORN CHAROENSUPPANIMIT, Ph.D. Co-advisor: Prof. BUNJERD JONGSOMJIT, Ph.D.

Field of Study: Chemical Engineering
Academic Year: 2020

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ACKNOWLEDGEMENTS

First of all, I would like to express my most profound appreciation and gratitude to Prof. Dr. Pongtorn Charoensuppanimit for being my thesis advisor, whose suggestion was invaluable in guiding me throughout the research. Correspondingly, I would like to prolong my gratitude to my thesis co-advisor, Prof. Dr. Bunjerd Jongsomjit, for his benevolence in assisting and encouraging me. Both of their counsels are so worthy that it would be impracticable to accomplish this research as good as it is without them.

I would like to give special thanks to the chairman, Asst. Prof. Dr. Sorada Kanokpanont, and also Asst. Prof. Dr. Paravee Vas-umnuay and Asst. Prof. Dr. Kanokwan Ngaosuwan for joining the thesis committee and revising my research thoroughly.

I, as well, would like to give thanks to the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University for supporting the ASPEN PLUS program license.

At last, I would like to give many thanks to my family who always encourages and supports me, especially for finances in doing this research.

Thanakarn Suthirojn

TABLE OF CONTENTS

Page

LIST OF TABLES

Page

LIST OF FIGURES

Chapter 1

Introduction

1.1 Background

In Thailand, the utilization of ethanol is generally for the production of gasohol, a greener fuel mixed between gasoline and ethanol used in automobiles. However, the demand for gasohol may decrease in the coming future due to the rapid development in energy storage used in the electrical vehicles (EV) [1]. In addition to the future prospect; fluctuation of oil price and increase in ethanol production plants, such advancement may cause the reduction of gasohol usage which could directly affect the ethanol demand. These may affect to fuel car ratio in the future. Due to bioethanol is fuel grade, it has low cost and value. To tackle this, ethanol may be utilized as a precursor for the synthesis of more valuable chemicals such as diethyl ether, acetaldehyde, etc.

In the coming future, organic chemical in industrial may shift into renewable raw materials instead of fossil raw materials. The approach of research of innovative economically friendly are increasing in recent years. Owing to ethanol is renewable chemical that derived from biomass such as molasses and cane juice from sugarcane, cassava chips and cassava roots, bioethanol becomes as a starting material for various chemical processes. Bio-ethanol is green feedstock for valuable chemical production. Moreover, in very recent years acetaldehyde global production is increasing and it is expected to grow exceed 104 million tons by 2024. [2]

In recent years, ethanol processing has been more interesting because the amounts of ethanol have become from biomass treatment (bio-ethanol). There is various research that studies the ethanol processing such as partial oxidation and steam reforming. Therefore, the non-oxidative dehydrogenation is an essential first step in ethanol steam reforming and ethanol partial oxidation reactions. Typically, there are two methods involved in acetaldehyde productions - e.g., partial oxidative dehydrogenation of ethanol and non-oxidative dehydrogenation of ethanol.

Acetaldehyde is a fine chemical product from large-scale end process in industry. Acetaldehyde is widely used as the starting material for synthesis of many industrial chemical products such as acetic acid, acetate esters, and pentaerythritol. Acetaldehyde is more costly than ethanol. Acetaldehyde has a wide range of applications such as food preservative and as a precursor to vinylphosphonic acid that is used as adhesive or ion conductive membrane. Acetaldehyde may become a major intermediate to produce several secondary intermediates.

This means acetaldehyde will be a significant role in the forthcoming. Therefore, in this work, the synthesis of acetaldehyde is selected due to previously several decent attributes.

Previous study, they have investigated the oxidation of ethylene. It was found that the production was significantly contracted when the more performance methanol carbonylation process to manufacture acetic acid were substituted to acetaldehyde oxidation processes, based on syngas can produced by ethylene steam reforming [3]. In case of ethanol dehydrogenation is the alternative pathway for acetaldehyde production and the by-product; hydrogen is attend significantly; the dehydrogenation or non-oxidative dehydrogenation of ethanol is chosen for process analysis and economic evaluation in this study.

In this research, Aspen Plus will be utilized for the process simulation of acetaldehyde production from ethanol. A useful sensitivity analysis of process parameters such as operating conditions, raw material and product sale prices as well as production capacities will be conducted to comprehend the impacts of these effects on the process feasibility. Lastly, the techno-economic results will be employed to justify whether the process is suitable for ethanol valorization. A profitable process that may be obtained in this work can generate benefit to the bio-ethanol which is one of the bio-refinery products receiving more interests in the near future.

1.2 Objectives

The aim of this work is to design and simulate the process of acetaldehyde production based on the lab results. The alternative pathway of valorization of bioethanol by converting into acetaldehyde via the non-oxidative dehydrogenation of ethanol will be utilized in this work. The factors that impact the process simulation will be study in this work. Then, the techno-economic analysis method will be conducted using Aspen Plus program for assessment of feasibility of the production.

1.3 Scopes of research

1. Analyze the acetaldehyde production process simulation using Aspen Plus program. The analyzed process converts bioethanol via the non-oxidative dehydrogenation and this study was conducted in Aspen Plus.

2. Evaluate the economic of acetaldehyde production process which benefits a future feasibility study using process simulator namely Aspen Plus.

3. This research will demonstrate processes in Aspen plus simulator to indicate minimum cost for highly profit with operating conditions and weight hourly space velocity (WHSV) is 22.9 ($g_{ethanol}g_{cat}^{-1}$) h^{-1} which based on literature [4]. Further details about operating conditions is given in Chapter 2.

Chapter 2

Theory and Literature reviews

This chapter describes the theoretical background that involves to this research, including the reviews of previous research study and relevant literature about ethanol dehydrogenation reaction to produce acetaldehyde. Acetaldehyde properties and its production and the reviews of separation process will be given in this chapter.

2.1 Theory

2.1.1 Acetaldehyde

Acetaldehyde is organic chemicals in classification of aldehydes. Acetaldehyde is used in the manufacturing of various chemicals such as acetic acid, pentaerythritol, vinyl acetate resins, flavors, and perfumes. In atmospheric pressure and room temperature, acetaldehyde appears as a clear colorless liquid. Acetaldehyde is miscible in water and most common organic solvents. Molecular structure of acetaldehyde is shown in Figure 1. Chemical and physical properties are listed in Table 2.

Figure 1 Molecular structure of acetaldehyde [5]

Table 1 Chemical and physical properties of acetaldehyde [6]

Properties	**Acetaldehyde**
Formula	CH_3CHO
Molecular Weight	44.05 g/mol
Appearance	Colorless liquid
Odor	Pungent and fruity odor
Boiling point	20.2 °C
Melting point	-123 °C
Vapor pressure	1.19 atm (at 25 °C), 0.99 atm (at 20 °C)
Specific gravity	0.785 g/mL (at 25 °C)
Solubility	Miscible in water, and most common organic solvents
Classification (National Fire Protection Association) *	Health: 3, Flammability: 4, Reactivity: 3, and no specification hazard

*NFPA704 is Standard System for the Identification of the Hazards of Materials for Emergency Response. Degree of health hazard at level 3 mean short exposure could cause serious temporary or moderate residual injury. Degree of Flammability level 4 mean this chemical can be ignited under almost all ambient temperature conditions. Degree of reactivity level 3 mean capable of detonation or explosive decomposition but requires a strong initiating source, must be heated under confinement before initiation, reacts explosively with water, or will detonate if severely shocked. [7]

2.1.2 Ethanol

Ethanol is a chemical compound, simple alcohol with the chemical formula C_2H_5OH. Ethanol can produce from fermentation of glucose obtained from sugar cranes, cassava chips, and molasses by yeasts or via petrochemical processes. Ethanol is a colorless liquid with a slight characteristic odor, flammable and volatile. Molecular structure of ethanol is shown in Figure 2. Chemical and physical properties are listed in Table 3.

Figure 2 Molecular structure of ethanol [8]

Table 2 Chemical and physical properties of ethanol [8]

Properties	**Acetaldehyde**
Formula	CH_3CH_2OH
Molecular Weight	46.069 g/mol
Appearance	Colorless liquid
Odor	Characteristic odor
Boiling point	78.24 °C
Melting point	-114.14 °C
Vapor pressure	0.059 atm (at 20 °C)
Specific gravity	0.7893 g/mL (at 20 °C)
Solubility	Miscible
Classification (National Fire Protection Association) *	Health: 2, Flammability: 3, Reactivity: 0, and no specification hazard

*NFPA704 is Standard System for the Identification of the Hazards of Materials for Emergency Response. Degree of health hazard at level 2 mean intense or continued but not chronic exposure could cause temporary incapacitation or possible residual injury. Degree of Flammability level 3 mean this chemical can be ignited under almost all ambient temperature conditions. Degree of reactivity level 0 mean normally stable, even under fire exposure conditions, and is not reactive with water. [7]

2.1.3 Ethanol utilization

As mentioned in Chapter 1, the bioethanol processing has been more interesting for a long time. In recent years, the utilization of ethanol is for gasohol production but in the present this utilization of ethanol may concern due to the decrease in demand of ethanol from coming of EV cars. Some of catalytic reactions of excess ethanol has been studied to convert into other products which is more valuable and higher cost than ethanol.

The products obtained from the catalytic reactions of ethanol are ethylene, acetaldehyde, diethyl ether, carbon monoxide, carbon dioxide and hydrogen. The following section is provided the chemical reactions which converts ethanol into more valuable products.

- Steam reforming of ethanol

Ethanol is catalytically transformed into hydrogen, carbon monoxide and carbon dioxide as following. [9]

$$CH_3CH_2OH + H_2O \longrightarrow 4H_2 + 2CO \quad (2.1)$$

$$CH_3CH_2OH + 3H_2O \longrightarrow 6H_2 + 2CO_2 \quad (2.2)$$

- Ethanol dehydrogenation or non-oxidative dehydrogenation of ethanol

  The endothermic reaction that produces acetaldehyde from ethanol as follow. [4]

$$CH_3CH_2OH \longrightarrow CH_3CHO + H_2 \quad (2.3)$$

- Oxidative dehydrogenation of ethanol

  The alternative route to the classical dehydrogenation of bioethanol to produced acetaldehyde as provided in the following reactions. [4]

$$CH_3CH_2OH + 1/2O_2 \longrightarrow CH_3CHO + H_2O \quad (2.4)$$

$$CH_3CH_2OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O \quad (2.5)$$

- Ethanol dehydration

  Ethylene and diethyl ether are produced via catalytic dehydration of ethanol as given in the following reactions. [4]

$$CH_3CH_2OH \longrightarrow C_2H_4 + H_2O \quad (2.6)$$

$$2CH_3CH_2OH \longrightarrow C_2H_5OC_2H_5 + H_2O \quad (2.7)$$

From equations (2.3) and (2.4), describe about the reaction of converting ethanol into acetaldehyde. The different between two equations are type of reaction, side reactions and by-products occurred from side reaction as shown and listed in Table 4.

Table 3 Comparison between non-oxidative dehydrogenation and oxidative dehydrogenation of ethanol.

	Non-oxidative dehydrogenation	**Oxidative dehydrogenation**
Type of reaction	Endothermic	Exothermic
Reactants	Ethanol	Ethanol and Oxygen
Primary Product	Acetaldehyde (CH_3CHO)	Acetaldehyde (CH_3CHO)
By-products	H_2	H_2O, CO_2
Phase of reaction	Vapor phase	Vapor phase

As mentioned in Table 4, it is clearly seen that two reactions for acetaldehyde production is totally different. Although the operating temperature of the non-oxidative dehydrogenation is higher than oxidative dehydrogenation that may cause the deactivation of catalyst, but the major priority must consider is safety of the process. The oxygen in oxidative dehydrogenation reaction may cause explosion of process if not controlling the process carefully. Owing to this reason, the non-oxidative dehydrogenation is operated easily than the other one. In the oxidative dehydrogenation, the feed including two components which effected to total flow rate of the process. Thus, the size of reactor use in the oxidative dehydrogenation is greater than the non-oxidative dehydrogenation from WHSV calculation, which is necessary for calculate the size of reactor. The by-products obtained from two reactions; the hydrogen obtained from the non-oxidative dehydrogenation has more valuable than H_2O and CO_2 which are waste and cannot use in other process.

As a result, the non-oxidative dehydrogenation reaction is also attractive and chosen for process analysis and economic evaluation for this study.

2.2 Literature reviews

2.2.1 Reaction and catalysts related to acetaldehyde productions

As mentioned in section 2.1.3, the non-oxidative dehydrogenation of ethanol is chosen to produce acetaldehyde. In acetaldehyde production, a typical catalyst used in ethanol dehydrogenation process in order to produce acetaldehyde is various. Various catalyst types and operating conditions for acetaldehyde production are listed in Table 5.

Table 4 List of catalyst types and operating conditions for ethanol dehydrogenation for acetaldehyde production. [4] [10-12]

Catalyst	Temperature (°C)	Pressure (atm)	Ethanol conversion (%)	Acetaldehyde Selectivity (%)	By-products occurred	WHSV (g/g_{cat}) h^{-1}
Cu/Zinc-Aluminate	500	1	80	96	DEE, H_2, H_2O, CO, ethylene, CH_4	-
CuO-Cr_2O_3/Al_2O_3	300	1	55	50	Ethylene, H_2O, CH_4, CO, CO_2, Isobutanol	1
Cu/[Si] Beta zeolite	300	1	85	82	No reported	1.99
V-Zr-La/SBA-15	400	1	80	48	DEE, H_2, H_2O, ethylene	22.9

From Table 5, For CuO-Cr_2O_3/Al_2O_3 catalyst, although this literature may report all the data required for process analysis; but the conversion of ethanol and selectivity of acetaldehyde obtained from this reaction is the lowest than the others due to lower WHSV. When compared Cu/Zinc-Aluminate, Cu/[Si] Beta zeolite and V-Zr-La/SBA-15 catalysts with high conversion of ethanol obtained. For Cu/Zinc-Aluminate catalyst, there is no reported for WHSV which required to evaluate reactor size for economic analysis. As to Cu/[Si] Beta zeolite catalyst, there is no reported about by-products occurred in reaction which is necessary for mass balance calculation as well.

To produce acetaldehyde, the best catalyst of ethanol dehydrogenation to produce acetaldehyde appears to be V-Zr-La/SBA-15 since the catalyst has all necessary data for process simulation with highest conversion of ethanol and acetaldehyde selectivity at temperature and pressure around 400 °C and 1 atm, respectively.

2.2.2 Separation processes for problematic by-products

As mentioned in section 2.1.3, there is water occurred during the chemical reaction as a by-product which can form azeotrope mixture with ethanol. There are three types of separation process must be considered to purify mixture into pure component; extractive distillation, pressure-swing distillation and pervaporation may consider in this section.

Distillation processes such as pressure-swing distillation and extractive distillation are widely used to separate azeotrope mixtures with close boiling points into pure components. Extractive distillation is used for the separation of mixtures with similar relative volatilities and azeotrope mixtures. Extractive distillation can modify or increase the relative volatility between heavy component and light component by adding a third component or an entrainer with high boiling point and miscible. [13, 14] The entrainer usually loading close to the top of azeotropic mixture with few stages below. The light component will distillate to the top of column with desire purity and the bottom of column will consist of heavy components and entrainer. Then, the bottom stream will feed into the recovery system for recycle to use in the first column repletely. The entrainer must not be form to azeotrope mixture with any components in the system. [15]

The pressure-swing distillation is based on a simple change in operating pressure and change relative volatility of azeotrope mixtures. The pressure-swing distillation is effective when the composition of azeotropes varies significantly and sensitive with the pressure change. An advantage of the pressure-swing distillation is environmental safety process. It does not need the separating agent while the extractive distillation required an efficient solvent [16-19]. Iqbal and Ahmad [20] reported that the water-ethanol azeotrope can be separate from each other by using pressure-swing distillation technique. They also reported that high purity of 99.7 mol% ethanol can be obtained at 10 atm of operating pressure in high pressure column and 1 atm of operating pressure in low pressure column. Nevertheless, the disadvantage of this technique is high operating cost to keep the operating condition in the column.

Pervaporation is a membrane separation technique in which liquid mixture can be separated by partial vaporization through a non-porous permselective membrane. In pervaporation process, a liquid mixture is in 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. Pervaporation is a complex process involving mass and heat transfer. Each step of diffusion, sorption and desorption is effected to the separation. [21, 22]

When compared pressure-swing distillation to pervaporation, the costs of membrane used in pervaporation process is higher than the costs in pressure-swing distillation leading to penalties in the operating costs and long payback time. The literature reports that higher electricity consumption in the pervaporation process and in this case may affected to an environmental. The pervaporation process configuration should consider to the development and design for more environmentally friendly process which is the major priority to considered for each process. [23]

Subaer et al. [24] have investigated that the selectivity was low influencing ethanol purity was the weakness of the membrane. Selectivity can be achieved if it coated with materials which can be reduced the hydrophilic properties of polymer to be used as membrane in pervaporation process and it effected to increasing of capital as well.

From all of the literature mentioned earlier and all separation techniques, the extractive distillation technique is chosen for this work. The reason can be summarized as follows:

- The extractive distillation is more economical than pressure-swing distillation and total annual cost of pressure-swing distillation is more than extractive distillation. Although extractive distillation needs much more steps than pressure-swing distillation, but the extractive distillation has energy demand lower than pressure-swing distillation. Due to capital cost of extractive distillation are obviously lower than pressure-swing distillation, extractive distillation appears to be better economically options for separation of ethanol-water mixture. [25-27]
- The pervaporation process could not perform in this acetaldehyde production process due to the desire reaction temperature for the process is quite high as 400 °C. Most of the membranes used in pervaporation process are made from polymer in the result of low capital cost. Polymer membrane for pervaporation technique had a limitation in a process temperature due to T_d (Decomposition temperature) of polymer membrane is low as 200 °C. If the process temperature has higher than 200 °C, the process must use the ceramic membrane which had better stability and higher cost than polymer membrane. [28, 29]
- Owing to disadvantages of the pervaporation process in case of environmentally friendly, operating costs and higher capital costs in the pressure-swing process, the extractive distillation is chosen for ethanol purification from ethanol-water mixture.

2.2.3 Previous work related to the simulation of acetaldehyde productions

There are a few literatures about process simulation of acetaldehyde production to be study and review in this section.

Johanna [30] had studied, designed and simulated the plant for manufacturing acetaldehyde. The study focused on the acetaldehyde production from oxidation of ethanol. The process simulation was used ChemCAD for sizing each units and economic evaluation. The results obtained from this process simulation are only production rate and total investment costs. The production rate of acetaldehyde was 2,122 kg/h, the total investment costs was 40.0 million SEK (Swedish Krona) and operating cost per ton of acetaldehyde was 7,081 SEK and results in a payback time of 2.6 years.

The simulation has several advantages such as they show possibility how to produce the acetaldehyde and the overview of the production before building plant in industrial process. The variables which could affect the processes can be obtain from the process simulation. Besides the overview of the production process, the economic analysis evaluator in the simulator can analyze the profitability index, internal rate of return and payout period.

The different catalysts use and operating conditions in the process may affected the conversion, selectivity and by-products occurred in the production. There is only Johanna's work performed the process simulation of acetaldehyde production and there's only oxidative dehydrogenation of ethanol process. This work, the non-oxidative dehydrogenation of ethanol will simulate to compare the factors which effect the acetaldehyde production process with difference purposes to Johanna's work as follows;

- Study of diethyl ether by-products occurred and effect directly to the process.
  As mentioned in section 2.1.3 and 2.2.2, the by-products occurred in the process can form the azeotrope mixture. This work will study the factors of azeotrope mixture which affect to purity of acetaldehyde, even though the only small amount of diethyl ether occurred. When azeotrope mixture formed in the process and different by-products occurred in the process, this leads to the different separation processes and separation investment costs to Johanna's work. As a result, the simulation results can be obtained and suggest for improvement of catalyst performance for next study.
- Study of CO_2 emission.
  The amount of CO_2 emission from the process is major factor must concern about the process performance. Since the production can emit the CO_2 or greenhouse gas to the atmosphere, it's impact to the environmental. According to Johanna's work, the study not calculated and evaluated the CO_2 emission. Thus, this work will provide this topic discussion which is one of important thing must concern about design the production in industrial process.

Lastly, as mention before, there is only one work and there is an oxidative dehydrogenation process to produced acetaldehyde from ethanol. There is not been found the literature about the process simulation of acetaldehyde production from ethanol via non-oxidative. Thus, this work will be the interesting study and benefit for improvement and development for feasibility of plant design in industrial process in the future.

2.2.4 Enhancement of energy efficiency

An important thing that would help to decide about the process simulation for industrial production is energy usage in the process. The energy usage could directly affect the total annual cost (TAC) and operating cost of the process. Thus, the energy recovery system is necessary for the production process. There is various research which have designed the energy recovery system in their process by several authors as shown and listed in Table 6 and Table 7.

Table 5 Comparison of energy consumption between before and after design heat exchanger network. [31-35]

Process	**Hot utilities consumption (kW)**		**Cold utilities consumption (kW)**	
	Before	**After**	**Before**	**After**
Synthesis and optimization of work and heat exchange networks using an MINLP model with a reduced number of decision variables.	5,275.9	4337.1	13,010.3	12,075.7
Optimization and utilities relocation approach for the improvement of heat exchanger network designs.	2,074.908	1,937.998	243.84	106.93
Heat integration of biochemical ethanol production from straw.	113,000	61,000	100,000	49,000
Enhancing strategy promoted by large step length for the structure optimization of heat exchanger networks.	25,880	24,454	33,600	32,173
An extended method for work and heat integration considering practical operating constraints.	21,454	7,850	54,958	37,688

Table 6 Comparison of total annual cost between before and after design heat exchanger network. [31-35]

Process	Total annual cost ($/year)	
	Before	After
Synthesis and optimization of work and heat exchange networks using an MINLP model with a reduced number of decision variables.	10,186,680	10,004,220
Optimization and utilities relocation approach for the improvement of heat exchanger network designs.	1,467,805	1,416,103
Heat integration of biochemical ethanol production from straw.	No data reported	No data reported
Enhancing strategy promoted by large step length for the structure optimization of heat exchanger networks.	2,942,000	2,901,696
An extended method for work and heat integration considering practical operating constraints.	No data reported	No data reported

From Table 6 and Table 7, it's clearly seen in reducing of both energy consumption and total annual cost (TAC) when working on heat exchanger network (HEN).

There is various interesting research have been conducted in heat exchanger network work apart from the listed in Table 6 and Table 7 and can be concluded as follows:

- The heat exchanger network can be utilizing for design the optimal energy usage for the process configuration. The total energy investment of process with heat exchanger network can be reduced when compared to base case. In addition to energy investment, A total annual cost of process with heat exchanger network was achieved significantly lower than the process without heat exchanger network. [36, 37]
- From the literatures, they studied on results from heat integration work. The process with full heat integration can considerably increase the net plant efficiency. Furthermore, when compared full heat integration process to process without heat integration, the process with full heat integration has superior economic to others. [38, 39]

As mentioned above, the process with heat exchanger network (HEN) can be saving energy usage and total annual cost of the production. As a result, heat exchanger network must be performed and work in this acetaldehyde production.

Chapter 3

Methodology

This chapter divided into 5 parts including design scope, feed preparation, block diagram, process flow diagram description, a method for economic analysis evaluation, and CO_2 emission evaluation.

3.1 Design scope

As mentioned in previous chapter, the suitable operating conditions for acetaldehyde production was chosen from literature. There are two interesting operating conditions to be simulated and compared the factors that impacted the process. First process is 25% conversion of ethanol with 100% selectivity of acetaldehyde reacted in 200 °C reaction temperature and second process is 80% conversion of ethanol with 48 % selectivity of acetaldehyde reacted in 400 °C reaction temperature. Two processes with different operating conditions using the same catalyst are V-Zr-La/SBA-15 and atmospheric pressure. In this work, abbreviations are used instead as NOX-ethanol conversion-reaction temperature. The operating conditions of NOX-25-200 and NOX-80-400 are given in Table 8.

Table 7 Summary of interesting operating conditions [4]

	NOX-25-200	NOX-80-400
Temperature (°C)	200	400
Pressure (atm)	1	1
Ethanol conversion (%)	25	80
Selectivity (%)	100% acetaldehyde	48% acetaldehyde 51.29% ethylene 0.71% diethyl ether

The interesting operating conditions chosen for this work are the highest and the lowest conversion from the literature. The highest conversion is resulting from the high reaction temperatures but may result in decomposition process into another product which is result in low selectivity. When compared with the lowest conversion process, the factor that effect the process would be distinguished.

From Table 8, the definitions of the parameters can be defined for mass balance calculation in section 3.2 as follows:

$$\text{Conversion} = \frac{\text{The amount of reactant consumed}}{\text{The amount of feed}} \tag{3.1}$$

$$\text{Yield} = \frac{\text{The amount of product produced}}{\text{The amount of product would be produced}} \tag{3.2}$$

$$\text{Selectivity} = \frac{\text{The amount of product}}{\text{The amount of by-product}} \tag{3.3}$$

3.2 Feed preparation

The non-oxidative dehydrogenation of ethanol for acetaldehyde production uses only one raw material in feed stream. Raw material using in both processes was 99.5%wt ethanol and received from external source.

Before simulated two processes, calculation to determine the feed amount of ethanol is necessary for feed preparation system. There are two actual production capacity to study in this work – 12,000 and 120,000 tons/year [40, 41]. In addition, three production capacities are added to this work to study trend of process production from low to high capacity. As mentioned in section 2.1.3, chemical equation (2.2), (2.6) and (2.7) were used to determine the amount of ethanol utilized in both process NOX-25-200 and NOX-80-400 by mass balance calculation. NOX-25-200 process used only equation (2.2) due to its selectivity is 100% acetaldehyde. NOX-80-400 is used all chemical equations as mentioned above. The results of mass balance are given in Table 9 and calculation method of each capacities are provided in appendix A.

Table 8 Amount of ethanol in feed stream for acetaldehyde production

Capacity (tons/year)	**Amount of fresh feed ethanol (tons/year)**	
	NOX-25-200	**NOX-80-400**
12,000	12,608.62	26,453.93
30,000	31,521.33	66,135.98
60,000	63,042.65	132,271.5
90,000	94,563.52	198,406.55
120,000	126,084.84	264,541.61

3.3 Block diagram

In this section, Figure 3 showed the block diagram of NOX-25-200 process and Figure 4 showed the block diagram of NOX-80-400 process. The description for two processes of non-oxidative dehydrogenation – NOX-25-200 and NOX-80-400, would be mentioned in section 3.4.

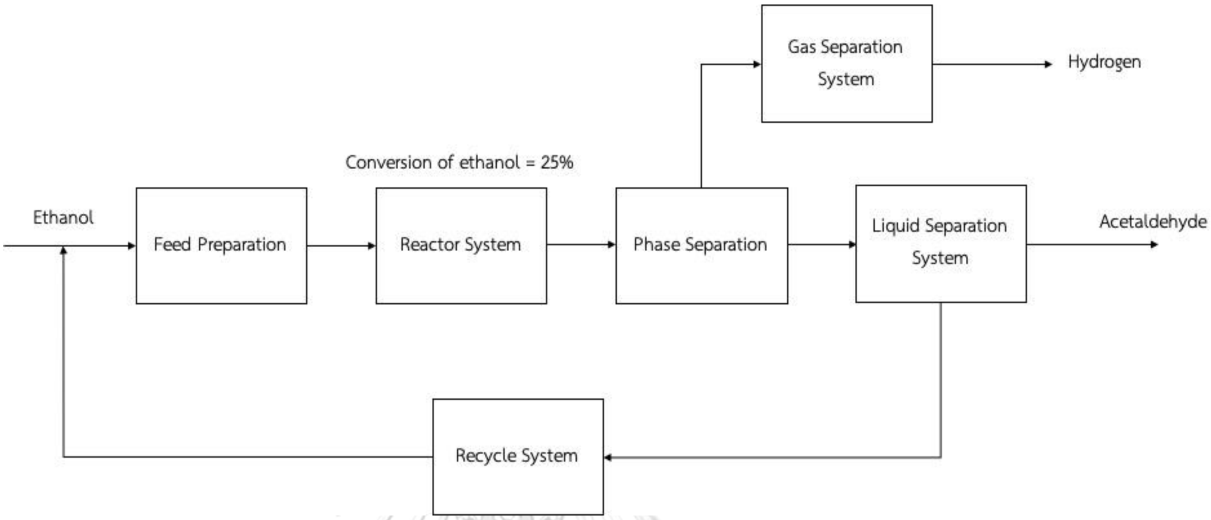


Figure 3 Block diagram of NOX-25-200 process

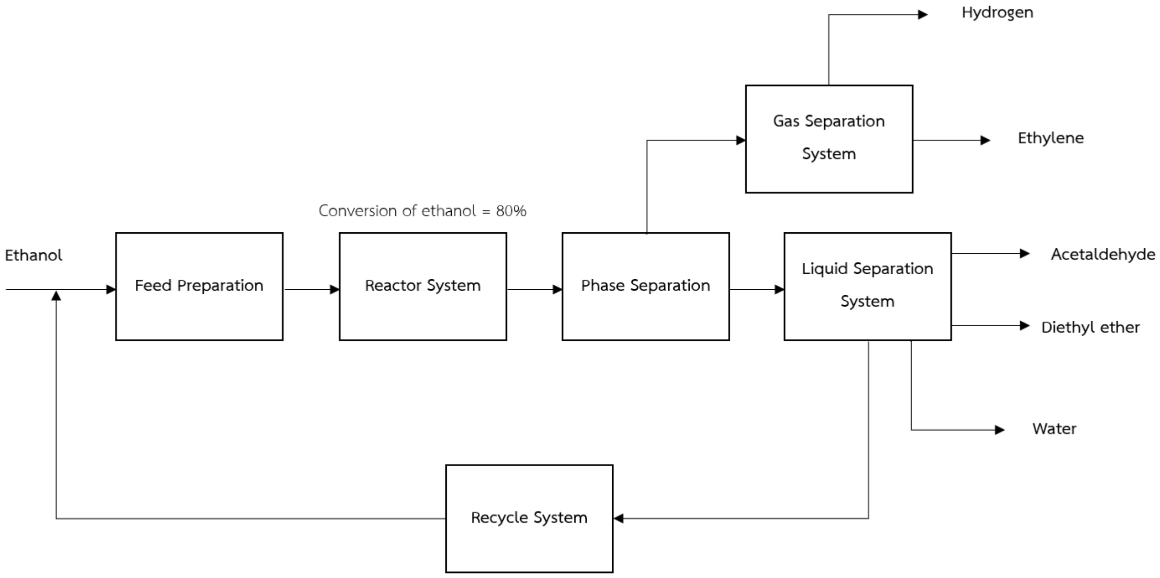


Figure 4 Block diagram of NOX-80-400 process

Acetaldehyde plant was designed with production capacity of 12,000 30,000 60,000 90,000 and 120,000 tons of acetaldehyde per year. Due to the high production rate, the production will operate as a continuous process. The production will design as Figure 3 for NOX-25-200 process and Figure 4 for NOX-80-400 process including each system as follows:

3.3.1 Feed preparation system

Due to ethanol fresh feed is from storage at 30 °C, 1 atm but the suitable conditions for acetaldehyde production pressure was 1 atm and temperature was 200 °C and 400 °C as mentioned in previous section. Thus, it’s necessary to has the feed preparation system.

3.3.2 Reactor system

For the acetaldehyde production, the reactions take place in the reactor using V-Zr-La/SBA-15 catalyst. The reaction including only one reaction for NOX-25-200 process (100% selectivity acetaldehyde) and three reactions for NOX-80-400 process; one main reaction and two side reactions. All reactions can take place under the same desired temperature and pressure.

Acetaldehyde production reactor is designed to Rstoic model by stoichiometric coefficient. The length of reactor, length of bed and reactor diameter were calculated from WHSV chosen from literature mentioned in previous chapter and given in appendix B.

3.3.3 Phase separation system

When the products steam delivered from the reactor, the steam including main products and by products from the reactions. Two states of product occurred in the steam; liquid and gaseous. The liquid is acetaldehyde, diethyl ether, water and ethanol remain from the reactions. The gaseous is hydrogen and ethylene. Thus, it is necessary to separate two phases for next system by phase separation system. Phase separation unit for both processes are use flash unit. Flash separation unit is designed to be operated at a constant pressure of 0 atm with adiabatically condition.

3.3.4 Separation system

After phase separation system, there is mixture components in liquid stream, e.g. acetaldehyde, water and ethanol in NOX-25-200 process and acetaldehyde, diethyl ether, water and ethanol in NOX-80-400 process. The separation system will purify the acetaldehyde into desired purity.

For the acetaldehyde purification column, the RadFrac model was used to perform this process. The column contained stages in rectifying section and stages in the stripping section with a total stage excluding the condenser and the reboiler. By utilizing the Design Specification feature, the optimal reflux ratio was computed for the distillation section which corresponded to the mass purity of 99.0 wt% in the product stream.

3.3.5 Recycle system

Owing to ethanol conversion of both processes is not 100%; 25% conversion for NOX-25-200 and 80% conversion for NOX-80-200. There is ethanol remain from the reaction. To conserved raw material, the process must have the recycle system to recycling the ethanol to feed preparation system repletely.

3.4 Process flow diagram description

The assumption for process simulation in this work is divided into 2 parts, the vapor-liquid equilibrium unit and reactor unit. The vapor-liquid equilibrium is simulated based on the thermodynamics model. The reactor unit assumption is simulated based on literature results which are conversion and selectivity.

This section will describe about the process flow diagram for two acetaldehyde productions which showed in Figure 5 and Figure 6. In this process simulation, all acetaldehyde production processes were simulated by Aspen Plus. The NRTL model was used in the simulation with NIST TDE database. Since the suitable conditions for acetaldehyde production was 1 atm and temperature was 200 °C and 400 °C, predictive split models suitable for low pressure reaction, polar molecules and azeotropic mixtures (acetaldehyde and diethyl ether, ethanol and water) – e.g., NRTL, UNIQUAC and Wilson were selected as a result to Eric Carlson’s recommendation [42]. The description for two processes of non-oxidative dehydrogenation is listed as below.

3.4.1 Non-oxidative dehydrogenation for acetaldehyde production at 200 °C

In relation to Figure 5, the fresh feed of 99.5 wt% ethanol (ETOH-F) is mixed with the recycle ethanol from recycling stream (ETOH-RE) in mixer M-1. The mixed stream (stream 1) is delivered to furnace (E-1) to heat the stream to 400 °C, a proper temperature for acetaldehyde production. The stream discharged from E-1 (stream 2) is fed to reactor (R-1), and all reactions take place in R-1. All vapor products from reactor R-1 (stream 3) are sent into heat exchanger (E-2, E-3 and E-4) to cooled down temperature using boiler feed water, cooling water and glycol solution respectively. The product stream 6 was cooled to 10 °C and then the stream was sent to knock-out drum (S-1) where the separation between gas and liquid phases occurred. The liquid in stream 7 was sent to pump (P-1) to raise the pressure to about 2.3 atm which was proper for acetaldehyde separation by using distillation column, S-2. The distillation column was used to distillated acetaldehyde from other components. There were three product streams from this column including stream 9, 10 and 11. The product’s purity is designed to be 99.00 wt%

acetaldehyde according to acetaldehyde suppliers [43]. The liquid stream (stream 11) that contains unreacted ethanol and water. According to water and ethanol is an azeotropes mixture, the extractive distillation column (S-3) was used to extracted ethanol from water by using ethylene glycol. The ethanol was used as the recycled stream (ETOH-RE) for mixing with ETOH-F and then fed to reactor repeatedly. Then, the stream 13 from S-3 column which contains water-ethylene glycol mixture is sent to column S-4 to separate ethylene glycol for use in S-3 as recycle ethylene glycol (EG-RE). Lastly, the acetaldehyde in stream 10 was sent into heat exchanger (E-5) to reducing temperature to 30 °C using chilled water to achieve the final stream (ACET) which is proper temperature to store acetaldehyde product.

3.4.2 Non-oxidative dehydrogenation for acetaldehyde production at 400 °C

In relation to Figure 6, the fresh feed of 99.5 wt% ethanol (ETOH-F) is mixed with the recycle ethanol from recycling stream (ETOH-RE) in mixer M-1. The mixed stream (stream 1) is delivered to furnace (E-1) to heat the stream to 400 °C, a proper temperature for acetaldehyde production. The stream discharged from E-1 (stream 2) is fed to reactor (R-1), and all reactions take place in R-1. All vapor products from reactor R-1 (stream 3) are sent into compressor (C-1) to raise the pressure heat exchanger (E-2, E-3 and E-4) to cool down temperature using boiler feed water, cooling water and glycol solution respectively. The product stream 8 was cooled to 10 °C and then the stream was sent to knock-out drum (S-1) where the separation between gas and liquid phases occurred. The liquid in stream 9 was sent to valve (V-1) to reduce the pressure to about 2.3 atm which was proper for acetaldehyde separation by using distillation column, S-2. The distillation column was used to distillate acetaldehyde-diethyl ether azeotrope mixture from other components. The stream 12 is sent into column S-3 to separate acetaldehyde from diethyl ether. The product’s purity is designed to be 99.00 wt% acetaldehyde according to acetaldehyde suppliers [43]. The liquid stream (stream 13) that contains unreacted ethanol and water. According to water and ethanol is an azeotropes mixture, the extractive distillation column (S-4) was used to extract ethanol from water by using ethylene glycol. The ethanol was used as the recycled stream (ETOH-RE) for mixing with ETOH-F and then fed to reactor repeatedly. Then, the stream 18 from S-4 column which contains water-ethylene glycol mixture is sent to column S-5 to separate ethylene glycol for use in S-4 as recycle ethylene glycol (EG-RE). Lastly, the acetaldehyde in stream 10 was sent into heat exchanger (E-6) to reduce temperature to 30 °C using chilled water to achieve the final stream (ACET) which is proper temperature to store acetaldehyde product.

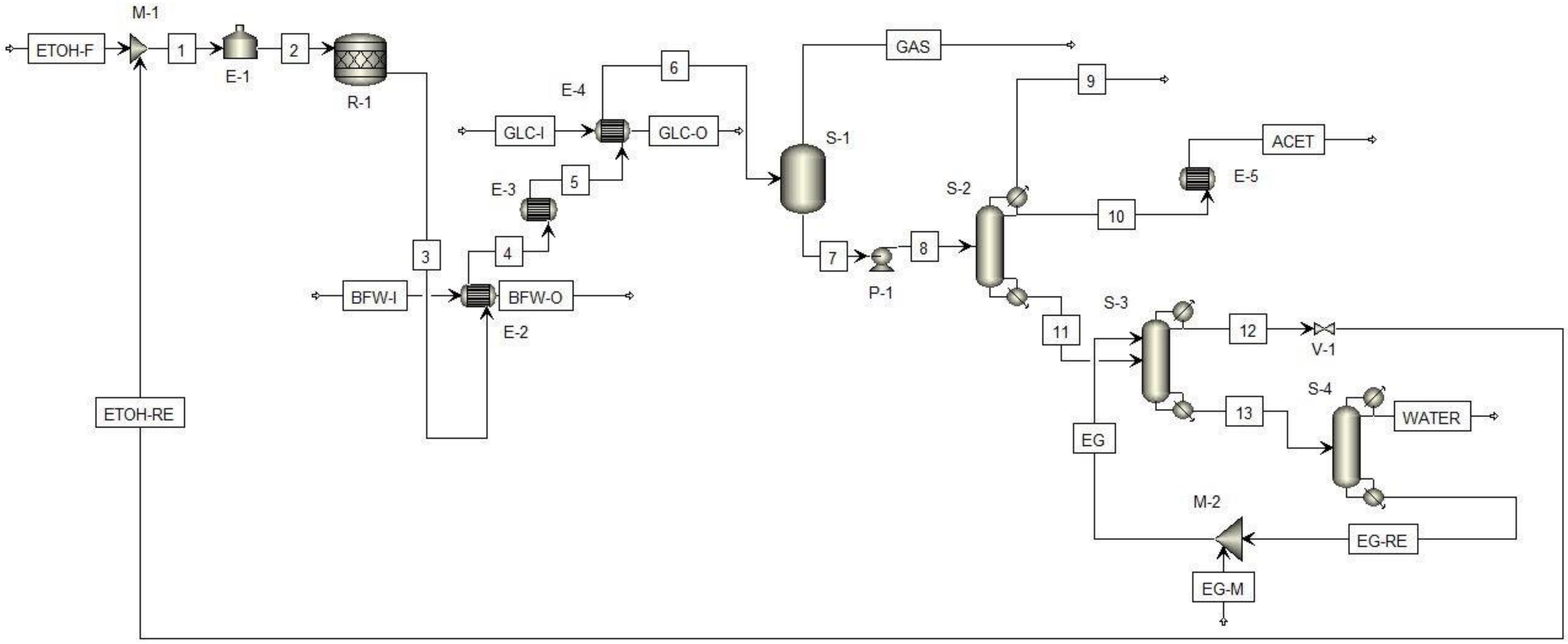


Figure 5 Process flow diagram of NOX-25-200

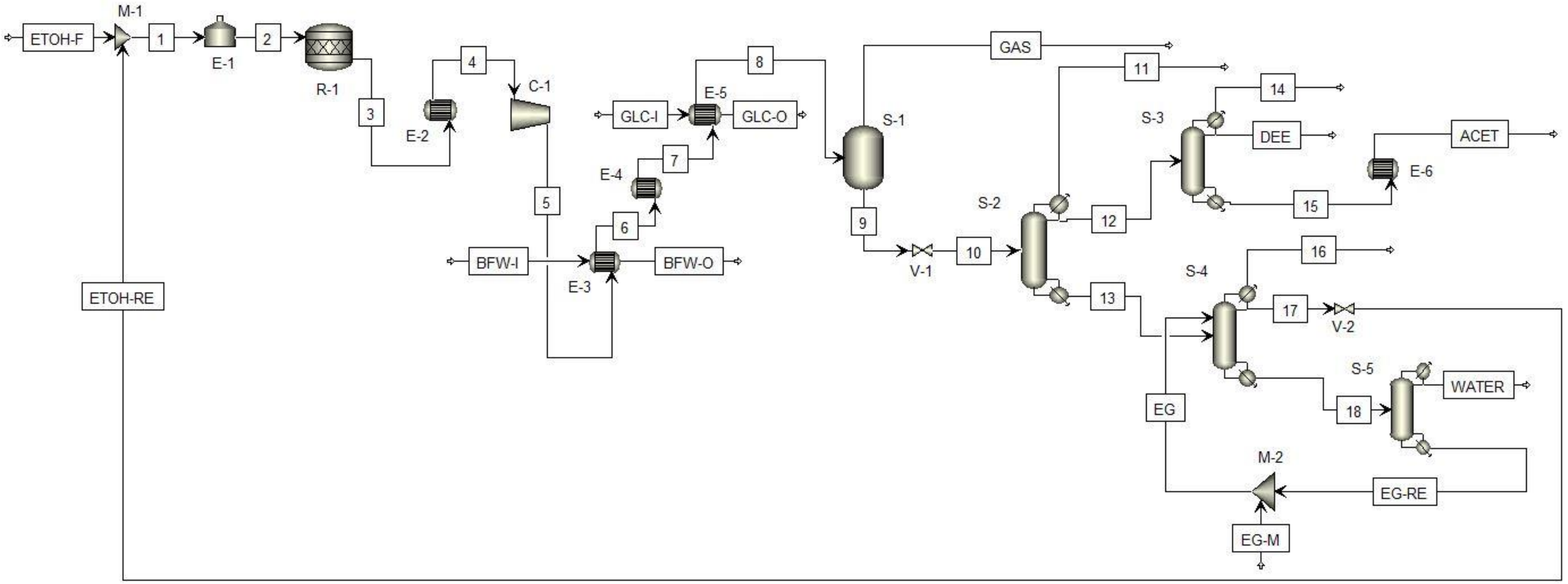


Figure 6 Process flow diagram of NOX-80-400

3.5 Economic analysis

In this work, the ethanol's cost was assumed to be 0.49 US$ per liter [44] for raw material cost. The purity of ethanol was assumed to be 99%. The acetaldehyde's price which is product from this process is 1.01 US$ per kilogram [43] was used as a basis for economic analysis. The costs of utility were obtained from the Analysis, Synthesis and Design of Chemical Processes [45] and giving in the Table 7.

Table 9 Summary of utilities price [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

In the final, unit operation sizing including cost estimations and costs of all equipment in acetaldehyde production process were performed by Aspen Economic Evaluation to obtained Internal Rate of Return (IRR), Profitability Index (PI) and Payout Period (POP).

The economic parameter which determines the feasibility of process is profitability index (PI) and can be calculated from equation (3.1).

$$\mathrm{PI} = \frac{\text{The present value of future cash flow}}{\text{Initial investment}} \tag{3.3}$$

The feasible of process's profitability can be determined as follows:

PI < 1 means the process cannot gain profit

PI > 1 means the profitability of process Is feasible

3.6 CO_2 emission evaluation

For plant design, the first thing that must be concerned is about greenhouse gas emission such as CO_2 from new petrochemicals plant. Net CO_2 emission can calculate based on CO_2 feed into the process and CO_2 can release from the process by

1. The process or waste stream
2. The utilities usage which potentially produce CO_2

Net CO_2 emission is calculated by using equation (3.2)

$$\text{Net } CO_2 \text{ emission} = CO_2 \text{ outlet} - CO_2 \text{ inlet} \tag{3.2}$$

Direct CO_2 that released from the production plant and indirect CO_2 can compute from plant's energy – e.g., the electricity is defined as CO_2 outlet.

3.7 Evaluation of energy utilization

The energy utilization is the important factor which must be concerned for feasible work. In this work, the specific energy consumption (SEC) is used to determine the process performance. The specific energy consumption is calculated by equation (3.3)

$$\text{SEC} = \frac{\text{Energy used}}{\text{The amount of product}} \tag{3.3}$$

The process's energy efficiency can be improved by heat recovery system.

Chapter 4

Results and Discussion

This chapter included the explanation and discussion of results from this study. This part contained 6 topics discussion includes evaluation of raw material utilization, simulation results of acetaldehyde production, evaluation of CO_2 emission, heat recovery system, energy utilization and economic evaluation.

4.1 Evaluation of raw material utilization

In this study, the only raw material using in acetaldehyde production via non-oxidative dehydrogenation is ethanol. Thus, the evaluation of raw material utilization is necessary to be discussed in this part. Before simulating the process, the feed amount of raw material is necessary to be determined.

As mentioned in previous chapter, the mass balance calculation is necessary for this work. The mass balance of non-oxidative dehydrogenation is calculated which is depended on stoichiometric ratio of chemical equation. Table 11 shows the amount of fresh feed ethanol from mass balance calculation. As seen in the Table, the amount of ethanol is calculated based on perfect separation's assumption.

Table 10 The amount of fresh feed ethanol and recycle amount from mass balance calculation

Process	Capacity (tons/year)	The amount of ethanol (tons/year)	
		Fresh feed	Recycle
NOX-25-200	**12,000**	12,608.62	37,825.87
	30,000	31,521.33	94,563.98
	60,000	63,042.65	189,127.96
	90,000	94,563.52	283,690.55
	120,000	126,084.84	378,254.53
NOX-80-400	**12,000**	26,453.93	6,613.51
	30,000	66,135.98	16,534.11
	60,000	132,271.50	33,067.76
	90,000	198,406.55	49,601.87
	120,000	264,541.61	66,135.52

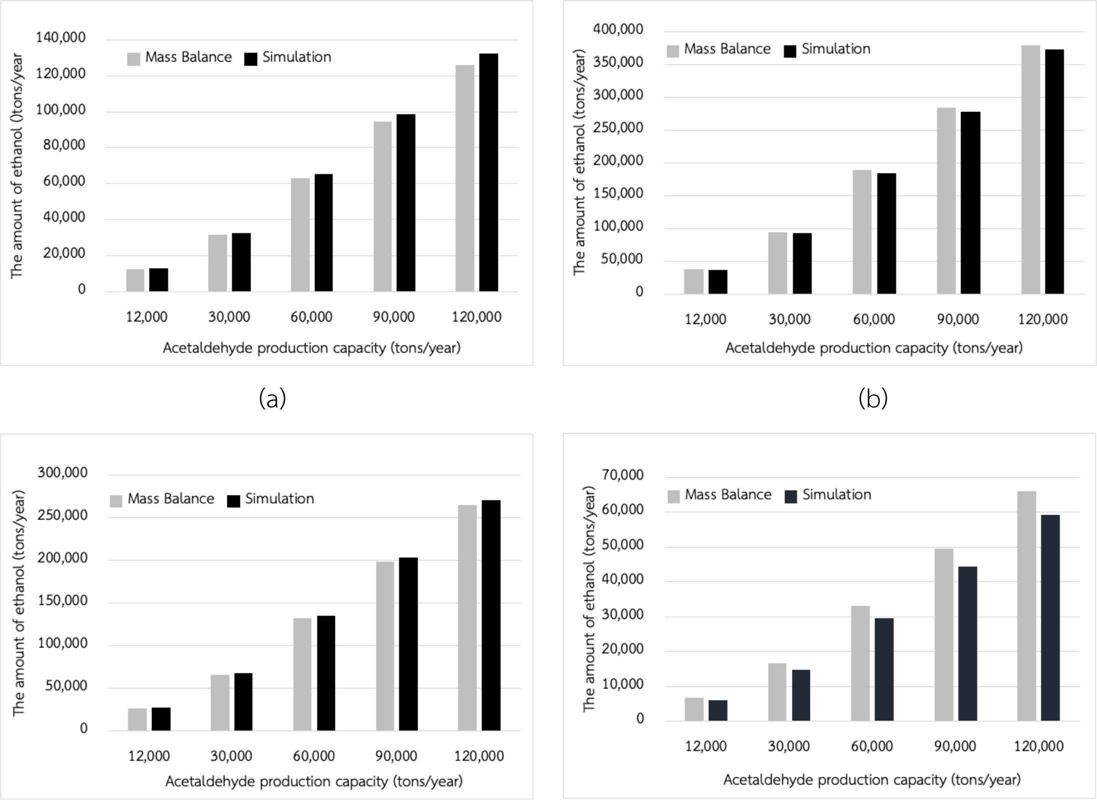
Table 11 shows that both processes of non-oxidative dehydrogenation have not reacted completely in the reactor. As mentioned above, these results are based on only perfectly separation's assumption. The practical process of acetaldehyde production could not be complete perfectly separation. Table 12 has concluded the results obtained from simulated process, the ethanol fresh feed and ethanol recycle stream.

According to the Table, the results show that the amount of ethanol from calculation is not equal to the amount of ethanol from process simulation. Due to infeasibility of perfect separation, the amount of ethanol may lose during separation process.

Table 11 The amount of fresh feed ethanol and recycle amount from simulation results

Process	Capacity (tons/year)	The amount of ethanol (tons/year)	
		Fresh feed	Recycle
NOX-25-200	12,000	12,941.1	36,854.8
	30,000	32,537.8	92,734.3
	60,000	65,642.5	185,445
	90,000	98,463.2	278,178
	120,000	132,627	374,943
NOX-80-400	12,000	27,106.2	5,928.12
	30,000	67,767	14,820.6
	60,000	135,533	29,641
	90,000	203,299	44,461.66
	120,000	271,065	59,281.9

The compared results from Table 11 and Table 12 is shown in Figure 7. The results show that the amount of fresh feed ethanol obtained from mass balance calculation is less than the amount of fresh feed ethanol from simulation (see Figure 7 (a) and (c)). In contrast, the amount of recycle ethanol obtained from mass balance calculation is more than the amount of recycle ethanol from simulation (see Figure 7 (b) and (d)).

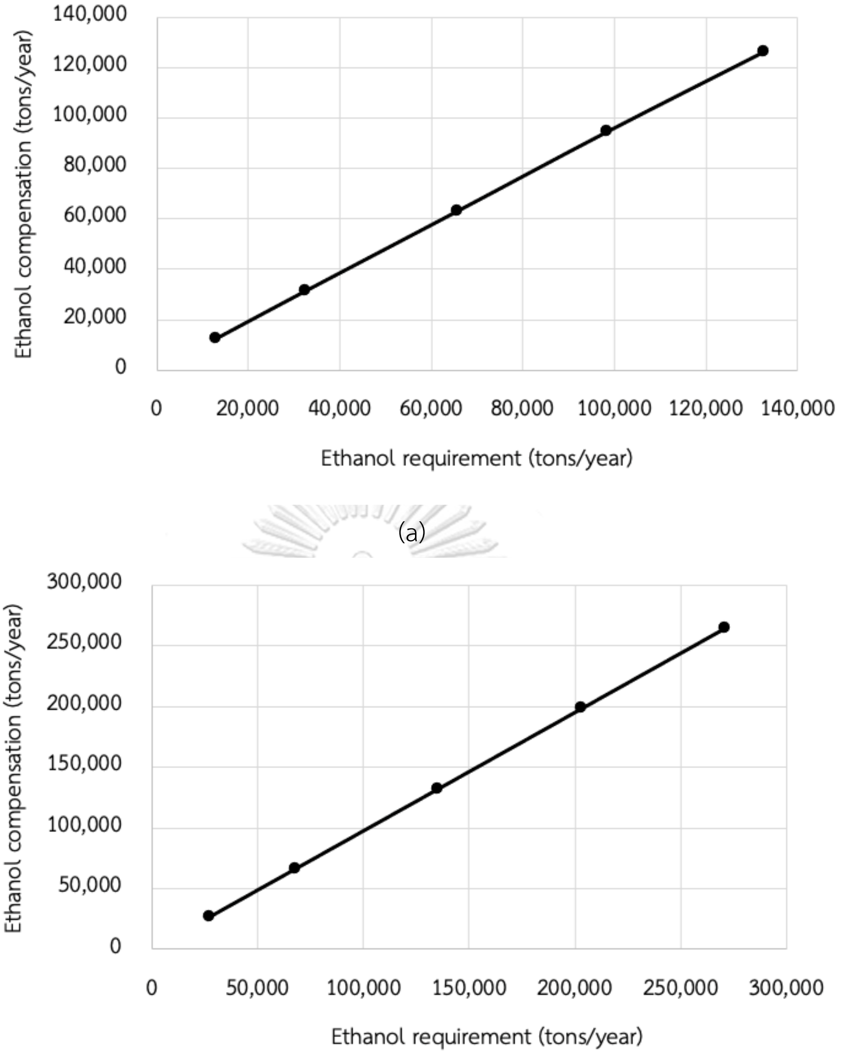


(a) (b)

(c) (d)

Figure 7 Comparison of calculation and simulation of (a) the amount of fresh feed ethanol in NOX-25-200 process (b) the amount of recycle ethanol in NOX-25-200 process (c) the amount of fresh feed ethanol in NOX-80-400 process (d) the amount of recycle ethanol in NOX-25-200 process

There may be a loss of ethanol during the separation and purification process of acetaldehyde production. Therefore, it is resulting in less amount of recycle ethanol in simulated work than the calculation. In the same way, the make-up of ethanol in fresh feed stream is required to compensate for this loss. Thus, the amount of fresh feed ethanol obtained from simulated work is more than calculation as depicted in the Figure. As seen in the Figure, all the results have shown the trend in linear function between ethanol utilization and acetaldehyde production capacity.



(a)

(b)

Figure 8 Relationship between ethanol requirement and ethanol compensation of (a) NOX-25-200 process (b) NOX-80-400 process

According to Figure 8, the ethanol requirement for acetaldehyde process is used to compare the compensated ethanol. The compensation percentages are about 3.7% for NOX-25-200 and 2.4% for NOX-80-400 process. By way of explanation, while the NOX-25-200 and NOX-80-400 process is working, approximately 96.3% and 97.6% of the overall conversion of the ethanol amount obtained respectively. In additionally, the mass balance calculation for this work is corrected by confirmed with ethanol increased in linearly trend.

4.2 Simulation results of acetaldehyde production

According to process flow diagrams mentioned in previous chapter, section 3.4, stream results of acetaldehyde productions from process simulator, namely Aspen Plus, are provided in Table 13 and Table 14. Table 13 and Table 14 show summary of stream results of NOX-25-200 and NOX-80-400 processes, respectively. However, there are only the result of 120,000 tons per year of acetaldehyde capacity shown in this part. The other stream results of each capacity is provide in Appendix C.

Table 12 Stream results of NOX-25-200 process with capacity of 120,000 tons/year

Stream no.	**Unit**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Temperature	°C	78.4607	200	200	121	45	10	10	10.0739	38.9159
Pressure	atm	1	1	1	1	1	1	1	2.3	2
Molar Vapor Fraction	-	0.723241	1	1	1	0.357956	0.216326	0	0	1
Mole flow	kmol/hr	1143.16	1143.16	1426.84	1426.84	1426.84	1426.84	1118.18	1118.18	2.67734
Mass flow	tons/year	507660	507660	507660	507660	507660	507660	491331	491331	1081.65
Ethanol	tons/year	505122	505122	378841	378841	378841	378841	376033	376033	0.538159
Acetaldehyde	tons/year	50.0452	50.0452	120805	120805	120805	120805	112818	112818	1078.14
Hydrogen	tons/year	-	-	5525.76	5525.76	5525.76	5525.76	2.88066	2.88066	2.77012
Water	tons/year	1029.05	1029.05	1029.05	1029.05	1029.05	1029.05	1018.16	1018.16	0.205989
Ethylene Glycol	tons/year	1459.2	1459.2	1459.2	1459.2	1459.2	1459.2	1459.19	1459.19	1.82E-16

Table 13 Stream results of NOX-25-200 process with capacity of 120,000 tons/year (continued)

Stream no.	Unit	10	11	12	13	ACET	BFW-I	BFW-O	EG
Temperature	°C	38.9159	101.101	97.0553	203.915	30	111	111	227.186
Pressure	atm	2	2.3	2	2.3	2	1.4606	1.4606	2.3
Molar Vapor Fraction	-	0	0	0	0	0	0	0.9999	1.62E-09
Mole flow	kmol/hr	265.057	850.442	842.693	293.015	265.057	201	201	285.266
Mass flow	tons/year	112818	377431	374943	173562	112818	34989.9	34989.9	171074
Ethanol	tons/year	1088.86	374943	373069	1874.73	1088.86	-	-	0.0176723
Acetaldehyde	tons/year	111690	50.0437	50.031	0.0126824	111690	-	-	1.11E-07
Hydrogen	tons/year	0.110547	2.19E-17	0	0	0.110547	-	-	-
Water	tons/year	32.209	978.748	361.852	623.649	32.209	34989.9	34989.9	6.75269
Ethylene Glycol	tons/year	9.54E-11	1459.19	1462.85	171064	9.54E-11	-	-	171068

Table 13 Stream results of NOX-25-200 process with capacity of 120,000 tons/year (continued)

Stream no.	Unit	EG-M	EG-RE	ETOH-F	ETOH-RE	GAS	GLC-I	GLC-O	WATER
Temperature	°C	227.243	227.184	30	97.0553	10	0	10	112.801
Pressure	atm	2.3	2.3	1	1	1	1	1	2
Molar Vapor Fraction	-	0	0	0	0	1	0	0	0
Mole flow	kmol/hr	11.769	273.515	300.251	842.693	308.662	17848.2	17848.2	19.5
Mass flow	tons/year	7058.56	164027	132627	372943	16329.2	3.95E+06	3.95E+06	9535.71
Ethanol	tons/year	-	0.0176767	131964	373069	2808.57	-	-	1874.71
Acetaldehyde	tons/year	-	1.11E-07	-	50.031	7986.85	-	-	0.0126822
Hydrogen	tons/year	-	-	-	-	5522.87	-	-	-
Water	tons/year	-	6.75232	663.134	361.852	10.8891	2.76E+06	2.76E+06	616.896
Ethylene Glycol	tons/year	7058.56	164020	-	1462.85	0.0043422	1.18E+06	1.18E+06	7044.08

Table 13 Stream results of NOX-80-400 process with capacity of 120,000 tons/year

Stream no.	**Unit**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Temperature	°C	78.2432	400	400	90	238.719	124	45	10
Pressure	atm	1	1	1	1	5	5	5	5
Molar Vapor Fraction	-	1	1	1	1	1	1	0.5576	0.461396
Mole flow	kmol/hr	747.565	747.565	1329.92	1329.92	1329.92	1329.92	1329.92	1329.92
Mass flow	tons/year	330347	330347	330347	330347	330347	330347	330347	330347
Ethanol	tons/year	328695	328695	65739	65739	65739	65739	65739	65739
Acetaldehyde	tons/year	75.2786	75.2786	119922	119922	119922	119922	119922	119922
Ethylene	tons/year	6.85E-09	6.85E-09	81544.7	81544.7	81544.7	81544.7	81544.7	81544.7
Diethyl Ether	tons/year	0.0150309	0.0150309	2988.04	2988.04	2988.04	2988.04	2988.04	2988.04
Hydrogen	tons/year	-	-	5484.22	5484.22	5484.22	5484.22	5484.22	5484.22
Water	tons/year	1565.6	1565.6	54657.4	54657.4	54657.4	54657.4	54657.4	54657.4
Ethylene Glycol	tons/year	10.8377	10.8377	10.8377	10.8377	10.8377	10.8377	10.8377	10.8377

Table 14 Stream results of NOX-80-400 process with capacity of 120,000 tons/year (continued)

Stream no.	**Unit**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
Temperature	^{o}C	10	9.96968	38.0645	38.0645	103.837	34.4005	40.4438	96.6341
Pressure	atm	5	2.3	2	2	2.3	1.7	2	2
Molar Vapor Fraction	-	0	0.00097758	1	0	0	1	0	1
Mole flow	kmol/hr	716.302	716.302	25.9392	233.452	456.911	1.24049	208.643	14.8785
Mass flow	tons/year	229586	229586	10803.9	99282.4	119499	566.202	88090.2	6578.91
Ethanol	tons/year	65516.7	65516.7	0.316789	65.5166	65450.9	4.14E-16	65.5166	6464.47
Acetaldehyde	tons/year	107008	107008	10002.1	96842.7	163.755	469.514	87209.3	88.3797
Ethylene	tons/year	477.295	477.295	476.376	0.918977	7.12E-08	0.916593	2.64E-34	6.43E-08
Diethyl Ether	tons/year	2096.25	2096.25	294.806	1801.42	0.0247545	95.7623	243.587	0.00969903
Hydrogen	tons/year	2.16759	2.16759	2.15911	0.0084808	6.45E-15	0.00828316	1.86E-34	-
Water	tons/year	54474	54474	28.2031	571.845	53874	0.00104845	571.799	25.9384
Ethylene Glycol	tons/year	10.8377	10.8377	2.39E-17	1.35E-12	10.8377	-	-	0.118177

Table 14 Stream results of NOX-80-400 process with capacity of 120,000 tons/year (continued)

Stream no.	**Unit**	**17**	**18**	**ACET**	**BFW-I**	**BFW-O**	**DEE**	**EG**	**EG-M**
Temperature	^{o}C	96.6341	159.098	30	114	114	34.4005	227.242	227.243
Pressure	atm	2	2.3	2	1.61297	1.61297	1.7	2.3	2.3
Molar Vapor Fraction	-	0	0	0	0	0.999562	0	0	0
Mole flow	kmol/hr	133.907	858.163	208.643	203	203	23.5693	550.038	3.477
Mass flow	tons/year	59281.9	383528	88090.2	35338.1	35338.1	10626	329889	2085.36
Ethanol	tons/year	58985.5	0.966686	65.5166	-	-	1.89E-13	5.44E-15	-
Acetaldehyde	tons/year	75.3756	6.23E-06	87209.3	-	-	9163.91	2.39E-15	-
Ethylene	tons/year	6.87E-09	1.04E-20	2.64E-34	-	-	0.00238434	-	-
Diethyl Ether	tons/year	0.0150554	6.65E-11	243.587	-	-	1462.07	-	-
Hydrogen	tons/year	-	-	1.86E-34	-	-	0.000197638	-	-
Water	tons/year	210.18	53638.1	571.799	35338.1	35338.1	0.0449438	0.269243	-
Ethylene Glycol	tons/year	10.8384	329889	-	-	-	-	329889	2085.36

Table 14 Stream results of NOX-80-400 process with capacity of 120,000 tons/year (continued)

Stream no.	Unit	EG-RE	ETOH-F	ETOH-RE	GAS	GLC-I	GLC-O	WATER
Temperature	°C	227.242	30	96.6341	10	0	10	121.032
Pressure	atm	2.3	1	1	5	1	1	2
Molar Vapor Fraction	-	0	0	0	1	0	0	0
Mole flow	kmol/hr	546.572	613.658	133.907	613.621	11213.2	11213.2	311.591
Mass flow	tons/year	327811	271065	59281.9	100761	2.48E+06	2.48E+06	55717.3
Ethanol	tons/year	5.44E-10	269710	58985.5	222.246	-	-	0.966686
Acetaldehyde	tons/year	2.39E-15	-	75.3756	12913.9	-	-	6.23E-06
Ethylene	tons/year	-	-	6.87E-09	81067.4	-	-	-
Diethyl Ether	tons/year	-	-	0.0150554	891.785	-	-	-
Hydrogen	tons/year	-	-	-	5482.06	-	-	-
Water	tons/year	0.26926	1355.32	210.18	183.374	1.74E+06	1.74E+06	53637.9
Ethylene Glycol	tons/year	327810	-	10.8384	1.98E-05	744014	744014	2078.43

Table 14 Percentages of acetaldehyde yield achieved from simulation

Process	Capacity (tons/year)	Acetaldehyde (tons/year)	Acetaldehyde yield (%)
NOX-25-200	**12,000**	10,978.4	91.56
	30,000	27,565.2	91.88
	60,000	55,241.1	92.07
	90,000	82,864.4	92.07
	120,000	111,690	93.08
NOX-80-400	**12,000**	8,712.76	72.61
	30,000	21,780.6	72.60
	60,000	43,563.9	72.61
	90,000	65,346.6	72.61
	120,000	87,209.3	72.67

According to Table 15, the size of plant is not affected to the acetaldehyde percentages yield obtained from the simulation. The acetaldehyde yield from NOX-25-200 process is approximately to 92% and NOX-80-400 process is approximately to 72.6%. Thus, the accuracy of this work is confirmed by these results.

4.3 Evaluation of CO_2 emission

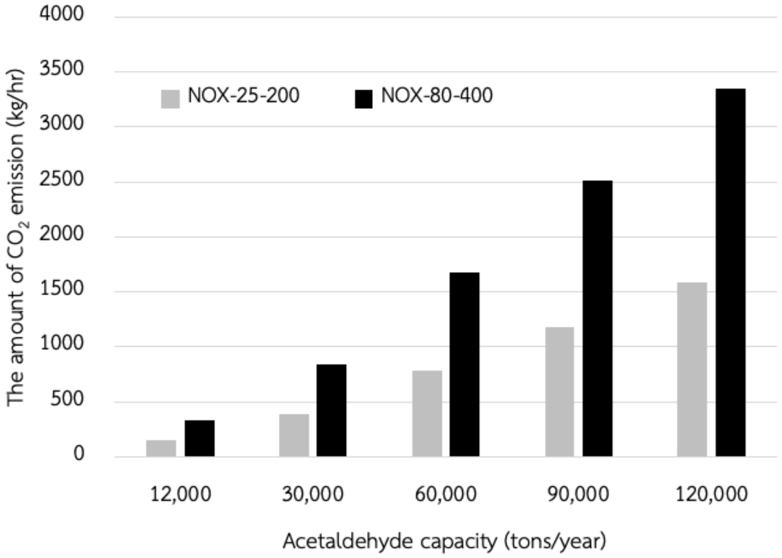
As mentioned in previous chapter, the first thing that must be concerned for plant design is greenhouse gas assessment. Some of greenhouse gas might be occurred in this work is CO_2 gas. The method for calculating net carbon dioxide emission is mentioned in section 3.6. Net CO_2 emission, which based on CO_2 flow rate, is used to evaluate CO_2 emission in this section.

For this work, there is no CO_2 fed into both processes of acetaldehyde production. Due to the CO_2 emitted from both processes are from thermal utilities and electrical utilities, the CO_2 outlet from both processes are indirect outlet. Hence, net CO_2 emission is calculated from only CO_2 outlet from the process. Net CO_2 emission from the acetaldehyde productions are provided in Table 16.

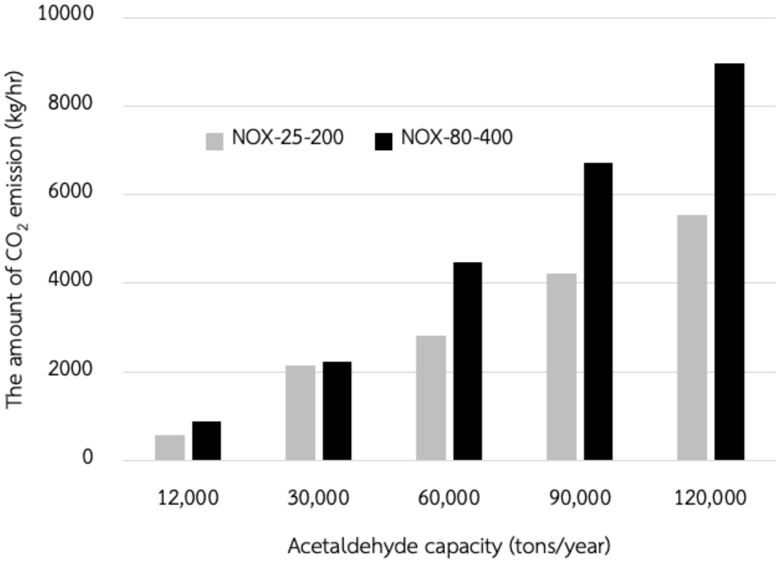
Table 15 Net CO_2 emission

Process	Capacity (tons/year)	Inlet	Outlet		Net CO_2 emission (kg/hr)
		Inlet CO_2 (kg/hr)	Direct outlet (kg/hr)	Indirect outlet (kg/hr)	
NOX-25-200	**12,000**	0	0	744.22	744.22
	30,000	0	0	2,551.95	2,551.95
	60,000	0	0	3,595.15	3,595.15
	90,000	0	0	5,393.81	5,393.81
	120,000	0	0	7,130.28	7,130.28
NOX-80-400	**12,000**	0	0	1,328.91	1,328.91
	30,000	0	0	3,319.00	3,319.00
	60,000	0	0	6,641.19	6,641.19
	90,000	0	0	9,964.09	9,964.09
	120,000	0	0	13,307.36	13,307.36

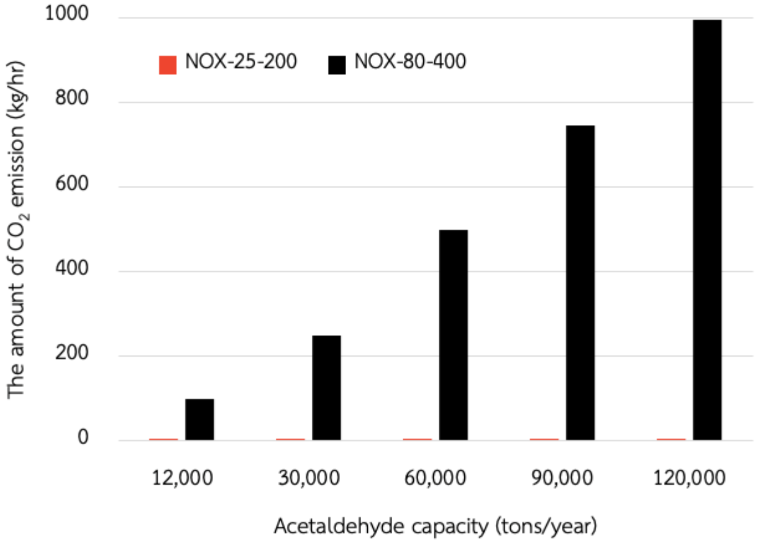
As a result, the mainly outlet of CO_2 is coming from the utilities usage which is indirect CO_2 outlet in the acetaldehyde production. Moreover, the results in Table above could be determined the amount of CO_2 emitted per acetaldehyde 1 kg. The amount of CO_2 emitted per acetaldehyde 1 kg is approximately to 0.68 $kg_{CO_2}/kg_{acetaldehyde}$ for NOX-25-200 process and 1.46 $kg_{CO_2}/kg_{acetaldehyde}$ for NOX-80-400 process. It is clearly seen that CO_2 emitted per 1 kg of acetaldehyde of NOX-25-200 is lower than NOX-80-400 process. The factor that affected the large amount of CO_2 emitted in NOX-80-400 was mainly from compressor which shown in Figure 9.



(a) Furnace



(b) Distillation columns



(c) Pump for NOX-25-200 and compressor for NOX-80-400 process

Figure 9 The amount of CO2 emissions from each unit operation

Carbon dioxide gas is still produced even there is no CO_2 consumption in this process. As seen in Figure 9, the CO_2 gas is still occurred in the process. The CO_2 gas was produced from furnace and distillation column unit in both processes; NOX-25-200 and NOX-80-400. While the CO_2 generation from NOX-25-200 process was produced by pump, NOX-80-400 process was generated by compressor.

In conclusion, the amount of CO_2 emission from NOX-80-400 process is higher than NOX-25-200 process. As a result of higher CO_2 emission rate in NOX-80-400 process can be caused by 1) the furnace outlet temperature of NOX-80-400 process is higher than NOX-25-200 process (400 °C and 200 °C) 2) the number of distillation columns in NOX-80-400 process is more than in NOX-25-200 process (4 columns and 3 columns) 3) compressor usage in NOX-80-400 process while NOX-25-200 used pump.

4.4 Evaluation of energy utilization

In this study, the energy can be divided into two main types including thermal and electrical duty. The total duty used in this work are presented in Table 17.

Table 16 Summary of thermal and electrical duty in NOX-25-200 and NOX-80-400 process

Process	Acetaldehyde capacity (tons/year)	Energy consumption (MW)	
		Electrical duty	Thermal duty
NOX-25-200	**12,000**	6.5E-04	7.460
	30,000	1.17E-03	24.729
	60,000	1.97E-03	36.708
	90,000	2.73E-03	55.071
	120,000	3.49E-03	73.075
NOX-80-400	**12,000**	0.286	11.345
	30,000	0.716	28.840
	60,000	1.431	57.708
	90,000	2.147	86.583
	120,000	2.862	115.640

As seen in Table 17, the process performance can be significantly defined by energy efficiency. In this work, the factor that used to define the energy efficiency is specific energy consumption (SEC). The specific energy consumption can be measured by dividing energy used by the amount of product. In this work, the specific energy consumption of electrical duty has been obtained. The specific energy consumption of electrical duty for NOX-25-200 and NOX-80-400 is approximately to 0.0015 MJ/kg and 1.13 MJ/kg respectively. As a result, these values can be indicated that the NOX-80-400 process use more electrical duty than NOX-25-200 process significantly.

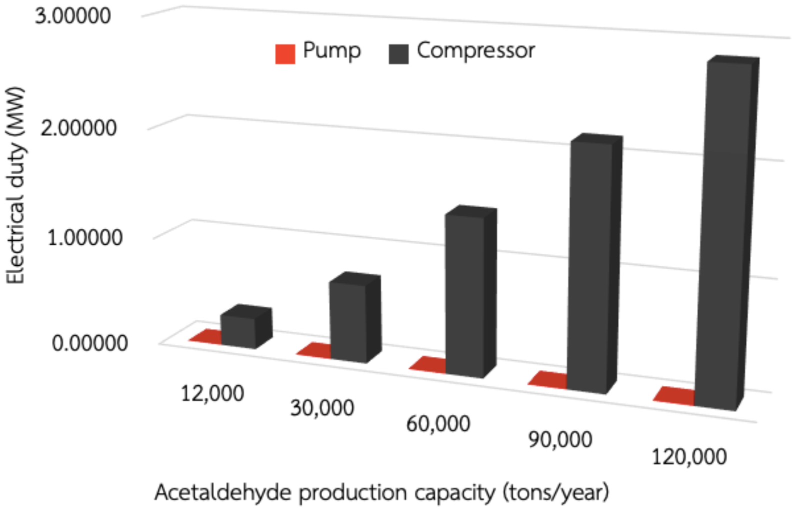


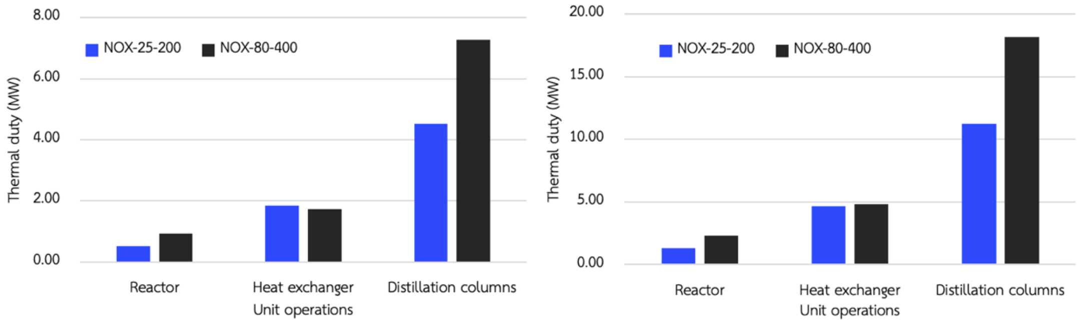
Figure 10 Electrical duty in NOX-25-200 and NOX-80-400 process

Figure 10 shows the total summary of electrical used in each process of acetaldehyde production. It is clearly seen that the process with the compressor unit is consuming a lot of electrical which accounted for 99% of all electrical consumed. This is because there are several vapor products exiting the reactor and only heat exchanger using cannot reached the acetaldehyde to desired yield in NOX-80-400 process. Thus, it is necessary to used compressor before entering the phase separation process.

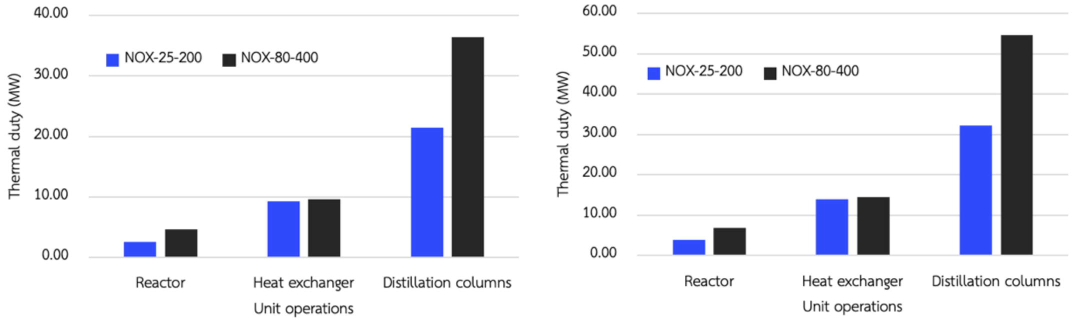
In contrary, the NOX-25-200 process, there are fewer product coming out the reactor and easier to separate vapor and liquid phase. The stream pressuring process can be used after the phase separation process for only liquid. Therefore, it is not necessary to use compressor in the NOX-25-200 process.

According to Table 17, the specific energy consumption of thermal duty can be achieved as well. The specific energy consumption of thermal duty is approximately to 24.50 MJ/kg and 45.44 MJ/kg for NOX-25-200 and NOX-80-400 process respectively. This indicates that the NOX-80-400 process consumed a lot of thermal energy when compared to NOX-25-200 process.

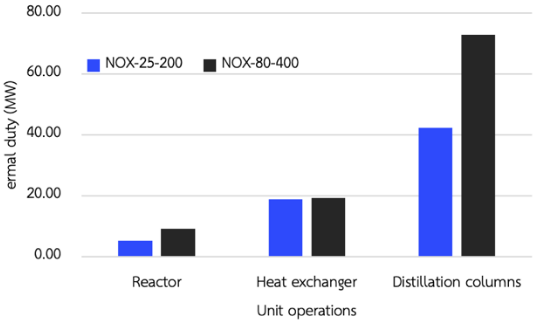
When compare thermal duty of each unit from both processes and represent in Figure 11, most of the thermal energy consumption is from the distillation columns unit. The thermal energy used in distillation column is approximately to 63% of all thermal energy consumed.



(a) 12,000 tons/year (b) 30,000 tons/year



(c) 60,000 tons/year (d) 90,000 tons/year



(e) 120,000 tons/year

Figure 11 Thermal duty in NOX-25-200 and NOX-80-400 process

As seen in Figure 11, it is clearly seen that thermal duty used in distillation columns for NOX-80-400 process is higher than NOX-25-200 for all production capacities. The higher number of distillation columns can cause higher thermal duty consumption. In addition to higher temperature reaction of NOX-80-400 process, the thermal duty used for furnace and reactor in NOX-80-400 process is higher than NOX-25-200 for all capacities as well.

4.5 Heat recovery system

Heat recovery system has been used in this research. Heat recovering in this work is conducted by using heat exchanger unit E-2 and E-3 in NOX-25-200 process and NOX-80-400 process, respectively. The utility involved in the heat recovery system is boiler feed water (BFW), the saturated steam which vaporized from water.

The heat recovery system for heat exchanger unit namely E-2 in NOX-25-200 process is used to exchange the heat between the process stream and boiler feed water. The boiler feed water is used as utility in this unit operation for absorbed heat that released from the process stream (stream 3) and reduced temperature from 200 °C to 121 °C (stream 4). Then, the boiler feed water which absorbed heat from the process stream can be used as utility for reboiler section in distillation column S-2.

Heat recovery system in NOX-80-400 process is working as same as the system in NOX-25-200 process. Heat recovery system occurred in NOX-80-400 by using heat exchanger unit namely E-3. The utility used in this unit operation is boiler feed water (BFW) as well. The boiler feed water is used to absorb heat from process stream (stream 5) and reduced temperature from 239 °C to 124 °C (stream 6). Then, the heat absorbed boiler feed water can be used as utility for reboiler section in distillation column S-2 also.

4.6 Economic evaluation

In this work, the analysis tool using for evaluating the economic is Aspen Economic Analyzer. The production capacity of acetaldehyde has divided into five cases; 12,000 30,000 60,000 90,000 and 120,000 tons/year. The evaluation of each acetaldehyde production capacity is based on fixed ethanol price to 0.49 US$ per liter. As mentioned in chapter 3, the acetaldehyde selling price use in this work is 1.01 US$ per kilogram based on price reference from ICIS data [43]. However, according to the price, the economic evaluation of this production cannot make a profit. Thus, it is necessary to find the new selling price of acetaldehyde.

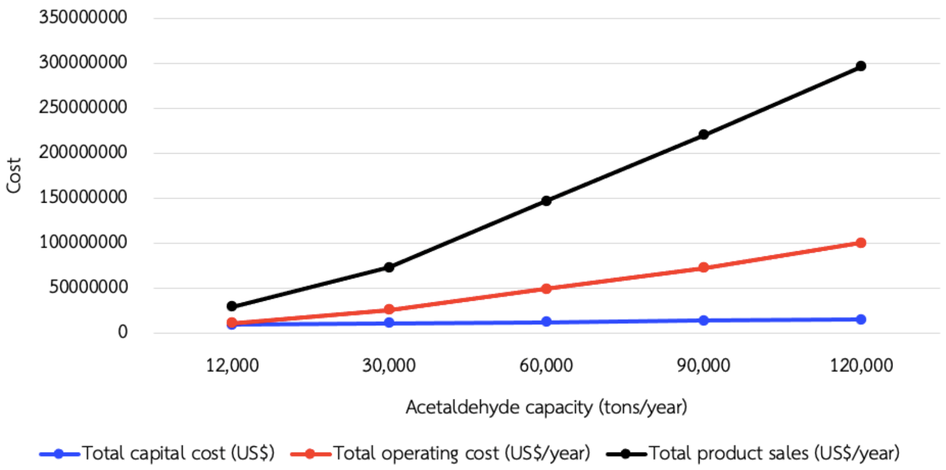
For economic evaluation of acetaldehyde production, the selling price of acetaldehyde must be determined. The new selling price of acetaldehyde start evaluated from 120,000 tons/year with assumption that the higher production capacity, the higher profitability of acetaldehyde production achieved. Thus, the highest capacity of acetaldehyde may give the highest profitability by assuming of this work. Furthermore, the economic evaluation procedure is working based on five years of payout period (POP). Then, the new price will be chosen for evaluate the economic feasibility of acetaldehyde production which acetaldehyde capacity is suitable for acetaldehyde production.

The economic analysis of acetaldehyde production is conducted by simulator namely Economic Evaluator in Aspen Plus. The results of evaluation are used to compare the feasibility of each acetaldehyde production capacity. The minimum selling price of acetaldehyde that can return profit to the process is 1.07 US$ per kilogram and 2.69 US$ per kilogram for NOX-25-200 and NOX-80-400 process respectively. As mentioned above, the POP of this production is fixed with 5 years. The price of acetaldehyde that could return a profit to the process in 5 years is 1.20 US$ per kilogram and 2.89 US$ per kilogram for NOX-25-200 and NOX-80-400 respectively. Thus, the acetaldehyde price using for evaluating economic feasibility of acetaldehyde production is 2.89 US$ per kilogram. The economic analysis results are shown in Table 18.

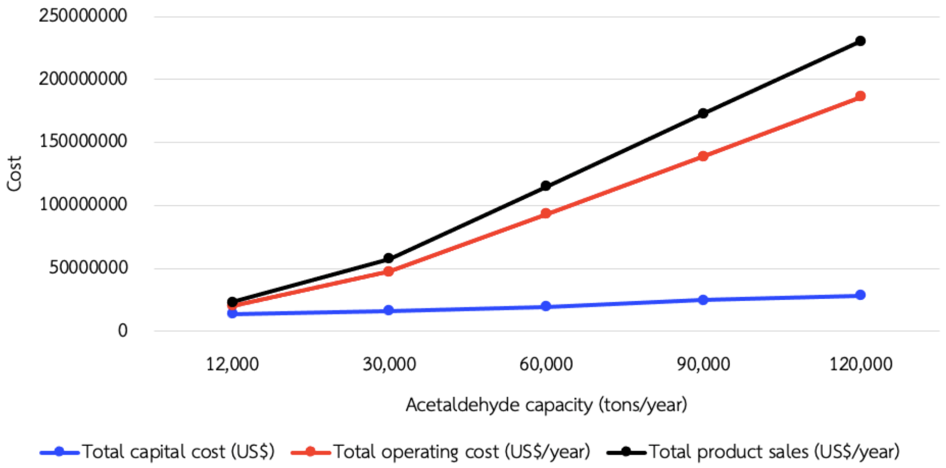
Table 17 The economic analysis results for NOX-25-200 and NOX-80-400 process

Process	**Acetaldehyde capacity (tons/year)**	**Economic parameter**		
		Profitability index (PI)	**POP (year)**	**%IRR**
NOX-25-200	**12,000**	1.46	2.05	121.076
	30,000	1.56	1.55	224.291
	60,000	1.62	1.34	356.633
	90,000	1.63	1.32	382.726
	120,000	1.63	1.31	397.671
NOX-80-400	**12,000**	0.95	-	-
	30,000	1.04	7.04	28.614
	60,000	1.07	5.43	36.919
	90,000	1.07	5.01	39.973
	120,000	1.07	4.98	40.258

According to Table 18, the assumption can be confirmed by the economic analysis results. In case of 12,000 tons/year of acetaldehyde capacity in NOX-80-400, the result shows that profitability index (PI) of the process is less than 1. Thus, the process cannot make a profit. For the NOX-25-200 process, all cases are economically feasible with acetaldehyde price 2.89 US$ per kilogram. In addition, all capacities in NOX-80-400 process except 12,000 tons/year of acetaldehyde capacity cannot gain the profit.



(a) NOX-25-200 process



(b) NOX-80-400 process

Figure 12 Trend of total capital cost, total operating cost and total product sales of both processes

As seen in Figure 12, the rate of increasing of the total product sales is the function of the acetaldehyde production capacity. The total product sales are higher than total capital cost and total operating cost in both processes. Thus, this is the reason of results obtained in Table 18 that higher profitability of the production achieved with increasing production capacity of acetaldehyde.

In this work, the process with the highest internal rate of return had been chosen. The process with maximum capacity was chosen by the reasonable results in profitability index value and internal rate of return. Thus, the NOX-25-200 with 120,000 tons/year of acetaldehyde capacity is the most profitable for acetaldehyde production process.

As mentioned above, NOX-25-200 process provided higher internal rate of return (%IRR) and optimum payout period (POP). This may cause by more factors involved than previously mentioned listed as below.

1) Total acetaldehyde amount obtained from the process

As mentioned before in section 4.2, the amount of acetaldehyde product obtained from the process is the factor must be considered about economic feasibility. When comparing two processes of acetaldehyde production with different operating conditions, ethanol conversion and acetaldehyde selectivity, the amount of acetaldehyde obtained from the different process is significantly different.

In case of NOX-25-200 process, there is only one main product occurred in this process which is acetaldehyde with 100% selectivity. The acetaldehyde product in this process can be separated easier than the NOX-80-400. The NOX-80-400 process has various product occurred in the process. This can cause the purity of acetaldehyde product. The essential factor that caused the amount of acetaldehyde in NOX-80-400 process is by-product occurred during the process reaction; diethyl ether. The diethyl ether can form azeotrope mixture with acetaldehyde, and it is difficult to purify or separate acetaldehyde from this by-product. Thus, acetaldehyde to be selling may be loss during separation process of NOX-80-400.

2) Total cost of raw material used

The amount of ethanol required for acetaldehyde production process are shown in Table 19 It is clearly seen that the amount of ethanol required for NOX-80-400 process is more than the amount of ethanol required in NOX-25-200 process. As mentioned previously in section 4.1, NOX-80-400 has achieved higher conversion of ethanol than NOX-25-200. Thus, the amount of ethanol obtained from external source in NOX-80-400 is higher than NOX-25-200 process.

Table 18 The amount of ethanol required for acetaldehyde production

Acetaldehyde capacity (tons/year)	**The amount of ethanol required (tons/year)**	
	NOX-25-200	**NOX-80-400**
12,000	12,941.1	27,106.2
30,000	32,537.8	67,767
60,000	65,642.5	135,533
90,000	98,463.2	203,299
120,000	132,627	271,065

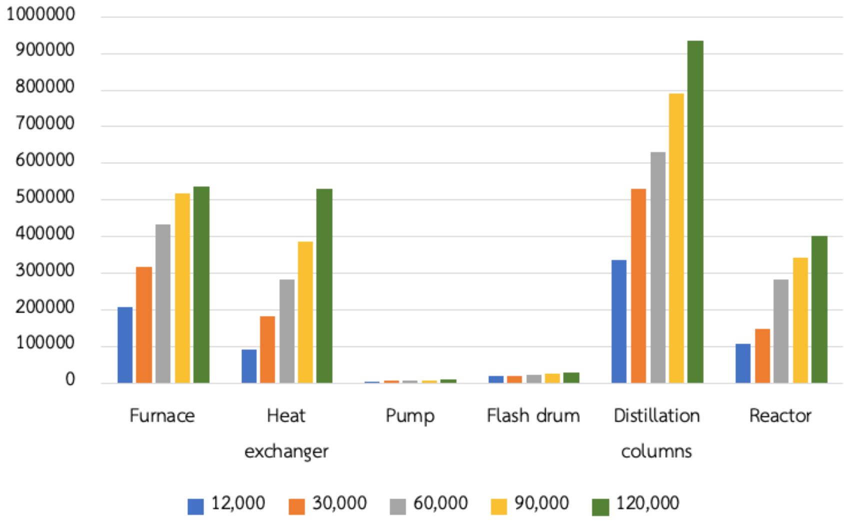
3) Total equipment cost

Total equipment cost of each process are shown in Table 19. When comparing total equipment cost of each capacity, it is clearly seen that NOX-80-400 has higher total equipment cost for all capacity. The results show that NOX-80-400 process is require much more payment than NOX-25-200 process.

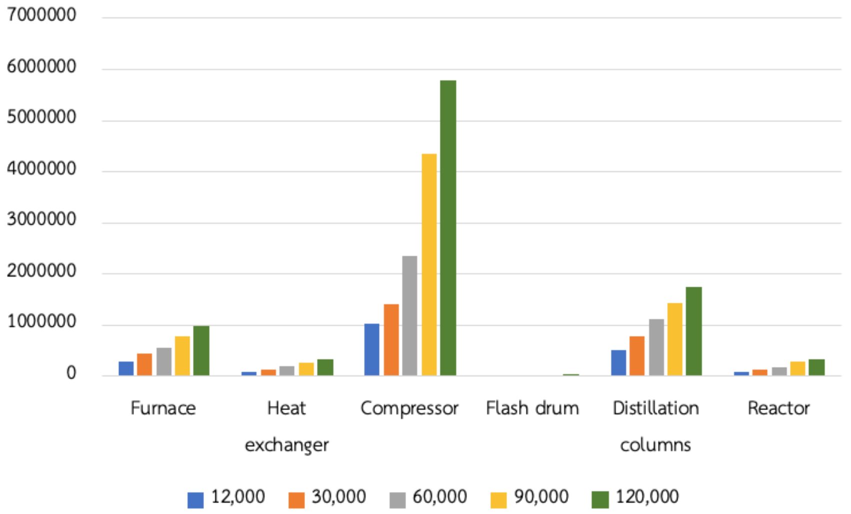
Table 19 Total equipment cost for acetaldehyde production

Process	Acetaldehyde capacity (tons/year)	Total equipment cost (US$)
NOX-25-200	12,000	818,500
	30,000	1,287,100
	60,000	1,775,700
	90,000	2,217,200
	120,000	2,602,500
NOX-80-400	12,000	2,209,400
	30,000	3,213,300
	60,000	4,898,500
	90,000	7,921,300
	120,000	10,186,500

When divided total equipment cost into each unit, the equipment cost of each unit for the acetaldehyde production are shown in Figure 13. The major cost of acetaldehyde production is the compressor in NOX-80-400 process which cost is the highest among all other units. In NOX-25-200 process, the major cost is in the purification and recycle unit.



(a) NOX-25-200 process



(b) NOX-80-400 process

Figure 13 Equipment cost of each unit operation

Chapter 5

Conclusion

Due to the rapid development in energy storage used in the electrical vehicles (EV), the demand for gasohol may decrease. Moreover, fluctuation of oil price may cause the reduction of gasohol usage which could directly affect the ethanol demand. In this work, organic chemical in industrial may shift into renewable raw materials instead of fossil raw materials. Thus, Aspen Plus will be utilized for the process simulation of acetaldehyde production from ethanol.

Two processes of acetaldehyde production with different operating conditions have been conducted in this study: NOX-25-200 and NOX-80-400 process. The operating conditions were obtained from the literature. The non-oxidative dehydrogenation of ethanol using V-Zr-La/SBA-15 catalyst was chosen under two different operating conditions. First, the non-oxidative dehydrogenation using V-Zr-La/SBA-15 catalyst under 1 atm of operating pressure and 200 °C of operating temperature (NOX-25-200). The other one is the non-oxidative dehydrogenation under 1 atm of operating pressure and 400 °C of operating temperature (NOX-80-400).

First, the results from raw material utilization show that the amount of ethanol utilization in mass balance calculation does not equal to the acetaldehyde production process. The infeasibility of perfect separation can cause the ethanol to lose during separation process. The overall conversion of ethanol obtained from NOX-25-200 and NOX-80-400 process is 96.3% and 97.6% respectively.

Second, the results from CO_2 emission show that the NOX-25-200 process released 0.68 $kg_{CO_2}/kg_{acetaldehyde}$ and 1.46 $kg_{CO_2}/kg_{acetaldehyde}$ for NOX-80-400 process. All of CO_2 emitted from both processes are indirect CO_2 emission from using utilities. Likewise, the acetaldehyde production capacity does not affect on CO_2 emission.

Third, the energy utilization for both processes of acetaldehyde production are defined by specific energy consumption (SEC). The specific energy consumption of electrical duty for NOX-25-200 and NOX-80-400 is approximately to 0.0015 MJ/kg and 1.13 MJ/kg respectively. Owing to this, the energy usage in NOX-80-400 process is higher than NOX-25-200 process. The energy consumption in both processes can be divided into two types. The electrical duty is come from pump and compressor. The thermal duty is come from utilities usage in distillation columns, reactor and heat exchanger.

Lastly, the economic analysis results are feasible to all acetaldehyde production except 12,000 acetaldehyde capacity of NOX-80-400 process. Due to the highest %IRR, 120,000 tons/year capacity of acetaldehyde production in NOX-25-200 process is suitable for acetaldehyde production. Moreover, NOX-25-200 process with 120,000 tons/year is utilized raw material than the other process. As a result of equipment cost, the NOX-25-200 process spend lower equipment cost than NOX-80-400 process. Finally, the NOX-25-200 process with 120,000 tons/year of acetaldehyde production can make a profit returning to the production within 1.31 years with 397.67 of internal rate of return (%IRR).

In conclusion, the several results obtained from lab-scale reaction of the non-oxidative dehydrogenation of ethanol for acetaldehyde production is only focused on the highest conversion achieved. Meanwhile, the working on acetaldehyde production plant must be considered in the separation process also. The highest conversion of ethanol can produce several by-products which may form azeotropic mixtures to main product. This azeotropic mixtures can be causing in the separation process and losing the main product. Hence, the catalyst designed for using in the non-oxidative dehydrogenation must be considered to these factors.

For the future study, the alternative way to make this process more economic feasibility is to produce the acetaldehyde via higher operating pressure. This can cause in lower operating cost of unit operating which involved the pressure.

Thus, this research might be a benefit for improvement and development for feasibility of plant design in the future. It would be result in understanding in process and a procedure of process simulation that will be the important part which directly to commercial scale.

Chapter 6

Recommendation

As a result, energy consumption and economic evaluation study in previously section shows that the compressor can be cause the economic feasibility of the process. Thus, the operating conditions of 10 atm has been worked with the expectation to reduce cost of compressor. The reaction at operating pressure 10 atm is expected to enhance the process separation efficiency. In NOX-80-400 process, the compressor is used for pressuring the vapor phase. Instead of that, this recommendation to increase the pressure before the reaction occurred. In feed preparation system, all reactants are in liquid phase. Using pump instead of compressor may reduce cost of operating conditions.

Please note that this work is only changes the operating pressure, not all the process parameters and conditions. The process flow diagram of this recommend work are shown in Figure 14.

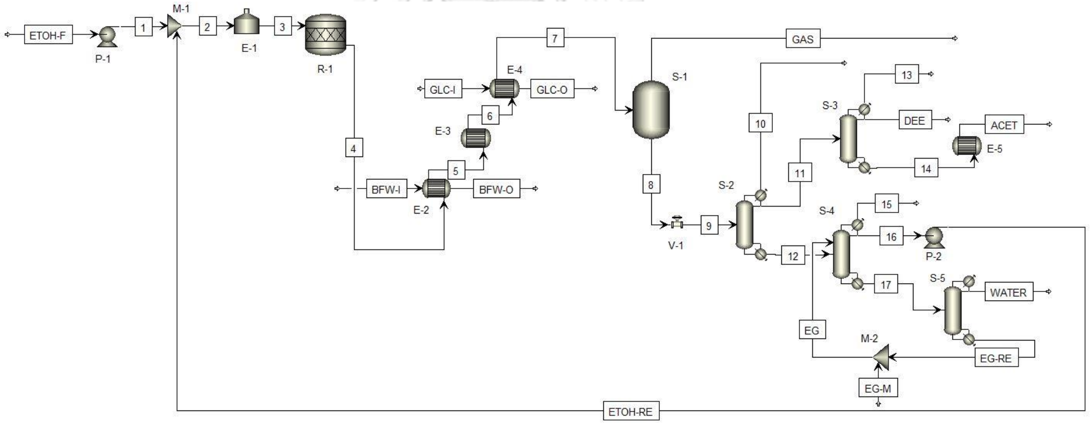


Figure 14 Process flow diagram of acetaldehyde production at 400 °C and 10 atm

As seen in the figure, the pump is used in feed preparation instead of compressor where place after the reactor. Pump using in this process may cause the lower operating cost and other economic parameter as shown in Table 21.

Table 20 The comparison of economic analysis result of operating conditions between 1 atm and 10 atm at 200 °C and 400 °C

Operating conditions	PI	POP (year)	%IRR	Total equipment cost (US$)
200 °C and 1 atm	1.63	1.31	397.671	2,602,500
200 °C and 10 atm	1.62	1.53	240.149	6,684,700
400 °C and 1 atm	1.07	4.98	40.258	10,186,500
400 °C and 10 atm	1.14	3.42	60.205	4,334,200

According to the table, increased pressure of 10 atm can increased the profitability of the acetaldehyde process in operating condition of 400 °C. In contrast, increasing pressure of 10 atm in operating condition of 200 °C is not improved the profitability feasible for this process. For further study, the catalytic reaction of non-oxidative dehydrogenation must be investigated in 10 atm condition. This work is just an example case and study guide for the catalytic reaction at other operating conditions.

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APPENDIX

APPENDIX A Calculation of ethanol required and feed amount for non-oxidative dehydrogenation of ethanol for acetaldehyde production

For acetaldehyde capacity basis of 12,000 tons/year

$$\frac{12{,}000\ \frac{\text{tons}}{\text{year}} \times \frac{10^6}{1}\ \frac{\text{g}}{\text{tons}}}{44\ \frac{\text{g}}{\text{mol}}} = 272.73 \times 10^6\ \frac{\text{mol}}{\text{year}}$$

The reaction in reactor for NOX-80-400 process

$C_2H_5OH \longrightarrow CH_3CHO + H_2$

$2C_2H_5OH \longrightarrow C_2H_5OC_2H_5 + H_2O$

$C_2H_5OH \longrightarrow C_2H_4 + H_2O$

Mass balance calculation for determine ethanol utilization in each process

From selectivity of this process

48% selectivity of acetaldehyde = 272.73×10^6 mol/year

51.29% selectivity of ethylene = 291.42×10^6 mol/year

0.71% selectivity of ethylene = 4.03×10^6 mol/year

Calculate the ethanol utilization for the acetaldehyde process from stoichiometric coefficient

Acetaldehyde 272.73×10^6 mol/year consuming ethanol = 272.73×10^6 mol/year

Ethylene 291.42×10^6 mol/year consuming ethanol = 291.42×10^6 mol/year

Ethylene 0.71×10^6 mol/year consuming ethanol = 4.03×10^6 mol/year

Thus, the amount of total ethanol required for the acetaldehyde production = 572.21×10^6 mol/year. When convert into tons/year unit, the amount of ethanol is equal to 26,321.66 tons/year feed of ethanol. However, this acetaldehyde production is utilized 99.5 wt% of ethanol. Therefore, the actual ethanol fresh feed required for this production is $\frac{26{,}321.66}{0.995}$ = 26,453.93 tons/year.

APPENDIX B Reactor sizing

The catalyst weight (W_{cat})

Weight hourly space velocity (WHSV) of this process is 22.9 ($g_{ethanol}g_{cat}^{-1}$) h^{-1}. Basis of 120,000 tons/year of acetaldehyde production capacity, flow rate of ethanol for reactor is approximately to 3,741.08 kg/hr.

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

From equation, the mass of catalyst can calculate as follows;

$$\text{Catalyst weight } (W_{cat}) = \frac{3{,}741.08\ \frac{kg_{ethanol}}{hr}}{22.9\ \frac{kg_{ethanol}}{kg_{cat}\cdot h}}$$

$$= 163.37\ kg_{cat}$$

The diameter of reactor (D)

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

Where; G = mass velocity (kg/m^2s)

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

D = vessel diameter (m)

Mass velocity (G) is equal to 1.35 $\frac{kg}{m^2 \cdot s}$ for a vapor-phase packed bed reactor.

$$\text{Diameter (D)} = \left(\frac{4 \times 3{,}741.08\ \frac{kg}{hr} \times \frac{1\ hr}{3{,}600\ s}}{1.35\ \frac{kg}{m^2 \cdot s} \times \pi}\right)^{\frac{1}{2}}$$

$$= 5.6166\ m$$

The volume of catalyst bed (V_{bed})

In this work, V-Zr-La/SBA-15 catalyst is used with a bulk density of 0.067 g/cm^3.

$$\text{Catalyst bed volume } (V_{bed}) = \frac{W_{cat}}{\rho_b}$$

$$= \frac{163.37 \text{ kg}_{cat}}{0.067 \frac{\text{g}_{cat}}{\text{cm}^3} \times \frac{1 \text{ kg}_{cat}}{1{,}000 \text{ g}_{cat}} \times \frac{10^6 \text{ cm}^3}{1 \text{ m}^3}}$$

$$= 2.44 \text{ m}^3$$

The length of and catalyst bed (L_B) the length of reactor (L_R)

For the catalyst bed length (L_B)

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

$$L_B = \frac{4 \times 2.44 \text{ m}^3}{\pi \times (0.99 \text{ m})^2}$$

$$= 3.17 \text{ m}$$

For the reactor length (L_R)

$$L_R = L_B + 0.942$$

$$= 3.17 + 0.942$$

$$= 4.112 \text{ m}$$

Table 21 Summary of reactor sizing for economic analysis

Process	Acetaldehyde capacity (tons/year)	D (m)	L_B (m)	L_R (m)
NOX-25-200	12,000	1.22	3.17	4.112
	30,000	1.93		
	60,000	2.76		
	90,000	3.43		
	120,000	3.88		
NOX-80-400	12,000	0.99	3.17	4.112
	30,000	1.57		
	60,000	2.22		
	90,000	2.72		
	120,000	3.10		

APPENDIX C Stream results of NOX-25-200 and NOX-80-400 process

Table 22 Stream results of NOX-25-200 with capacity of 12,000 tons/year

Stream no.	**Unit**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Temperature	°C	78.4709	200	200	121	45	10	10	10.14	38.9165
Pressure	atm	1.01325	1.01325	1.01325	1.01325	1.01325	1.01325	1.01325	2.33048	2.0265
Molar Vapor Fraction	-	0.725598	1	1	1	0.358004	0.216369	0	0	1
Mole flow	kmol/hr	112.339	112.339	140.223	140.223	140.223	140.223	109.883	109.883	0.263158
Mass flow	tons/year	49900.5	49900.5	49900.5	49900.5	49900.5	49900.5	48295.3	48295.3	106.32
Ethanol	tons/year	49651	49651	37238.3	37238.3	37238.3	37238.3	36962.1	36962.1	0.0530396
Acetaldehyde	tons/year	4.93047	4.93047	11874.5	11874.5	11874.5	11874.5	11089.3	11089.3	105.976
Hydrogen	tons/year	0	0	543.155	543.155	543.155	543.155	0.28311	0.28311	0.272165
Water	tons/year	94.2534	94.2534	94.2534	94.2534	94.2534	94.2534	93.2553	93.2553	0.0189121
Ethylene Glycol	tons/year	150.318	150.318	150.318	150.318	150.318	150.318	150.318	150.318	1.88E-17

Table C.1 Stream results of NOX-25-200 with capacity of 12,000 tons/year (continued)

Stream no.	Unit	10	11	12	13	ACET	BFW-I	BFW-O	EG
Temperature	°C	38.9165	101.107	97.0606	205.988	30	111	111	227.242
Pressure	atm	2.0265	2.33048	2.0265	2.33048	2.0265	1.47995	1.47995	2.33048
Molar Vapor Fraction	-	0	0	0	0	0	0	0.999772	0
Mole flow	kmol/hr	26.0526	83.5673	82.8036	31.978	26.0526	19.76	19.76	31.2143
Mass flow	tons/year	11089.3	37099.7	36854.8	18965.9	11089.3	3439.8	3439.8	18721
Ethanol	tons/year	107.284	36854.8	36670.5	184.274	107.284	0	0	1.21E-05
Acetaldehyde	tons/year	10978.4	4.91706	4.91534	0.00171588	10978.4	0	0	1.06E-10
Hydrogen	tons/year	0.0109445	2.16E-18	0	0	0.0109445	0	0	0
Water	tons/year	3.59806	89.6384	28.6275	61.0168	3.59806	3439.8	3439.8	0.00593075
Ethylene Glycol	tons/year	9.87E-12	150.318	150.731	18720.6	9.87E-12	0	0	18721

Table C.1 Stream results of NOX-25-200 with capacity of 12,000 tons/year (continued)

Stream no.	Unit	EG-M	EG-RE	ETOH-F	ETOH-RE	GAS	GLC-I	GLC-O	WATER
Temperature	°C	227.243	227.242	30	97.0606	10	0	10	109.901
Pressure	atm	2.33048	2.33048	1.01325	1.01325	1.01325	1.01325	1.01325	2.0265
Molar Vapor Fraction	-	0	0	0	0	1	0	0	0
Mole flow	kmol/hr	0.9241	30.2901	29.2971	82.8036	30.34	1754.18	1754.18	1.68795
Mass flow	tons/year	554.237	18166.7	12941.1	36854.8	1605.21	387976	387976	799.174
Ethanol	tons/year	0	1.21E-05	12876.4	36670.5	276.145	0	0	184.274
Acetaldehyde	tons/year	0	1.06E-10	0	4.91534	785.197	0	0	0.00171588
Hydrogen	tons/year	0	0	0	0	542.872	0	0	0
Water	tons/year	0	0.00593051	64.7055	28.6275	0.998092	271583	271583	61.0109
Ethylene Glycol	tons/year	554.237	18166.7	0	150.731	0.000447651	116393	116393	553.887

Table 23 Stream results of NOX-25-200 with capacity of 30,000 tons/year

Stream no.	**Unit**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Temperature	°C	78.3274	200	200	121	45	10	10	10.0999	38.9073
Pressure	atm	1.01325	1.01325	1.01325	1.01325	1.01325	1.01325	1.01325	2.33048	2.0265
Molar Vapor Fraction	-	0.72426	1	1	1	0.357248	0.215677	0	0	1
Mole flow	kmol/hr	283.133	283.133	353.132	353.132	353.132	353.132	276.97	276.97	0.661096
Mass flow	tons/year	125270	125270	125270	125270	125270	125270	121245	121245	266.933
Ethanol	tons/year	124643	124643	93482.5	93482.5	93482.5	93482.5	92792.3	92792.3	0.127731
Acetaldehyde	tons/year	12.4172	12.4172	29809.7	29809.7	29809.7	29809.7	27843.6	27843.6	266.019
Hydrogen	tons/year	0	0	1363.53	1363.53	1363.53	1363.53	0.712525	0.712525	0.687903
Water	tons/year	510.865	510.865	510.865	510.865	510.865	510.865	505.518	505.518	0.0986485
Ethylene Glycol	tons/year	103.065	103.065	103.065	103.065	103.065	103.065	103.065	103.065	1.20E-17

Table C.2 Stream results of NOX-25-200 with capacity of 30,000 tons/year (continued)

Stream no.	Unit	10	11	12	13	ACET	BFW-I	BFW-O	EG
Temperature	°C	38.9073	101.024	96.9762	205.642	30	111	111	226.916
Pressure	atm	2.0265	2.33048	2.0265	2.33048	2.0265	1.47995	1.47995	2.33048
Molar Vapor Fraction	-	0	0	0	0	0	0	0.999219	9.97E-08
Mole flow	kmol/hr	65.4485	210.86	209.477	50.152	65.4485	49.65	49.65	48.7689
Mass flow	tons/year	27843.6	93134.6	92734.3	29633.5	27843.6	8643.03	8643.03	29233.2
Ethanol	tons/year	259.503	92532.6	92270.7	261.992	259.503	0	0	0.0121416
Acetaldehyde	tons/year	27565.2	12.4171	12.4171	2.77E-05	27565.2	0	0	1.16E-09
Hydrogen	tons/year	0.0246225	5.10E-18	0	0	0.0246225	0	0	0
Water	tons/year	18.9088	486.511	348.19	145.004	18.9088	8643.03	8643.03	6.68323
Ethylene Glycol	tons/year	6.33E-12	103.065	103.065	29226.5	6.33E-12	0	0	29226.5

Table C.2 Stream results of NOX-25-200 with capacity of 30,000 tons/year (continued)

Stream no.	Unit	EG-M	EG-RE	ETOH-F	ETOH-RE	GAS	GLC-I	GLC-O	WATER
Temperature	^oC	227.243	226.909	30	96.9762	10	0	10	107.672
Pressure	atm	2.33048	2.33048	1.01325	1.01325	1.01325	1.01325	1.01325	2.0265
Molar Vapor Fraction	-	0	0	0	0	1	0	0	0
Mole flow	kmol/hr	1.0491	47.7195	73.6617	209.477	76.1627	4412.2	4412.2	2.43249
Mass flow	tons/year	629.207	28603.9	32537.8	92734.3	4024.47	975857	975857	1029.68
Ethanol	tons/year	0	0.012143	32375.1	92270.7	690.201	0	0	261.98
Acetaldehyde	tons/year	0	1.16E-09	0	12.4171	1966.11	0	0	2.77E-05
Hydrogen	tons/year	0	0	0	0	1362.82	0	0	0
Water	tons/year	0	6.68292	162.689	348.19	5.34732	683100	683100	138.321
Ethylene Glycol	tons/year	629.207	28597.2	0	103.065	0.000303244	292757	292757	629.382

Table 24 Stream results of NOX-25-200 with capacity of 60,000 tons/year

Stream no.	Unit	1	2	3	4	5	6	7	8	9
Temperature	°C	78.4712	200	200	121	45	10	10	10.0842	38.9166
Pressure	atm	1.01325	1.01325	1.01325	1.01325	1.01325	1.01325	1.01325	2.33048	2.0265
Molar Vapor Fraction	-	0.723088	1	1	1	0.358012	0.216378	0	0	1
Mole flow	kmol/hr	565.242	565.242	705.548	705.548	705.548	705.548	552.883	552.883	1.32414
Mass flow	tons/year	251089	251089	251089	251089	251089	251089	243012	243012	534.981
Ethanol	tons/year	249834	249834	187375	187375	187375	187375	185986	185986	0.267016
Acetaldehyde	tons/year	24.7299	24.7299	59750.1	59750.1	59750.1	59750.1	55799.1	55799.1	533.251
Hydrogen	tons/year	0	0	2733.04	2733.04	2733.04	2733.04	1.42451	1.42451	1.36936
Water	tons/year	467.808	467.808	467.808	467.808	467.808	467.808	462.853	462.853	0.0939134
Ethylene Glycol	tons/year	762.91	762.91	762.91	762.91	762.91	762.91	762.908	762.908	9.56E-17

Table C.3 Stream results of NOX-25-200 with capacity of 60,000 tons/year (continued)

Stream no.	Unit	10	11	12	13	ACET	BFW-I	BFW-O	EG
Temperature	°C	38.9166	101.108	97.0613	206.292	30	111	111	227.229
Pressure	atm	2.0265	2.33048	2.0265	2.33048	2.0265	1.47995	1.47995	2.33048
Molar Vapor Fraction	-	0	0	0	0	0	0	0.999048	1.93E-10
Mole flow	kmol/hr	131.09	420.469	416.634	163.411	131.09	99.5	99.5	159.576
Mass flow	tons/year	55799.1	186678	185445	96937.3	55799.1	17320.9	17320.9	95704.8
Ethanol	tons/year	540.07	185445	184518	927.227	540.07	0	0	0.00226168
Acetaldehyde	tons/year	55241.1	24.7398	24.7307	0.00903341	55241.1	0	0	2.07E-08
Hydrogen	tons/year	0.0551439	1.09E-17	0	0	0.0551439	0	0	0
Water	tons/year	17.8656	444.893	140.093	305.744	17.8656	17320.9	17320.9	0.943562
Ethylene Glycol	tons/year	5.01E-11	762.908	762.404	95704.3	5.01E-11	0	0	95703.8

Table C.3 Stream results of NOX-25-200 with capacity of 60,000 tons/year (continued)

Stream no.	Unit	EG-M	EG-RE	ETOH-F	ETOH-RE	GAS	GLC-I	GLC-O	WATER
Temperature	°C	227.243	227.228	30	97.0613	10	0	10	106.706
Pressure	atm	2.33048	2.33048	1.01325	1.01325	1.01325	1.01325	1.01325	2.0265
Molar Vapor Fraction	-	0	0	0	0	1	0	0	0
Mole flow	kmol/hr	3.382	156.199	148.607	416.634	152.665	8826.45	8826.45	7.212
Mass flow	tons/year	2028.38	93679.2	65642.5	185445	8077.22	1.95E+06	1.95E+06	3258.1
Ethanol	tons/year	0	0.00226142	65314.3	184518	1389.58	0	0	927.225
Acetaldehyde	tons/year	0	2.07E-08	0	24.7307	3951.06	0	0	0.00903339
Hydrogen	tons/year	0	0	0	0	2731.62	0	0	0
Water	tons/year	0	0.943542	328.212	140.093	4.9545	1.37E+06	1.37E+06	304.801
Ethylene Glycol	tons/year	2028.38	93678.2	0	762.404	0.00227229	585650	585650	2026.07

Table 25 Stream results of NOX-25-200 with capacity of 90,000 tons/year

Stream no.	Unit	1	2	3	4	5	6	7	8	9
Temperature	°C	78.4714	200	200	121	45	10	10	10.0778	38.9166
Pressure	atm	1.01325	1.01325	1.01325	1.01325	1.01325	1.01325	1.01325	2.33048	2.0265
Molar Vapor Fraction	-	0.723101	1	1	1	0.358013	0.216378	0	0	1
Mole flow	kmol/hr	847.887	847.887	1058.35	1058.35	1058.35	1058.35	829.349	829.349	1.98628
Mass flow	tons/year	376647	376647	376647	376647	376647	376647	364530	364530	802.499
Ethanol	tons/year	374763	374763	281073	281073	281073	281073	278988	278988	0.400555
Acetaldehyde	tons/year	37.0975	37.0975	89628.2	89628.2	89628.2	89628.2	83701.4	83701.4	799.904
Hydrogen	tons/year	0	0	4099.71	4099.71	4099.71	4099.71	2.13683	2.13683	2.0541
Water	tons/year	700.875	700.875	700.875	700.875	700.875	700.875	693.452	693.452	0.140709
Ethylene Glycol	tons/year	1145.26	1145.26	1145.26	1145.26	1145.26	1145.26	1145.25	1145.25	1.44E-16

Table C.4 Stream results of NOX-25-200 with capacity of 90,000 tons/year (continued)

Stream no.	Unit	10	11	12	13	ACET	BFW-I	BFW-O	EG
Temperature	°C	38.9166	101.108	97.0614	206.339	30	111	111	227.229
Pressure	atm	2.0265	2.33048	2.0265	2.33048	2.0265	1.47995	1.47995	2.33048
Molar Vapor Fraction	-	0	0	0	0	0	0	0.999416	1.83E-10
Mole flow	kmol/hr	196.642	630.721	624.968	245.757	196.642	149.2	149.2	240.004
Mass flow	tons/year	83701.4	280026	278178	145790	83701.4	25972.6	25972.6	143941
Ethanol	tons/year	810.164	278178	276787	1390.89	810.164	0	0	0.00343897
Acetaldehyde	tons/year	82864.4	37.1106	37.097	0.013649	82864.4	0	0	3.18E-08
Hydrogen	tons/year	0.0827284	1.63E-17	0	0	0.0827284	0	0	0
Water	tons/year	26.7675	666.543	209.187	458.791	26.7675	25972.6	25972.6	1.43405
Ethylene Glycol	tons/year	7.52E-11	1145.25	1144.6	143940	7.52E-11	0	0	143940

Table C.4 Stream results of NOX-25-200 with capacity of 90,000 tons/year (continued)

Stream no.	Unit	EG-M	EG-RE	ETOH-F	ETOH-RE	GAS	GLC-I	GLC-O	WATER
Temperature	°C	227.243	227.228	30	97.0614	10	0	10	106.704
Pressure	atm	2.33048	2.33048	1.01325	1.01325	1.01325	1.01325	1.01325	2.0265
Molar Vapor Fraction	-	0	0	0	0	1	0	0	0
Mole flow	kmol/hr	5.065	234.939	222.909	624.968	229.005	13240.1	13240.1	10.818
Mass flow	tons/year	3037.78	140903	98463.2	278178	12116.3	2.93E+06	2.93E+06	4886.76
Ethanol	tons/year	0	0.00343889	97970.9	276787	2084.45	0	0	1390.88
Acetaldehyde	tons/year	0	3.18E-08	0	37.097	5926.81	0	0	0.0136489
Hydrogen	tons/year	0	0	0	0	4097.57	0	0	0
Water	tons/year	0	1.43396	492.316	209.187	7.42298	2.05E+06	2.05E+06	457.357
Ethylene Glycol	tons/year	3037.78	140902	0	1144.6	0.00341114	878503	878503	3038.5

Table 26 Stream results of NOX-80-400 with capacity of 12,000 tons/year

Stream no.	**Unit**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Temperature	°C	78.2432	400	400	90	238.719	124	45	10
Pressure	atm	1	1	1	1	5	5	5	5
Molar Vapor Fraction	-	0.0507641	1	1	1	1	1	0.5576	0.461395
Mole flow	kmol/hr	74.7559	74.7559	132.991	132.991	132.991	132.991	132.991	132.991
Mass flow	tons/year	33034.4	33034.4	33034.4	33034.4	33034.4	33034.4	33034.4	33034.4
Ethanol	tons/year	32869.2	32869.2	6573.84	6573.84	6573.84	6573.84	6573.84	6573.84
Acetaldehyde	tons/year	7.51688	7.51688	11992.1	11992.1	11992.1	11992.1	11992.1	11992.1
Ethylene	tons/year	6.82E-10	6.82E-10	8154.4	8154.4	8154.4	8154.4	8154.4	8154.4
Diethyl Ether	tons/year	0.00149711	0.00149711	298.801	298.801	298.801	298.801	298.801	298.801
Hydrogen	tons/year	0	0	548.417	548.417	548.417	548.417	548.417	548.417
Water	tons/year	156.57	156.57	5465.7	5465.7	5465.7	5465.7	5465.7	5465.7
Ethylene Glycol	tons/year	1.08376	1.08376	1.08376	1.08376	1.08376	1.08376	1.08376	1.08376

Table C.5 Stream results of NOX-80-400 with capacity of 12,000 tons/year (continued)

Stream no.	**Unit**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
Temperature	°C	10	9.96968	38.0653	38.0653	103.837	34.4043	40.4448	96.6347
Pressure	atm	5	2.3	2	2	2.3	1.7	2	2
Molar Vapor Fraction	-	0	0.000977578	1	0	0	1	0	1
Mole flow	kmol/hr	71.6296	71.6296	2.594	23.346	45.6896	0.125015	20.8457	1.48784
Mass flow	tons/year	22958.4	22958.4	1080.41	9928.31	11949.6	57.0444	8800.77	657.884
Ethanol	tons/year	6551.61	6551.61	0.0316821	6.55161	6545.03	4.18E-17	6.55161	646.451
Acetaldehyde	tons/year	10700.7	10700.7	1000.22	9684.17	16.3515	47.3431	8712.76	8.82513
Ethylene	tons/year	47.729	47.729	47.6371	0.0918599	7.10E-09	0.0916218	2.59E-35	6.42E-09
Diethyl Ether	tons/year	209.623	209.623	29.4808	180.14	0.00247176	9.60873	24.1046	0.000968468
Hydrogen	tons/year	0.216757	0.216757	0.215908	0.000849364	6.44E-16	0.000829584	1.79E-35	0
Water	tons/year	5447.36	5447.36	2.82949	57.3561	5387.18	0.000106131	57.3515	2.59525
Ethylene Glycol	tons/year	1.08376	1.08376	2.39E-18	1.34E-13	1.08376	0	0	0.0118158

Table C.5 Stream results of NOX-80-400 with capacity of 12,000 tons/year (continued)

Stream no.	Unit	17	18	ACET	BFW-I	BFW-O	DEE	EG	EG-M
Temperature	°C	96.6347	159.093	30	114	114	34.4043	227.241	227.243
Pressure	atm	2	2.3	2	1.61297	1.61297	1.7	2.3	2.3
Molar Vapor Fraction	-	0	0	0	0	0.999553	0	0	0
Mole flow	kmol/hr	13.3906	85.8002	20.8457	20.3	20.3	2.37528	54.989	0.136
Mass flow	tons/year	5928.12	38343.7	8800.77	3533.81	3533.81	1070.5	32980	81.5672
Ethanol	tons/year	5898.48	0.0966229	6.55161	0	0	1.91E-14	6.48E-11	0
Acetaldehyde	tons/year	7.5264	6.21E-07	8712.76	0	0	924.069	2.68E-16	0
Ethylene	tons/year	6.86E-10	1.04E-21	2.59E-35	0	0	0.000238144	0	0
Diethyl Ether	tons/year	0.00150329	6.63E-12	24.1046	0	0	146.427	0	0
Hydrogen	tons/year	0	0	1.79E-35	0	0	1.98E-05	0	0
Water	tons/year	21.0291	5363.59	57.3515	3533.81	3533.81	0.00454922	0.0371353	0
Ethylene Glycol	tons/year	1.08362	32980	0	0	0	0	32980	81.5672

Table C.5 Stream results of NOX-80-400 with capacity of 12,000 tons/year (continued)

Stream no.	Unit	EG-RE	ETOH-F	ETOH-RE	GAS	GLC-I	GLC-O	WATER
Temperature	°C	227.241	30	96.6347	10	0	10	120.823
Pressure	atm	2.3	1	1	5	1	1	2
Molar Vapor Fraction	-	0	0	0	1	0	0	0
Mole flow	kmol/hr	54.8522	61.3653	13.3906	61.3615	1121.31	1121.31	30.948
Mass flow	tons/year	32898	27106.2	5928.12	10076	248003	248003	5445.69
Ethanol	tons/year	6.48E-11	26970.7	5898.48	22.2245	0	0	0.0966229
Acetaldehyde	tons/year	2.68E-16	0	7.5264	1291.38	0	0	6.21E-07
Ethylene	tons/year	0	0	6.86E-10	8106.67	0	0	0
Diethyl Ether	tons/year	0	0	0.00150329	89.1777	0	0	0
Hydrogen	tons/year	0	0	0	548.201	0	0	0
Water	tons/year	0.0371328	135.531	21.0291	18.3373	173602	173602	5363.55
Ethylene Glycol	tons/year	32897.9	0	1.08362	1.98E-06	74400.8	74400.8	82.0371

Table 27 Stream results of NOX-80-400 with capacity of 30,000 tons/year

Stream no.	**Unit**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Temperature	°C	78.2432	400	400	90	238.719	124	45	10
Pressure	atm	1	1	1	1	5	5	5	5
Molar Vapor Fraction	-	0.0507631	1	1	1	1	1	0.557601	0.461396
Mole flow	kmol/hr	186.893	186.893	332.484	332.484	332.484	332.484	332.484	332.484
Mass flow	tons/year	82587.5	82587.5	82587.5	82587.5	82587.5	82587.5	82587.5	82587.5
Ethanol	tons/year	82174.6	82174.6	16434.9	16434.9	16434.9	16434.9	16434.9	16434.9
Acetaldehyde	tons/year	18.8154	18.8154	29980.9	29980.9	29980.9	29980.9	29980.9	29980.9
Ethylene	tons/year	1.71E-09	1.71E-09	20386.4	20386.4	20386.4	20386.4	20386.4	20386.4
Diethyl Ether	tons/year	0.0037583	0.0037583	747.018	747.018	747.018	747.018	747.018	747.018
Hydrogen	tons/year	0	0	1371.07	1371.07	1371.07	1371.07	1371.07	1371.07
Water	tons/year	391.324	391.324	13664.4	13664.4	13664.4	13664.4	13664.4	13664.4
Ethylene Glycol	tons/year	2.7945	2.7945	2.7945	2.7945	2.7945	2.7945	2.7945	2.7945

Table C.6 Stream results of NOX-80-400 with capacity of 30,000 tons/year (continued)

Stream no.	**Unit**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
Temperature	°C	10	9.96968	38.0645	38.0645	103.837	34.4053	40.4442	96.6344
Pressure	atm	5	2.3	2	2	2.3	1.7	2	2
Molar Vapor Fraction	-	0	0.000977582	1	0	0	1	0	1
Mole flow	kmol/hr	179.077	179.077	6.4849	58.3641	114.228	0.312717	52.1097	3.71963
Mass flow	tons/year	57397.1	57397.1	2701.02	24820.9	29875.1	142.682	22000.7	1644.74
Ethanol	tons/year	16379.4	16379.4	0.0791886	16.3793	16362.9	1.05E-16	16.3793	1616.14
Acetaldehyde	tons/year	26752.4	26752.4	2500.55	24210.9	40.927	118.444	21780.6	22.0885
Ethylene	tons/year	119.325	119.325	119.096	0.229461	1.78E-08	0.228866	6.59E-35	1.61E-08
Diethyl Ether	tons/year	524.07	524.07	73.703	450.36	0.00618875	24.0066	60.6167	0.00242471
Hydrogen	tons/year	0.541903	0.541903	0.539787	0.00211601	1.61E-15	0.00206674	4.65E-35	0
Water	tons/year	13618.6	13618.6	7.05167	143.022	13468.5	0.000265858	143.011	6.47483
Ethylene Glycol	tons/year	2.79449	2.79449	6.17E-18	3.47E-13	2.79449	0	0	0.0304734

Table C.6 Stream results of NOX-80-400 with capacity of 30,000 tons/year (continued)

Stream no.	Unit	17	18	ACET	BFW-I	BFW-O	DEE	EG	EG-M
Temperature	°C	96.6344	160.23	30	114	114	34.4053	227.239	227.243
Pressure	atm	2	2.3	2	1.61297	1.61297	1.7	2.3	2.3
Molar Vapor Fraction	-	0	0	0	0	0.999571	0	1.19E-10	0
Mole flow	kmol/hr	33.4767	222.017	52.1097	50.75	50.75	5.94162	144.985	0.085
Mass flow	tons/year	14820.6	100366	22000.7	8834.52	8834.52	2677.58	86955.7	50.9795
Ethanol	tons/year	14746.5	0.263253	16.3793	0	0	4.79E-14	3.04E-10	0
Acetaldehyde	tons/year	18.8385	1.94E-06	21780.6	0	0	2311.83	1.20E-15	0
Ethylene	tons/year	1.72E-09	4.89E-21	6.59E-35	0	0	0.000594795	0	0
Diethyl Ether	tons/year	0.00376404	2.53E-11	60.6167	0	0	365.737	0	0
Hydrogen	tons/year	0	0	4.65E-35	0	0	4.93E-05	0	0
Water	tons/year	52.466	13409.8	143.011	8834.52	8834.52	0.0113955	0.231046	0
Ethylene Glycol	tons/year	2.79468	86955.5	0	0	0	0	86955.5	50.9795

Table C.6 Stream results of NOX-80-400 with capacity of 30,000 tons/year (continued)

Stream no.	Unit	EG-RE	ETOH-F	ETOH-RE	GAS	GLC-I	GLC-O	WATER
Temperature	^{o}C	227.239	30	96.6344	10	0	10	120.72
Pressure	atm	2.3	1	1	5	1	1	2
Molar Vapor Fraction	-	0	0	0	1	0	0	0
Mole flow	kmol/hr	144.9	153.416	33.4767	153.407	2803.32	2803.32	77.117
Mass flow	tons/year	86904.7	67767	14820.6	25190.5	620017	620017	13460.8
Ethanol	tons/year	3.04E-10	67428.1	14746.5	55.5622	0	0	0.263253
Acetaldehyde	tons/year	1.20E-15	0	18.8385	3228.51	0	0	1.94E-06
Ethylene	tons/year	0	0	1.72E-09	20267.1	0	0	0
Diethyl Ether	tons/year	0	0	0.00376404	222.948	0	0	0
Hydrogen	tons/year	0	0	0	1370.53	0	0	0
Water	tons/year	0.231037	338.835	52.466	45.844	434012	434012	13409.6
Ethylene Glycol	tons/year	86904.5	0	2.79468	5.10E-06	186005	186005	51.0046

Table 28 Stream results of NOX-80-400 with capacity of 60,000 tons/year

Stream no.	**Unit**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Temperature	°C	78.2432	400	400	90	238.719	124	45	10
Pressure	atm	1	1	1	1	5	5	5	5
Molar Vapor Fraction	-	0.0507625	1	1	1	1	1	0.557601	0.461397
Mole flow	kmol/hr	373.783	373.783	664.963	664.963	664.963	664.963	664.963	664.963
Mass flow	tons/year	165174	165174	165174	165174	165174	165174	165174	165174
Ethanol	tons/year	164348	164348	32869.6	32869.6	32869.6	32869.6	32869.6	32869.6
Acetaldehyde	tons/year	37.676	37.676	59961.5	59961.5	59961.5	59961.5	59961.5	59961.5
Ethylene	tons/year	3.44E-09	3.44E-09	40772.6	40772.6	40772.6	40772.6	40772.6	40772.6
Diethyl Ether	tons/year	0.00752803	0.00752803	1494.03	1494.03	1494.03	1494.03	1494.03	1494.03
Hydrogen	tons/year	0	0	2742.13	2742.13	2742.13	2742.13	2742.13	2742.13
Water	tons/year	782.482	782.482	27328.5	27328.5	27328.5	27328.5	27328.5	27328.5
Ethylene Glycol	tons/year	5.70453	5.70453	5.70453	5.70453	5.70453	5.70453	5.70453	5.70453

Table C.7 Stream results of NOX-80-400 with capacity of 60,000 tons/year (continued)

Stream no.	**Unit**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
Temperature	°C	10	9.96968	38.0643	38.0643	103.837	34.4053	40.4438	96.6343
Pressure	atm	5	2.3	2	2	2.3	1.7	2	2
Molar Vapor Fraction	-	0	0.000977586	1	0	0	1	0	1
Mole flow	kmol/hr	358.152	358.152	12.9695	116.726	228.456	0.62508	104.224	7.43915
Mass flow	tons/year	114793	114793	5401.94	49641.3	59750.2	285.196	44003.9	3289.46
Ethanol	tons/year	32758.5	32758.5	0.158393	32.7585	32725.6	2.10E-16	32.7585	3232.25
Acetaldehyde	tons/year	53504.5	53504.5	5001.02	48421.6	81.9086	236.762	43563.9	44.2061
Ethylene	tons/year	238.649	238.649	238.19	0.459584	3.56E-08	0.458393	1.33E-34	3.22E-08
Diethyl Ether	tons/year	1048.13	1048.13	147.403	900.719	0.0123834	47.9711	121.59	0.00485155
Hydrogen	tons/year	1.0838	1.0838	1.07956	0.00423985	3.23E-15	0.00414111	9.13E-35	0
Water	tons/year	27236.8	27236.8	14.0908	285.714	26937	0.000531945	285.691	12.9321
Ethylene Glycol	tons/year	5.70452	5.70452	1.26E-17	7.09E-13	5.70452	0	0	0.0621963

Table C.7 Stream results of NOX-80-400 with capacity of 60,000 tons/year (continued)

Stream no.	**Unit**	**17**	**18**	**ACET**	**BFW-I**	**BFW-O**	**DEE**	**EG**	**EG-M**
Temperature	°C	96.6343	160.964	30	114	114	34.4053	227.241	227.243
Pressure	atm	2	2.3	2	1.61297	1.61297	1.7	2.3	2.3
Molar Vapor Fraction	-	0	0	0	0	0.999564	0	2.82E-10	0
Mole flow	kmol/hr	66.9524	454.019	104.224	101.5	101.5	11.8765	299.954	0.544
Mass flow	tons/year	29641	206719	44003.9	17669	17669	5352.17	179899	326.269
Ethanol	tons/year	29492.8	0.557095	32.7585	0	0	9.59E-14	5.43E-10	0
Acetaldehyde	tons/year	37.7025	4.50E-06	43563.9	0	0	4620.99	2.77E-15	0
Ethylene	tons/year	3.44E-09	1.47E-20	1.33E-34	0	0	0.00119151	0	0
Diethyl Ether	tons/year	0.00753183	6.64E-11	121.59	0	0	731.158	0	0
Hydrogen	tons/year	0	0	9.13E-35	0	0	9.87E-05	0	0
Water	tons/year	104.791	26819.6	285.691	17669	17669	0.0228005	0.283957	0
Ethylene Glycol	tons/year	5.70388	179899	0	0	0	0	179899	326.269

Table C.7 Stream results of NOX-80-400 with capacity of 60,000 tons/year (continued)

Stream no.	Unit	EG-RE	ETOH-F	ETOH-RE	GAS	GLC-I	GLC-O	WATER
Temperature	°C	227.241	30	96.6343	10	0	10.0001	120.795
Pressure	atm	2.3	1	1	5	1	1	2
Molar Vapor Fraction	-	0	0	0	1	0	0	0
Mole flow	kmol/hr	299.412	306.831	66.9524	306.812	5606.6	5606.6	154.607
Mass flow	tons/year	179574	135533	29641	50380.6	1.24E+06	1.24E+06	27144.9
Ethanol	tons/year	5.42E-10	134855	29492.8	111.124	0	0	0.557095
Acetaldehyde	tons/year	2.77E-15	0	37.7025	6457	0	0	4.50E-06
Ethylene	tons/year	0	0	3.44E-09	40533.9	0	0	0
Diethyl Ether	tons/year	0	0	0.00753183	445.892	0	0	0
Hydrogen	tons/year	0	0	0	2741.04	0	0	0
Water	tons/year	0.283942	677.666	104.791	91.6873	868017	868017	26819.3
Ethylene Glycol	tons/year	179574	0	5.70388	1.04E-05	372007	372007	325.054

Table 29 Stream results of NOX-80-400 with capacity of 90,000 tons/year

Stream no.	**Unit**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Temperature	°C	78.2432	400	400	90	238.719	124	45	10
Pressure	atm	1	1	1	1	5	5	5	5
Molar Vapor Fraction	-	0.0507651	1	1	1	1	1	0.5576	0.461395
Mole flow	kmol/hr	560.677	560.677	997.447	997.447	997.447	997.447	997.447	997.447
Mass flow	tons/year	247761	247761	247761	247761	247761	247761	247761	247761
Ethanol	tons/year	246522	246522	49304.4	49304.4	49304.4	49304.4	49304.4	49304.4
Acetaldehyde	tons/year	56.4483	56.4483	89942.2	89942.2	89942.2	89942.2	89942.2	89942.2
Ethylene	tons/year	5.14E-09	5.14E-09	61158.8	61158.8	61158.8	61158.8	61158.8	61158.8
Diethyl Ether	tons/year	0.0112744	0.0112744	2241.04	2241.04	2241.04	2241.04	2241.04	2241.04
Hydrogen	tons/year	0	0	4113.19	4113.19	4113.19	4113.19	4113.19	4113.19
Water	tons/year	1174.36	1174.36	40993.4	40993.4	40993.4	40993.4	40993.4	40993.4
Ethylene Glycol	tons/year	7.98548	7.98548	7.98548	7.98548	7.98548	7.98548	7.98548	7.98548

Table C.8 Stream results of NOX-80-400 with capacity of 90,000 tons/year (continued)

Stream no.	**Unit**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
Temperature	°C	10	9.96968	38.0653	38.0653	103.837	34.4043	40.4447	96.6345
Pressure	atm	5	2.3	2	2	2.3	1.7	2	2
Molar Vapor Fraction	-	0	0.000977578	1	0	0	1	0	1
Mole flow	kmol/hr	537.23	537.23	19.4552	175.097	342.677	0.93762	156.345	11.159
Mass flow	tons/year	172190	172190	8103.2	74463.3	89623.5	427.836	66006.6	4934.2
Ethanol	tons/year	49137.7	49137.7	0.237618	49.1378	49088.4	3.14E-16	49.1378	4848.43
Acetaldehyde	tons/year	80256.7	80256.7	7501.74	72632.3	122.649	355.081	65346.6	66.1953
Ethylene	tons/year	357.972	357.972	357.283	0.688975	5.33E-08	0.687189	1.94E-34	4.81E-08
Diethyl Ether	tons/year	1572.2	1572.2	221.108	1351.07	0.0185399	72.0609	180.866	0.00726434
Hydrogen	tons/year	1.6257	1.6257	1.61933	0.00636971	4.83E-15	0.00622137	1.34E-34	0
Water	tons/year	40855.8	40855.8	21.2172	430.098	40404.5	0.000796083	430.063	19.4816
Ethylene Glycol	tons/year	7.98546	7.98546	1.76E-17	9.91E-13	7.98546	0	0	0.0870744

Table C.8 Stream results of NOX-80-400 with capacity of 90,000 tons/year (continued)

Stream no.	**Unit**	**17**	**18**	**ACET**	**BFW-I**	**BFW-O**	**DEE**	**EG**	**EG-M**
Temperature	°C	96.6345	158.445	30	114	114	34.4043	227.241	227.243
Pressure	atm	2	2.3	2	1.61297	1.61297	1.7	2.3	2.3
Molar Vapor Fraction	-	0	0	0	0	0.999239	0	0	0
Mole flow	kmol/hr	100.431	631.062	156.345	152.3	152.3	17.8148	399.975	0.764
Mass flow	tons/year	44461.6	280115	66006.6	26512.3	26512.3	8028.82	239888	458.216
Ethanol	tons/year	44239.2	0.69076	49.1378	0	0	1.43E-13	4.38E-10	0
Acetaldehyde	tons/year	56.4536	4.11E-06	65346.6	0	0	6930.64	1.63E-15	0
Ethylene	tons/year	5.14E-09	5.43E-21	1.94E-34	0	0	0.00178615	0	0
Diethyl Ether	tons/year	0.0112755	3.91E-11	180.866	0	0	1098.14	0	0
Hydrogen	tons/year	0	0	1.34E-34	0	0	0.000148341	0	0
Water	tons/year	157.857	40227.5	430.063	26512.3	26512.3	0.0341235	0.278798	0
Ethylene Glycol	tons/year	7.98577	239887	0	0	0	0	239887	458.216

Table C.8 Stream results of NOX-80-400 with capacity of 90,000 tons/year (continued)

Stream no.	Unit	EG-RE	ETOH-F	ETOH-RE	GAS	GLC-I	GLC-O	WATER
Temperature	°C	227.241	30	96.6345	10	0	10	120.789
Pressure	atm	2.3	1	1	5	1	1	2
Molar Vapor Fraction	-	0	0	0	1	0	0	0
Mole flow	kmol/hr	399.206	460.246	100.431	460.217	8409.95	8409.95	231.856
Mass flow	tons/year	239426	203299	44461.6	75570.9	1.86E+06	1.86E+06	40689
Ethanol	tons/year	4.38E-10	202283	44239.2	166.686	0	0	0.69076
Acetaldehyde	tons/year	1.63E-15	0	56.4536	9685.46	0	0	4.11E-06
Ethylene	tons/year	0	0	5.14E-09	60800.8	0	0	0
Diethyl Ether	tons/year	0	0	0.0112755	668.843	0	0	0
Hydrogen	tons/year	0	0	0	4111.56	0	0	0
Water	tons/year	0.278785	1016.5	157.857	137.531	1.30E+06	1.30E+06	40227.2
Ethylene Glycol	tons/year	239426	0	7.98577	1.46E-05	558015	558015	461.134

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