Glycerol Carbonate Production from Glycerol and Diethyl Carbonate: A Comparative Study Between A Separated Reaction/Distillation (SRD) Process and A Reactive Distillation (RD) Process

Mr. Chayanin Sriharuethai

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 2022

การผลิตกลีเซอรอลคาร์บอเนตจากกลีเซอรอล และไดเอทิลคาร์บอเนต การศึกษาเปรียบเทียบระหว่างกระบวนการแบบแยกส่วนปฏิกิริยากับกระบวนการกลั่น และ กระบวนการกลั่นแบบมีปฏิกิริยา

นายชญานิน ศรีหฤทัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2565

Thesis Title	Glycerol Carbonate Production from Glycerol and Diethyl Carbonate: A Comparative Study Between A Separated Reaction/Distillation (SRD) Process and A Reactive Distillation (RD) Process
By	Mr. Chayanin Sriharuethai
Field of Study	Chemical Engineering
Thesis Advisor	Assistant Professor PONGTORN CHAROENSUPPANIMIT, Ph.D.

Accepted by the FACULTY OF ENGINEERING, Chulalongkorn University in Partial Fulfillment of the Requirement for the Master of Engineering

.... Dean of the FACULTY OF ENGINEERING
(Professor SUPOT TEACHAVORASINSKUN, Ph.D.)

THESIS COMMITTEE

.... Chairman
(AKAWAT SRIRISUK, Ph.D.)
.... Thesis Advisor
(Assistant Professor PONGTORN CHAROENSUPPANIMIT, Ph.D.)
.... Examiner
(Professor SUTTICHAI ASSABUMRUNGRAT, Ph.D.)
.... Examiner
(KRITCHART WONGWAILIKHIT, Ph.D.)
.... External Examiner
(Associate Professor Kanokwan Ngaosuwan, Ph.D.)

ชญานิน ศรีหฤทัย : การผลิตกลีเซอรอลคาร์บอเนตจากกลีเซอรอล และไดเอทิลคาร์บอเนต การศึกษาเปรียบเทียบระหว่างกระบวนการแบบแยกส่วนปฏิกิริยากับกระบวนการกลั่นและ กระบวนการกลั่นแบบมีปฏิกิริยา. (Glycerol Carbonate Production from Glycerol and Diethyl Carbonate: A Comparative Study Between A Separated Reaction/Distillation (SRD) Process and A Reactive Distillation (RD) Process) อ.ที่ปรึกษาหลัก : ผศ. ดร.พงศ์ธร เจริญศุภนิมิตร

กลีเซอรอลคาร์บอเนต เป็นหนึ่งในผลิตภัณฑ์ที่มีมูลค่าสูงที่สามารถผลิตจากกลีเซอรอลซึ่งเป็นผลิตภัณฑ์ข้างเคียงจากอุตสาหกรรมการผลิตไบโอดีเซล ในงานวิจัยนี้จะเป็นการออกแบบกระบวนการแบบต่อเนื่องในการผลิตกลีเซอรอลคาร์บอเนตผ่านปฏิกิริยาทรานส์เอสเทอร์ริฟิเคชันจากกลีเซอรอลดิบ และไดเอทิลคาร์บอเนต โดยจะใช้โปรแกรม Aspen Plus ในการจำลองกระบวนการ ในงานนี้จะมีการศึกษากระบวนการสองแบบ คือ 1. กระบวนการแบบแยกส่วนปฏิกิริยากับกระบวนการกลั่น ซึ่งจะประกอบด้วยเครื่องปฏิกรณ์แบบถังกวนต่อเนื่องสำหรับการทำปฏิกิริยา และหอกลั่นที่ใช้สำหรับการแยกสารให้บริสุทธิ์ และ 2. กระบวนการกลั่นแบบมีปฏิกิริยาซึ่งจะประกอบไปด้วยหอกลั่นแบบมีปฏิกิริยาที่จะสามารถทำปฏิกิริยา และทำการกลั่นได้ภายในหอเดียวกัน, และหอกลั่นแบบธรรมดาเพื่อใช้ในการกลั่นแยกสารให้บริสุทธิ์ หลังจากทำการออกแบบเสร็จสิ้น จะมีการหาสภาวะของกระบวนการที่ทำให้กระบวนการมีประสิทธิภาพสูงที่สุด โดยการเชื่อมต่อโมเดลที่สร้างขึ้นในโปรแกรม Aspen Plus กับโปรแกรม MATLAB และใช้ขั้นตอนวิธีเชิงพันธุกรรม ในการหาสภาวะที่ทำให้กระบวนการมีประสิทธิภาพสูงที่สุด จากผลการทดลอง จะแสดงให้เห็นว่ากระบวนการกลั่นแบบมีปฏิกิริยาจะให้ผลที่ดีกว่ากระบวนการแบบแยกส่วนปฏิกิริยากับกระบวนการกลั่น ทั้งในแง่ของประสิทธิภาพ และผลทางเศรษฐศาสตร์ โดยกระบวนการกลั่นแบบมีปฏิกิริยาสามารถเลื่อนสมดุลของปฏิกิริยาไปข้างหน้า ทำให้กลีเซอรอลสามารถแปลงมาเป็นผลิตภัณฑ์ได้มาก นอกจากนั้นเมื่อพิจารณาผลทางเศรษฐศาสตร์ จะพบว่ากระบวนการกลั่นแบบมีปฏิกิริยาให้ผลที่ดีกว่าในแง่ของ ต้นทุนการลงทุนที่ต่ำกว่า, ค่าใช้จ่ายในการดำเนินงานที่ต่ำกว่า, ค่าใช้จ่ายต่อปีที่ต่ำกว่า, ใช้ระยะเวลาในการคืนทุนน้อยกว่า, และมีอัตราผลตอบแทนการลงทุนที่สูงกว่า

สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต	....
ปีการศึกษา	2565	ลายมือชื่อ อ.ที่ปรึกษาหลัก	....

6470012621 : MAJOR CHEMICAL ENGINEERING

KEYWORD: Glycerol carbonate, Reactive distillation, Process design, Process optimization, Techno-economics analysis

Chayanin Sriharuethai : Glycerol Carbonate Production from Glycerol and Diethyl Carbonate: A Comparative Study Between A Separated Reaction/Distillation (SRD) Process and A Reactive Distillation (RD) Process. Advisor: Asst. Prof. PONGTORN CHAROENSUPPANIMIT, Ph.D.

Glycerol carbonate is one of the valuable products that can be converted from glycerol produced in the biodiesel industry. In this work, the continuous process of glycerol carbonate production via transesterification from crude glycerol and diethyl carbonate will be developed using Aspen Plus simulation. There are two processes to be considered. First, the separated reaction/distillation (SRD) process consists of a continuously stirred tank reactor for the reaction section and a distillation column for the purification section. Second, the reactive distillation (RD) process consists of a reactive distillation column that can accommodate both the reaction and purification in a single column, and a conventional distillation column for the purification section. After the design is complete, the optimization will be done by connecting the model in Aspen Plus to MATLAB and using the Genetic Algorithm to optimize the model. The results show that the RD process is superior to the SRD process in terms of both performance and economics. The RD process can shift the reaction equilibrium, resulting in high conversion and a large quantity of product. Moreover, when considering the economic value, the RD process is also better due to its lower total capital cost, lower operational cost, lower total annual cost, shorter payback period, and higher %IRR.

Field of Study:	Chemical Engineering	Student's Signature ....
Academic Year:	2022	Advisor's Signature ....

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my thesis advisor, Asst. Prof. Dr. Pongtorn Charoensuppanimit, for his excellent guidance, care, and the conducive research atmosphere he provided. His encouragement and insightful comments have inspired me to broaden my research from various perspectives. I am extremely grateful to him for the time he spent reviewing my thesis work.

I am also grateful to my thesis chairman, Dr. Akawat Sirisuk, as well as the members of my thesis committee: Prof. Dr. Suttichai Assabumrungrat, Assoc. Prof. Dr. Kanokwan Ngaosuwan, and Dr. Kritchart Wongwailikhit. Their insightful comments and suggestions have made significant contributions to the improvement of this work.

Finally, I am deeply grateful to my family and friends who have consistently provided me with unwavering support, motivation, and comprehension during my academic journey.

Chayanin Sriharuethai

TABLE OF CONTENTS

Page

LIST OF TABLES

Page

LIST OF FIGURES

Page

CHAPTER 1

INTRODUCTION

1.1 Background

Glycerol is the major byproduct of biodiesel production through the transesterification of vegetable oils or animal fat with alcohol. In the last two decades, biodiesel industries have risen significantly due to the global demand of sustainable alternatives to petrochemicals and oil-derived fuels. A large and rapidly growing of biodiesel at present causes a large amount of glycerol, which is inexpensive to sell so that the glycerol can be transformed into a high-value product, e.g., Propanediol for automotive antifreeze additive, Acetals for fuel additive in gasoline, and Epichlorohydrin for converting to epoxy resins [1, 2].

Glycerol carbonate is one of the high-value products that can be produced from glycerol by transesterification reaction. Glycerol carbonate can be used as a solvent and a surfactant in the beauty and skincare businesses. Moreover, it may also be used as an electrolyte for lithium batteries and a reactant for synthesizing polymers such as polyesters, polyurethanes, and polycarbonates [3].

There are many methods for transesterification reactions, such as conventional stirred tank reactors, bio-processing processes [4], membrane reactors [5], microreactors [6], reactive distillation [7], etc. The reactive distillation process has drawn increased attention in recent years from industrial and academic research due to its significant potential for process intensification, especially in equilibrium reactions, as it can shift equilibrium and lead to higher conversions and selectivity. Moreover, it could also reduce investment and operational costs [8].

The transesterifications of glycerol with dimethyl carbonate using reactive distillation were studied by Bor-Yih Yu [9], showing that the reactive distillation process can reduce the total annual cost by about 33.1% and reduce CO_2 emission by 36.1% compared with the separated reaction/distillation process. However, there have not been any studies on glycerol transesterifications with diethyl carbonate using reactive distillation, so this work will focus on that area.

The process modelling program, namely Aspen Plus, will be utilized in this work to simulate the continuous process of glycerol carbonate production from glycerol and diethyl carbonate, as well as the Aspen Economic Analyzer for evaluating the economics of the process.

1.2 Objectives of this research

1.2.1 To develop a continuous process for glycerol carbonate production from crude glycerol and diethyl carbonate using a conventional stirred tank reactor and reactive distillation.

1.2.2 To provide the economic analysis of the process.

1.2.3 To provide a comparative study of the separated reaction/distillation process (SRD) process and reactive distillation (RD) process.

1.3 Scopes of this research

1.3.1 The crude glycerol from biodiesel production will be pretreated to get purified glycerol.

1.3.2 The purified glycerol and diethyl carbonate will be the reactant of the transesterification reaction to be converted into glycerol carbonate and ethanol as products.

1.3.3 The reaction takes place at a temperature not exceeding 80 ^{O}C to avoid side reactions, and the catalyst used in this work is Ce-NiO.

1.3.4 The process model of glycerol carbonate production is simulated by Aspen Plus, and the economic analysis is evaluated by Aspen Economic Analyzer.

1.3.5 The separated reaction/distillation (SRD) process and the reactive distillation (RD) process of glycerol carbonate production will compare on the topic of performance, economics, and environmental impact.

CHAPTER 2

THEORY AND LITERATURE REVIEWS

This chapter will provide the related theory and literature review along with the useful information for the research, including the general information on the chemical used, the reactive distillation information, and the past literature, which will help to simulate the continuous process of glycerol carbonate production in this work.

2.1 Biodiesel production

Biodiesel is a monoalkyl ester of long-chain fatty acids derived from renewable lipid feedstocks, such as vegetable oils or animal fats. Biodiesel is typically used as pure (B100) or blended with petrodiesel (B5, B20) for diesel engines due to their similar properties [10].

The current approach for biodiesel production in a biorefinery plant is through the transesterification of vegetable oils. First, the oil is treated to reduce acidity. Then, excess methanol and a base catalyst are added to react with the oil for transesterification reactions. Phase separation occurs after the reaction proceeds; the bottom phase is rich in glycerol but also contains methanol and the base catalyst, whereas the upper phase corresponds to biodiesel and methanol. Following separation, methanol is recovered through the distillation process. Afterwards, crude glycerol and biodiesel are purified, resulting in pure glycerol and biodiesel for commercial use. The simplified procedure for producing biodiesel from vegetable oils through transesterification is shown in **Figure 1** [1].

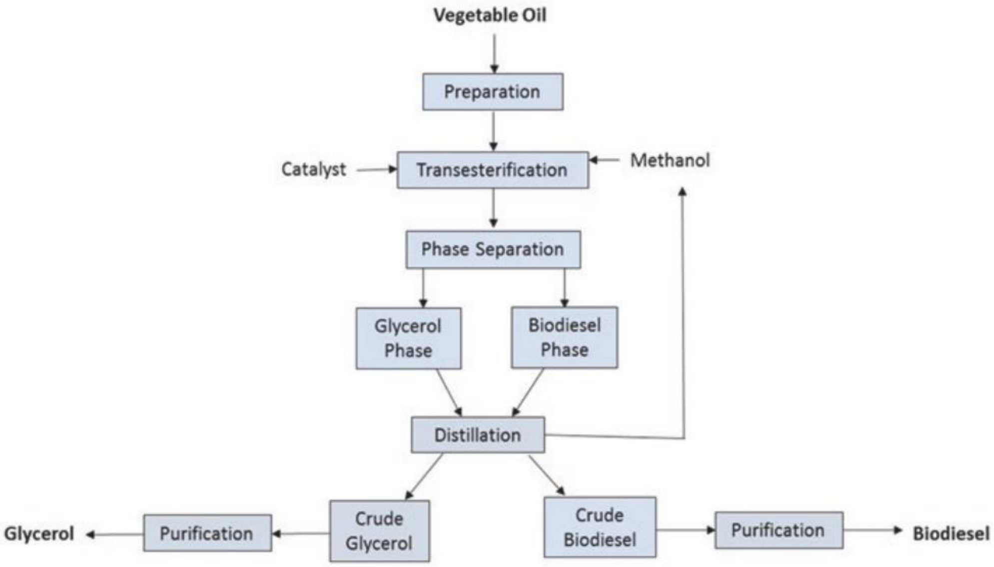

Figure 1 The scheme of biodiesel production through the transesterification of vegetable oil [1].

2.2 Chemical

2.2.1 Glycerol (GL)

The concern of biodiesel production is its byproduct; every 100 kg of biodiesel produced, 10 kg of crude glycerol is typically produced as a byproduct, which has low economic value and leads to an oversupply of glycerol [11]. For this reason, scientists have been working to find ways to turn glycerol into a more valuable product, as shown in **Figure 2**. The number of published scientific articles with glycerol as a keyword increased significantly between the years 1996 and 2016 [1].

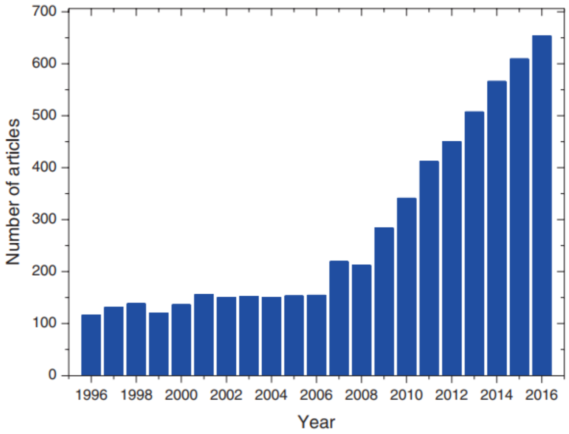

Figure 2 The number of published scientific articles with glycerol as a keyword [1].

An alternate method for disposing of glycerol and solving its surplus issues is by transforming it into value-added products which have a wide application in the fields of personal care, pharmaceutical industries, food industries, chemical solvent, chemical intermediates, etc. [12, 13]. The example of value-added products from glycerol and its routes are shown in **Figure 3** [14].

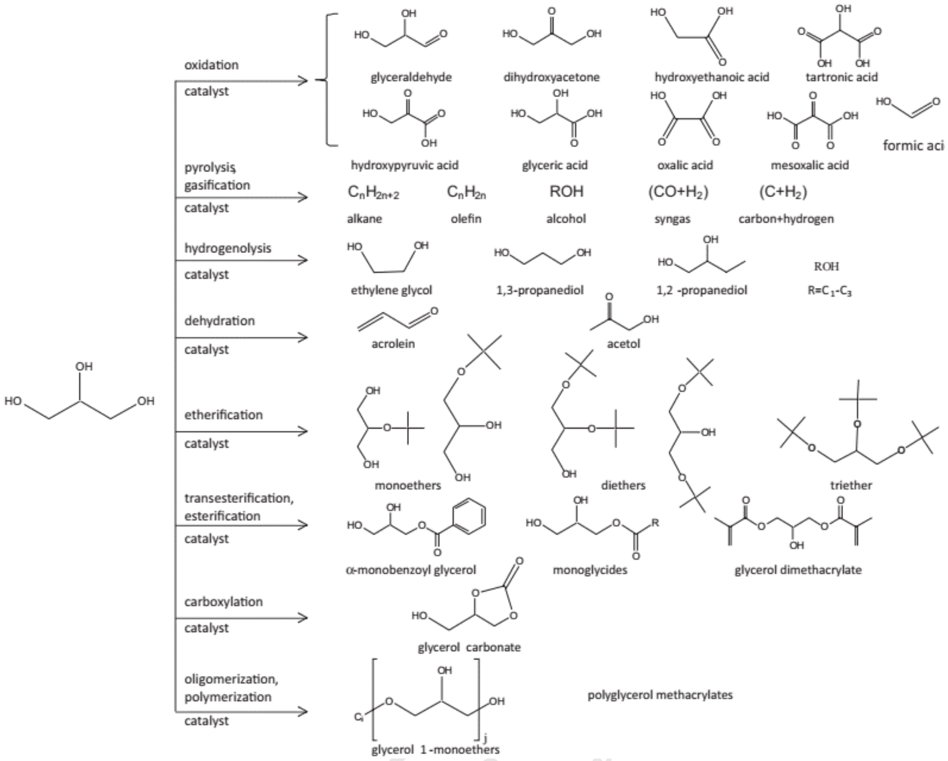

Figure 3 Value-added products from glycerol [14].

2.2.2 Diethyl carbonate (DEC)

Diethyl carbonate is the organic compound in the carbonate family, which has recently gained interest due to its green properties (polarity, low toxicity, biodegradability). Diethyl carbonate is a potential replacement for methyl tert-butyl ether (MTBE) as a gasoline additive because it can increase gasoline's octane number and emit fewer particles than MTBE. Additionally, the synthesis of diethyl carbonate is also a green route since it can be converted from CO_2 via carbonylation, which helps utilize carbon dioxide. Other routes for the synthesis of diethyl carbonate are oxidative carbonylation of ethanol, trans-esterification of carbonate, and alcoholysis of urea [15, 16].

2.2.3 Glycerol carbonate (GC)

Glycerol carbonate is a nonflammable, nontoxic, biodegradable, water-soluble chemical with high flash point properties. It is widely used in the chemical industry as a solvent, surfactant, detergent, electrolyte for batteries, additive to cosmetics, additive to diesel, and chemical intermediate [15]. Due to its higher value compared to glycerol, glycerol carbonate has become an intriguing value-added product derived from glycerol. The synthesis of glycerol carbonate from glycerol can occur via different routes and feedstocks, as shown in **Figure 4** [16].

The first route involves a reaction with phosgene ($COCl_2$), which is dangerous due to the generation of highly toxic gas. The second route requires the use of urea as a feedstock, which is necessary to continuously remove ammonia to shift the equilibrium. The third route involves carboxylation with CO/CO_2, which has gained the attention of researchers due to its use of two waste streams as reactants to provide valuable products, but the reaction yield is low. Therefore, this work will focus on the last route, which involves the transesterification of glycerol using dimethyl carbonate or diethyl carbonate as a feedstock.

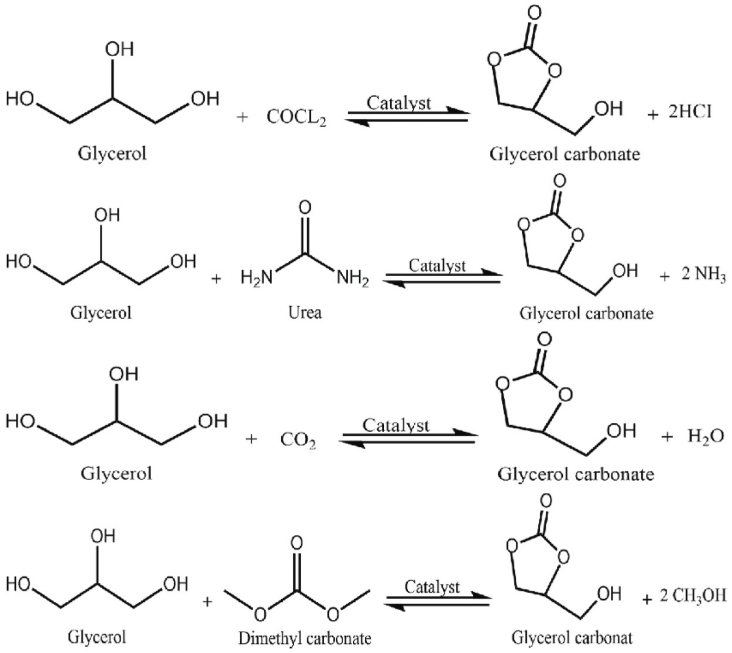

Figure 4 Different routes for producing glycerol carbonate [16].

2.2.4 Ethanol (EtOH)

Ethanol or Ethyl alcohol is one of the most common organic compounds used in industrial and consumer products. Most of the ethanol produced globally is derived by fermenting the sugar in the starches of grains such as corn, sorghum, and barley, as well as the sugar in sugar cane and sugar beets [17]. The characteristic of ethanol is a colorless liquid and flammable compound. Ethanol can be used to produce drugs, plastics, lacquers, plasticizers, cosmetics, etc. Furthermore, it is also used in commercial products such as beverages, perfumes, mouthwashes, hand sanitizer, rubbing alcohol, etc. [18].

2.3 Reactive distillation

Reactive distillation is the process which is a combination of a reactor and distillation column. In other words, reactive distillation can create chemical reactions and separation simultaneously in a single column. The first concept of reactive distillation was made public in 1921 by A.A. Backhaus [19], which was patented to produce ester in a continuous process. However, this concept wasn't used at that time.

After 60 years, the industrial use of the reactive distillation method has begun. In 1978, the Eastman-Kodak Company developed a reactive distillation process to produce high-purity of methyl acetate. Due to the existence of two azeotropes between methyl acetate and methanol and between methyl acetate and water, the conventional method for producing methyl acetate consisted of eight distillation columns. In contrast, the reactive distillation contains only a single column to produce high-purity methyl acetate, as shown in **Figure 5.** In addition, it was reported that the single reactive distillation column reduced five times energy consumption and capital investment costs less than the conventional process [20].

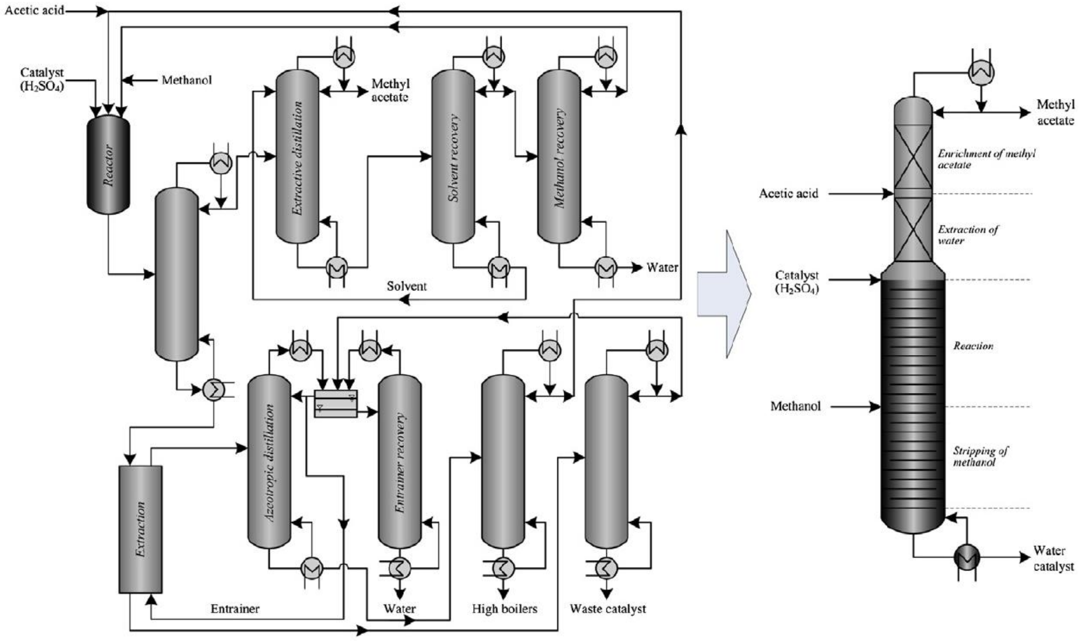

Figure 5 (left) Conventional process, (right) Reactive distillation process of methyl acetate production [20].

Reactive distillation has garnered a great deal of interest, particularly for chemical equilibrium-limited reactions that generally need a large excess of one of the reactants. The advantages of reactive distillation are as follows: [20]

- **Increased conversion** - In equilibrium-limited reactions, reactive distillation can increase conversion by continuously removing the product from the system. As a result, the reaction will go forward and achieve a higher conversion.
- **Increased selectivity** - For a system with a side reaction, continuous removal of main products from the reaction zone help reduce the opportunity for occurring undesired products.
- **Reduced energy consumption** - For exothermic reactions, the heat of the reaction can use directly to supply the heat of vaporization. For this reason, the energy required for the reboiler will be reduced.
- **Capital savings** – The investment cost is reduced due to the reactive distillation process is combined the reaction unit and separation unit in a single column.

- **Separation of close-boiling components** - A reactive entrainer can be employed to react with one of the components, resulting in an intermediate product with a boiling point possible for separation.

The partitions of the reactive distillation column can be divided into three parts consisting of a rectifying section, a reactive section, and a stripping section, as shown in **Figure 6** [21].

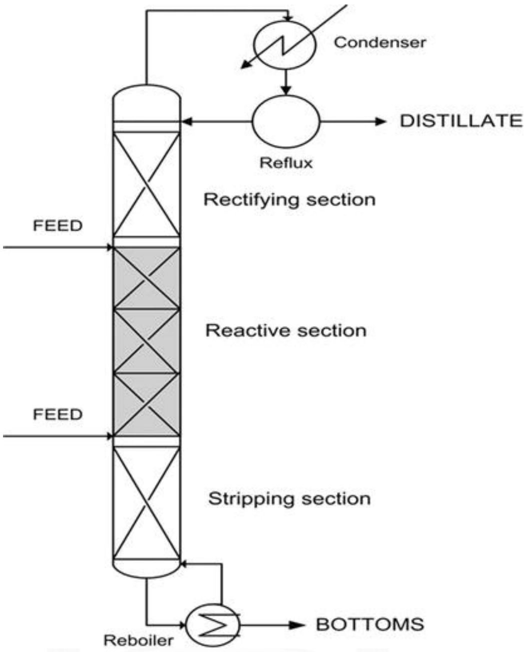

Figure 6 Schematic diagram of reactive distillation column [21].

2.4 Literature review

2.4.1 Crude glycerol pretreatment

According to Kanchanasuta et al. [22], crude glycerol obtained from the biodiesel industry typically contains approximately 83% glycerol. However, it also contains impurities such as water, ash, methanol, and matter organic non-glycerol (MONG). The matter organic non-glycerol (MONG) are constituents of free fatty acids, triglycerides, phospholipids, sterols, waxes, etc. It is necessary to remove these impurities to achieve a higher glycerol conversion during the reaction stage [23].

2.4.2 Reactive distillation of glycerol carbonate production from glycerol

N. Lertlukkanasuk et al. [24] studied the synthesis of glycerol carbonate using glycerol and urea as feedstock on the Co_3O_4/ZnO catalyst. The comparison of conventional processes and reactive distillation process shows that the conversion of glycerol can increase from 72.5% to 93.6% by using reactive distillation. In the same way, the overall energy consumption can also decrease from 0.324 to 0.215 kW/mol glycerol carbonate in a reactive distillation system.

Bor-Yih Yu et al. [9, 25] studied the economic and environmental analysis of the conventional process compared with the reactive distillation process on glycerol carbonate production from glycerol and dimethyl carbonate using zinc/lanthanum mixed-oxide (Zn_4La_1) as a catalyst. The results showed that the reactive distillation process required a lower total annual cost than the conventional process – 1,561 and 2,334 kUS$/year, respectively. Moreover, reactive distillation can reduce CO_2 emissions by about 36.1 % (0.207 kg CO_2/kg Glycerol carbonate) compared with the conventional process (0.322 kg CO_2/kg Glycerol carbonate).

2.4.3 Glycerol transesterification with diethyl carbonate

The glycerol carbonate production from diethyl carbonate and glycerol will be the reaction used in this study. The route of the reaction is shown in **Figure 7**.

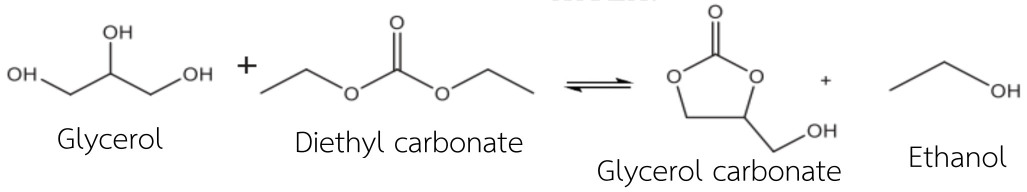

Figure 7 Glycerol transesterification with diethyl carbonate.

J. Zhang et al. [26] studied the kinetics of glycerol carbonate synthesis from glycerol and diethyl carbonate over Ce–NiO catalyst. First, the equilibrium constant (K_c) was calculated by experimenting the reaction in a 50 mL isothermal batch reactor in a temperature range of 338-358 K using a feed of glycerol and diethyl carbonate in a ratio of 1:3 and catalyst in the amount of 5 wt% of glycerol. The reaction time is 6 hours to confirm that reactions are in equilibrium. The measurement results of the concentration (mol/L) at equilibrium conditions versus temperature are shown in **Table 1**.

Table 1 Experimental data of the reaction equilibrium [26].

Temperature (K)	C_{A0}	C_{B0}	C_A	C_B	C_C	C_D
338	2.197	6.592	1.082	5.478	1.117	2.234
343	2.197	6.592	0.801	5.198	1.398	2.795
348	2.197	6.592	0.781	5.178	1.418	2.836
353	2.197	6.592	0.549	4.947	1.650	3.299
358	2.197	6.592	0.434	4.832	1.765	3.530

The experimental data were used to calculate the equilibrium constant based on **Eq.1**, and the result was found by linear fitting of Ln K_c versus 1/T shown in **Eq.2**; The unit of C is in mol/L, and T is in Kelvin.

$$K_C = \frac{C_{GC} C_{EtOH}^2}{C_{Gly} C_{DEC}} \quad \textbf{(1)}$$

$$\text{Ln } K_C = -\frac{13{,}918}{T} + 41 \quad \textbf{(2)}$$

Then, the reaction kinetics was developed by fitting the kinetic equation to the experimental data. The rate equation can be written as **Eq.3**, and the calculated Arrhenius equation can be shown as **Eq.4**.

$$-\frac{dC_{Gly}}{dt} = kC_{Gly}^2 C_{DEC} \quad \textbf{(3)}$$

$$k = k_r \exp\left(-\frac{E_a}{RT}\right) \quad \textbf{(4)}$$

Where, $k_r = 4.07E+11$

$E_a = 87.90$ kJ/mol.

Moreover, the author also reported the effect of conversion and selectivity on the reaction time and temperature, as shown in **Figure 8**. Therefore, the recommended condition for this reaction is a reaction time of 4-6 hours and a temperature of 353-358 K to avoid the occurrence of glycidol (GD) as an undesired product [26].

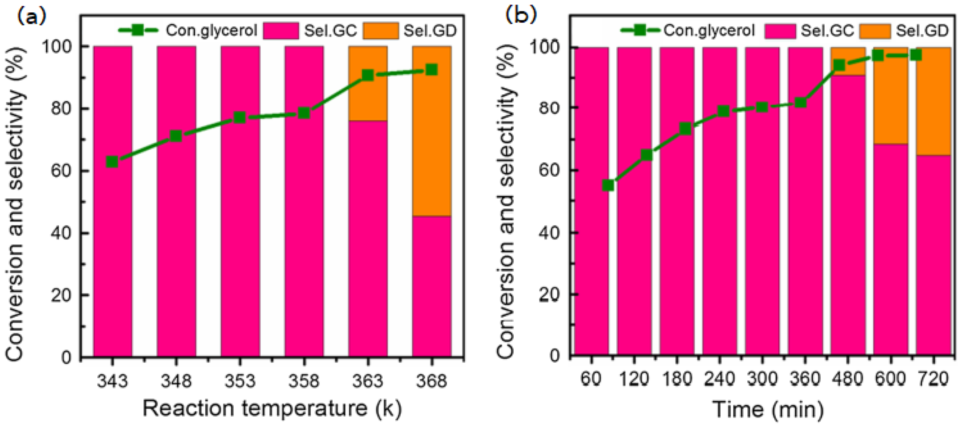

Figure 8 The effect of (a) Reaction temperature, (b) Reaction time on the conversion and selectivity [26].

J. Liu et al. [27] studied the liquid-liquid equilibrium of glycerol transesterification with diethyl carbonate at various temperatures, including 343.2 K, 363.2 K, 383.2 K, and 403.2 K. The experiment has resulted in two ternary systems consisting of glycerol – diethyl carbonate – glycerol carbonate, as shown in **Figure 9** and glycerol – diethyl carbonate – ethanol, as shown in **Figure 10**.

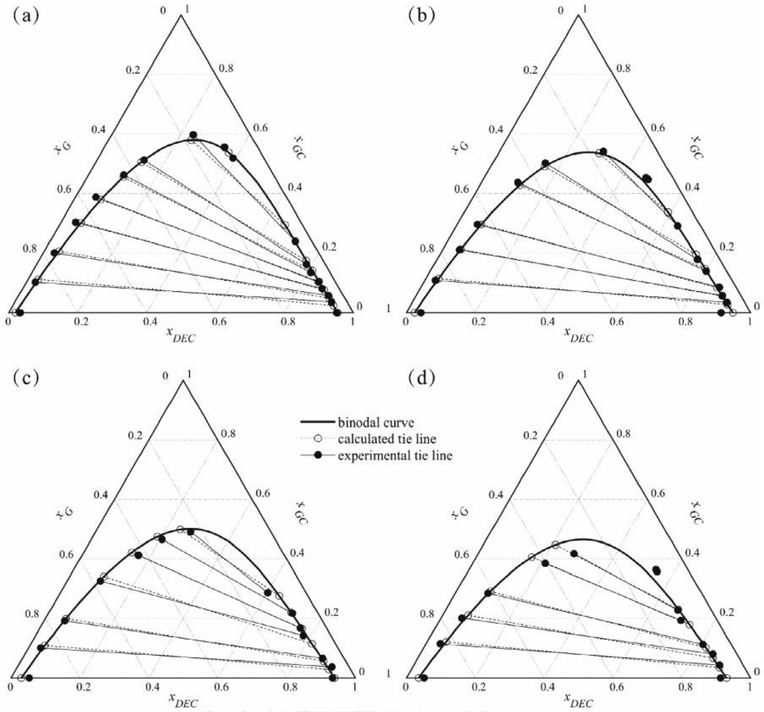

Figure 9 Ternary diagram of glycerol (G) – diethyl carbonate (DEC) – glycerol carbonate (GC) at temperature (a) 343.2 K, (b) 363.2 K, (c) 383.2 K, (d) 403.2 K [27].

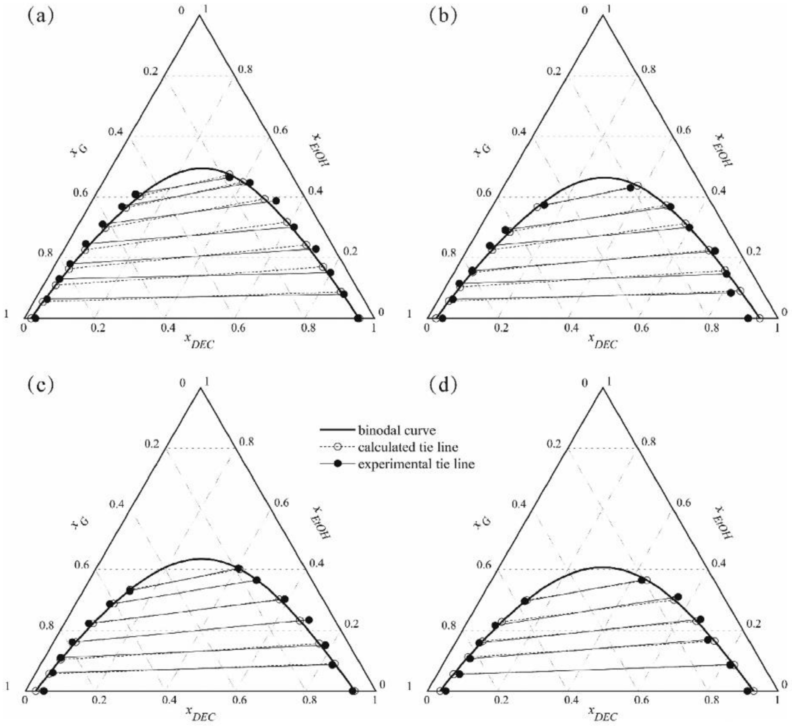

Figure 10 Ternary diagram of glycerol (G) – diethyl carbonate (DEC) – ethanol (EtOH) at temperature (a) 343.2 K, (b) 363.2 K, (c) 383.2 K, (d) 403.2 K [27].

According to **Figures 9, 10.** The open circles connected dash lines are representative of the calculated tie line, which come from fitting the experimental data with the NRTL model. The NRTL model is shown in **Eq.5**, and the estimated NRTL interaction parameters of this reaction are shown in **Table 2**.

$$\ln\gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_j x_j G_{ji}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ji} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k x_k G_{kj}} \right) \qquad \textbf{(5)}$$

Where, $\tau_{ji} = \Delta g_{ij} / RT; \ \left(\Delta g_{ii} = 0 \right)$

$$G_{ij} = \exp\left(-\alpha_{ij} \tau_{ij} \right); \ \left(\alpha_{ij} = \alpha_{ji} \right)$$

Table 2 The estimated NRTL binary interaction parameters (α_{ij} = 0.3) [27].

Component pair		Parameters	
i	j	Δg_{ij}, J/mol	Δg_{ji}, J/mol
Glycerol	Diethyl carbonate	8,741.34	6,556.00
Glycerol	Glycerol carbonate	-1,065.27	1,132.53
Glycerol	Ethanol	-1,571.84	5,211.05
Diethyl carbonate	Glycerol	2,700.05	3,556.15
Diethyl carbonate	Ethanol	-1,312.28	1,296.57
Glycerol carbonate	Ethanol	1,152.99	-5,701.16

2.4.4 Process optimization

Since process simulation requires the input of several variables into the program, it is necessary to figure out the optimal value for each variable so that the process can operate in a cost-effective way.

X. Gao et al. [28] find the optimum process configuration of the isopropyl acetate production model in Aspen Plus by using Genetic algorithms (GA) to minimize the total annual cost (TAC) as an objective function for optimization. The total annual cost (TAC) equation can show in the equation as follows.

$$\text{Total annual cost (TAC)} = \frac{\text{Total capital cost}}{\text{Payback period}} + \text{Total operating cost} \qquad \textbf{(6)}$$

S.R. Pandit et al. [29] have described the method to communicate Aspen Plus with MATLAB by using the ActiveX server as an intermediary for connection. MATLAB, which includes the optimization algorithm, will generate the input for the process and send it to Aspen Plus by ActiveX server. Then, Aspen Plus has to run the simulation and send the results back to MATLAB via the ActiveX server again. The Aspen Plus and MATLAB communication steps can be shown in **Figure 11**.

Furthermore, on the MATLAB community website (www.mathworks.com), Andrés F. [30] has shared the source code for connecting MATLAB with Aspen Plus via ActiveX server for making sensitivity analysis, which will serve as an example source code for linking these two programs in this study.

Figure 11 A block diagram illustrating the integration of Aspen Plus with MATLAB [29].

Genetic Algorithm (GA) is a heuristic optimization method inspired by the process of natural selection and genetics. The GA is used to find approximate solutions to complex problems by mimicking the mechanics of natural evolution, such as selection, reproduction, and mutation. The steps of GA for finding the optimal solution can be shown in **Figure 12**. The GA starts by creating the initial population and scoring which populations have a high probability of survival (the populations that produce a satisfactory solution). Then, the high-scoring populations are selected to generate the next generation according to the selection rule. The new generation can occur from two approaches. First, the crossover rules by combining two parents to form a new child, and the mutation rules by slightly changing the parent to create a new child. The method to create a new generation can be illustrated in **Figure 13**. Then, the new generation is scored and used to calculate the next generation in a loop [31].

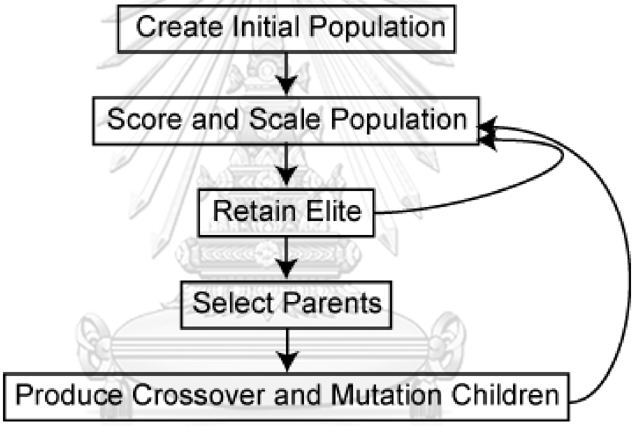

Figure 12 Flow chart of the genetic algorithm (GA) [31].

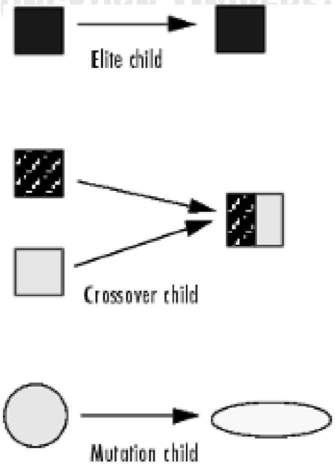

Figure 13 Different methods to create a new generation in GA [31].

CHAPTER 3

METHODOLOGY

This chapter describes the procedures and details for developing a simulation model of glycerol carbonate production from glycerol and diethyl carbonate. In addition, the method for evaluating the economic analysis and environmental impact is also included. The research step will divide into seven steps, as shown in **Figure 14**.

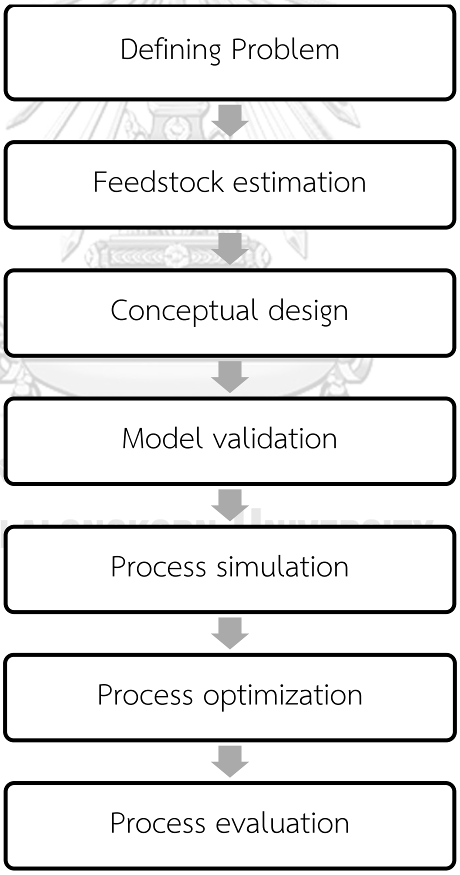

Figure 14 Research methodology procedure.

3.1 Defining Problem

To study the feasibility of using a reactive distillation (RD) process compared with the separated reaction/distillation (SRD) process for producing glycerol carbonate as a value-add chemical from an oversupply problem of crude glycerol. This process's successful development will help suggest a new direction for converting crude glycerol into a value-add product.

3.2 Feedstock estimation

In December 2020, Thailand had a biodiesel production rate of approximately 8.5 million liters per day, with 13 biodiesel plants registered with the Department of Energy Business [32]. The average biodiesel production rate per plant was 23,878 kg/h. For every 100 kilograms of biodiesel produced, 10 kilograms of crude glycerol were generated, resulting in a supply of 2,388 kg/h of crude glycerol and considering that 30 % of crude glycerol is used to produce glycerol carbonate. The feed rate of 716.4 kg/h of crude glycerol will be used as a basis for simulation. Furthermore, diethyl carbonate is excess in the feed stream on a ratio of 3:1 of crude glycerol, and Ce-NiO is used as a catalyst in the amount of 5 wt% of glycerol, according to J. Zhang et al. [26] experiment which studies the kinetic of this reaction using a batch reactor.

The cost of each raw material is set according to the commercial suppliers, as shown in **Table 3**.

Table 3 Cost of feedstock used in this study.

Component	Purity	Price	Ref
Crude glycerol	83.3 wt%	0.5 US$/kg	[33]
Diethyl carbonate	99.9 wt%	1.0 US$/kg	[34]

3.3 Conceptual design

The process flow diagram of the conceptual design for producing glycerol carbonate from crude glycerol and diethyl carbonate consists of 3 diagrams. First, the crude glycerol pretreatment process to produce purified glycerol. Second is the separated reaction/distillation (SRD) process, and Last is the reactive distillation (RD) process, as shown in **Figures 15, 16, and 17,** respectively.

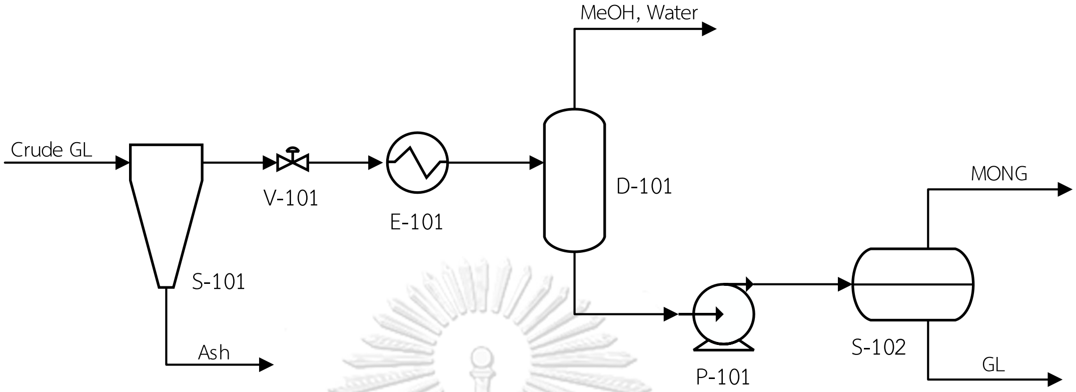

Figure 15 The crude glycerol pretreatment process.

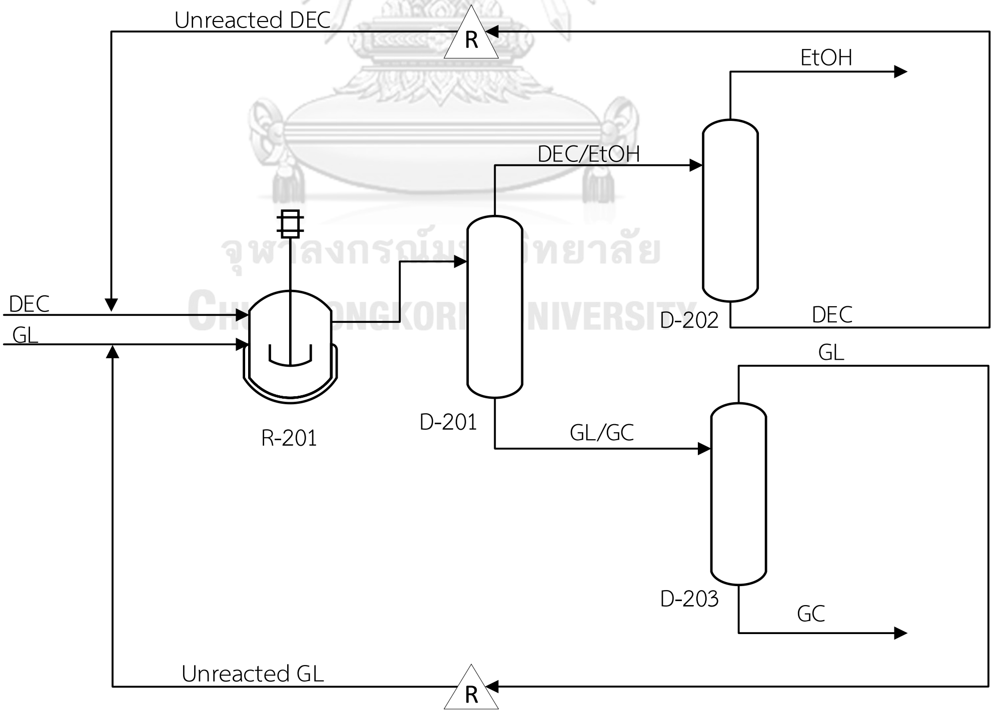

Figure 16 The separated reaction/distillation (SRD) process of glycerol carbonate production from diethyl carbonate.

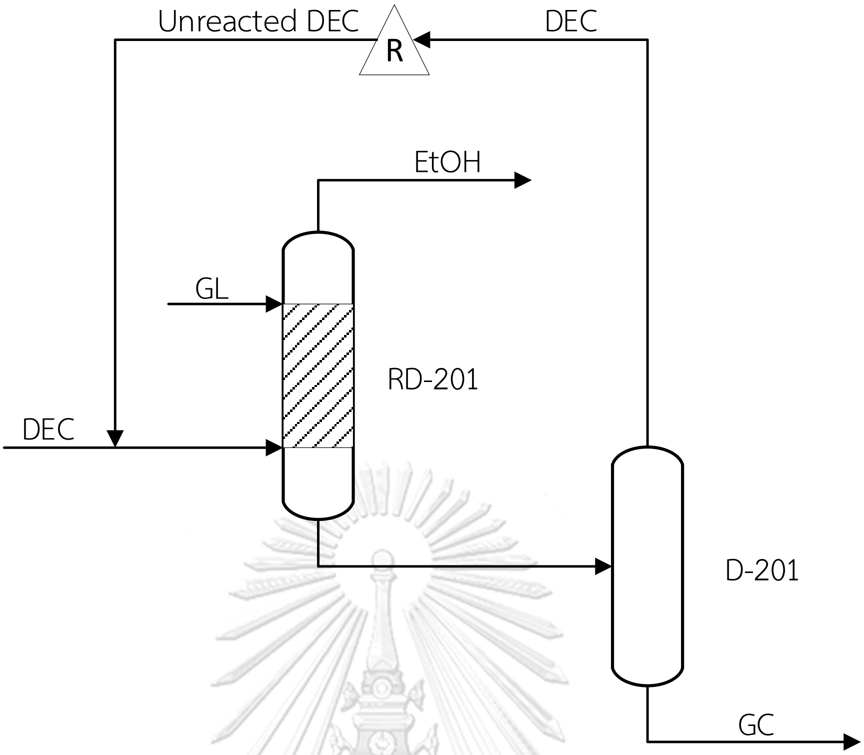

Figure 17 The reactive distillation (RD) process of glycerol carbonate production from diethyl carbonate.

3.3.1 Crude glycerol pretreatment process

The crude glycerol pretreatment process is designed based on the work of P. Thanahiranya et. al. [35], Ding [36], and the patent of Chang [37]. The process starts by feeding crude glycerol to a splitter to separate the solid phase from the crude glycerol. Then, the outlet stream from the splitter is pressurized to 0.1 bar and heated up to 95°C to flash at the flash tank to remove methanol and water. The remaining stream is then pressurized to 1.0 bar through a pump and sent to a decanter to separate MONG from the glycerol. The crude glycerol pretreatment process yields a 97.4 %wt purity of glycerol.

3.3.2 Feed preparation system

The feed preparation system is a mixing process that mixes the purified glycerol and diethyl carbonate with the unreacted substance from the recycling system before feeding into the reaction process. The dimethyl carbonate is excess in a ratio of 1:3 by mole of purified glycerol based on the work of J. Zhang et al. [26].

3.3.3 Reaction/Reactive distillation system

For the separated reaction/distillation (SRD) process, the transesterification of glycerol takes place in a continuously stirred tank reactor at a reaction temperature of 80°C and atmospheric pressure. The Ce–NiO catalyst is loaded into a reactor in the amount of 5 wt% of glycerol. According to J. Zhang et al. [26] experiment, the equilibrium constant of the reaction is used to calculate the reactor volume in this work.

For the reactive distillation (RD) process, the reactive distillation column will be used instead of the reactor and the first distillation column. The transesterification reaction takes place in the reactive zone, with glycerol and diethyl carbonate being fed at the top and bottom of the reactive zone, respectively. According to Bor-Yih Yu et al. research [9, 25], which has a similar reaction (transesterification of glycerol from dimethyl carbonate), glycerol was almost completely converted through a reactive distillation column. Therefore, the hypothesis for this work will be that the glycerol conversion is almost 100%, similar to the dimethyl carbonate reaction. So, there was no need to recycle glycerol back into the reaction system, as shown in **Figure 17.** The unreacted diethyl carbonate and product, including glycerol carbonate and ethanol, will be separated by sending the ethanol out through the top stream of the reactive distillation column, and the rest are sent to the separation system through the bottom stream.

3.3.4 Separation system

In the separation system, the distillation column is used to separate the unreacted reactant for recycling back into the reaction system. Additionally, it is used to purify the product to achieve high purity for commercial sale. The glycerol carbonate is commercially sold at a purity of 96.8 wt%, so the distillation column configuration in the simulation program will be set to achieve about 96.8 wt% purity for glycerol carbonate and 95.0 wt% purity for ethanol.

3.3.5 Recycle system

Due to the excess diethyl carbonate in feed and the reaction equilibrium limit, the unreacted diethyl carbonate and glycerol will need to be recycled back for use again in the reactor. The recycling system will be sent the unreacted reactant and then mixed with makeup in the feed preparation system.

3.4 Model validation

3.4.1 Thermodynamics model validation

In the crude glycerol pretreatment process, the UNIFAC model is used for simulation due to the missing property of MONG and the existence of polar and non-polar compounds in the system.

The transesterification of glycerol from diethyl carbonate reaction was operated at low-pressure conditions, and there was a non-ideal mixture. So, the activity coefficient model is used in this section. The nonrandom two-liquid model (NRTL) was selected according to J. Liu et al. [27] study, which reports the NRTL binary parameters for this system as shown in **Table 2**.

For the accuracy of the thermodynamics model, the NRTL binary parameters from J. Liu et al. [27] will be entered into Aspen Plus. After that, two tertiary diagrams will be simulated consisting of glycerol – diethyl carbonate – glycerol carbonate and glycerol – diethyl carbonate – ethanol for validation with the experimental data, as previously shown in **Figures 9, and 10**.

3.4.2 Reaction equilibrium constant validation

The equilibrium constant shown in **Eq.2** will be used in the simulation model to predict the reaction results. The predicted results will then be compared to the experimental data presented in **Table 1**. This comparison will serve to validate whether the equilibrium constant can accurately predict the reaction results.

3.5 Process simulation

After ensuring that the thermodynamics model is validated, the process of glycerol carbonate production from diethyl carbonate will be designed by simulating in the Aspen Plus program. The simulation will be divided into two cases, including the separated reaction/distillation (SRD) process and the reactive distillation (RD) process, to compare in each other.

3.6 Process optimization

The models in Aspen Plus will be first set to obtain the output concentration of each steam for commercial sale by using the design specifications function in Aspen Plus. However, there are still some variables that do not know what the optimum value is, such as the number of stages, feed location, and operating pressure of the distillation column. Therefore, optimization is required to find the optimum value. The method used in this work is by connecting the Aspen Plus model with MATLAB via ActiveX server and using the Genetic algorithm as a built-in optimization algorithm in MATLAB to find the optimum value for each parameter. The objective function for optimization is to minimize the total annual cost (TAC), as shown in the following equation.

$$\text{Total annual cost (TAC)} = \frac{\text{Total capital cost}}{\text{Payback period}} + \text{Total operating cost} \tag{7}$$

3.7 Process evaluation

After the model is optimized, the model obtained from Aspen Plus will be used for evaluating the process in terms of economics, energy, and environmental impact using Aspen Economic Analyzer as follows.

3.7.1 Profitability Index (PI)

The profitable index (PI) is a parameter that indicates whether the process is worth investing in or not. The equation for calculating PI is shown as follows [38].

$$\text{Profitable index (PI)} = \frac{\text{Present value of future cash flows}}{\text{Initial investment}} \qquad \textbf{(8)}$$

If, PI > 1; Project is generates value. So, the project should be accepted.

PI = 1; Project is at breaks even point.

PI < 1; Project destroys value. So, the project should be rejected.

The cost of product in the glycerol carbonate production from glycerol and diethyl carbonate is set based on the commercial sales, as shown in **Table 4**.

Table 4 Commercial chemical cost of glycerol carbonate production.

Component	Purity	Price	Ref
Glycerol carbonate	96.8 wt%	6.0 US$/kg	[39]
Ethanol	95.0 wt%	1.3 US$/kg	[40]

The utility cost is mainly obtained from a process design textbook, namely Analysis, Synthesis, and Design of Chemical Processes [41], while the cost of hot oil is calculated using the recommended equation by D. Ulrich et al.[42]. The cost of utility can be summarized in **Table 5**.

Table 5 List of utilities and prices.

Utility	Price	Unit	Ref
Electricity	0.0674	US$/kWh	[41]
Cooling water	0.378	US$/GJ	[41]
Chilled water	4.77	US$/GJ	[41]
Low-pressure steam	2.03	US$/GJ	[41]
High-pressure steam	5.66	US$/GJ	[41]
Fuel oil (350^{O}C)	8.67	US$/GJ	[42]

The catalyst used in this work is the Ce–NiO catalyst by loading at an amount of 5 wt% of glycerol. This catalyst was chosen because it has been previously experimented with by J. Zhang et al. [26], who obtained the equilibrium constant which used to simulate the model in this study. The cost of the catalyst is calculated assuming a price of 50 US$/kg [43]. Typically, the price of catalysts depends on the country, manufacturer, and the amount used, but the catalyst used in this work has no information on its cost. Therefore, the catalyst cost is assumed based on a higher cost due to the use of a small amount, using a higher cost of catalyst mentioned in the design textbook PRINCIPLES AND CASE STUDIES OF SIMULTANEOUS DESIGN by William L. Luyben [44]. In addition, the lifetime of the catalyst was also not known. Therefore, it is estimated to be the lowest time compared to studies where the lifespan of the catalyst is unknown[45, 46], which can be estimated to be around six months (change two times/year).

However, since the catalyst price calculations in this work are based on estimation, a sensitivity analysis of the catalyst price is conducted to determine the effect that would occur when the price of the catalyst changes. The sensitivity analysis of catalyst cost to the results of the process will show in **Appendix C**.

3.7.2 Internal Rate of Return (IRR)

The internal rate of return (IRR) is a discount rate that makes the net present value (NPV) of all cash flows equal to zero. The IRR will show an investment's potential profitability by using the following equations [47, 48].

$$0 = \text{NPV} = \sum_{t=1}^{T} \frac{C_t}{(1+\text{IRR})^t} - C_0 \tag{9}$$

Where, C_t = Net cash inflow during period t

C_0 = Total investment cost

t = Number of time periods

3.7.3 Payback Period

The payback period is the amount of time required to return the initial investment expense; a shorter payback period value means the project is more attractive for investment. The payback period can be calculated as follows [49].

$$\text{Payback Period} = \frac{\text{Cost of Investment}}{\text{Average Annual Cash Flow}} \tag{10}$$

3.7.4 Energy utilization

To evaluate the process's energy utilization, the specific energy consumption equation (SEC) is used to calculate the energy required to produce 1 kg of glycerol carbonate. The specific energy consumption (SEC) can be calculated as follows [50].

$$\text{Specific energy consumption (SEC)} = \frac{\text{Energy consumption}}{\text{Amount of GC produced}\,(\text{Kg})} \tag{11}$$

3.7.5 Environmental impact

The environmental impact of the process is determined by calculating the amount of CO_2 emitted per quantity of GC produced as follows.

$$CO_2\ \text{emission} = \frac{\text{Amount of } CO_2 \text{ emission}\left(\text{Kg}\right)}{\text{Amount of GC produced}\left(\text{Kg}\right)} \quad \textbf{(12)}$$

CHAPTER 4

RESULTS AND DISCUSSION

This chapter presents the results and explanation of the study by dividing it into four sections: the validation of the simulation model, the results of the separated reaction/distillation (SRD) process, the results of the reactive distillation (RD) process, and the comparison results between process in the term of process performance, economics results, and the environmental impact.

4.1 Model validation

4.1.1 Thermodynamics model validation

The nonrandom two-liquid (NRTL) model and also the NRTL binary interaction parameters for the system of glycerol, diethyl carbonate, glycerol carbonate, and ethanol from J. Liu et al. [27] study, as shown in **Table 2**, were entered into Aspen Plus for simulating the mixing between components. This section is dedicated to the validation of the NRTL model in accurately predicting the vapor-liquid and liquid-liquid equilibrium behaviors.

The simulation results are shown in ternary diagrams of the two systems: glycerol – diethyl carbonate – glycerol carbonate system, and glycerol – diethyl carbonate – ethanol system at the temperatures of 343.2 K, 363.2 K, 383.2 K, and 403.2 K as shown in **Figures 18, and 19**.

The results from the ternary diagram can be compared with **Figures 9, and 10** which show that the ternary diagrams from Aspen Plus have the same results published in J. Liu's experiments [27]. So, it can be interpreted that the NRTL thermodynamics model and input binary interaction parameters can be used as a representative for calculating and simulating the model in this process.

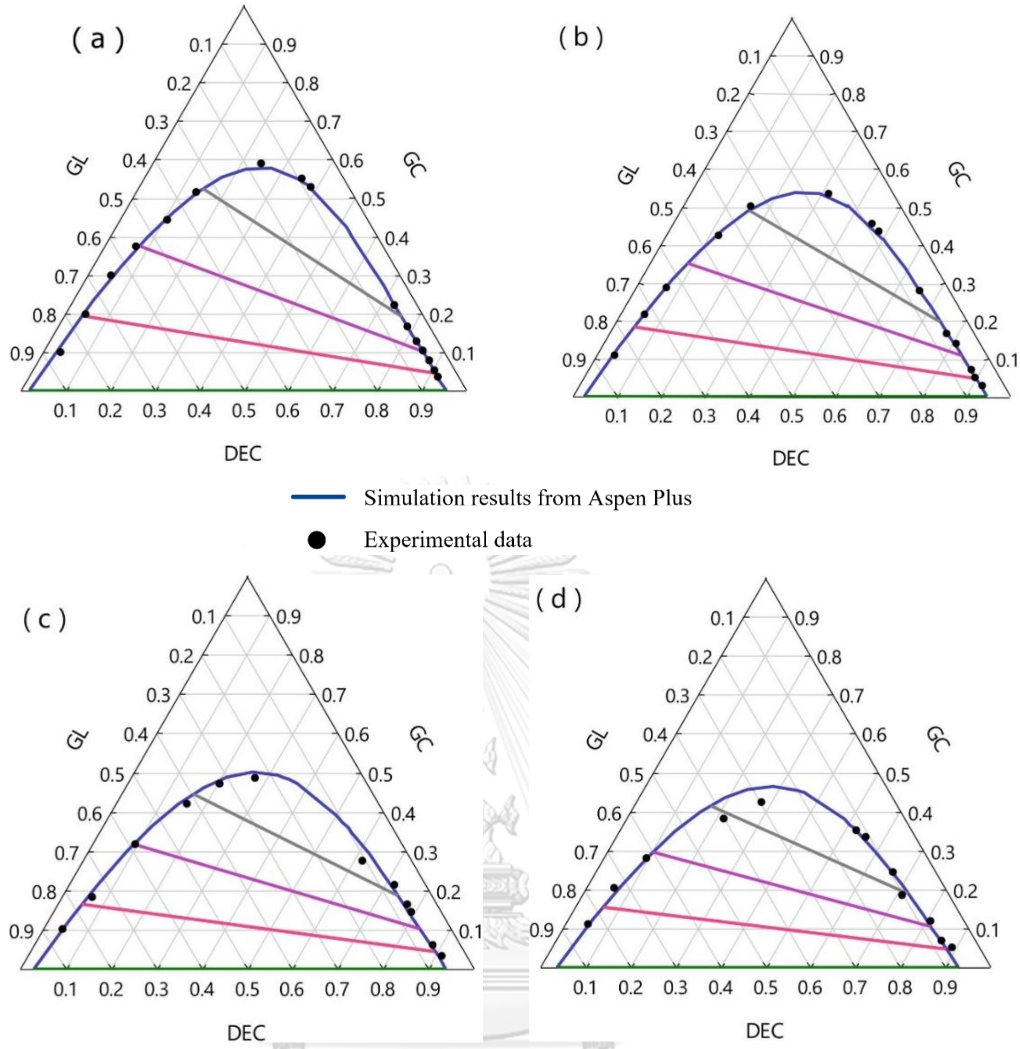

Figure 18 Ternary diagram of glycerol (GL) – diethyl carbonate (DEC) – glycerol carbonate (GC) system at temperature (a) 343.2 K, (b) 363.2 K, (c) 383.2 K, (d) 403.2 K.

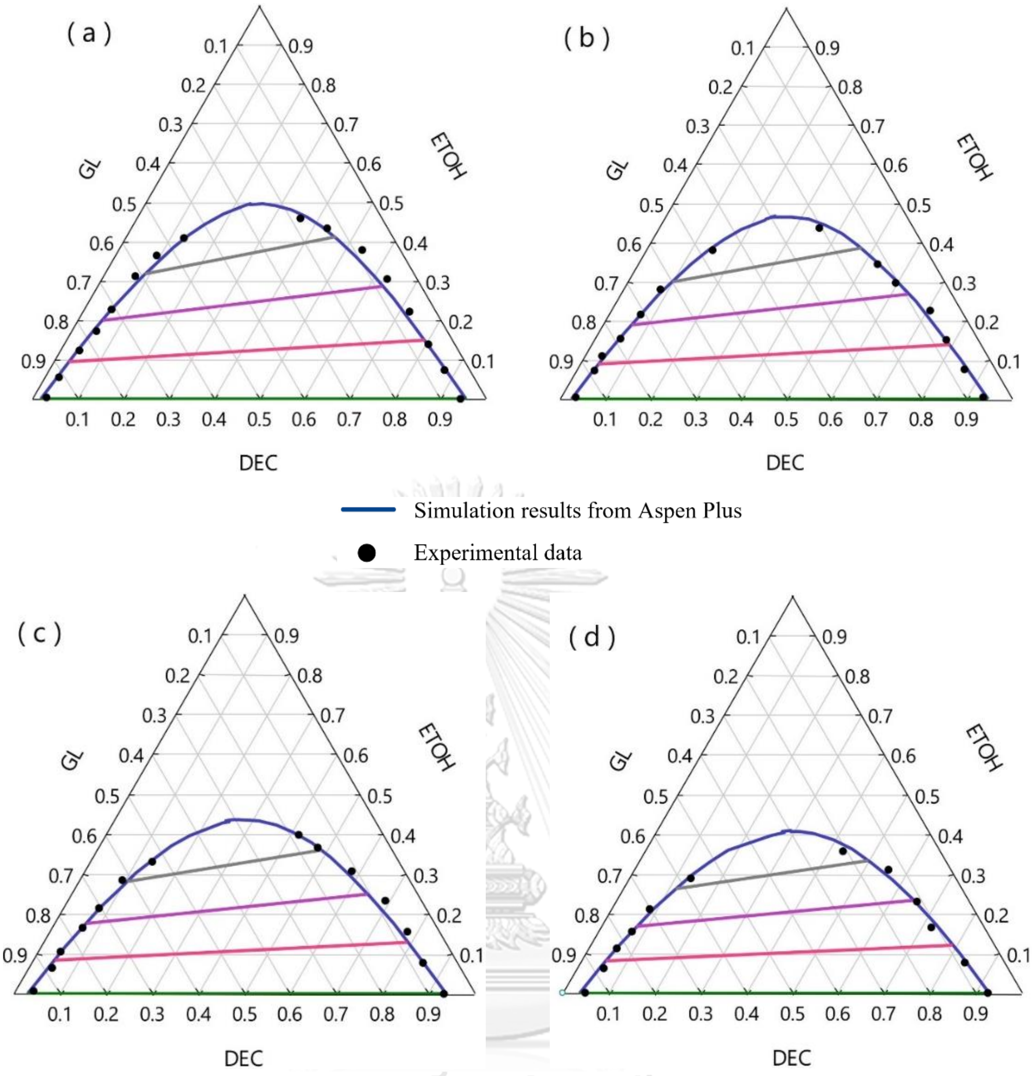

Figure 19 Ternary diagram of glycerol (GL) – diethyl carbonate (DEC) – ethanol (EtOH) system at temperature (a) 343.2 K, (b) 363.2 K, (c) 383.2 K, (d) 403.2 K.

4.1.2 Reaction equilibrium constant validation

The equilibrium constant shown in **Eq.2** was inserted into an RCSTR model in Aspen Plus to simulate the reaction at various temperatures for comparison with **Table 1**. The simulation results are present in **Table 6**. which shows that the reaction equilibrium constant can represent the experimental results and can be used to simulate the model in this work.

Table 6 Comparison results between the simulation results and experimental results.

Temperature (K)	C_{A0}	C_{B0}	C_A	C_B	C_C	C_D
338 [This work]	2.167	6.502	1.138	5.617	1.102	2.204
338 [26]	2.197	6.592	1.082	5.478	1.117	2.234
343 [This work]	2.167	6.502	0.968	5.426	1.261	2.521
343 [26]	2.197	6.592	0.801	5.198	1.398	2.795
348 [This work]	2.167	6.502	0.799	5.233	1.419	2.838
348 [26]	2.197	6.592	0.781	5.178	1.418	2.836
353 [This work]	2.167	6.502	0.636	5.046	1.569	3.139
353 [26]	2.197	6.592	0.549	4.947	1.650	3.299
358 [This work]	2.167	6.502	0.487	4.872	1.705	3.411
358 [26]	2.197	6.592	0.434	4.832	1.765	3.530

C is a concentration in the unit of mol/L.

According to the model validation in **sections 4.1.1 and 4.1.2**, the simulation model demonstrated the ability to predict thermodynamic and reaction results consistent with the experimental data. These findings suggest that the simulation model used in this study will likely produce accurate results that closely match the experimental data.

4.2 The Separated Reaction/Distillation (SRD) process

The process of SRD starts by feeding 716.4 kg/h of crude glycerol to the glycerol pretreatment process to remove the impurity of the crude stream. Then the purified glycerol is mixed with the glycerol recycle stream as well as the fresh diethyl carbonate stream with the diethyl carbonate recycled stream. Afterward, the mixed stream is fed into the continuously stirred tank reactor by controlling the glycerol and excess diethyl carbonate in a ratio of 1:3 by mole. The reactor (R-201) is designed to operate as an isothermal reactor at 80^{O}C, according to **Figure 8-a**, which shows that the reaction temperature should not exceed 80 ^{O}C to avoid side reactions. The residence time is set to 4 hr, according to **Figure 8-b**, which shows the appropriate reaction time that makes the reaction close to equilibrium and does not occur side reaction. The outlet stream from the reactor (R-201) is sent into the purification section consisting of 3 distillation columns. First, D-201 is used to separate diethyl carbonate and ethanol from glycerol and glycerol carbonate. Second, the distillation column D-202 is used to separate unreacted diethyl carbonate back into the reaction system and used to purify the ethanol to achieve 95.0 wt% purity for commercial sale. Last, the D-203 distillation column is used to separate unreacted glycerol and purify glycerol carbonate to reach 97.0 wt% purity for commercial sale. To find the optimum condition, the distillation column is set to obtain purity for commercial sale by using design specifications in Aspen Plus. At the same time, other parameters, including the number of stages, feed location, and operating pressure, are optimized using a Genetic algorithm in MATLAB.

The algorithm settings are shown in **Table 7**. The input settings for the algorithm included the variables to be optimized, its upper and lower bounds, the optimization constraints, and the stopping criteria were set using the optimization feature in MATLAB. An optimization constraint was applied to ensure that the feed stage had a value lower than the total number of stages. The stopping criteria were set based on the limitations of the computer being used. It should be noted that when using the genetic algorithm to optimize the process, a large population size and a high number of generations can result in a good optimization outcome. However, this also requires higher computer specifications to perform the calculations. Therefore, this work has set up an optimized option for the computer to be able to run the genetic algorithm effectively.

Table 7 Optimization variables setting of the SRD process.

Name	Variables	Types	Lower bound	Upper bound
x1	D-201 No. of stage	Integer	15	45
x2	D-201 Feed stage	Integer	5	44
x3	D-201 Pressure	Continuous	0.30	1.50
x4	D-202 No. of stage	Integer	15	45
x5	D-202 Feed stage	Integer	5	44
x6	D-202 Pressure	Continuous	0.30	1.50
x7	D-203 No. of stage	Integer	15	45
x8	D-203 Feed stage	Integer	5	44
x8	D-203 Pressure	Continuous	0.10	0.45

Optimization constraints: 1. x1 - x2 >= 1
2. x4 - x5 >= 1
3. x7- x8 >= 1

Solver: Genetic Algorithm

Options: 1. Population size: 50
2. Runtime limits: Max generations: 10

After running the optimization, The designed process diagram results are shown in **Figure 20,** and the stream results are shown in **Table 8**.

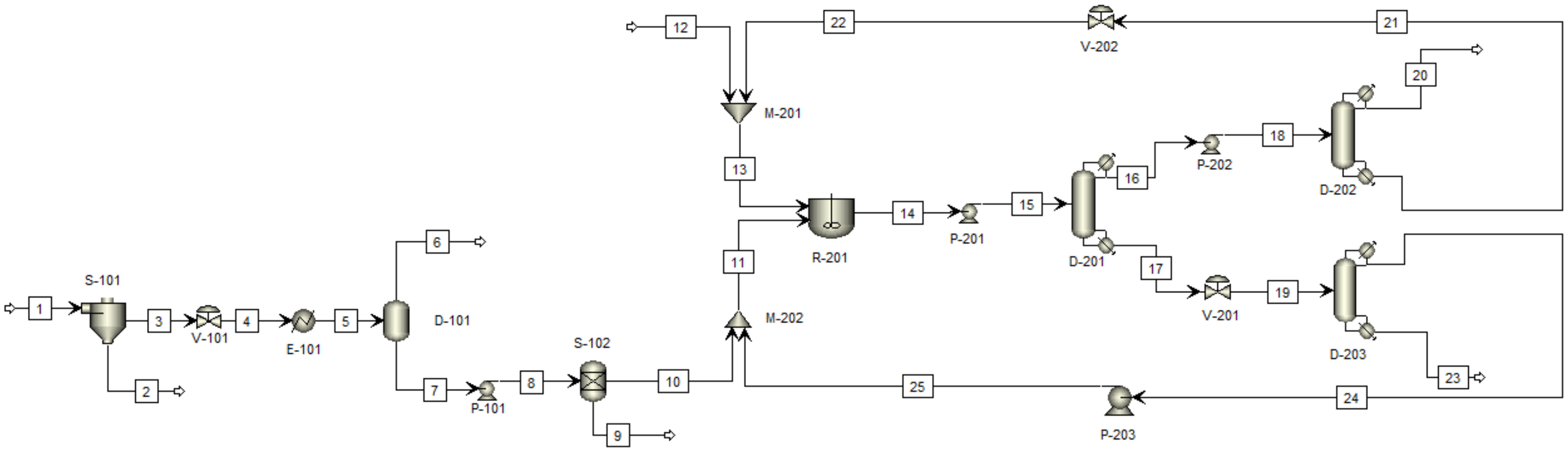

Figure 20 The designed process diagram results of the Separated Reaction/Distillation (SRD) process.

Table 8 Stream results of the Separated Reaction/Distillation (SRD) process.

Stream no.	1	2	3	4	5	6	7
Temperature (^{O}C)	30.0	30.0	30.0	30.0	95.0	95.0	95.0
Pressure (Bar)	1.00	1.00	1.00	0.10	0.10	0.10	0.10
Total mass flow (kg/h)	716.4	40.7	675.7	675.7	675.7	68.2	607.5
- GL (wt %)	83.32	14.67	87.46	87.46	87.46	0.78	97.19
- DEC (wt %)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
- GC (wt %)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
- EtOH (wt %)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
- Water (wt %)	11.24	1.98	11.79	11.79	11.79	94.77	2.47
- MeOH (wt %)	0.48	0.08	0.50	0.50	0.50	4.45	0.06
- MONG (wt %)	0.19	0.03	0.20	0.20	0.20	0.00	0.22
- ASH (wt %)	4.77	83.23	0.05	0.05	0.05	0.00	0.06

Table 8 Stream results of the Separated Reaction/Distillation (SRD) process (Cont'd).

Stream no.	8	9	10	11	12	13	14
Temperature (^{O}C)	95.1	95.1	95.1	112.0	30.0	106.4	80.0
Pressure (Bar)	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Total mass flow (kg/h)	607.5	7.4	600.1	782.1	735.6	3,228.3	4,010.4
- GL (wt %)	97.19	79.84	97.41	97.78	0.00	0.00	5.05
- DEC (wt %)	0.00	0.00	0.00	0.03	99.90	99.90	62.44
- GC (wt %)	0.00	0.00	0.00	0.20	0.00	0.00	18.01
- EtOH (wt %)	0.00	0.00	0.00	0.00	0.00	0.00	14.03
- Water (wt %)	2.47	2.03	2.48	1.90	0.10	0.10	0.45
- MeOH (wt %)	0.06	0.05	0.06	0.04	0.00	0.00	0.01
- MONG (wt %)	0.22	18.08	0.00	0.00	0.00	0.00	0.00
- ASH (wt %)	0.06	0.00	0.06	0.04	0.00	0.00	0.01

Table 8 Stream results of the Separated Reaction/Distillation (SRD) process (Cont'd).

Stream no.	15	16	17	18	19	20	21
Temperature (^{O}C)	80.0	97.5	287.5	97.5	234.7	79.5	128.1
Pressure (Bar)	1.01	1.01	1.01	1.06	0.12	1.06	1.06
Total mass flow (kg/h)	4,010.4	3,084.8	925.6	3,084.8	925.6	592.1	2,492.7
- GL (wt %)	5.05	0.00	21.88	0.00	21.88	0.00	0.00
- DEC (wt %)	62.44	81.17	0.03	81.17	0.03	2.31	99.90
- GC (wt %)	18.01	0.00	78.05	0.00	78.05	0.00	0.00
- EtOH (wt %)	14.03	18.24	0.00	18.24	0.00	95.00	0.00
- Water (wt %)	0.45	0.58	0.00	0.58	0.00	2.63	0.10
- MeOH (wt %)	0.01	0.01	0.00	0.01	0.00	0.06	0.00
- MONG (wt %)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
- ASH (wt %)	0.01	0.00	0.04	0.00	0.04	0.00	0.00

Table 8 Stream results of the Separated Reaction/Distillation (SRD) process (Cont'd).

Streams	22	23	24	25
Temperature (^{O}C)	126.0	239.7	174.5	174.6
Pressure (Bar)	1.00	0.12	0.12	1.00
Total mass flow (kg/h)	2,492.7	743.6	182.1	182.1
- GL (wt %)	0.00	3.00	99.00	99.00
- DEC (wt %)	99.90	0.00	0.14	0.14
- GC (wt %)	0.00	96.95	0.86	0.86
- EtOH (wt %)	0.00	0.00	0.00	0.00
- Water (wt %)	0.10	0.00	0.00	0.00
- MeOH (wt %)	0.00	0.00	0.00	0.00
- MONG (wt %)	0.00	0.00	0.00	0.00
- ASH (wt %)	0.00	0.05	0.00	0.00

4.3 The Reactive Distillation (RD) Process

The RD process starts by feeding 716.4 kg/h of crude glycerol to the glycerol pretreatment process and then to the reactive distillation column (RD-201). The fresh diethyl carbonate is mixed with unreacted diethyl carbonate from recycle stream and fed into the reactive distillation column (RD-201) at the same ratio in the SRD process. The reactive distillation column (RD-201) will be used instead of the reactor and the first distillation column in the SRD process; the reactive distillation column is set to separate ethanol first to shift the reaction equilibrium forward. The operating pressure of RD-201 is set to operate at a vacuum condition to control the temperature in the reaction zone not exceeding 80 ^{O}C to avoid side reactions [26]. The results from reactive distillation found that the reaction conversion is 100%, which shows that reactive distillation helps to shift the chemical equilibrium forward and leads to higher conversion. The bottom product from reactive distillation will be sent to the separation system in D-201 to purify 97 wt% glycerol carbonate for commercial sale and to recycle unreacted diethyl carbonate back into the reaction system. In the same way as the SRD process, the RD process is optimized using a genetic algorithm in MATLAB to find an optimum value of a number of stages, feed location, reflux ratio, and operating pressure for the RD-201 as well as D-201. The algorithm settings of the RD process are shown in **Table 9**.

In the RD process, the D-201 distillation column to separate diethyl carbonate and glycerol carbonate can be separated from each other easily, which makes the design specification feature in Aspen Plus cannot be used to find the optimal variable of reflux ratio. This problem is solved by adding the reflux ratio variable into the optimization setting and setting the constraint to achieve high diethyl carbonate recovery in the D-201 distillation column to ensure that D-201 is still operating effectively.

Table 9 Optimization variables setting of the RD process.

Name	Variables	Types	Lower bound	Upper bound
x1	RD-201 No. of stage	Integer	15	45
x2	RD-201 Feed stage 1	Integer	3	43
x3	RD-201 Feed stage 2	Integer	4	44
x4	RD-201 Reflux ratio	Continuous	0.1	5.0
x5	RD-201 Pressure	Continuous	0.10	0.40
x6	D-201 No. of stage	Integer	10	40
x7	D-201 Feed stage	Integer	2	39
x8	D-201 Reflux ratio	Continuous	0.1	5.0
x9	D-201 Pressure	Continuous	0.3	1.5

Optimization constraints:
1. x1 - x3 >= 2
2. x3 - x2 >= 2
3. x6 - x7 >= 1
4. Temperature at stage x3-1 <= 80 ^{O}C
5. DEC recovery at D-201 to recycle stream >= 95 %

Solver: Genetic Algorithm

Options:
1. Population size: 50
2. Runtime limits: Max generations: 10

The designed process diagram results are shown in **Figure 21,** and the stream results are shown in **Table 10**.

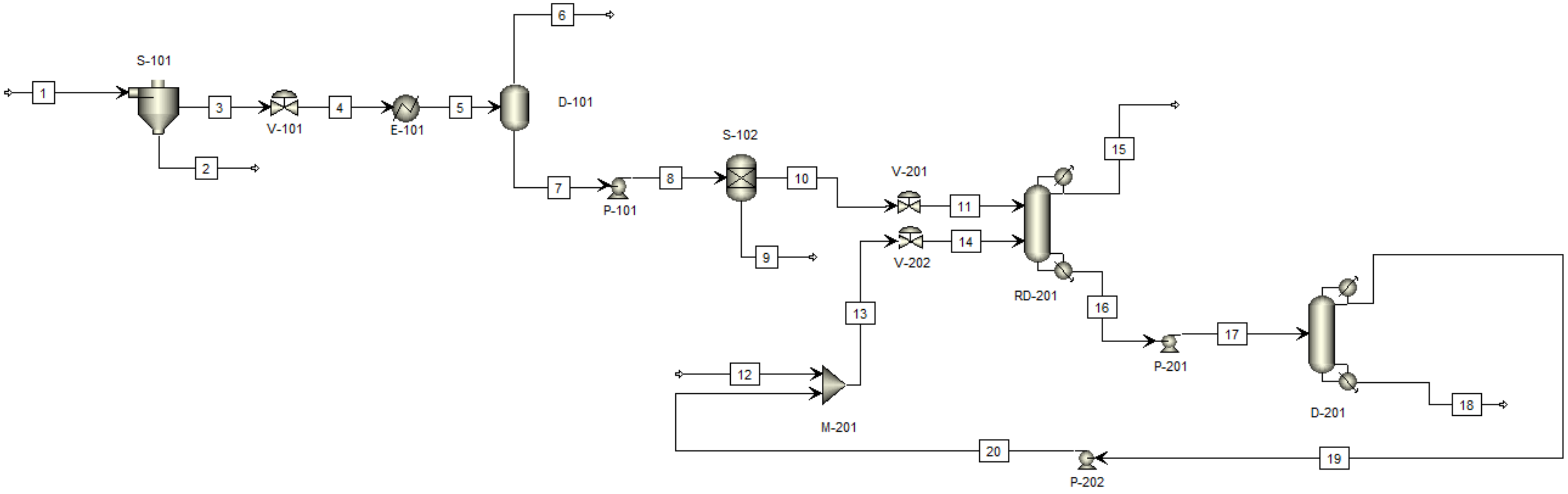

Figure 21 The designed process diagram results of The Reactive Distillation (RD) Process.

Table 10 Stream results of the Reactive Distillation (RD) Process.

Stream no.	1	2	3	4	5	6	7
Temperature (^{O}C)	30.0	30.0	30.0	30.0	95.0	95.0	95.0
Pressure (Bar)	1.00	1.00	1.00	0.10	0.10	0.10	0.10
Total mass flow (kg/h)	716.4	40.7	675.7	675.7	675.7	68.2	607.5
- GL (wt %)	83.32	14.67	87.46	87.46	87.46	0.78	97.19
- DEC (wt %)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
- GC (wt %)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
- EtOH (wt %)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
- Water (wt %)	11.24	1.98	11.79	11.79	11.79	94.77	2.47
- MeOH (wt %)	0.48	0.08	0.50	0.50	0.50	4.45	0.06
- MONG (wt %)	0.19	0.03	0.20	0.20	0.20	0.00	0.22
- ASH (wt %)	4.77	83.23	0.05	0.05	0.05	0.00	0.06

Table 10 Stream results of the Reactive Distillation (RD) Process (Cont'd).

Stream no.	8	9	10	11	12	13	14
Temperature (^{O}C)	95.1	95.1	95.1	92.4	30.0	96.2	73.7
Pressure (Bar)	1.00	1.00	1.00	0.17	1.00	1.00	0.17
Total mass flow (kg/h)	607.5	7.4	600.1	600.1	788.5	2,536.3	2,536.3
- GL (wt %)	97.19	79.84	97.41	97.41	0.00	0.00	0.00
- DEC (wt %)	0.00	0.00	0.00	0.00	99.90	99.96	99.96
- GC (wt %)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
- EtOH (wt %)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
- Water (wt %)	2.47	2.03	2.48	2.48	0.10	0.04	0.04
- MeOH (wt %)	0.06	0.05	0.06	0.06	0.00	0.00	0.00
- MONG (wt %)	0.22	18.08	0.00	0.00	0.00	0.00	0.00
- ASH (wt %)	0.06	0.00	0.06	0.06	0.00	0.00	0.00

Table 10 Stream results of the Reactive Distillation (RD) Process (Cont'd).

Stream no.	15	16	17	18	19	20
Temperature (°C)	39.0	78.8	78.9	220.6	124.9	124.9
Pressure (Bar)	0.17	0.17	0.96	0.96	0.96	1.00
Total mass flow (kg/h)	615.6	2,520.8	2,520.8	773.0	1,747.8	1,747.8
- GL (wt %)	0.00	0.00	0.00	0.00	0.00	0.00
- DEC (wt %)	2.40	70.24	70.24	3.00	99.99	99.99
- GC (wt %)	0.00	29.73	29.73	96.96	0.00	0.00
- EtOH (wt %)	95.00	0.00	0.00	0.00	0.00	0.00
- Water (wt %)	2.54	0.01	0.01	0.00	0.01	0.01
- MeOH (wt %)	0.06	0.00	0.00	0.00	0.00	0.00
- MONG (wt %)	0.00	0.00	0.00	0.00	0.00	0.00
- ASH (wt %)	0.00	0.01	0.01	0.04	0.00	0.00

4.4 Comparison

4.4.1 Process performance and energy utilization comparison

The process performance assessments for glycerol carbonate production from crude glycerol and diethyl carbonate via the separate reaction/distillation (SRD) process and the reactive distillation (RD) process are shown in **Table 11**.

Table 11 Process performance comparison between the SRD and RD processes.

	The SRD Process	The RD process
<u>Reaction</u>		
Glycerol Conversion (%)	73.5	100.0
GC production (kg GC/h)	743.6	773.0
<u>Energy utilization</u>		
Total heat duty (kW)	1,063.0	809.0
Total cooling duty (kW)	904.4	672.2
Energy consumption (kWh/kg GC)	2.65	1.92

The results indicate that the RD process has a higher conversion than the SRD process because it can shift the reaction equilibrium forward, resulting in 100% glycerol conversion without requiring a recycling system for glycerol, and the RD process will have a lower residence time than the SRD process. Additionally, the RD process yields a higher glycerol carbonate production rate compared to the SRD process. Although the SRD process incorporates a recycle stream to reuse unreacted glycerol in the CSTR, the unreacted glycerol is already lost in the separation system, leading to a lower glycerol carbonate production rate. The energy utilization results show that the RD process requires lower energy consumption per product compared to the SRD process because the RD process does not require a distillation tower to purify glycerol for recycling.

The glycerol conversion results in this work can be compared to other routes for producing glycerol carbonate using the reactive distillation system, as described in **CHAPTER 2**. The comparison results can be shown in **Table 12.** However, the energy utilization cannot be compared because N. Lertlukkanasuk et al. [24] only focused on a standalone reactive distillation column, and Bor-Yih Yu [25] did not report the energy consumption.

Table 12 Glycerol conversion comparison results.

Reactant with GL	Reactant : GL mole ratio	The SRD Process	The RD process	Reference
Urea	1 : 1	72.5	93.6	[24]
Dimethyl carbonate	2 : 1	80.4	98.2	[25]
Diethyl carbonate	3 : 1	73.5	100.0	This work

From **Table 12**, it can be inferred that the RD process is superior to the SRD process in terms of its ability to shift equilibrium and achieve higher conversion. However, the percentage results in this table cannot definitively determine which route is better since these three experiments utilize different reactant ratios to react with glycerol.

4.4.2 Process economics comparison

In terms of process economics, the two processes are evaluated using Aspen Economic Analyzer, resulting in **Table 13**.

Table 13 Process economics comparison between the SRD and RD process.

	The SRD Process	The RD process
Total capital cost (Million US$)	8.51	5.74
Total operating cost (Million US$/Year)	2.81	2.30
Total raw materials cost (Million US$/Year)	9.60	10.06
Total product sales (Million US$/Year)	45.81	47.63
Total utility cost (Million US$/Year)	0.30	0.19
Total Annual Cost (Million US$/Year)	7.63	6.23
Payback period (Year)	1.77	1.46
Profitability index	1.65	1.71
Internal rate of return (%)	163.6	266.48

From the results, the total capital cost of the RD process is lower than the SRD process because the RD process can reduce the need for distillation columns to purify the glycerol recycle stream and the distillation columns to purify ethanol. Moreover, the utility cost and the operating cost of the RD process, including labor and maintenance costs, are also lower compared to the SRD process due to the reduced number of unit operations. Regarding material terms, The RD process has higher raw materials cost and higher product sales than the RD process because in the SRD process, glycerol is lost by the separation system, but for the RD process, glycerol is all consumed in the reaction section.

For other economic parameters, the profitability index (PI) with a value greater than 1 indicates that both processes are profitable. Additionally, when comparing the internal rate of return (% IRR), payback period, and total annual cost, the RD process has a higher %IRR, shorter payback period, and lower total annual cost than the SRD process, indicating that the RD process is more attractive for investment than the SRD process.

The economic results cannot be compared with other routes because N. Lertlukkanasuk et al. [24] did not study the economic analysis, while Bor-Yih Yu [25] studied the economic analysis but calculated it on different methods and different calculation basis.

4.4.3 Environmental impact comparison

In terms of environmental impact assessment, the total carbon dioxide emissions from the use of utility are used to compare between the processes. The assessment of carbon dioxide emissions is presented in **Table 14**.

Table 14 Environmental impact comparison between the SRD and RD process.

	The SRD Process	The RD process
Low pressure steam (kg CO_2/h)	86.67	123.3
High pressure steam (kg CO_2/h)	0	68.2
Fuel-Oil (kg CO_2/h)	165.0	0
Total CO_2 emission (kg CO_2/h)	251.7	191.5
Specific CO_2 emission (kg CO_2/kg GC)	0.34	0.25

According to the environmental impact assessment, the results show that the RD process has lower carbon dioxide emissions compared to the SRD process. This is because the RD process consumes less energy than the SRD process, and the amount of energy used directly affects the amount of utility used as well as the carbon dioxide emissions. These results can also be compared to the glycerol production route with dimethyl carbonate by Bor-Yih Yu [25], which yields specific energy consumption values of 0.32 kg CO_2/kg GC for the SRD process and 0.21 kg CO_2/kg GC for the RD process. These values indicate that the energy consumption results are similar in the DME and DEC route.

CHAPTER 5

CONCLUSIONS

5.1 Conclusions

The increasing production of biodiesel has led to a surplus of glycerol, a byproduct from the biodiesel manufacturing process. To mitigate this oversupply, the conversion of glycerol into high-value substances has gained significant attention. One such valuable product is glycerol carbonate, which can be used as a solvent and additive in various industries. Therefore, this work aims to develop a continuous process model for producing glycerol carbonate from glycerol and diethyl carbonate by comparing two processes: the separate reaction/distillation (SRD) process and the reactive distillation (RD) process.

The SRD and RD processes are modelled in Aspen Plus, evaluated in Aspen Economics Analyzer, and optimized in MATLAB using genetic algorithms. The results show that the RD process is more efficient than the SRD process due to its ability to shift the reaction equilibrium forward, overcoming the chemical equilibrium problem. Additionally, the RD process combines the reaction and separation steps into a single unit, resulting in significant cost savings in capital investments, operating expenses, and utility expenses. Moreover, economic indicators were used to evaluate the two processes and determine which one was better. The results indicate that the RD process demonstrates a lower total annual cost, a shorter payback period, and a higher internal rate of return (%IRR), making it a more attractive option for investment.

However, it is essential to acknowledge that the RD process has complexities in operation due to the combination of reaction and separation in a single unit. The RD column has a small operating window due to limitations in apparatus, separation, and reaction.

5.2 Recommendations

5.2.1 Heat exchanger network

To enhance the energy efficiency of the process, an extra heat exchanger can be added to make a heat exchanger network to reduce the overall energy consumption. For example, in the SRD process, Aspen Plus recommends adding a heat exchanger (E-100) located before the condenser D-203 to allow the hot side fluid to exchange heat energy with the stream before reboiler D-202, as shown in **Figure 22**. This approach incurs an additional capital cost of 10,600 US$, resulting in energy cost savings of 14,600 US$/Year. Nevertheless, this method is impractical as it involves temperature adjustments in the product streams, making it challenging to control the product specifications within the distillation column. Therefore, the heat exchanger network was not applied in this work.

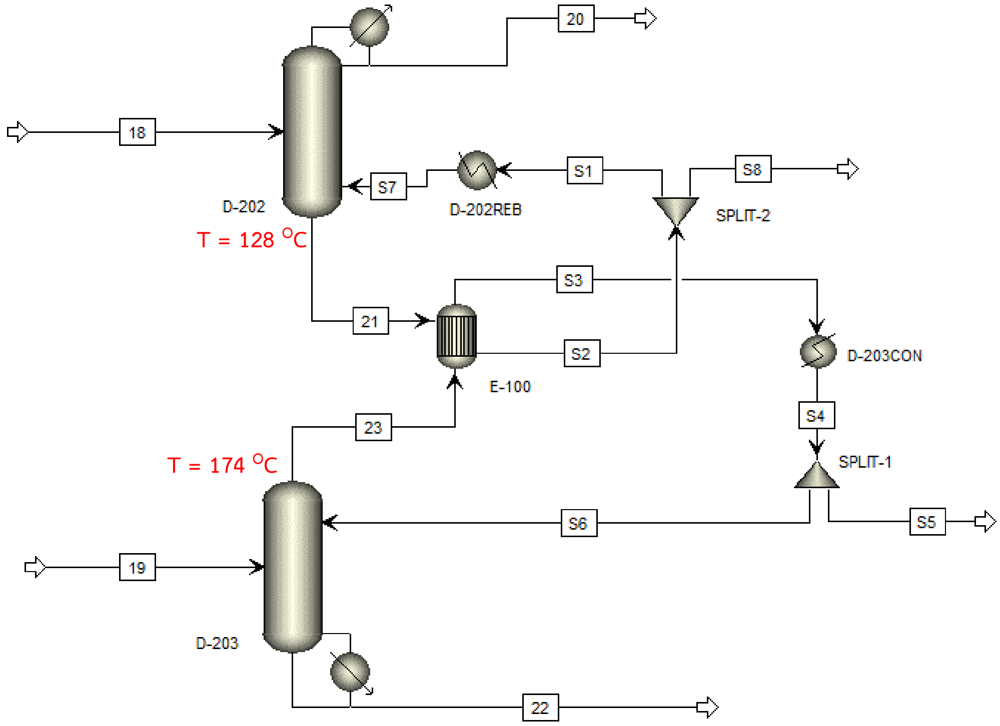

Figure 22 Heat exchanger network recommended by Aspen Plus.

5.2.2 Diethyl carbonate production

The diethyl carbonate (DEC) used in this work is calculated by purchasing it from the supplier. Therefore, DEC can be produced by reacting ethanol with carbon dioxide, as shown in **Figure 23**. This reaction has been studied and designed on a commercial scale by Bor-Yih Yu et al. [51]. If the Glycerol carbonate production plant in this work can be integrated with the DEC production plant, it would enable DEC and EtOH to be used in cycles and also serve as a plant for CO_2 utilization.

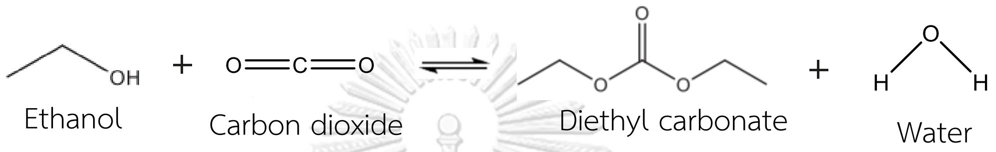

Figure 23 Reaction for producing DEC from EtOH and CO_2.

REFERENCES

1. Claudio J. A. Mota BPP, Ana Lúcia de Lima. Glycerol A Versatile Renewable Feedstock for the Chemical Industry: Springer; 2017.
2. Pagliaro M. Properties, applications, history, and market. Elsevier; 2017. p. 1-21.
3. Das A, Shi D, Halder G, Lalthazuala Rokhum S. Microwave-assisted synthesis of glycerol carbonate by transesterification of glycerol using Mangifera indica peel calcined ash as catalyst. Fuel. 2022;330:125511.
4. Lee JWY, Chia WY, Ong W-J, Cheah WY, Lim SS, Chew KW. Advances in catalytic transesterification routes for biodiesel production using microalgae. Sustainable Energy Technologies and Assessments. 2022;52:102336.
5. Sato T, Nagasawa H, Kanezashi M, Tsuru T. Transesterification membrane reactor with organosilica membrane in batch and continuous flow modes. Chemical Engineering Journal. 2022;450:137862.
6. Wang T, Li W, Ge X, Qiu T, Wang X. Kinetics measurement of ethylene-carbonate synthesis via a fast transesterification by microreactors. Chinese Journal of Chemical Engineering. 2022.
7. Petchsoongsakul N, Ngaosuwan K, Kiatkittipong W, Aiouache F, Assabumrungrat S. Process design of biodiesel production: Hybridization of ester-and transesterification in a single reactive distillation. Energy Conversion and Management. 2017;153:493-503.
8. Steinigeweg S, Gmehling J. Transesterification processes by combination of reactive distillation and pervaporation. Chemical Engineering and Processing: Process Intensification. 2004;43(3):447-56.
9. Yu B-Y. Development of two plant-wide glycerol carbonate production processes: Design, optimization and environmental analysis. Journal of the Taiwan Institute of Chemical Engineers. 2020;117:19-25.
10. Jan C. J. Bart NPaSC. Biodiesel science and technology: Woodhead publishing limited; 2010.
11. Leoneti AB, Aragão-Leoneti V, de Oliveira SVWB. Glycerol as a by-product of

biodiesel production in Brazil: Alternatives for the use of unrefined glycerol. Renewable Energy. 2012;45:138-45.

12. Aroua MK, Cognet P. Editorial: From Glycerol to Value-Added Products. Frontiers in Chemistry. 2020;8.
13. The Glycerin Market: High Demand, Low Prices and the Impact of Biodiesel Germany: chemondis; [Available from: https://blog.chemondis.com/2266/glycerin-on-chemondis/.
14. Aresta MaD. AngelaCatalysis for the Valorization of Low-Value C-Streams. Journal of the Brazilian Chemical Society. 2014;25:2215-28.
15. Liu J, Pan D, Zhang Q, Guan Y, Yang B. Liquid-liquid equilibrium of systems encountered in glycerol transesterification with dimethyl carbonate. Fluid Phase Equilibria. 2022;563:113588.
16. Sedghi R, Shahbeik H, Rastegari H, Rafiee S, Peng W, Nizami A-S, et al. Turning biodiesel glycerol into oxygenated fuel additives and their effects on the behavior of internal combustion engines: A comprehensive systematic review. Renewable and Sustainable Energy Reviews. 2022;167:112805.
17. Biofuels explained - Ethanol U.S. Energy Information Administration: Washington; 2022 [Available from: https://www.eia.gov/energyexplained/biofuels/ethanol.php.
18. Strohm B. Ethanol. In: Wexler P, editor. Encyclopedia of Toxicology (Third Edition). Oxford: Academic Press; 2014. p. 488-91.
19. Backhaus AA, inventor; U S INDUSTRIAL ALCOHOL Co US IND ALCOHOL CO, assignee. Continuous process for the manufacture of esters1921.
20. Keller T. Chapter 8 - Reactive Distillation. In: Górak A, Olujić Ž, editors. Distillation. Boston: Academic Press; 2014. p. 261-94.
21. Vandana S. Reactive Distillation: Modeling, Simulation, and Optimization. 2019.
22. Kanchanasuta S, Champreda V, Pisutpaisal N, Singhakant C. Optimization of bio-succinic fermentation process from crude glycerol by Actinobacillus succinogenes. Environmental Engineering Research. 2021;26(4).
23. Carvalho M, Matos M, Roca C, Reis MAM. Succinic acid production from glycerol by Actinobacillus succinogenes using dimethylsulfoxide as electron acceptor. New

Biotechnology. 2014;31(1):133-9.

24. Lertlukkanasuk N, Phiyanalinmat S, Kiatkittipong W, Arpornwichanop A, Aiouache F, Assabumrungrat S. Reactive distillation for synthesis of glycerol carbonate via glycerolysis of urea. Chemical Engineering and Processing: Process Intensification. 2013;70:103-9.
25. Yu B-Y, Chen W-J. Rigorous Simulation and Optimization of a Plant-wide Glycerol Carbonate (GC) Production Process. In: Pierucci S, Manenti F, Bozzano GL, Manca D, editors. Computer Aided Chemical Engineering. 48: Elsevier; 2020. p. 283-8.
26. Zhang J, Wu Y, Song X, Xu S, Li S, Zhu Y, et al. Thermodynamic and kinetic studies for synthesis of glycerol carbonate from glycerol and diethyl carbonate over Ce–NiO catalyst. Chemical Papers. 2018;72(11):2909-19.
27. Liu J, Pan D, Zhang Q, Guan Y, Yang B. Liquid-liquid equilibrium of immiscible systems involved in glycerol transesterification with diethyl carbonate. Fluid Phase Equilibria. 2022;558:113455.
28. Gao X, Yang Y, Chen M, Cheng Q, Lu K. Novel heat pump reactive distillation and dividing-wall column reactive distillation processes for synthesizing isopropyl acetate to save TAC and reduce CO2 emissions. Chemical Engineering and Processing - Process Intensification. 2022;171:108746.
29. Pandit SR, Jana AK. Transforming conventional distillation sequence to dividing wall column: Minimizing cost, energy usage and environmental impact through genetic algorithm. Separation and Purification Technology. 2022;297:121437.
30. Abril AF. Aspen Plus - Matlab Link 2018 [Available from: https://www.mathworks.com/matlabcentral/fileexchange/69464-aspen-plus-matlab-link.
31. What Is the Genetic Algorithm? [Available from: https://www.mathworks.com/help/gads/what-is-the-genetic-algorithm.html.
32. Tunpaiboon N. Industry Outlook 2021-2023: Biodiesel 2021 [Available from: https://www.krungsri.com/en/research/industry/industry-outlook/energy-utilities/biodiesel/io/io-biodiesel-21.
33. Hebei Disha Import and Export Trade Co. L. Crude Glycerine 80% 85% Industrial Grade [Available from: https://hbdisha.en.made-in-china.com/product/lQXYMihdCkWa/China-Crude-Glycerine-80-85-Industrial-Grade.html.

34. Anhui Eapearl Chemical Co. L. 99.99% Purity Diethyl Carbonate High Quality [Available from: https://eapearlchem.en.made-in-china.com/product/RFutBspDhPVT/China-Best-Sale-99-99-Purity-Diethyl-Carbonate-High-Quality.html.

35. Thanahiranya P, Charoensuppanimit P, Sadhukhan J, Soottitantawat A, Arpornwichanop A, Thongchul N, et al. Succinic Acid Production from Glycerol by Actinobacillus succinogenes: Techno-economic, environmental, and exergy analyses. Journal of Cleaner Production. 2023;404:136927.

36. Supramono D, Ashshiddiq JfA, editors. Economic potential of the manufacture of acrolein and propylene glycol from glycerol. AIP Conference Proceedings; 2021: AIP Publishing LLC.

37. Chang WM. Glycerol (medical grade) preparation method using a by-product of a bio-diesel process. Google Patents; 2011.

38. Team C. Profitability Index 2022 [Available from: https://corporatefinanceinstitute.com/resources/knowledge/accounting/profitability-index/.

39. Guedes PHPS, Luz RF, Cavalcante RM, Young AF. Process simulation for technical and economic evaluation of acrolein and glycerol carbonate production from glycerol. Biomass and Bioenergy. 2023;168:106659.

40. Xilong Scientific Co. L. Denatured Ethanol 95% Sda-40-B-190 Ethyl Alcohols for Disinfectant [Available from: https://xilongchemical.en.made-in-china.com/product/aXPJsKcxXrhZ/China-Denatured-Ethanol-95-Sda-40-B-190-Ethyl-Alcohols-for-Disinfectant.html.

41. Turton R, Bailie RC, Whiting WB, Shaeiwitz JA. Analysis, synthesis and design of chemical processes: Pearson Education; 2008.

42. Ulrich GD, Vasudevan PT. How to Estimate Utility Costs 2006 [66-9]. Available from: https://terpconnect.umd.edu/~nsw/chbe446/HowToEstimateUtilityCosts-UlrichVasudevan2006.pdf.

43. Bildea CS, Győrgy R, Sánchez-Ramírez E, Quiroz-Ramírez JJ, Segovia-Hernandez JG, Kiss AA. Optimal design and plantwide control of novel processes for di-n-pentyl ether production. Journal of Chemical Technology & Biotechnology. 2015;90(6):992-1001.

44. Luyben WL. Principles and case studies of simultaneous design: John Wiley & Sons; 2012.
45. Lee Y-L, Lim D, Lee B, Upadhyay M, Brigljević B, Roh H-S, et al. Comparative Techno-economic analysis of methanol production via carbon dioxide reforming of landfill gas using a highly active and stable Nickel-based catalyst. Energy Conversion and Management. 2022;259:115585.
46. Baddour FG, Snowden-Swan L, Super JD, Van Allsburg KM. Estimating Precommercial Heterogeneous Catalyst Price: A Simple Step-Based Method. Organic Process Research & Development. 2018;22(12):1599-605.
47. IRR and NPV: Demystified [Available from: https://www.graycapitalllc.com/irr-and-npv-demystified/.
48. Tamplin T. How to Calculate IRR | IRR Formula [Available from: https://learn.financestrategists.com/finance-terms/irr/irr-formula/.
49. Kagan J. Payback Period Explained, With the Formula and How to Calculate It 2022 [Available from: https://www.investopedia.com/terms/p/paybackperiod.asp.
50. Lawrence A, Thollander P, Andrei M, Karlsson M. Specific Energy Consumption/Use (SEC) in Energy Management for Improving Energy Efficiency in Industry: Meaning, Usage and Differences. Energies. 2019;12(2):247.
51. Yu B-Y, Wu P-J, Tsai C-C, Lin S-T. Evaluating the direct CO2 to diethyl carbonate (DEC) process: Rigorous simulation, techno-economical and environmental evaluation. Journal of CO2 Utilization. 2020;41:101254.

APPENDIX

Appendix A Equipment operating conditions

Table A-1 Equipment designed operating conditions of the SRD process.

Unit	Equipment type	Operating conditions	Design comments
S-101	SSplit	- Split fraction - MIXED stream: 0.99 - CISOLID stream: 0.01	Designed based on the work of P. Thanahiranya et al. [35]
V-101	Valve	- Outlet pressure: 0.1 bar	
E-101	Heater	- Outlet temperature: 95°C - Pressure drop: 0 bar	
D-101	Flash2	- Pressure drop: 0 bar - Duty: 0	
P-101	Pump	- Outlet pressure: 1 bar	
S-102	Sep	- MONG 99% separation	
M-201	Mixer	- Pressure drop: 0 bar	
M-202	Mixer	- Pressure drop: 0 bar	
R-201	RCSTR	- Pressure: 1 bar - Temperature: 80 °C - Residence time: 4 hours - Catalyst loading: 160 kg	Designed based on the reaction studied by J. Zhang et al. [26]
P-201	Pump	- Outlet pressure: 1.01 bar	
D-201	RadFrac	- Number of stages: 26 - Feed stages: 8 - Pressure: 1.01 bar	From optimization
		- Reflux ratio: 0.07 - D/F ratio: 0.81	From design specifications
P-202	Pump	- Outlet pressure: 1.06 bar	
V-201	Valve	- Outlet pressure: 0.12 bar	

Table A-1 Equipment designed operating conditions of the SRD process. (Cont'd).

Unit	Equipment type	Operating conditions	Design comments
D-202	RadFrac	- Number of stages: 19 - Feed stages: 9 - Pressure: 1.06 bar	From optimization
		- Reflux ratio: 0.78 - D/F ratio: 0.38	From design specifications
D-202	RadFrac	- Number of stages: 24 - Feed stages: 12 - Pressure: 0.12 bar	From optimization
		- Reflux ratio: 3.19 - D/F ratio: 0.24	From design specifications
V-202	Valve	- Outlet pressure: 1 bar	
P-203	Pump	- Outlet pressure: 1 bar	

Table A-2 Equipment designed operating conditions of the RD process.

Unit	Equipment type	Operating conditions	Design comments
S-101	SSplit	- Split fraction - MIXED stream: 0.99 - CISOLID stream: 0.01	Designed based on the work of P. Thanahiranya et al. [35]
V-101	Valve	- Outlet pressure: 0.1 bar	
E-101	Heater	- Outlet temperature: 95°C - Pressure drop: 0 bar	
D-101	Flash2	- Pressure drop: 0 bar - Duty: 0	
P-101	Pump	- Outlet pressure: 1 bar	
S-102	Sep	- MONG 99 % separation	
V-201	Valve	- Outlet pressure: 0.17 bar	
M-201	Mixer	- Pressure drop: 0 bar	
V-202	Valve	- Outlet pressure: 0.17 bar	

Table A-2 Equipment designed operating conditions of the RD process. (Cont'd).

Unit	Equipment type	Operating conditions	Design comments
RD-201	RadFrac	- Number of stages: 21 - S11 Feed stage: 6 - S14 Feed stage: 19 - Pressure: 0.17 bar - Reflux ratio: 1.99	From optimization
		- D/F ratio: 0.48	From design specifications
		- Raschig ring packed in reaction stages with catalyst loading 122 kg	Estimate catalyst loading from packed section volume
P-201	Pump	- Outlet pressure: 0.96 bar	
D-201	RadFrac	- Number of stages: 12 - Feed stages: 11 - Pressure: 0.96 bar - Reflux ratio: 0.31	From optimization
		- D/F ratio: 0.69	From design specifications
P-201	Pump	- Outlet pressure: 1 bar	

Appendix B Estimate catalyst amount in a reactor

According to research that conducted experiments to measure the reaction and report the equilibrium constant for use in our work, The experiments were set by using a 50 mL batch reactor, filled the reactant of glycerol and diethyl carbonate in a ratio of 1:3 by mole, and using a catalyst in an amount of 5 wt% of glycerol. However, the process in this work has been scaled up to a commercial level, and the operation mode has been changed to continuous processing. Therefore, this work has no straightforward way to calculate the catalyst consumption in a reactor. This work calculates the amount of catalyst loading following these steps.

1. Find the reaction volume – for the SRD process, the reaction volume is a reactor volume, and for the RD process, the reaction volume is calculated from the volume of the reaction zone.
2. Find the initial volume of glycerol in the reactor.
3. The catalyst loading amount is 5 wt% of initial glycerol in the reactor.

<u>The separated reaction/distillation process (SRD) process</u>

- The calculated reactor volume is 16 m^3.
- If the volume of the reaction is 1 m^3, in a reactant mole ratio of 1:3, the amount of glycerol is 200.7 kg.
- So, the catalyst loading is 200.7 x 16 x 0.05 = 160 kg.

<u>The reactive distillation (RD) process</u>

- The volume of the reaction zone in the RD process is calculated from.

$$V_{\text{reaction zone}} = \frac{\pi D^2}{4} \times \text{Section height} \times \text{No. of reaction stages} = 12\ m^3$$

- So, the catalyst loading is 200.7 x 12 x 0.05 = 122 kg.

Appendix C Sensitivity analysis of catalyst cost to the process evaluation

The separated reaction/distillation process (SRD) process

Table C-1 Sensitivity analysis of catalyst cost of the SRD process.

Catalyst cost [US$/kg]	50	100	300	500
Total Capital Cost [million USD]	8.51	8.51	8,51	8.51
Total Raw Materials Cost [million USD/Year]	9.60	9.62	9.68	9.74
Total operating cost [Million US$/Year]	2.83	2.83	2.84	2.84
Total Product Sales [million USD/Year]	45.81	45.81	45.81	45.81
Payback period [Year]	1.767	1.767	1.771	1.774
Profitability index	1.65	1.65	1.65	1.64
Internal rate of return (%)	163.56	163.26	162.83	162.07

The reactive distillation (RD) process

Table C-2 Sensitivity analysis of catalyst cost of the RD process.

Catalyst cost [US$/kg]	50	100	300	500
Total Capital Cost [million USD]	5.74	5.74	5.74	5.74
Total Raw Materials Cost [million USD/Year]	10.06	10.08	10.13	10.18
Total operating cost [Million US$/Year]	2.30	2.30	2.30	2.31
Total Product Sales [million USD/Year]	47.63	47.63	47.63	47.63
Payback period [Year]	1.46	1.46	1.46	1.46
Profitability index	1.71	1.71	1.71	1.71
Internal rate of return (%)	266.48	266.20	265.11	264.02

Appendix D Utilities specifications

Table D Utilities specifications.

Utility type	Type	Temperature (^{O}C)	
		Inlet	Outlet
Chilled water	Water	5	15
Cooling water	Water	30	45
Low pressure steam	Steam	160	160
High pressure steam	Steam	254	254
Fuel-Oil	Oil	350	340

Appendix E Economics analysis

Table E Economics analysis calculations basis.

Description	Units	Value
Time period		
Operating Hours per Period	Hours/Year	8,766
Number of Weeks per Period	Weeks/Year	52
Number of Periods for Analysis	Year	20
Capital costs parameters		
Working Capital Percentage	Percent/Year	5
Operating costs parameters		
Operating Supplies (lump-sum)	USD/Year	0
Laboratory Charges (lump-sum)	USD/Year	0
User Entered Operating Charges (as percentage)	Percent/Year	25
Plant Overhead (Percent of Operating Labor and Maintenance Costs)	Percent/Year	25
G and A Expenses (Percent of Subtotal Operating Costs)	Percent/Year	8
General investment parameters		
Tax Rate	Percent/Year	40
Interest Rate	Percent/Year	20
Economic Life of Project	Year	10
Salvage Value (Fraction of Initial Capital Cost)	Percent	20
Depreciation Method		Straight Line
Escalation		
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

VITA

NAME	Chayanin Sriharuethai
DATE OF BIRTH	20 September 1998
PLACE OF BIRTH	Bangkok, Thailand
INSTITUTIONS ATTENDED	B.Eng., Chemical Engineering, Mahidol University, 2021
HOME ADDRESS	111/14 Phornthana village, Moo.6, Thapma, Rayong, 21000, Thailand