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Research Article

Enhancing Propylene Glycol Product Yield by Modifying the Glycerol Hydrogenation Process

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Abstract

The production of propylene glycol from glycerol is an emerging and sustainable approach in the chemical industry that can be considered completely renewable. Glycerol, a byproduct of biodiesel production, has gained attention as an alternative feedstock for the synthesis of value-added chemicals such as propylene glycol. This paper evaluates how to perform process modification for optimization of propylene glycol product yield. The process modification was carried out by adding compressor unit before entering a heater, adding heater unit before entering a mixer, and adding 2 separator unit before entering a distillation column. By modifying the addition of compressor unit, heater unit, and 2 separator unit, it has been proven that it can optimizing the propylene glycol product yield by up to 99.75%.

Keywords: Propylene glycol; process modification; process Optimization; Product yield

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1. Introduction

Propylene glycol is an organic compound derived from propylene which has the chemical formula $C_3H_8O_2$ with the IUPAC name 1,2-propanediol [1]. Propylene glycol is used as a raw material to produce polyester resins, liquid detergents, pharmaceuticals, cosmetics, and paints [2]. Propylene glycol is produced by hydrogenation of glycerol. Glycerol is a polyol with three hydroxyl groups and interesting physicochemical properties that allow its application in different industries [3]. Glycerol is the main by-product of biodiesel production that always increase due to the continuous increase in biodiesel supply [4]. In biodiesel suppliers, glycerol production is abundant, where one biodiesel company, The Archer Daniels Midlands Company (ADM) in the USA has proven that they produce 100 kt/t of PG using bio-diesel derived glycerol [5]. The hydrogenation process carried out refers to the conversion of glycerol into propylene glycol (PG) through a catalytic process that previously through dehydration process that involving the release of water molecules [6].

In previous research, the conversion of glycerol to propylene glycol was carried out in two stages: the hydrolysis of propylene oxide to glycerol, followed by the hydrogenation of glycerol to PG. The hydrolysis process is carried out of weak acid conditions, with a molar ratio of propylene oxide and water of 1:15. This process produced glycerol, which was then subjected to hydrogenation to form propylene glycol. The hydrogenation was conducted with a nickel catalyst at temperatures between 110 °C - 150 °C,

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and pressures ranging from 2 MPa-4 MPa that produced propylene glycol, dipropylene glycol, tripropylene glycol, and other by-products, which were separated using a distillation column. The propylene glycol product yield achieved in this process was limited up to 73.50% [7].

The purpose of this process modification is to optimizing propylene glycol product yield by modifying the glycol hydrogenation process. In this modification, variations in addition of some unit are introduced. The aim of these modifications is to observe their impact on the outcomes obtained in the propylene glycol production.

2. Methods

Process modifications were carried out using Aspen HYSYS V11 software by selecting NRTL and UNIQUAC as fluid-package type. In this simulation, the modification for optimizing the propylene glycol product yield starts with doing an addition of pump (P-102) at the beginning of the process to increasing the pressure of glycerol and compressor (K-100) for increasing the pressure of hydrogen. Then, the cooler (E-100) was added after adding pump for reducing the temperature of glycerol and heater (E-101) for increasing the temperature of hydrogen. Adding two separator (V-100) and (V-101) in this modification aims to separate excess hydrogen from the desired product from reactor, namely propylene glycol. In addition, there is an additional compressor (TEE-100) to produce purge and ensure the efficiency of H_2O purification. After adding two separators, then adding splitter (X-101) to forcibly separate the product from hydrogen so that the hydrogen can be recycled and reused to form propylene glycol again. Adding cooler (E-102) after the distillation unit aims to ensure that the main product (propylene glycol) is at room temperature. To optimizing the propylene glycol yield, a process modification was carried out by adding a recycle (RCY-1) from the top product of splitter to returned it to the mixer.

From the modifications that have been made, the results obtained show an increase in propylene glycol product yield by optimizing model of the process with adding several unit so that a high yield is obtained. Propylene glycol product yield can be calculated using Equation (1):

$$Yield\ of\ Propylene\ Glycol\ (\%) = \frac{Mol\ of\ Propylene\ Glycol\ prodcut}{Total\ mol\ of\ feed} \times 100\% \quad (1)$$

From Equation (1), we get the result that shown in Table 2 contain the comparison of product yield results by using the modification and unmodification processes.

Based on the data obtained from hysys in modified process and unmodified process, the purity of the propylene glycol product produced can be determined. Purity of propylene glycol can be calculate using Equation (2):

$$Purity\ (\%) = \frac{mass\ of\ propylene\ glycol}{total\ product\ mass} \times 100\% \quad (2)$$

The results were analyzed and compared between the unmodified process system and the modified process of propylene glycol production to assess the efficiency of each process.

3. Result and Discussion

3.1 Basic Chemical Process and Simulation

Propylene glycol is obtained from glycerol through a hydrogenolysis reaction that involves breaking the chemical bonds of CO and adding hydrogen simultaneously [8]. The catalysts commonly used are derived from precious metals, such as Pt, Rh, Ru, Pd, Ir, and Re, as they exhibit high selectivity to propylene glycol and high glycol erol conversion [9]. However, non-precious metals, such as Cu, Co, and Ni, can present catalytic activity as high as precious metal catalysts, in addition to having lower costs. Nickel-based catalysts have high activity for producing hydropower plants because they are typical catalysts for glycerol reform [10]. Yun *et al.* [11] studied bimetallic Cu-Ni catalysts supported on mesoporous alumina for glycerol hydrogenolysis in a batch reactor, obtaining 60% of glycerol conversion and 20% of propylene glycol yield at 220 °C, under atmospheric pressure. More recently, Seretis and Tsiakaras [12] studied aqueous phase reforming and hydrogenolysis of glycerol in a batch reactor, using 65%Ni catalyst supported on SiO_2/Al_2O_3; the maximum propylene glycol yield was 22% after 4 h of reaction at 240 °C, under autogenous pressure.

Total chemical reaction [11]:

$$C_3H_8O_{3(l)} + H_{2(g)} \rightarrow C_3H_8O_{2(l)} + H_2O_{(g)} \quad (3)$$
$$\Delta H_{r298} = -\ 80500\ J/mol$$
$$\Delta H_{r500} = -79861.39\ J/mol$$

The reaction was carried out at a temperature of 500 K. From the calculation above, so it is concluded that the reaction that occurs is exothermic [13].

Calculation of ΔG_f Reaction (3) as a main reaction with respect to the ΔGf value for each component in Table 1:

$$\Delta G_{f298} = [(G_{f298}C_3H_8O_{2(l)} + G_{f298}\ H_2O_{(g)}) - (G_{f298}\ C_3H_8O_{3(l)} + G_{f298}\ H_{2(g)})]\ J/mol$$

ΔG_{f298} = [(– 304480 + (–228600)) – (–448490 +0)] J/mol

ΔG_{f298} = –84590 J/mol

$\Delta G_{298} = -RT \ln K_{298}$

$\ln K_{298} = -\frac{\Delta G_{298}}{RT}$

$\ln K_{298} = -\frac{-84590 \text{ J/mol}}{(8.314 \text{ J/mol K}) \times 298 \text{ K}}$

$K_{298} = 6.7268 \times 10^{14}$

At operating temperature 500 K:

$\ln \frac{K_{500}}{K_{298}} = \frac{(-\Delta Hr\ 298\ K)}{R} \times \left(\frac{1}{T} - \frac{1}{298\ K}\right)$

$\ln \frac{K_{500}}{6.7268 \times 10^{14}} = \frac{(-(-80500 \text{ J/mol}))}{8.314 \text{ J/mol K}} \times \left(\frac{1}{500\ K} - \frac{1}{298\ K}\right)$

$K_{500} = 1.3397 \times 10^{9}$

Because the value of $K_{500} > 1$, thus, the main reaction is irreversible.

Therefore, the production of propylene glycol through gas-liquid phase glycerol hydrogenation is preferred. This hydrogenation process involves reacting glycerol ($C_3H_8O_3$) with hydrogen (H_2) to produce propylene glycol ($C_3H_8O_2$) along with by-products water (H_2O) [11]. Process flow diagram of glycerol hydrogenation without modification is shown in Figure 1. The manufacture of propylene glycol is by the process of hydrogenation of glycerol. In general, to determine the effect of temperature, it can be determined by the Arrhenius equation:

$$k = A.e^{-Ea/RT} \quad (4)$$

It is known that increasing the reaction temperature will increase the value of the reaction rate constant (k), which means accelerating the reaction rate.

Table 1. Data of ΔG_f for each component at temperature 298 K [17]

Compound	ΔH_{f298} (kJ/mol)	ΔG_{f298} (kJ/mol)
$C_3H_8O_3$	-582.8	-448.49
H_2	0	0
$C_3H_8O_2$	-421.5	-304.48
H_2O	-241.8	-228.6

According to Jiménez *et al.* [14] the process of making propylene glycol from glycerol has the equation for the value of k:

$$k_1 = 1.54 \times 10^7.e^{-86.56/RT} \quad (5)$$

$$k_2 = 7.16 \times 10^6.e^{-57.8/RT} \quad (6)$$

3.2 Modified Process Flowsheet and Simulation

To optimizing the propylene glycol product yield, this modified process starts with adding pump (P-102) at the beginning of the process to increasing the pressure of glycerol and compressor (K-100) for increasing the pressure of hydrogen. Then, the cooler (E-100) was added after adding pump for reducing the temperature of glycerol and heater (E-101) for increasing the temperature of hydrogen that can speed up the reaction rates also helps reach the consistent thermal conditions, which that conditions is important for maximizing product yield. Adding two separator in this modification aims to increase purity of product (propylene glycol). The bottom result of both separators produced a good amount of propylene glycol product yield that up to 47.61% and 58.71% which then combined using a mixer. In addition, there is an additional compressor (TEE-100) to produce purge and ensure the efficiency of H_2O purification. After adding two separator, then adding splitter (X-101) to forcibly separate the product from hydrogen until the composition was 100%, so that the hydrogen can be recycled and reused to form propylene glycol again [15]. After that, the bottom product of two separators and splitter was mixed before entering the distillation column for efficient recovery of several product [16]. Distillation column is used to separated propylene glycol until 99.75% yield and H_2O untul 98.62% yield. After the distillation column, adding cooler (E-102) to ensure that the main product (propylene glycol) is at room temperature. To optimizing the propylene glycol yield, a process modification was carried out by adding a recycle (RCY-1) from the top product of splitter to

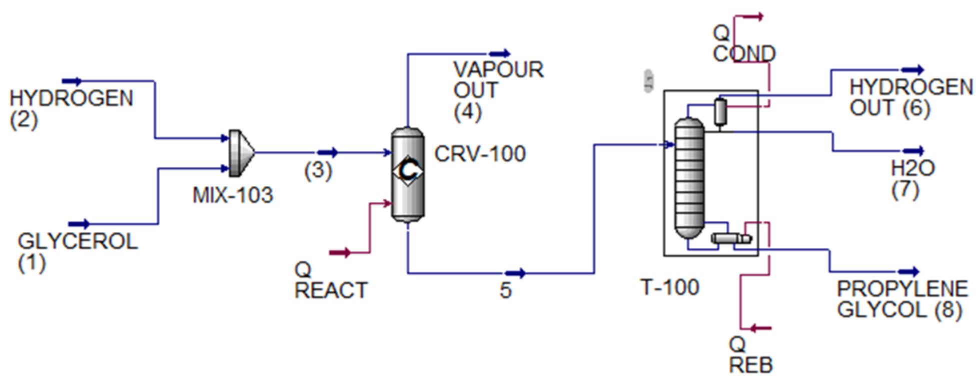

Figure 1. Unmodified flowsheet system process

returned it to the mixer that aims to minimizing the use of raw materials, as well as optimize energy use in the system which improve process sustainability. Simulation of the process modification of propylene glycol production is shown in Figure 2 and Figure 3, while the result of heat and material balance after the modified process is presented in the Table S1 (Supporting Information).

3.3 Improvement of Product Yield Due to The Process Modifications

The improvement of product yield due to the modification of the propylene glycol production process have a significant increase up to 99.75%. The process modification applied to the simulation of propylene glycol production involves adding one heater unit, one compressor unit, and two separators unit. The improvement in the yield of propylene glycol also influenced by recycling the top product hydrogen) of second separator and returned it to the mixer. The following is a calculation of the product yield with unmodified and modified process.

Propylene glycol product yield in unmodified process (%) = (0.7350/1) × 100% = 73.5%
Propylene glycol product yield in modified process (%) = (0.9975/1) × 100% = 99.75%

The comparison results of unmodified process and modified process are shown in Table 2.

3.4 Improvement of Product Purity Due to The Process Modifications

The quality of propylene glycol products acts as a benchmark for assessing both the factory's performance and the overall standard of manufactured products. Greater product purity reflects enhanced quality in the product and the factory [18]. To evaluate the percentage purity in the two simulated processes, calculations were performed using Equation (2). The mass of the propylene glycol product and the total product mass were derived from Aspen HYSYS data. Table 3 provides the data for the total product mass in the unmodified process design. Using the

Table 2. Comparison propylene glycol yield with unmodified process and modified process

Process	Propylene Glycol Yield (%)
Unmodified process	73.5
Modified process	99.75

Table 3. Composition of unmodified process system product

Composition	Mass fraction
Glycerol	0.2639
Hydrogen	0
Propylene glycol	0.7350
Water (H_2O)	0.0011
Total product	1

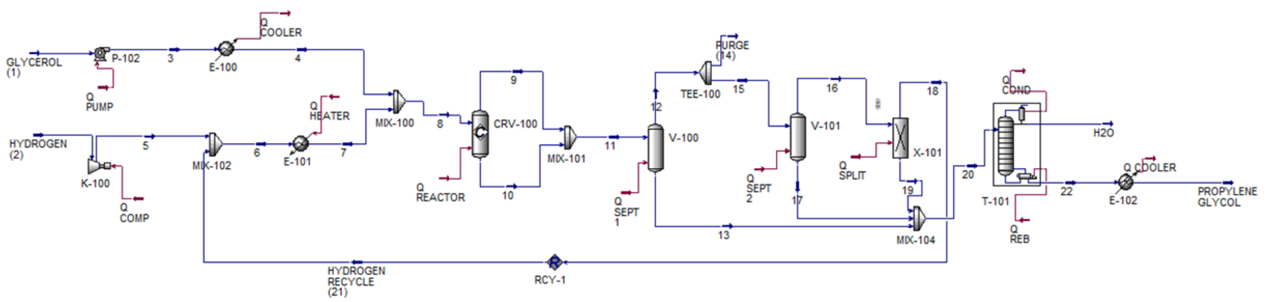

Figure 2. HYSYS simulation of modified process

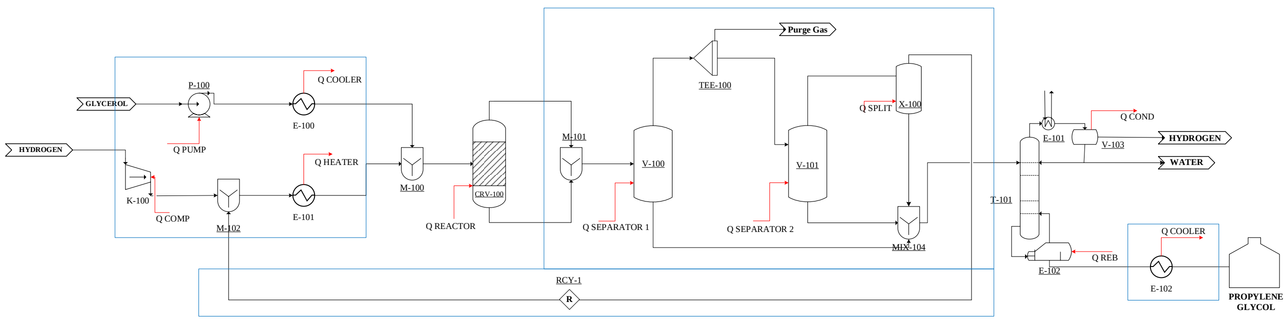

Figure 3. Process flow diagram (PFD) of modified process of propylene glycol production

information in Table 3, the purity of propylene glycol in unmodified process system was calculated as follows:

Purity in unmodified process (%) = (0.7350/1) x 100% = 73.5%

The calculation shows that the methyl chloride produced in the unmodified process system has an estimated purity of 73.5%. Table 4 provides the data for the total product mass in the modified process design. To compare this with the modified process, the purity of methyl chloride in the modified process was also determined using the same method, as follows:

Purity in modified process (%) = (0.9969/1) x 100% = 99.69%

A comparison of the product purity for both processes is summarized in Table 5. According to the purity results, the propylene glycol produced using the modified process exhibits higher purity, with a value of 99.69%. This reflects a residual of 26.19% between the two processes.

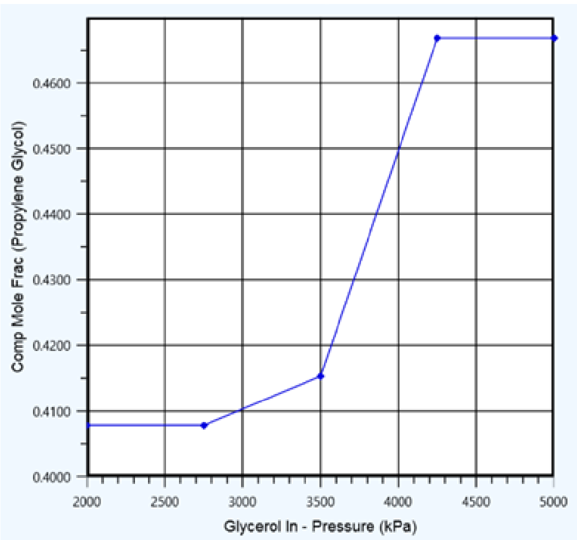

Figure 4. Sensitivity analysis with varying glycerol in-pressure

Table 4. Composition of modified process system product

Composition	Mass fraction
Glycerol	0.31
Hydrogen	0
Propylene glycol	0.9969
Water (H_2O)	0
Total product	1

3.5 Sensitivity Analysis of Reactor Operating Conditions

The sensitivity analysis investigated the impact of varying glycerol pressure, considered the independent variable, on the dependent variable, which is the mole fraction of liquid propylene glycol. The analysis was conducted using the Case Study tool, with glycerol pressure adjusted to 2000 kPa, 2750 kPa, 3500 kPa, 4250 kPa, and 5000 kPa. Table 6 presents the results of this analysis, demonstrating how changes in glycerol pressure influence the propylene glycol mole fraction in the reactor's output stream.

The case study revealed that as glycerol pressure increases, the yield of liquid products leaving the reactor increase. Since propylene glycol is the primary product, maintaining a high yield is crucial for simplifying downstream separation processes [19]. To minimize the load on the separation unit, operating at higher glycerol pressures is recommended. Figure 4 illustrates the correlation between glycerol pressure and the propylene glycol mole fraction.

Another sensitivity analysis focused on varying the ratio of glycerol mass flow to hydrogen gas mass flow, again targeting the liquid propylene glycol mole fraction as the dependent variable. Using the Case Study tool in HYSYS, the analysis examined mass flow ratios of 0.9; 1.05; 1.20; 1.35; and 1.5. The results, displayed in the Table 7, show the effect of these variations on the propylene glycol mole fraction.

The findings indicate that increasing the glycerol-to-hydrogen mass flow ratio leads to a higher yield of propylene glycol products exiting the reactor. A higher mass flow ratio improves the yield of the desired product, while a lower

Table 5. Purity of unmodified propylene glycol product of unmodified and modified process

Unmodified process (wt%)	Modified process (wt%)
73.5	99.69
Residual	26.19

Table 6. Sensitivity analysis of operating condition of reactor by varying pressure of glycerol

Reactor Pressure (kPa)	Propylene glycol mole fraction leaving the reactor
2000	0.4079
2750	0.4079
3500	0.4153
4250	0.4668
5000	0.4668

ratio increases the formation of by-products [20]. Figure 5 depicts the relationship between the glycerol-to-hydrogen mass flow ratio and the propylene glycol mole fraction leaving reactor.

4. Conclusion

Process modifications in propylene glycol production are essential for enhancing efficiency and sustainability. By optimizing unit operations such as compressors, heaters, and separators, and splitter the process achieved increased yield and improved product purity from 73.5% to 99.75%. Recycling unreacted hydrogen further reduced raw material consumption and energy use. These improvements demonstrate the potential for more sustainable and efficient chemical production through targeted process adjustments. Further studies on economic feasibility and environmental impact are recommended to ensure long-term viability and compliance with environmental regulation.

CRediT Author Statement

Author Contributions: A.S.N. Syahidah: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization, Project administration; M. Vania: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data Curation, Writing - Original Draft, Writing - Review & Editing; N. Aulia: Conceptualization, Methodology, Software, Validation, Investigation, Resources, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization, Supervision; N. Hidayah: Conceptualization, Methodology, Resources, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization; I. Varado: Software, Formal analysis, Investigation. All authors have read and agreed to the published version of the manuscript.

Table 7. Sensitivity analysis of operating condition of reactor by varying the ratio mass flow of glycerol to propylene glycol.

Ratio mass flow of glycerol to propylene glycol	Propylene glycol mole fraction leaving the reactor
0.9	0.4073
1.05	0.4075
1.20	0.4236
1.35	0.4683
1.5	0.5107

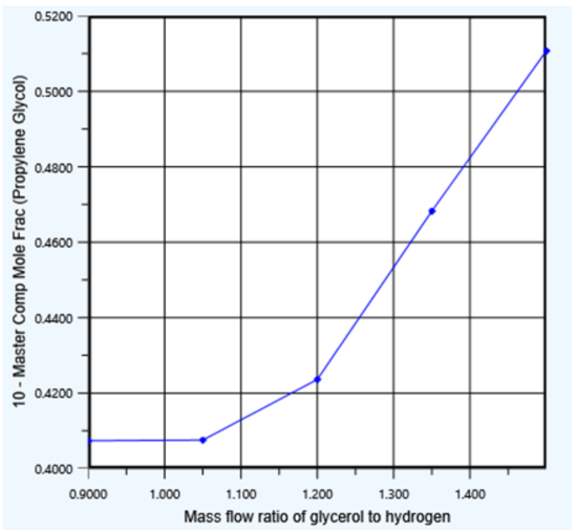

Figure 5. Sensitivity analysis with varying the ratio of glycerol mass flow to H_2 gas mass flow

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