

Comparison of techno-economic analysis of 1,3-propanediol  
production from crude glycerol via chemical and biological  
methods



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การเปรียบเทียบเชิงเทคนิคและเศรษฐศาสตร์วิเคราะห์ของกระบวนการผลิต  
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chemical and biological methods  
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ศัวัญญา บริบูรณ์ : การเปรียบเทียบเชิงเทคนิคและเศรษฐศาสตร์วิเคราะห์ของกระบวนการผลิต 1,3 โพรเพนไดออลจากกลีเซอรอลดิบด้วยวิธีทางเคมีและชีวภาพ. ( Comparison of techno-economic analysis of 1,3-propanediol production from crude glycerol via chemical and biological methods) อ.ที่ปรึกษาหลัก : ศศ. ดร.พงค์ธร เจริญศุภนิมิตร

ปัจจุบันอุตสาหกรรมไบโอดีเซลกำลังขยายตัวอย่างรวดเร็วเป็นผลทำให้เกิดอุปทานส่วนเกินของผลิตภัณฑ์พลอยได้กลีเซอรอลดิบ ซึ่งหนึ่งในวิธีจัดการกลีเซอรอลดิบคือการเปลี่ยนเป็นสารเคมีที่มีมูลค่าเพิ่ม เช่น 1,3-โพรเพนไดออล (1,3-PDO) ในงานวิจัยนี้จึงได้ศึกษาการผลิต 1,3-PDO ผ่านตัวเร่งปฏิกิริยา โดยใช้ตัวจำลองกระบวนการเพื่อประเมินประสิทธิภาพด้านเทคโนโลยีและเศรษฐกิจตลอดจนผลกระทบต่อสิ่งแวดล้อม ผลลัพธ์ที่ได้จะถูกนำไปเปรียบเทียบกับการผลิต 1,3-PDO แบบเดิมเพื่อให้เห็นถึงข้อดีของการผลิตผ่านตัวเร่งปฏิกิริยาทั้งในแง่ของเศรษฐกิจ การใช้พลังงาน การใช้วัตถุดิบ และผลกระทบต่อสิ่งแวดล้อม



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At present, the biodiesel industry is expanding rapidly which could lead to an oversupply of the by-product, crude glycerol. To manage this, crude glycerol should be converted into value-added chemicals such as 1,3-propanediol (1,3-PDO). In this study, the production of 1,3-PDO via catalytic reaction is simulated using a process simulator to evaluate its techno-economic performance as well as its environmental impact. The obtained results will be compared with the conventional production of 1,3-PDO to point out the advantages that the catalytic reaction can offer in terms of economic, energy utilization, raw material utilization, and environmental impacts.



Field of Study: Chemical Engineering

Student's Signature

Academic Year: 2022

Advisor's Signature

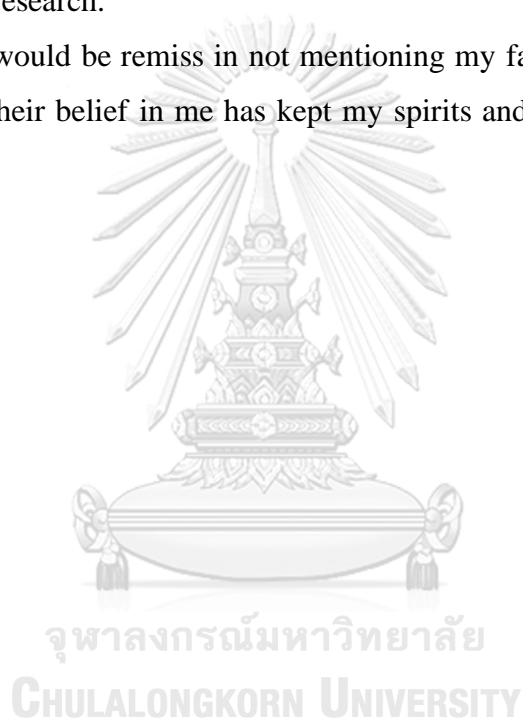
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## Chapter 1

### Introduction

#### 1.1 Background

Crude glycerol (CG) is the main byproduct of biodiesel production – about 1 kg of crude glycerol is produced in 10 kg of biodiesel production [1]. At present, the biodiesel industry expands rapidly which could lead to an oversupply of crude glycerol. Most crude glycerol generally constitutes 65-85%(w/w) of glycerin [2]. Since crude glycerol does not have a high value, it should be refined to obtain high-quality glycerin that can be utilized in the food, pharmaceutical, or cosmetic industries. Therefore, biodiesel producers need to find ways to exploit crude glycerol.

Crude glycerol can be used as feedstocks for various value-added industrial products, such as biopolymers, polyunsaturated fatty acids, ethanol, hydrogen, and n-butanol production [1]. Another option that holds great promise is to produce propanediol in particular, 1,3-propanediol (1,3-PDO) from crude glycerol. 1,3-PDO is used extensively in polyesters, glues, coatings, laminates, medicinal products, etc. [1], [3].

Typically, 1,3-PDO can be produced by three principal routes, petrochemical, biological, and heterogeneous catalysis routes. Each route has its advantages and disadvantages. The petrochemical route has been replaced gradually by the biological route to improve process sustainability. However, the major disadvantages of the biological method are that 1) the effluent is rich with a by-product that reduces the yield of 1,3-PDO, 2) the bacteria have less efficacy in high glycerol concentration, and 3) biocatalysts are relatively costly.

Therefore, the alternative reaction route using heterogeneous catalysis has been studied to overcome these drawbacks [4]. According to this work, the catalyst was employed using water as a solvent. The high selectivity of 1,3-PDO at 72 % was obtained at a relatively low operating temperature. In addition, it did not produce toxic by-products or corrosion problems that could harm the environment. Furthermore, according to the literature, a comparative study that dedicates to the 1,3-PDO production via biological and heterogenous catalysis routes has not been undertaken. Thus, in this study, 1,3-PDO production processes from crude glycerol will be simulated by the biological and chemical routes. Then, the obtained results will be compared in terms of economic, energy utilization, and environmental impacts.

## **1.2 Objectives of this research**

- 1.2.1 To establish a process design for 1,3-propanediol via heterogeneous catalysis.
- 1.2.2 To provide a comparative study of 1,3-PDO production via biological and heterogeneous catalysis.

## **1.3 Scopes of this research**

- 1.3.1 The process will produce 99.5 wt% of 1,3-PDO at 12,000 tonnes/yr.
- 1.3.2 The crude glycerol will be converted into 1,3-PDO via the biological and the heterogenous catalysis routes with the same production capacity.
- 1.3.3 The reaction takes place at 80 bar, 119.85°C, and uses Ir-ReO<sub>x</sub>/TiO<sub>2</sub> for the heterogeneous catalysis.

1.3.4 The reaction takes place at 1 bar, 33°C, and uses *Clostridium diolis* DSM 15410 for the biological catalysis.

1.3.5 The process performances will be evaluated in terms of economic, energy utilization, and environmental impact with the assumed 20-year plant life

#### 1.4 Schedule plans

No.	Activity	Plan																			
		2021										2022									
		6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10			
1	Find an appropriate research topic.	■																			
2	Literature research and identification of theories to be investigated in the project		■							■	■	■									
3	Calculation over mass balance			■	■						■	■									
4	Establish a process design			■	■						■	■									
5	Simulate a process design in Aspen plus simulation program					■	■	■	■				■	■	■	■	■	■	■	■	
6	Enhance the system for maximum efficiency.									■	■	■									
7	Analyze and verify the result of the process design										■	■									
8	Economic analysis													■	■	■	■	■	■	■	
9	Compare and Conclusion the economic result														■	■	■	■	■	■	

## Chapter 2

### Theory and literature reviews

#### 2.1 Crude glycerol information

Crude glycerol has the following main components, 38 % to 96 % of glycerol, 0 % to 16 % of moisture, 0 % to 29 % of ash, 0.01 % to 13 % of methanol, and 1% to 57 % of other organic matter. The compositions are different depending on the raw material and process used to produce biodiesel [5].

##### 2.1.1 Crude glycerol pretreatment

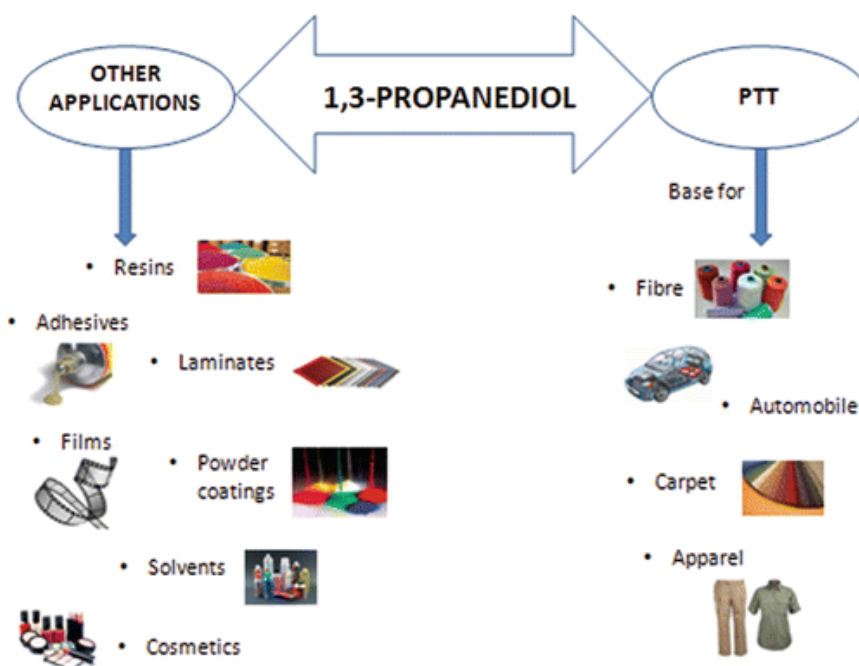
Pretreatment is a necessary process for eliminating the undesired material from crude glycerol before the fermentation process that produces 1,3-PDO.

In previous work [5], Five grades of crude glycerol (obtained from biodiesel preparation using jatropha, soybean, sunflower, rice bran, and linseed oils) were pre-treated by 4 different non-polar solvents, including hexane, heptane, octane, and petroleum ether. Then, the production yield of 1,3-PDO was compared with the 1,3-PDO production using pure glycerol. According to this work, it was concluded that, if the solvent was appropriately selected, using the pre-treated crude glycerol would be as effective as pure glycerol with petroleum ether showing the highest effectiveness

#### 2.2 1,3-PDO

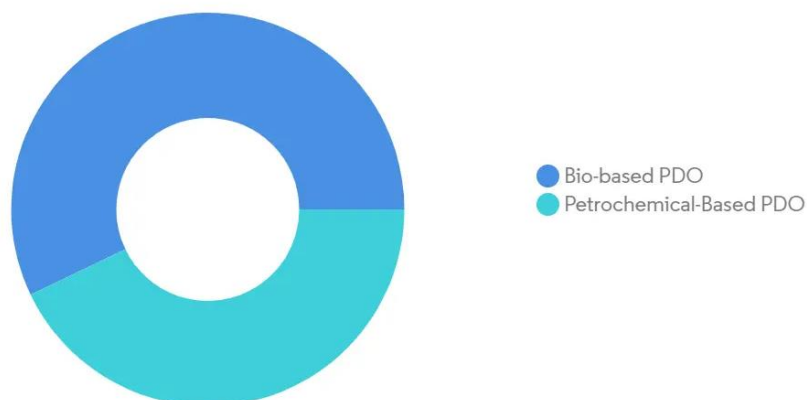
The Global Market of 1,3-PDO is expected to expand from 401.7 million USD in 2020 to 690.6 million USD by 2025 with the CAGR growing at 11.4 % [6]. The main products expected to be key drivers for an increased production capacity of 1,3-PDO are Polyurethane (PU), cosmetics, polytrimethylene terephthalate (PTT), self-care, and cleaning agents [6-8]





**Figure 1.** The 1,3-propanediol (1,3-PDO) applications [8]

1,3-PDO can be produced from two major sources, petrochemical-based and bio-based as depicted in **Figure 1**. Due to environmental and instability concerns, 1,3-PDO production via the bio-based route has a higher contribution than the petrochemical route according to **Figure 2**. Typically, the bio-based route uses sugar and glycerol as major feedstocks for the production of 1,3-PDO [9]. Since this work will provide insight to biodiesel producers to handle the surplus of crude glycerol, the production of 1,3-PDO will be focusing on using crude glycerol as its raw material.



**Figure 2.** The global revenue of 1,3-propanediol (PDO) by source [8, 10]

## 2.3 Literature reviews

In this section, both biological and heterogenous catalysis routes will be discussed starting from the biological route to the heterogenous catalysis route.

### 2.3.1 Biological route

Zhang et al. [11] compared *Klebsiella pneumoniae* DA-1HB (normal bacteria) with *Klebsiella pneumoniae* YMU2 (modified bacteria). The modified bacteria inhibited the genes *aldA* encoded aldehyde dehydrogenase (ALDH) that hindered the production of ethanol (by-products) and resulted in an increase of 1,3-PDO production. The yield of 1,3 PDO from glycerol by normal bacteria and modified bacteria were 0.355 mol/mol and 0.699 mol/mol, respectively. In other words, this suggested that more by-products reduced the yield of 1,3-PDO.

According to Szymanowska-Powalowska [12], this research studied the effects of initial glycerol concentrations on the metabolism and growth of *Clostridium butyricum* DSP1. The adaptability of *C. butyricum* DSP1 was evaluated with a crude

glycerol concentration of 50 g/L to 170 g/L. Resultantly, the maximum concentration of a substrate that did not interfere with the metabolic activity of bacterial cells is 70 g/L of crude glycerol. As seen from this, a high concentration of crude glycerol (130 g/L) inhibited bacterial growth which was a drawback of using bio-based catalyst.

According to Lee et al. [13], more than half of the cost of production was contributed to raw materials, particularly bio-based catalysts. Furthermore, comparing the prices of chemical catalysts and biocatalysts in laboratory grades, they were priced at € 1045/L and € 22/g to € 132.6/g, respectively. Typically, prices of the bio-based catalysts are higher than chemical catalysts leading to higher costs of production.

As seen from the compiled literature, the major disadvantages in the biological methods are that 1) the effluent was rich with a by-product that reduced the yield of 1,3-PDO, 2) bacteria could not function well, particularly in a high glycerol concentration environment, and 3) biocatalysts had a higher cost than heterogeneous catalysts.

### 2.3.2 Heterogeneous catalysis

For the heterogeneous catalysis, most catalytic reactions took place in liquid acids, especially sulfolane which could lead to the corrosion problem. Kubisztal et al. [14] investigated the effect of water concentration (0 to 6 vol.%) in sulfolane on the corrosion resistance of AISI 1010 steel. The result showed that if the water was in excess of 4 vol.%, this would lead to degradation of the corroded product layer and also to the deterioration of the corrosion resistance of AISI 1010 steel. Also, they usually operated at high pressure and temperature [13]. Although the heterogeneous catalysis requires high operating pressure and temperature and reacts well in an acidic

medium, the reaction could take place in an aqueous medium while providing a high yield of 1,3-PDO.

According to Liu et al. [4], the study examined the rhenium-oxide-modified iridium nanoparticles coating rutile Titania support as a catalyst in gas phase and liquid phase reactions, using 4% Ir of Ir-ReO<sub>x</sub>/TiO<sub>2</sub> at a ratio of Re/Ir between 0.063-1 and reacting for 4 hours with 67% glycerol. The experimental result of 4% Ir of Ir-ReO<sub>x</sub>/TiO<sub>2</sub> at a ratio of Re/Ir 0.30 in the gas phase at 573 K (G,573) resulted in 52 % conversion and 57 % selectivity of 1,3-PDO, and the liquid phase at 473 K (L,473) resulted in 31 % conversion and 72 % selectivity of 1,3-PDO [4]. The gas phase has a better percentage yield of 1,3-PDO (%yield = (%conversion x %selectivity)/100) than the liquid phase. However, the percentage yield of 1,3-PDO is not much different. Additionally, a gas phase requires a higher temperature and more complex distillation, which should require more energy than a liquid phase. Therefore, in this study, the selected condition is the liquid phase at 473 K.

**Table 1. Glycerol hydrogenolysis over 4 wt.% Ir Ir-ReO<sub>x</sub>/TiO<sub>2</sub> catalysts was reduced under different conditions [4]**

Entry	Catalyst	Reduction condition	Conversion (%)	Selectivity (%)				
				1,3-PDO	1,2-PDO	1-PrOH	2-PrOH	other
7	Ir-	(L,473)	31	72	5	15	7	1
8	ReO <sub>x</sub> /rutile,	(L,473)	46	59	3	31	6	1
9	Re/Ir =	(G,573)	52	57	2	34	5	2
10	0.30* (1)	(G,673)	36	61	4	28	6	1
11		(G,773)	17	65	10	17	7	1

Reaction conditions: catalyst amount = 150 mg, glycerol = 4 g, H<sub>2</sub>O = 2 g, P(H<sub>2</sub>) = 8 MPa, T = 393 K, t = 4 h. Reduction conditions: 30 cm<sup>3</sup>\*min<sup>-1</sup> H<sub>2</sub> at desired temperature for 1 h or P(H<sub>2</sub>) = 8 MPa at 473 K for 1 h (L, 473).

### 2.3.3 1,3-PDO production via biological route

As mentioned in the objective that the process performances of heterogeneous catalysis and biological routes for 1,3-PDO production will be compared, this section is given to provide information regarding the biological route. Please note that the biological route will be re-simulated and the process economic will be reevaluated in Aspen Plus. This is undertaken to ensure that the comparison between the biological route and the heterogenous catalysis route was performed using the same basis (Aspen Econ).

Espinel-Rios et al. [3] studied the biotechnological route for the production of 1,3-PDO from crude glycerol with *Clostridium* DMS 15410 and calculated economic profitability. The optimization of fermentation parameters was also analyzed for making investment decisions. The fermentation parameters were determined based on maximum substrate concentration and minimum dilution rate which resulted in 98.3 g/l and 0.05 h<sup>-1</sup> respectively to reach the maximum 1,3-PDO productivity. Furthermore, the best scenario for profitability was found at the maximum selling price of 1,3-PDO and the minimum cost of crude glycerol. However, even using the highest cost of crude glycerol, the ROI (Return on Investment) was still positive [3]. According to their work, the project payback period was 5.7 years with an investment of approximately \$25.3 million. In addition, 45% of operating costs were spent on utility due to the relatively high energy consumption of the process. In addition, changing some units or fermentation methods appeared to affect the process investment cost [3].

## Chapter 3

### Methodology

This chapter describes the steps involved in developing a process model describing the conversion of crude glycerol to 1,3-PDO and the main parameters that affect the feasibility of the process. In addition, there are 7 steps involved in this research as follows:

1. Problem definition
2. Collection of required data for process flow sheet construction
3. Calculation of required feed amounts
4. Design of process flowsheet
5. Simulation of process and result verification
6. Economic analysis
7. Energy utilization
8. Environmental impact

#### 3.1 Problem definition

To produce value-added chemicals, e.g., 1,3-PDO from the oversupply of crude glycerol which is a by-product obtained from the fast-growing biodiesel process.

#### 3.2 Collection of required data for process flow sheet construction

##### 3.2.1 Feedstock

In this study, the typical composition of crude glycerol is obtained from commercially available crude glycerol [15]. The MONG is the impurity such as soap, alcohol, and methyl ester [16]. In the previous study, the major component of crude

glycerol is oleate [17]. Then in this study, the MONG is Methyl oleate (methyl ester).

The major components and their compositions are given in **Table 2**.

**Table 2. Main components of crude glycerol [15-17]**

Main component	Mass Composition (%)
Glycerol	80
Methanol	0.5
Potassium hydroxide	1.5
Water	15
MONG (Methyl oleate)	3

### 3.2.2 Pretreatment

#### 3.2.2.1 Neutralization

In this process, acidification is required for neutralization. The 85 wt.% phosphoric acid is added to achieve a pH of 3.5. The mixture is stirred at 25 °C for 15 min [18]. The operating conditions are provided in **Table 3**.

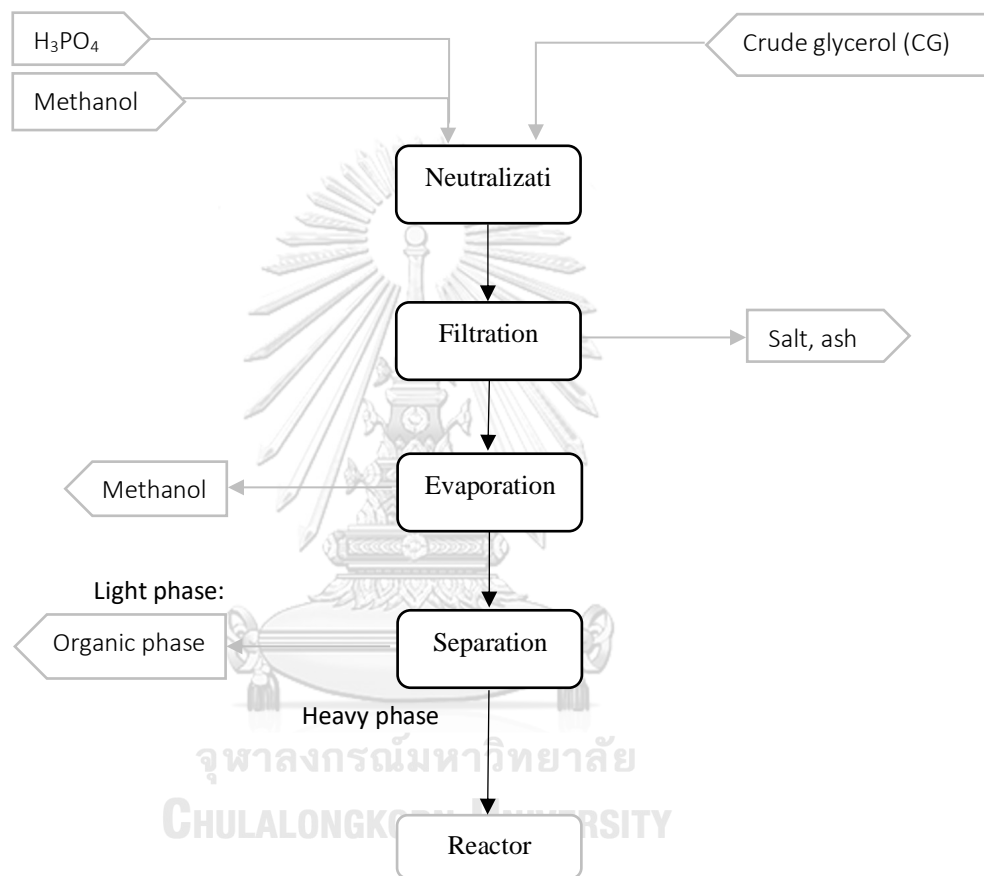
**Table 3. Operating conditions for the pretreatment process [18]**

Operating condition	Value
Temperature (°C)	25
Pressure (bar)	1
Reaction time (min.)	15
H <sub>3</sub> PO <sub>4</sub> concentration (wt.%)	85
pH	3.5

The acidification transforms the soap into free fatty acid and inorganic salt [18]. Furthermore, the mixture removes salt and ash by filtration after acidification, gets rid of excess methanol, and separates into 2 phases that consist of the light phase and the heavy phase. The lower phase is rich in glycerol. In addition, the precipitation yield increased with the amount of methanol since KH<sub>2</sub>PO<sub>4</sub> is insoluble in methanol.

Therefore, the methanol solvent content is calculated using the precipitation equation to be sufficient [18].

$$\text{Yield of precipitation (\%)} = 0.3042W_{\text{met}} + 84.74 \quad (\text{Eq.1})$$



**Figure 3.** Diagram of the pretreatment process



### 3.2.3 Reaction

#### 3.2.3.1 Biological route

In this process, the biological process is operated at 33 °C and under anaerobic conditions for 20 hrs. The glycerol concentration starts at 98.3 g/l. The operating conditions and reactions are provided in **Tables 4 and 5**.

**Table 4.** Operating conditions for the biological process [3]

Operating condition	Value
Temperature (°C)	33
Pressure (bar)	1
Reaction time (hrs.)	20
Glycerol concentration (g/l)	98.3

**Table 5.** The reaction of the biological process [19, 20]

Reaction	Main product
1) $C_3H_8O_3 + H_2 \rightarrow C_3H_8O_2 + H_2O$ (Eq.2)	1,3-PDO
2) $2C_3H_8O_3 \rightarrow C_4H_8O_2 + 4H_2 + 2CO_2$ (Eq.3)	Butyric acid
3) $C_3H_8O_3 + H_2O \rightarrow CH_3COOH + 3H_2 + CO_2$ (Eq.4)	Acetic acid

The fermentation stoichiometry equation was developed previously with the main products 1,3-PDO, butyric acid, acetic acid, and a small amount of unidentified products which were not characterized in the experimental work [3]. Since these unidentified products presented in small quantities, the product distribution was renormalized based on three major products including 1,3-PDO, butyric acid and acetic acid as shown in **Table 6**.

**Table 6.** Conversion and selectivity of the biological process [3]

Conversion	selectivity		
	1,3-PDO	Butyric acid	Acetic acid
94.2%	75.3%	7.4%	17.3%

### 3.2.3.2 Heterogeneous catalysis

In this process, the chemical process is operated at 393 K, 80 bars, and under anaerobic conditions for 4 hrs. The glycerol concentration starts at 67 wt.%. The operating conditions, reactions, conversion, and selectivity are provided in **Tables 7, 8, and 9.**

**Table 7.** Operating conditions for the chemical process [4]

Operating condition	Value
Temperature (°C)	119.85
Pressure (bar)	80
Reaction time (hrs.)	4
Glycerol concentration (%)	67
Liquid loading (%)	50

**Table 8.** The reaction of the chemical process [4]

Reaction	Main product
$C_3H_8O_3 + H_2 \rightarrow C_3H_8O_2 + H_2O$ (Eq.6)	1,2-PDO, and 1,3-PDO
$C_3H_8O_3 + 2H_2 \rightarrow C_3H_8O + 2H_2O$ (Eq.7)	1-PrOH, and 2-PrOH

**Table 9.** Conversion and selectivity of the chemical process [4]

Conversion	selectivity			
	1,3-PDO	1,2-PDO	1-PrOH	2-PrOH
31.0%	72.7%	5.1%	15.2%	7.1%

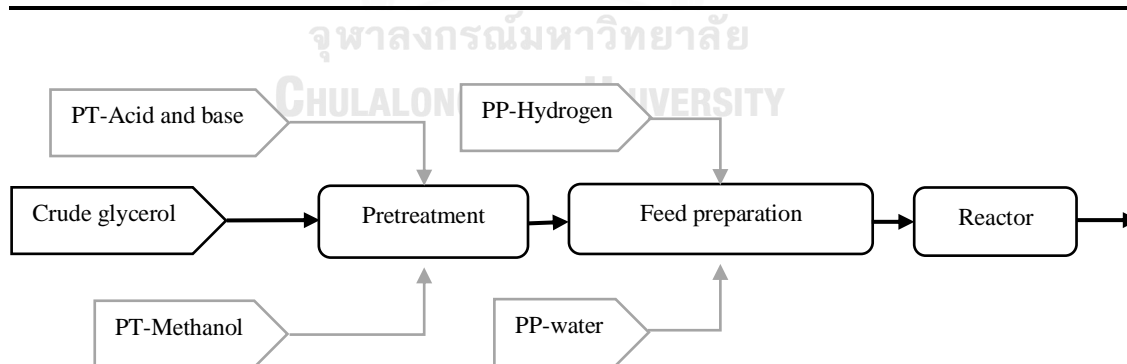
### 3.3 Calculation of required feed amounts

The data in section 3.2 can be used to calculate the inlet for each feed stream. Additionally, by assuming the production capacity of 12,000 tonnes/year with 99.9 wt % of 1,3-propanediol, the amount of required crude glycerol can be estimated. Then, other impurities contained in crude glycerol can be computed also. Moreover,

in the fermentation method, the same amount of initial crude glycerol as the chemical method is used for further comparison. The calculated data for the feed stream are tabulated in **Table 10**.

**Table 10.** The calculated feed stream of the chemical and biological methods

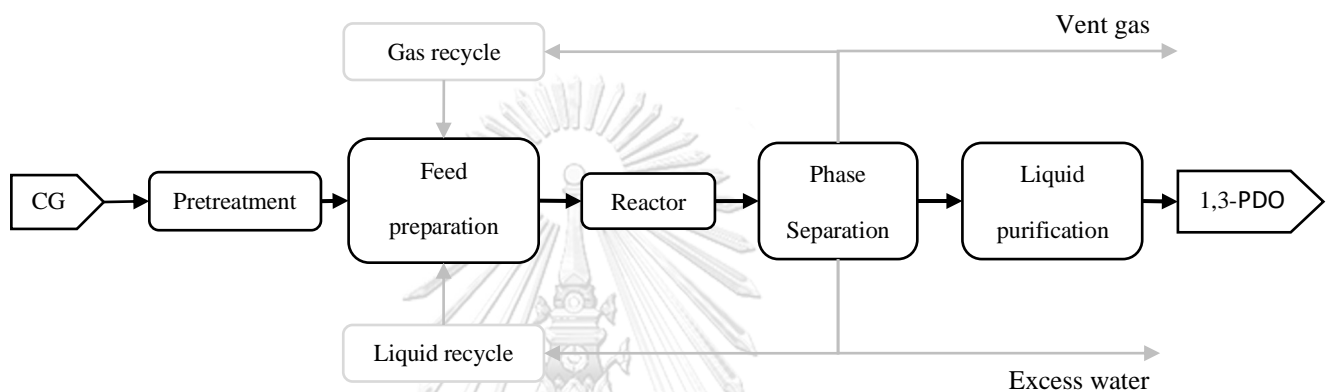
	Stream	Description	Mass flow rate (kg/h)
Pretreatment	Crude glycerol		12,500
	PT-Methanol		3,250
	PT-Acid	Phosphoric acid 85 wt.%	593
	PT-Base	Sodium hydroxide 85 wt.%	92
Chemical method	PP-Water	Water in fermentation (Ratio of glycerol and water is 2:1)	2,561
	PP-Hydrogen	Hydrogen added to make an anaerobic condition and reaction (Total H <sub>2</sub> = H <sub>2</sub> overhead space + H <sub>2</sub> used in reaction)	494
Biological method	PP-Water	Water in fermentation (Glycerol concentration = 98.3 g/l)	96,021
	PP-Hydrogen	Hydrogen added to make an anaerobic condition and reaction (Total H <sub>2</sub> = H <sub>2</sub> overhead space + H <sub>2</sub> used in reaction)	274



**Figure 4.** Block flow diagram of the feed stream

### 3.4 Design process flowsheet

The design flowsheet has 5 sections consisting of pretreatment, reactor feed preparation, reactor, phase separation, and liquid purification. Additionally, the part of the recycling process depends on the purity of the mixture. Then, the process may or may not contain some of these sections.



**Figure 5.** The process block flow diagram

### 3.5 Simulation of process and result verification

After creating the designed process flowsheet base on the information obtained from the previous step, the flowsheet is simulated using Aspen Plus, and the results will be verified – in case the execution and results are inconsistent with the experimental data, the simulated model will be corrected and re-simulated.

### 3.6 Economic Analysis

The model obtained from the previous step is used as a based case design. Then, the economic performance of the process is evaluated using Aspen Economic

Analyzer. The parameters used in the assessment of economic performances include the Profitability Index (PI), Internal Rate of Return (IRR), and Payback period (PB).

### 3.6.1 Profitability Index (PI)

The value of the PI is an indication of whether this project is worth the investment or not. The PI equation can be calculated as follows [21].

$$\text{Profitability index (PI)} = \frac{\text{Present value of future cash flows}}{\text{Initial investment}} \quad (\text{Eq. 8})$$

- $PI > 1$ , the project should be accepted.
- $PI = 0$ , the project should be at the break-even point.
- $PI < 1$ , the project should be rejected.

### 3.6.2 Internal Rate of Return (IRR)

The Internal Rate of Return (IRR) is a discounted cash flow technique that provides a rate of return earned from a project. The Internal Rate of Return is the discount rate when the sum of initial disbursements and discounted cash inflows equals zero. The IRR equation can be calculated as follows [22, 23].

$$0 = \sum_{n=0}^n \frac{CF_n}{(1+IRR)^n} \quad (\text{Eq. 9})$$

where  $CF_n$  are cash flows in time period, IRR is internal rate of return and  $n$  is time period.

- $IRR > \text{Capital cost}$ , the project should be accepted.
- $IRR < \text{Capital cost}$ , the project should be rejected.

### 3.6.3 Payout Period (PO)

The payout period (PO) measures how long it takes to recover the cost of an initial investment using the cash flows generated by the investment. A short period of PB is preferable since it indicates that the project would meet the break-even point in a shorter period [22, 24]. The PO equation can be calculated as follows [24].

$$\text{PO} = \text{Years before break-even point} + \frac{\text{Unrecovered amount}}{\text{Cash flow in recovery year}} \quad (\text{Eq. 10})$$

### 3.7 Energy utilization

Energy efficiency has been quantified using specific energy consumption (SEC) as Eq. (11). Based on this term, the SEC described the amount of energy needed to produce 1 kg of DEE - The smaller the SEC, the greater the efficiency with which energy is used [25]

$$\text{SEC} = \frac{\text{Total amount of utilized energy [kW]}}{\text{Total rate of 1,3-PDO production [kg/h]}} \quad (\text{Eq. 11})$$

### 3.8 Environmental impact

The direct and indirect CO<sub>2</sub> emissions have been estimated using the CO<sub>2</sub> tracking available in Aspen Plus V11. State that direct CO<sub>2</sub> emissions were CO<sub>2</sub> emitted from fuel combustion to produce heat while indirect CO<sub>2</sub> is produced by consuming utilities such as steam and electricity. In general, a process that was more energy-efficient had the potential to produce lower CO<sub>2</sub> emissions. The term used for quantifying net CO<sub>2</sub> emissions was given in Eq. (12) [25]

$$\text{Net CO}_2 \text{ emission} = \sum F_{\text{CO}_2, \text{inlet}} - \sum F_{\text{CO}_2, \text{outlet}} \quad (\text{Eq. 12})$$

## Chapter 4

### Result and discussion

The process simulation is performed through Aspen Plus. In this research, crude glycerol is converted to 1,3-PDO through four major processes, including crude glycerol pretreatment, fermentation, phase separation, and liquid purification. The production rate of 1,3-PDO represents about a quarter of the national demand based on the forecast total demand in 2022 [7]. The crude glycerol feed rate of 120,000 tons/year is estimated.

#### 4.1 Crude glycerol pretreatment system

In this study, both production simulation methods (e.g., biological route and catalysis route) are based on the same preparation system as shown in **Figure 6**. The typical composition of crude glycerol is obtained from commercially available crude glycerol [15]. The alkaline contained in crude glycerol (CG) is neutralized using 85 wt.% phosphoric acid (ACID) with methanol as the solvent. Methanol (METOH) is added to the pretreatment to facilitate salt precipitation. The ratio is calculated from **Eq.1**. Then, the precipitated salt (SALT) is filtered from stream 1 through a 110  $\mu\text{m}$  filter [18]. Methanol (stream 4) and methyl oleate (P-METHY1) are separated via T-101 tower and D-101 decanter, respectively. Before recycling, the methanol will be separated at the desired rate and will reduce the temperature to be used in the reaction as METOH. Additionally, methyl oleate and glycerol are separate layers so that they can be separated by the decanter.

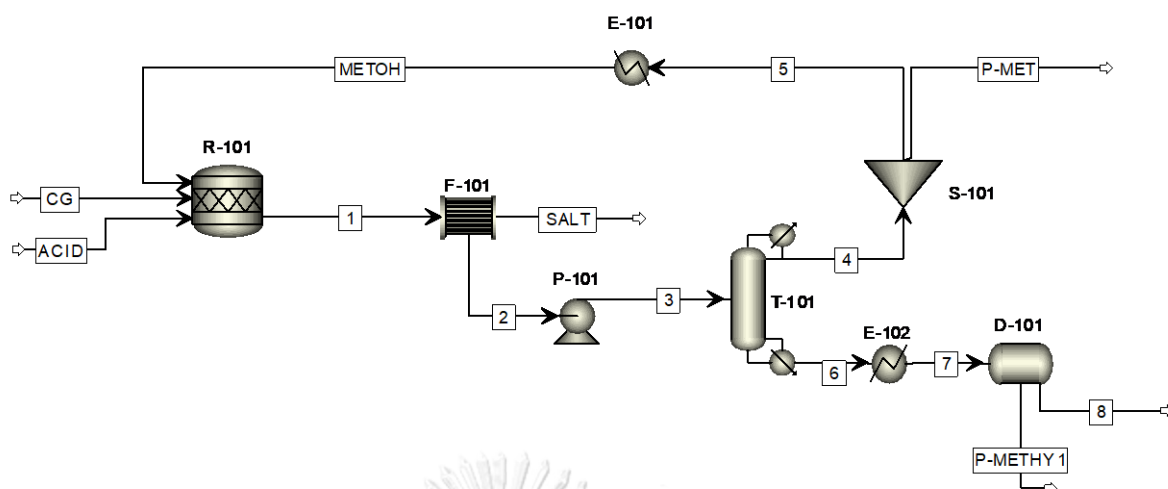


Figure 6. Diagram of crude glycerol pretreatment process

Table 11. Result of crude glycerol pretreatment (1)

Stream name	CG	ACID	METOH	SALT	1
Temperature °C	25.00	25.00	25.00	25.00	25
Pressure bar	1.00	1.00	1.00	1.00	1
Mass Flows kg/hr	12,500	409.28	12,137	478.47	25046
Mass Fractions					
H <sub>2</sub>	0.000	0.000	0.000	0.000	0.000
CO <sub>2</sub>	0.000	0.000	0.000	0.000	0.000
WATER	0.150	0.200	0.005	0.004	0.083
ACETIC	0.000	0.000	0.000	0.000	0.000
BUTYRIC	0.000	0.000	0.000	0.000	0.000
1,3-PDO	0.000	0.000	0.000	0.000	0.000
GLYCEROL	0.800	0.000	0.000	0.021	0.399
SALTK	0.000	0.000	0.000	0.949	0.018
METOH	0.005	0.000	0.995	0.025	0.485
METHYL	0.030	0.000	0.000	0.001	0.015
ACID	0.000	0.800	0.000	0.000	0.000
BASE	0.015	0.000	0.000	0.000	0.000



**Table 12.** Result of crude glycerol pretreatment (2)

Stream name		4	6	8	P-MET	P-METHY1
Temperature	°C	64.34	136.83	15.00	64.34	15
Pressure	bar	1.00	1.33	1.33	1.00	1.33
Mass Flows	kg/hr	12187	12380	12005	50.46	375.11
<b>Mass Fractions</b>						
H <sub>2</sub>		0.000	0.000	0.000	0.000	0.000
CO <sub>2</sub>		0.000	0.000	0.000	0.000	0.000
WATER		0.005	0.163	0.168	0.005	0.001
ACETIC		0.000	0.000	0.000	0.000	0.000
BUTYRIC		0.000	0.000	0.000	0.000	0.000
1,3-PDO		0.000	0.000	0.000	0.000	0.000
GLYCEROL		0.000	0.807	0.832	0.000	0.000
SALTK		0.000	0.000	0.000	0.000	0.002
METOH		0.995	0.000	0.000	0.995	0.000
METHYL		0.000	0.030	0.000	0.000	0.996
ACID		0.000	0.000	0.000	0.000	0.000
BASE		0.000	0.000	0.000	0.000	0.000

## 4.2 Biological route

### 4.2.1 Biological system

**Figure 7** provides the process flow diagram of the biological system. The treated glycerol (stream 8) is combined with recycled glycerol (stream 33) and make-up glycerol (GLYM). The amount of make-up glycerol (GLYM) substitutes the amount of glycerol that has been separated to eliminate the impurity (P-GLY). Next, set the glycerol concentration to 98.3 g/l with water (WATER). Since bacteria cannot tolerate high-concentrations of glycerol, water must be fed in large quantities [3, 12]. The hydrogen gas (H<sub>2</sub>M) will be added for the reaction and recycled (stream 22) from the tank's airspace for anaerobic condition. The reaction took place in R-201 in a liquid phase at 33 °C and 1 bar as shown in Figure7.

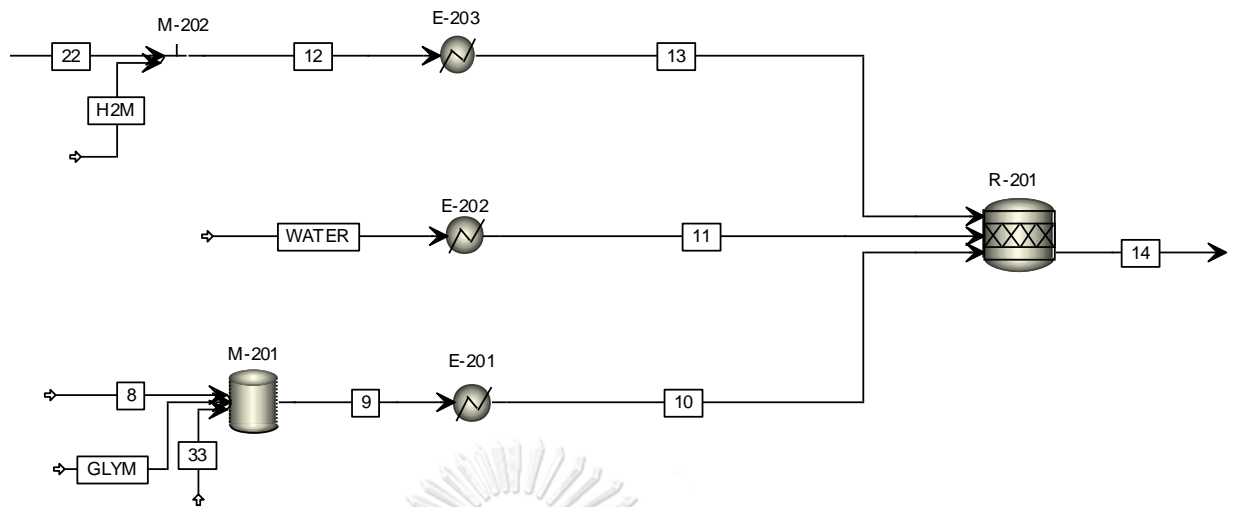


Figure 7. Diagram of the biological fermentation process

Table 13. Result of biological fermentation (1)

Stream name		GLYM	WATER	H2M	10	11
Temperature	°C	25.00	25.00	25.00	33.00	33.00
Pressure	bar	1.00	1.33	1.00	1.00	1.33
Mass Flows	kg/hr	21.16	96021	20.65	12615	96021
Mass Fractions						
H <sub>2</sub>		0.000	0.000	1.000	0.000	0.000
CO <sub>2</sub>		0.000	0.000	0.000	0.000	0.000
WATER		0.001	1.000	0.000	0.160	1.000
ACETIC		0.000	0.000	0.000	0.000	0.000
BUTYRIC		0.000	0.000	0.000	0.000	0.000
1,3-PDO		0.000	0.000	0.000	0.000	0.000
GLYCEROL		0.999	0.000	0.000	0.840	0.000
SALTK		0.000	0.000	0.000	0.000	0.000
METOH		0.000	0.000	0.000	0.000	0.000
METHYL		0.000	0.000	0.000	0.000	0.000
ACID		0.000	0.000	0.000	0.000	0.000
BASE		0.000	0.000	0.000	0.000	0.000

**Table 14.** Result of biological fermentation (2)

Stream name	13	14	22	33
Temperature °C	33.00	33.00	-160.00	15.05
Pressure bar	1.00	1.00	1.00	1.33
Mass Flows kg/hr	274.70	108911	254.05	588.78
<b>Mass Fractions</b>				
H <sub>2</sub>	0.999	0.002	0.999	0.000
CO <sub>2</sub>	0.001	0.011	0.001	0.000
WATER	0.000	0.911	0.000	0.000
ACETIC	0.000	0.010	0.000	0.000
BUTYRIC	0.000	0.003	0.000	0.000
1,3-PDO	0.000	0.057	0.000	0.001
GLYCEROL	0.000	0.006	0.000	0.999
SALTK	0.000	0.000	0.000	0.000
METOH	0.000	0.000	0.000	0.000
METHYL	0.000	0.000	0.000	0.000
ACID	0.000	0.000	0.000	0.000
BASE	0.000	0.000	0.000	0.000

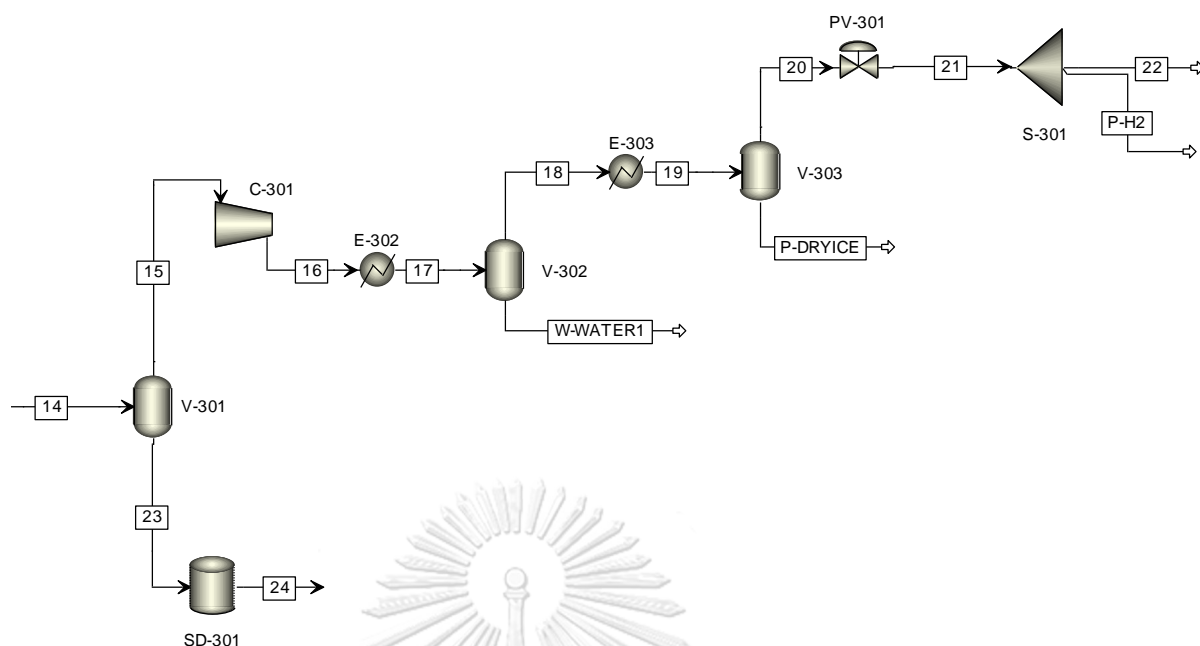
#### 4.2.2 Biological phase separation

In this section, gas, liquid, and solid catalyst contained in the reactor effluent (Stream 14) are separated as shown in **Figure 8**. First, the separation of the excess gas (stream 15) from a liquid (stream 23) is undertaken via V-301. Then, the gas line (stream 15) pressure is increased, and the temperature is decreased to condense the remaining liquid (W-WATER1) in the gas line. **Table 15** shows that recycling hydrogen (case II) is more profitable than selling it as a synthetic gas (case I). As synthetic gas costs \$0.1/cum, which is cheaper than the hydrogen gas price of \$3.9/cum. Consequently, the cost of reducing utilities cannot compensate for the difference. Then, Carbon dioxide (P-DRYICE) will be separated in the form of dry ice at -160 °C to purify the hydrogen for recycling in the fermentation process. The impurity is then removed at P-H2 and recirculation stream 22 to the preparation unit.

As for the liquid line, solid catalyst (yeast cells and bacteria) cannot be simulated directly, to account for the cost of yeast and bacteria separation, the sedimentor unit (SD-301) is set up for cost calculation. The batch bottom-suspended centrifuge or sedimentor use for separation due to the high quantity of water. Finally, stream 24, which contains primarily the valuable products in a form of a liquid mixture will be sent to the liquid purification system.

**Table 15** Summary of economic indicators evaluated for Cases I, II, and III.

Parameter	Case I	Case II	Case III
Description	Synthetic gas and 1,3-PDO only product	H <sub>2</sub> Recycle and 1,3-PDO only product	H <sub>2</sub> Recycle and 1,3-PDO and Acetic acid as a product
Total Capital Cost [Million USD]	43.6	81.6	93.5
Total Operating Cost [Million USD/Year]	279	174	337
Total Raw Materials Cost [Million USD/Year]	199	92.6	92.6
Total Product Sales [Million USD/Year]	313	319	377
Total Utilities Cost [Million USD/Year]	55.6	60.3	210
Desired Rate of Return [Percent/Year]	20	20	20
P.O. Period [Year]	8.09	2.99	9.94
Equipment Cost [Million USD]	13.1	39.1	44.8
Total Installed Cost [Million USD]	26.8	57.9	66.1



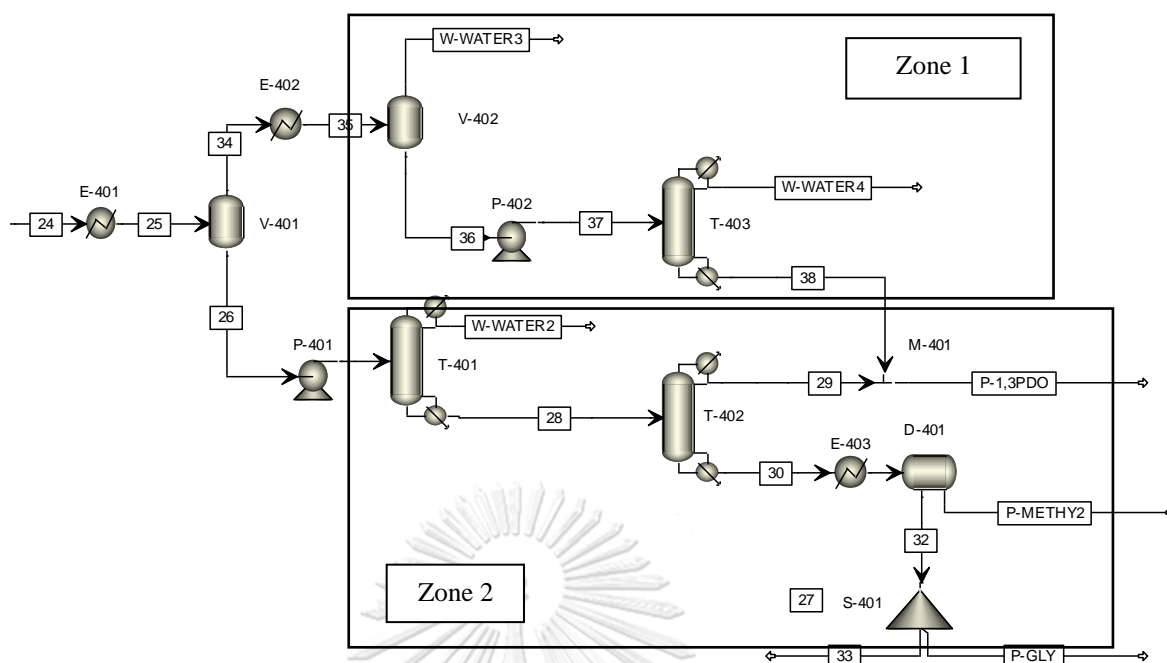
**Figure 8.** Diagram of the biological phase separation process

**Table 16.** Result of biological phase separation (1)

Stream name		15	24	W- WATER1	P- DRYICE	P-H2
Temperature	°C	33.00	33.00	30.00	-160.00	-160.00
Pressure	bar	1.00	1.00	15.00	15.00	1.00
Mass Flows	kg/hr	1187.3	107724	137.62	794.43	1.17
<b>Mass Fractions</b>						
H2		0.215	0.000	0.000	0.000	0.999
CO2		0.670	0.004	0.060	0.991	0.001
WATER		0.114	0.919	0.929	0.009	0.000
ACETIC		0.001	0.010	0.007	0.000	0.000
BUTYRIC		0.000	0.003	0.003	0.000	0.000
1,3-PDO		0.000	0.058	0.000	0.000	0.000
GLYCEROL		0.000	0.006	0.000	0.000	0.000
SALTK		0.000	0.000	0.000	0.000	0.000
METOH		0.000	0.000	0.000	0.000	0.000
METHYL		0.000	0.000	0.000	0.000	0.000
ACID		0.000	0.000	0.000	0.000	0.000
BASE		0.000	0.000	0.000	0.000	0.000

#### 4.2.3 Biological liquid purification

**Figure 9** illustrates the process flow diagram of the liquid purification process for biological route. Almost all the water and the remaining gas in the liquid line (stream 34) are separated from the heavy liquid components in stream 26 (e.g., Glycerol and 1,3-PDO) via V-401. Zone 1, The substances attached to the water are acetic acid, butyric acid, and 1,3-PDO. Since acetic acid and butyric acid are low volumes, difficult to separate from water, and inexpensive, it should not be separated via distillation as shown in Table 15 as case III. Consequently, there is only one separation for 1,3-PDO (stream 38) via T-403. Moreover, water (W-WATER3 and 4) could not be recycled unless it was treated. As a result, there is no water recycling in this system since treating water for recycling is not cost-effective. Zone 2 involves the separation of 1,3-PDO and glycerol. T-402 separates glycerol (stream 32) for recycling and desired product 1,3-PDO (stream 29) at 99.9% purity. Due to the small amount of glycerol (stream 32), the amount of methyl oleate affects recycling and should be separated as P-METHY2.



**Figure 9.** Diagram of the biological liquid purification process

**Table 17.** Result of biological liquid purification in zone 1

Stream name	35	37	38	W- WATER3	W- WATER4
Temperature °C	100.00	100.02	222.54	100.00	99.65
Pressure bar	1.00	1.33	1.33	1.00	1.00
Mass Flows kg/hr	92474.77	10341.52	517.44	82133.25	9824.08
<b>Mass Fractions</b>					
H <sub>2</sub>	0.000	0.000	0.000	0.000	0.000
CO <sub>2</sub>	0.004	0.000	0.000	0.005	0.000
WATER	0.976	0.931	0.001	0.982	0.980
ACETIC	0.010	0.016	0.000	0.010	0.017
BUTYRIC	0.003	0.002	0.000	0.003	0.002
1,3-PDO	0.006	0.050	0.997	0.000	0.000
GLYCEROL	0.000	0.000	0.002	0.000	0.000
SALTK	0.000	0.000	0.000	0.000	0.000
METOH	0.000	0.000	0.000	0.000	0.000
METHYL	0.000	0.000	0.000	0.000	0.000
ACID	0.000	0.000	0.000	0.000	0.000
BASE	0.000	0.000	0.000	0.000	0.000

**Table 18.** Result of biological liquid purification in zone 2(1)

Stream name		27	28	29	30	32
Temperature	°C	15.00	104.00	212.99	104.00	222.54
Pressure	bar	1.33	1.00	1.00	1.00	1.33
Mass Flows	kg/hr	0.91	15249.25	5661.56	92475.06	517.44
<b>Mass Fractions</b>						
H <sub>2</sub>		0.000	0.000	0.000	0.000	0.000
CO <sub>2</sub>		0.000	0.000	0.000	0.004	0.000
WATER		0.000	0.575	0.000	0.976	0.001
ACETIC		0.000	0.011	0.000	0.010	0.000
BUTYRIC		0.000	0.003	0.000	0.003	0.000
1,3-PDO		0.000	0.371	0.999	0.006	0.997
GLYCEROL		0.000	0.040	0.000	0.000	0.002
SALTK		0.000	0.000	0.000	0.000	0.000
METOH		0.000	0.000	0.000	0.000	0.000
METHYL		1.000	0.000	0.000	0.000	0.000
ACID		0.000	0.000	0.000	0.000	0.000
BASE		0.000	0.000	0.000	0.000	0.000

**Table 19.** Result of biological liquid purification in zone 2(2)

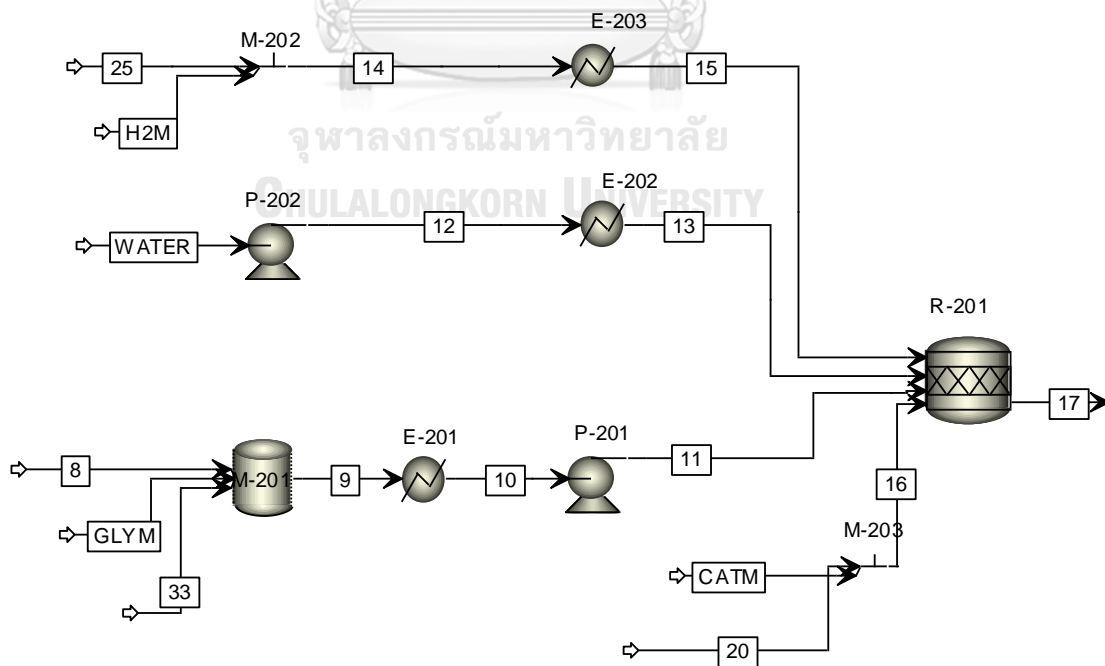
Stream name		33	P-1,3PDO	P-METHY2	P-GLY
Temperature	°C	15.05	213.00	15.00	15.05
Pressure	bar	1.33	1.00	1.33	1.33
Mass Flows	kg/hr	588.78	6179.0	0.91	24.53
<b>Mass Fractions</b>					
H <sub>2</sub>		0.000	0.000	0.000	0.000
CO <sub>2</sub>		0.000	0.000	0.000	0.000
WATER		0.000	0.000	0.000	0.000
ACETIC		0.000	0.000	0.000	0.000
BUTYRIC		0.000	0.000	0.000	0.000
1,3-PDO		0.001	0.999	0.000	0.001
GLYCEROL		0.999	0.000	0.000	0.999
SALTK		0.000	0.000	0.000	0.000
METOH		0.000	0.000	0.000	0.000
METHYL		0.000	0.000	1.000	0.000
ACID		0.000	0.000	0.000	0.000
BASE		0.000	0.000	0.000	0.000



### 4.3 Heterogeneous catalysis

#### 4.3.1 Chemical system

**Figure 10** provides the process flow diagram of the heterogeneous catalytic system. The treated glycerol (stream 8) is combined with recycled glycerol (stream 33) and make-up glycerol (GLYM). The amount of make-up glycerol (GLYM) substitutes the amount of glycerol that has been separated to eliminate the impurity (P-GLY). Next, set the glycerol concentration to 67 wt.% with water (WATER). The hydrogen gas (H<sub>2</sub>M) will be added for the reaction and recycled (stream 25) from the tank's airspace for anaerobic condition. The reaction took place in R-201 in a liquid phase at 473 K as shown in Figure 10. Additionally, the recycled catalyst (stream 20) is combined with make-up catalyst (CATM). The amount of make-up catalyst (CATM) replaces the amount of catalyst which reactivates degraded catalysts (P-CAT) by approximately 15% [4].

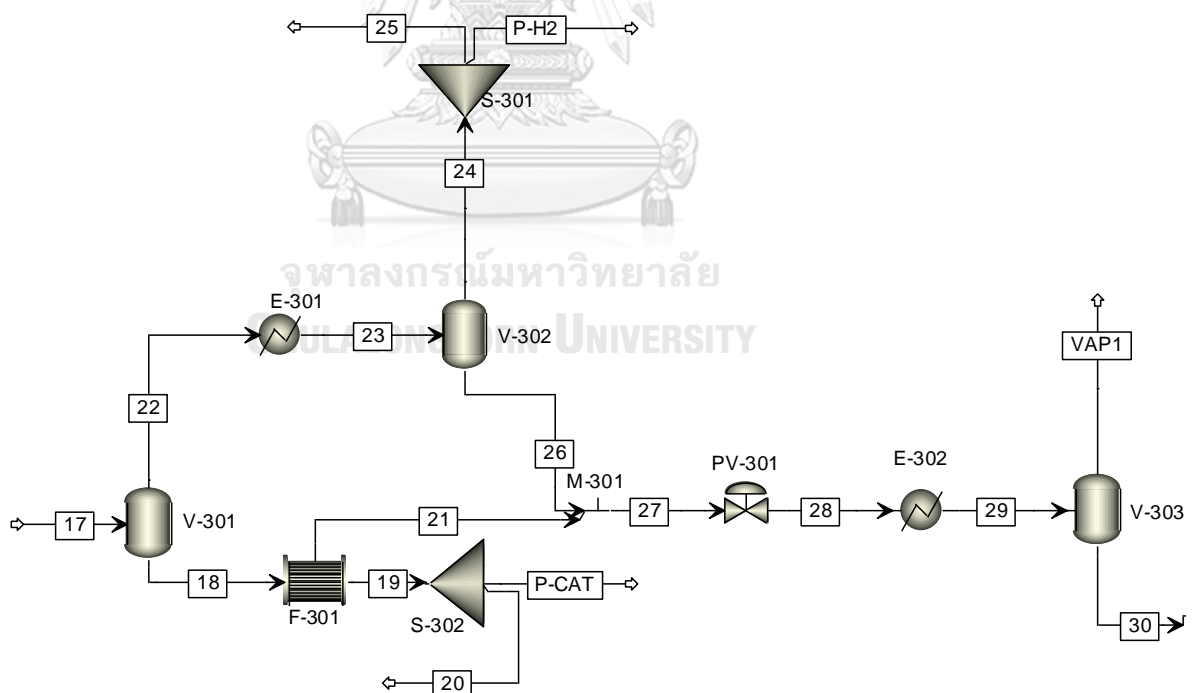


**Figure 10.** Diagram of chemical fermentation process



#### 4.3.2 Chemical phase separation system

In this section, gas, liquid, and solid catalyst contained in the reactor effluent (stream 17) are separated as shown in **Figure 11**. First, the separation of the excess gas (stream 22) from a liquid (stream 18) is undertaken via V-301. Then the gas line temperature (stream 22) is decreased to condense the remaining liquid (stream 26) in the gas line (stream 23). The liquid (stream 18) from V-301 is passed through a filter 0.156 nm (F-301) to separate the solid catalyst. The liquids from F-301 and V-302 (stream 21 and 26) are combined to stream 27. Given a minute amount of gas present in Stream 27, the stream pressure and temperature are reduced to remove the gas (VAP1). Finally, stream 30, which contains primarily the valuable products in a form of a liquid mixture will be sent to the liquid purification system.



**Figure 11.** Diagram of chemical phase separation process

**Table 22.** Result of chemical phase separation (1)

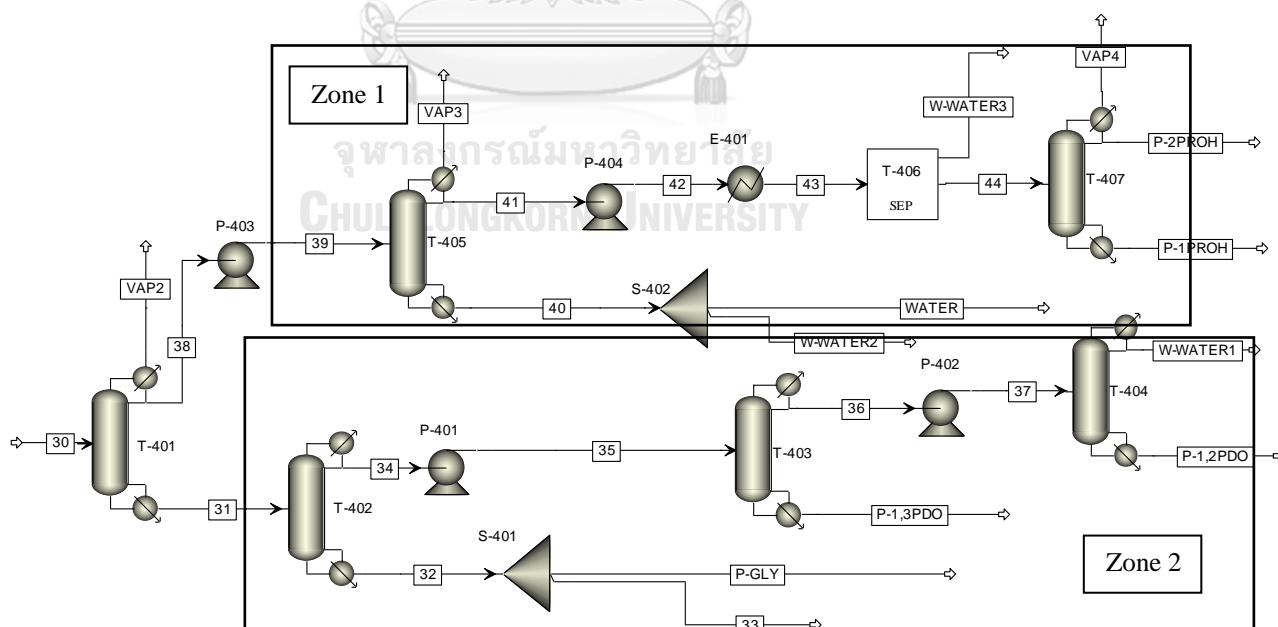
Stream name		18	21	22	24	26
Temperature	°C	119.85	119.85	119.85	35.00	35.00
Pressure	bar	80.00	80.00	80.00	80.00	80.00
Mass Flows	kg/hr	50140.80	48495.21	240.72	196.69	44.04
<b>Mass Fractions</b>						
H <sub>2</sub>		0.000	0.000	0.802	0.981	0.001
2-PROH		0.009	0.009	0.029	0.006	0.130
1-PROH		0.020	0.020	0.037	0.007	0.173
WATER		0.368	0.380	0.131	0.006	0.691
1,2-PDO		0.008	0.009	0.000	0.000	0.001
1,3-PDO		0.120	0.124	0.001	0.000	0.003
GLYCEROL		0.443	0.458	0.000	0.000	0.000
TIO <sub>2</sub>		0.032	0.000	0.000	0.000	0.000
SALTK		0.000	0.000	0.000	0.000	0.000
METOH		0.000	0.000	0.000	0.000	0.000
METHYL		0.000	0.000	0.000	0.000	0.000
ACID		0.000	0.000	0.000	0.000	0.000
BASE		0.000	0.000	0.000	0.000	0.000

**Table 23.** Result of chemical phase separation (2)

Stream name		29	30	P-CAT	P-H2	VAP1
Temperature	°C	35.00	35.00	119.85	35.00	35.00
Pressure	bar	1.33	1.33	80.00	80.00	1.33
Mass Flows	kg/hr	48539.25	48519.40	246.84	3.93	19.84
<b>Mass Fractions</b>						
H <sub>2</sub>		0.000	0.000	0.000	0.981	0.708
2-PROH		0.009	0.009	0.000	0.006	0.036
1-PROH		0.020	0.020	0.001	0.007	0.051
WATER		0.380	0.380	0.011	0.006	0.205
1,2-PDO		0.009	0.009	0.000	0.000	0.000
1,3-PDO		0.124	0.124	0.004	0.000	0.000
GLYCEROL		0.457	0.457	0.013	0.000	0.000
TIO <sub>2</sub>		0.000	0.000	0.971	0.000	0.000
SALTK		0.000	0.000	0.000	0.000	0.000
METOH		0.000	0.000	0.000	0.000	0.000
METHYL		0.000	0.000	0.000	0.000	0.000
ACID		0.000	0.000	0.000	0.000	0.000
BASE		0.000	0.000	0.000	0.000	0.000

#### 4.3.3 Chemical liquid purification system

**Figure 12.** illustrates the process flow diagram of the liquid purification process. The column T-401 is used to separate 1-propanol and 2-propanol (stream 38) from the heavy liquid components in stream 31 (e.g., 1,2-PDO and 1,3-PDO). Zone 1 involves the unit operations responsible for the separation of 1-propanol and 2-propanol. Since both alcohols form azeotrope with water, T-405 is used to distill water from stream 39 to the azeotrope point and process water (stream 40) will be split to recycle. Then adjust the pressure and temperature as stream 43 for pressure swing adsorption (T-406) to remove the remaining water (W-WATER3). Thus, these alcohols are successfully separated using T-407. Zone 2 involves the separation of 1,3-PDO and 1,2-PDO. Since these compounds do not form azeotrope with water, the separation can be undertaken easily using the columns T-402, T-403 and T-404. Finally, the desired product purity of 1,3-PDO at 99.9% is obtained [26].



**Figure 12.** Diagram of chemical liquid purification process

**Table 24.** Result of chemical liquid purification in zone 1 (1)

Stream name		38	40	41	43	44
Temperature	C	89.16	107.77	84.45	121.00	121.00
Pressure	bar	1.00	1.33	1.00	3.10	3.10
Mass Flows	kg/hr	18765	16440	2319.8	2319.9	1418.9
Mass Fractions						
H <sub>2</sub>		0.000	0.000	0.000	0.000	0.000
2-PROH		0.024	0.000	0.194	0.194	0.317
1-PROH		0.052	0.000	0.417	0.417	0.682
WATER		0.924	1.000	0.389	0.389	0.001
1,2-PDO		0.000	0.000	0.000	0.000	0.000
1,3-PDO		0.000	0.000	0.000	0.000	0.000
GLYCEROL		0.000	0.000	0.000	0.000	0.000
TIO <sub>2</sub>		0.000	0.000	0.000	0.000	0.000
SALTK		0.000	0.000	0.000	0.000	0.000
METOH		0.000	0.000	0.000	0.000	0.000
METHYL		0.000	0.000	0.000	0.000	0.000
ACID		0.000	0.000	0.000	0.000	0.000
BASE		0.000	0.000	0.000	0.000	0.000

**Table 25.** Result of chemical liquid purification in zone 1 (2)

Stream name		P-1PROH	P-2PROH	W-WATER2	W-WATER3
Temperature	°C	298.40	196.97	223.87	99.54
Pressure	bar	1.33	1.33	1.33	1.00
Mass Flows	kg/hr	1110.55	413.06	5999.69	1090.07
Mass Fractions					
H <sub>2</sub>		0.000	0.000	0.000	0.000
2-PROH		0.000	0.000	0.000	0.000
1-PROH		0.000	0.000	0.000	0.001
WATER		0.000	0.000	0.000	0.999
1,2-PDO		0.000	0.997	0.001	0.000
1,3-PDO		0.000	0.003	0.999	0.000
GLYCEROL		0.999	0.000	0.000	0.000
TIO <sub>2</sub>		0.000	0.000	0.000	0.000
SALTK		0.000	0.000	0.000	0.000
METOH		0.000	0.000	0.000	0.000
METHYL		0.001	0.000	0.000	0.000
ACID		0.000	0.000	0.000	0.000
BASE		0.000	0.000	0.000	0.000

**Table 26.** Result of chemical liquid purification in zone 2 (1)

Stream name		31	32	34	36
Temperature	°C	193.73	298.40	125.27	101.94
Pressure	bar	1.33	1.33	1.00	1.00
Mass Flows	kg/hr	29713.78	22210.97	7502.81	1503.12
Mass Fractions					
H <sub>2</sub>		0.000	0.000	0.000	0.000
2-PROH		0.000	0.000	0.000	0.000
1-PROH		0.000	0.000	0.000	0.000
WATER		0.037	0.000	0.145	0.724
1,2-PDO		0.014	0.000	0.056	0.274
1,3-PDO		0.202	0.000	0.799	0.001
GLYCEROL		0.747	0.999	0.000	0.000
TIO <sub>2</sub>		0.000	0.000	0.000	0.000
SALTK		0.000	0.000	0.000	0.000
METOH		0.000	0.000	0.000	0.000
METHYL		0.001	0.001	0.000	0.000
ACID		0.000	0.000	0.000	0.000
BASE		0.000	0.000	0.000	0.000

**Table 27.** Result of chemical liquid purification in zone 2 (2)

Stream name		P-GLY	P-1,2PDO	P-1,3PDO	W-WATER1
Temperature	°C	298.40	196.97	223.87	99.54
Pressure	bar	1.33	1.33	1.33	1.00
Mass Flows	kg/hr	1110.55	413.06	5999.69	1090.06
Mass Fractions					
H <sub>2</sub>		0.000	0.000	0.000	0.000
2-PROH		0.000	0.000	0.000	0.000
1-PROH		0.000	0.000	0.000	0.001
WATER		0.000	0.000	0.000	0.999
1,2-PDO		0.000	0.997	0.001	0.000
1,3-PDO		0.000	0.003	0.999	0.000
GLYCEROL		0.999	0.000	0.000	0.000
TIO <sub>2</sub>		0.000	0.000	0.000	0.000
SALTK		0.000	0.000	0.000	0.000
METOH		0.000	0.000	0.000	0.000
METHYL		0.001	0.000	0.000	0.000
ACID		0.000	0.000	0.000	0.000
BASE		0.000	0.000	0.000	0.000

## 4.4 Comparison

### 4.4.1 Economic comparison

Economic assessments of 1,3-PDO production from crude glycerol via chemical and biological methods are given in **Tables 28 and 29**. As seen in the tables, the capital cost of chemical production is lower than the biological production. The main contribution is R-201 units that are used for fermentation. Since the biological fermentation takes a long reaction time and is performed at low concentrations of glycerol, which require a substantial amount of water to dilute the system, this makes the biological fermentation tanks big and demands a lot of tanks to function as a continuous process resulting in the high equipment and installed costs while chemical production is expensive from special materials due to the use of Inconel as a shell material. However, there are fewer tanks and smaller size means lower installation costs. Furthermore, separation of the high amount of water also increases operating and utility costs in biological route.

Moreover, chemical production generates more revenue than biological production, as not only the main product can be sold, but also the by-products (**Fig. 13**). **Table 29** shows that the chemical production offers the possibility of higher return on investment when compared to biological production as seen from the NPV, IRR, and PI values. Furthermore, the pay-out-period of the chemical production is shorter than the biological production which means that the chemical production can reach the brake-even point faster than biological production.

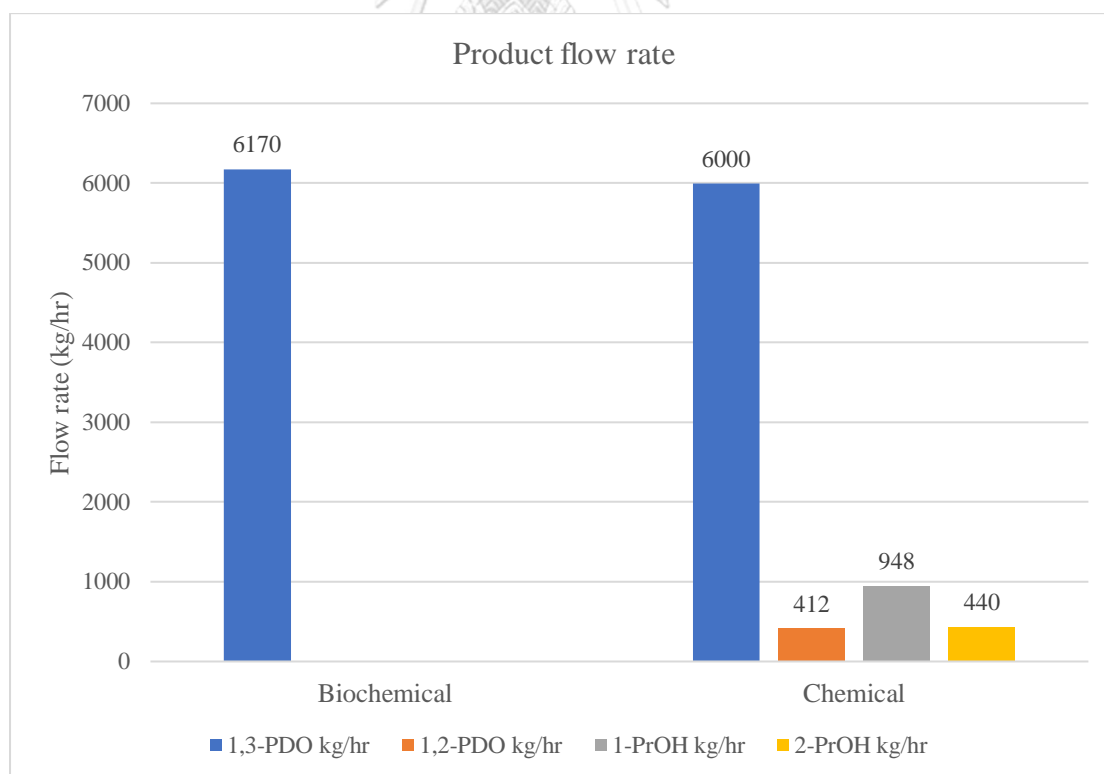


**Table 28.** Cost summary of biological and chemical production

Parameter	unit	Biological	Chemical
Total Operating Cost	Million USD/Year	174	228
Total Raw Materials Cost	Million USD/Year	92.6	173
Total Utilities Cost	Million USD/Year	60.3	28.2
Total Product Sales	Million USD/Year	319	423
Equipment Cost	Million USD	39.1	45.7
Total Installed Cost	Million USD	57.9	56.9
Total Project Capital Cost	Million USD	81.6	71.9

**Table 29.** Economic parameters and value of biological and chemical production

Parameter	unit	Biological	Chemical
NPV (Net Present Value)	Million USD	430	604
IRR (Internal Rate of Return)	Percent	77.4	89.2
PO (Pay-out-period)	Period	2.99	2.58
PI (Profitability Index)		1.33	1.34

**Figure 13.** Product flow rate of biological and chemical production

#### 4.4.3 Energy utilization comparison

Energy consumption (SEC) of 1,3-PDO production from crude glycerol via chemical and biological methods are summarized in **Table 30**. As seen in the table, the chemical production is more energy efficient than biological production since the production rate of 1,3-PDO for both productions is not significantly different. There, the main factor affecting the SEC value is the energy used. As mentioned above, biological production requires large amounts of water. Consequently, the purification unit requires much energy to evaporate the water from the product.

**Table 30.** SEC comparison between biological and chemical production

Parameter	unit	Biological	Chemical
1,3-PDO	kg/hr	6,170	6,000
Utility usage	kW	135,000	84,600
SEC	kw*hr/kg	22.3	14.1

#### 4.4.2 CO<sub>2</sub> emission comparison

As indicated in **Table 31**, the CO<sub>2</sub> emission from chemical production is 2.4 times lower than that of biological production. This observation can be deduced since 1) the chemical production does not emit carbon dioxide in the reaction and 2) the chemical production does not require an enormous amount of energy to evaporate a large amount of water like biological production.

**Table 31.** CO<sub>2</sub> emission comparison between biological and chemical catalytic production

Parameter	unit	Biological	Chemical
Direct CO <sub>2</sub> emission	tons/year	11,400	0
Indirect CO <sub>2</sub> emission	tons/year	222,000	98,700
Total CO <sub>2</sub> emission	tons/year	233,400	98,700

## Chapter 5

### Conclusions

#### 5.1 Comparison process conclusions

The production of 1,3-PDO via chemical and biological methods have been both successfully simulated. The main product purity, e.g., 1,3- PDO meets the salable specification. The production rate of the 1,3-PDO is not significantly different, but energy consumption, SEC value, and CO<sub>2</sub> emissions relative to chemical production are approximately half of the biological production. Furthermore, the economic performance appears to be higher in the chemical method than the biological one.

According to the analyses, chemical production is clearly another attractive investment option. However, chemical production still uses high pressure for fermentation reactions. If chemical production can be undertaken at low to moderate pressure, the biological production could easily be substituted by the chemical production.

#### 5.2 Recommendations

##### 5.2.1 Chemical production

- Reactor shell require special materials in order to operate at high pressure. If the pressure can be brought down, the cost of the equipment can be decreased.
- The cost of catalysts is expensive due to the use of expensive noble metals. If it can change the catalyst or use fewer quantities, it can reduce the cost of the raw material.

### 5.2.2 Biological production

- This process takes a long reaction time, which requires a large number of tanks to function as a continuous process. If it can reduce the reaction time, it can reduce the size and number of tanks that affect the cost of materials and installation costs.

- Since bacteria can not react well at high concentrations, thus a large amount of water is required for dilution. This results in the need for a large tank, and a lot of energy to evaporate water. Moreover, some products cannot be distilled because of the excessive water ratio. Therefore, if bacteria can be developed to react at high concentrations, it can reduce Equipment and installation costs from the smaller size of the fermentation tank, reduce utility costs from the evaporation process, and increase product sales that may be refined further.

## Appendix

### Stacker batch reactor

Total reactor (batch) = Total time (h) x Set of batches (set/h) x Number of batch (batch/set)

Total time (h) = Reaction time (h) + Uploading time (h) + Unloading time (h)

Set of batch (set/h) = 1/ (Unloading time (h))

Number of batch (batch/set) = Volume flow rate (L/h)/ (Set of batch x Liquid loading x Volume of reactor)

### Calculate total reactor

Chemical production:

Assume: Uploading time = Unloading time = 30 mins., Liquid loading = 75%,

Reactor size = 30,000 L, Reaction time = 4 h.

Total time = 4 + 0.5 + 0.5 = 5 h.

Set of batch = 1/ (0.5) = 2 set/h.

Number of batch = 44,257/ (2 x 0.75 x 30,000) = 0.984 = 1 batch/set

Total reactor = 5 x 2 x 1 = 10 batch

Biological production:

Assume: Uploading time = Unloading time = 30 mins., Liquid loading = 75%,

Reactor size = 75,000 L, Reaction time = 20 h.

Total time = 20 + 0.5 + 0.5 = 21 h.

Set of batch = 1/ (0.5) = 2 set/h.

Number of batch = 107,628 / (2 x 0.75 x 75,000) = 0.957 = 1 batch/set

Total reactor = 21 x 2 x 1 = 42 batch

Reactor shell material

Chemical production: Inconel

Biological production: SS316

Economic summary

Project summary basis:

Description	Units	
<b>Time period</b>		
Operating Hours per Period	Hours/Year	8,770
Number of Weeks per Period	Weeks/Year	52
Number of Periods for Analysis	Year	20
<b>Capital costs parameters</b>		
Working Capital Percentage	Percent/Year	5
<b>Operating costs parameters</b>		
Operating Supplies (lump-sum)	USD/Year	0
Laboratory Charges (lump-sum)	USD/Year	0
User Entered Operating Charges (as percentage)	Percent/Year	25
Operating Charges (Percent of Operating Labor Costs)	Percent/Year	25
Plant Overhead (Percent of Operating Labor and Maintenance Costs)	Percent/Year	50
G and A Expenses (Percent of Subtotal Operating Costs)	Percent/Year	8
<b>General investment parameters</b>		
Tax Rate	Percent/Year	40
Interest Rate	Percent/Year	20
Economic Life of Project	Year	20
Salvage Value (Fraction of Initial Capital Cost)	Percent	20
Depreciation Method	Straight Line	
<b>Escalation</b>		
Project Capital Escalation	Percent/Year	5
Products Escalation	Percent/Year	5
Raw Material Escalation	Percent/Year	3.5
Operating and Maintenance Labor Escalation	Percent/Year	3
Utilities Escalation	Percent/Year	3

## Project result summary:

Description	Units	Chemical	Biological
Total Project Capital Cost	Million USD	71.9	81.6
Total Raw Materials Cost	Million USD/Year	173	92.6
Total Products Sales	Million USD/Year	423	319
Total Operating Labor and Maintenance Cost	Million USD/Year	6.13	5.33
Total Utilities Cost	Million USD/Year	28.2	60.3
Total Operating Cost	Million USD/Year	228	174
Operating Labor Cost	Million USD/Year	1.18	1.18
Maintenance Cost	Million USD/Year	4.94	4.14
Operating Charges	Million USD/Year	0.30	0.30
Plant Overhead	Million USD/Year	3.06	2.66
Subtotal Operating Cost	Million USD/Year	211	161
G and A Cost	Million USD	16.9	12.9

## Engineering summary:

Description	Chemical		Biological	
	Total cost (USD)	Manhours (H)	Total cost (USD)	Manhours (H)
Basic Engineering	1,350,000	11,400	1,540,000	13,000
Detail Engineering	3,280,000	30,200	4,240,000	38,500
Material Procurement	1,100,000	0	1,100,000	0
Home Office	157,000	1,530	357,000	3,460
Total Design, Eng, Procurement Cost	5,880,000	0	7,240,000	0

## Operating labor and maintenance costs:

Description	Units	Chemical	Biological
Operating Labor			
Operators per Shift		5	5
Unit Cost	USD/Operator/H	20	20
Total Operating Labor Cost	USD/Year	876,000	876,000
Maintenance			
USD/8000 Hours		4,510,000	3,780,000
Total Maintenance Cost	USD/Year	4,940,000	4,140,000
Supervision			
Supervisors per Shift		1	1
Unit Cost	USD/Supervisor/H	35	35
Total Supervision Cost	USD/Year	307,000	307,000

## Utility resource summary:

Description	Fluid	Rate Units	Chemical	Biological	Cost Units	Chemical	Biological
Electricity		KW	953	5,630	USD/H	57.2	337
AP-UTIL-CHILL	Water	BTU/H	17,800,000	7,920,000	USD/H	83.0	37.0
AP-UTIL-CW	Water	BTU/H	121,000,000	114,000,000	USD/H	45.2	42.6
AP-UTIL-HP	Steam	BTU/H	69,400,000	287,000,000	USD/H	1300	5,360
AP-UTIL-LP	Steam	BTU/H	19,700,000	4,530,000	USD/H	275	63.4
AP-UTIL-MP	Steam	BTU/H	32,000,000	28,200,000	USD/H	479	423
AP-UTIL-REFRIG	Propane	BTU/H	-	1,130,000	USD/H	-	305
AP-UTIL-SHP	Steam	BTU/H	25,200,000	7,880,000	USD/H	974	304

## Raw material summary:

Description	Rate Units	Chemical	Biological	Cost Units	Chemical	Biological
Phosphoric acid (ACID)	LB/H	902.	902	USD/H	331	332
Glycerol (GLYM)	LB/H	2,430	46.7	USD/H	2,510	48.3
Crude glycerol (CG)	LB/H	27,600	27,600	USD/H	6,870	6,870
Hydrogen (H2M)	LB/H	629	45.5	USD/H	171	990
Water (WATER)	LB/H	-	212,000	USD/H	-	2,310
Catalyst (CATM)	LB/H	925	-	USD/H	9,860	-



## Chemical production

Description	Units	Total Cost	Design, Eng, Procurement	Construction		Construction Manpower	Construction Indirects
				Material	Manhours		
Purchased Equipment	USD	48,900,000	-	48,900,000	-	-	-
Equipment Setting	USD	148,000	-	-	4,350	148,000	-
Piping	USD	5,380,000	-	4,170,000	36,300	1,210,000	-
Civil	USD	696,000	-	398,000	11,000	298,000	-
Steel	USD	577,000	-	492,000	2,700	84,600	-
Instrumentation	USD	4,700,000	-	3,970,000	21,600	733,000	-
Electrical	USD	1,120,000	-	938,000	5,690	185,000	-
Insulation	USD	924,000	-	474,000	17,800	451,000	-
Paint	USD	176,000	-	52,700	4,960	124,000	-
Other	USD	15,800,000	5,880,000	6,090,000	-	-	3,790,000
Subcontracts	USD	-	-	-	-	-	-
G and A Overheads	USD	2,180,000	-	1,967,000	-	97,000	114,000
Contract Fee	USD	2,150,000	265,000	1,350,000	-	247,000	289,000
Escalation	USD	-	-	-	-	-	-
Contingencies	USD	14,900,000	1,110,000	12,400,000	-	644,000	755,000
Special Charges	USD	-	-	-	-	-	-
Total Project Cost	USD	97,600,000	-	-	-	-	-
Adjusted Total Project Cost	USD	71,900,000	-	-	-	-	-

## Biological production

Description	Units	Total Cost	Design, Eng, Procurement	Construction Material	Construction Manhours	Construction Manpower	Construction Indirects
Purchased Equipment	USD	42,000,000	-	42,000,000	-	-	-
Equipment Setting	USD	423,000	-	-	12,400	423,000	-
Piping	USD	7,390,000	-	5,050,000	70,400	2,340,000	-
Civil	USD	1,710,000	-	1,000,000	26,600	710,000	-
Steel	USD	1,450,000	-	1,240,000	6,710	210,000	-
Instrumentation	USD	8,440,000	-	6,980,000	43,100	1,460,000	-
Electrical	USD	3,780,000	-	3,340,000	13,400	439,000	-
Insulation	USD	2,010,000	-	1,030,000	38,500	973,000	-
Paint	USD	244,000	-	75,800	6,770	168,000	-
Other	USD	21,300,000	7,240,000	6,220,000	-	-	7,800,000
Subcontracts	USD	-	-	-	-	-	-
G and A Overheads	USD	2,440,000	-	2,010,000	-	202,000	234,000
Contract Fee	USD	2,660,000	304,000	1,380,000	-	450,000	522,000
Escalation	USD	-	-	-	-	-	-
Contingencies	USD	16,900,000	1,360,000	12,700,000	-	1,330,000	1,540,000
Special Charges	USD	-	-	-	-	-	-
Total Project Cost	USD	111,000,000	-	-	-	-	-
Adjusted Total Project Cost	USD	81,600,000	-	-	-	-	-

## Product summary:

Description	Rate Units	Chemical	Biological	Cost Units	Chemical	Biological
1,3-propanediol (P-1,3PDO)	LB/H	13,200	13,600	USD/H	38,200	39,400
1,2-propanediol (P-1,2PDO)	LB/H	911	-	USD/H	1,880	-
N-propanol (P-1PROH)	LB/H	2,110	-	USD/H	2,120	-
Isopropanol (P-2PROH)	LB/H	1,020	-	USD/H	1,150	-
Methanol (P-MET)	LB/H	111	111	USD/H	142	142
Hydrogen (P-H2)	LB/H	8.68	2.59	USD/H	2.00	21.3
Glycerol (P-GLY)	LB/H	2,450	54.1	USD/H	2,530	55.9
Methyl oleate (P-METHYL)	LB/H	827	829	USD/H	780	782
Salt (SALT)	LB/H	1,060	1,060	USD/H	718	718
Dry ice (P-DRYICE)	LB/H	-	1,750	USD/H	-	1,030
Catalyst (P-CAT)	LB/H	544	-	USD/H	687	-
Water treatment (W-WATERX)	LB/H	10,000	223,000	USD/H	-0.203	-5,730

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