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Research Article

Enhancing Mass and Yield Product of Propylene Glycol Production through Glycerol Hydrogenolysis

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Abstract

The chemical industry in Indonesia continues to experience significant growth in both innovation and technology. One of the significant areas of improvement is in supporting materials, exemplified by propylene glycol. The process of producing propylene glycol from glycerol involves hydrogenolysis. The hydrogenolysis process of propylene glycol is the reaction of glycerol with hydrogen gas under specific conditions. The effects of process innovation or modification with the aim of enhancing mass efficiency and yield of propylene glycol. Methods to increase mass efficiency and yield using the Aspen HYSYS V11 simulator tool and implemented effectively. From the process modifications that have been implemented, it can be concluded that this design is quite effective as it mass and yields more efficiency, with one notable improvement being mass efficiency of propylene glycol from 7304 ton/year to 10012 ton/year and the percentage yield of propylene glycol in the final product increasing from 70% to 98%.

Keywords: Glycerol; Hydrogenolysis; Propylene Glycol; Mass efficiency; Yield efficiency

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1. Introduction

Propylene glycol is an intermediate molecule with wide applications in the chemical industry. Its most successful renewable production technology is based on hydrogenolysis of glycerol, subproduct of the biodiesel industry, which has been commercially produced since the early 2010s [1]. Propylene glycol stands out with its superior economic value and versatile uses, including its incorporation as an additive in the polymer industry, Propylene glycol is a promising chemical with numerous applications including as an antifreeze, cosmetics, moisturizers, solvents, surfactants, and preservatives [2].

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Many studies have been conducted previously to obtain a high conversion in the hydrogenolysis process of glycerol into propylene glycol. Seretis & Tsiakaras [3] reported experimental trials of glycerol hydrogenolysis were carried out at reaction temperatures of 200 °C, 220 °C, and 240 °C, along with autogenous pressures of 16, 23.5, and 33.5 bar, respectively. The maximum glycerol conversion observed in these assessments reached 73.5%.

Modifications to the production process of propylene glycol, based on existing literature, are being implemented to enable the direct synthesis of propylene glycol from glycerol through a hydrogenolysis process with an annual capacity of 10.000 tons per year. The molar ratio of hydrogen to glycerol setted by 5:1 [4]. An excess amount of hydrogen is used to minimize side reactions, thus increasing the selectivity of the glycerol introduced into the process and producing propylene glycol with a high yield [5]. Operating conditions of the conversion reactor inlet feed used at an operating temperature of 490.75 K and a pressure of 4000 kPa operating continuously.

In the previous study, the glycerol that came out as the bottom result of the second separation column was very high in purity, and no separate glycerol recycling flow was carried out, as additional glycerol with the reactor feed. thus causing the mass flowrate and yield of propylene glycol produced to be not maximized [6]. Glycerol should not be wasted because it has a high market value and its production process is difficult and expensive. pure glycerol involves a complex and costly process, so any wasted volume will be economically detrimental. Therefore, glycerol that still contains high purity should be reused to reduce waste and maximize its economic potential [7].

In previous studies, the specification of the separation order in the distillation column has been identified as a factor leading to convergence, where in practice the separation order of the distillation column significantly affects the product yield of propylene glycol [8]. Similarly, simulation success for some units can be hampered by inconsistencies in the material balance. For example, the distillation column simulation in this journal may fail if the product specifications are not consistently aligned with the feed [9].

Based on these problems, the purpose of this research is to innovate by changing the separation sequence, namely separating glycerol in the first separation column so that the remaining glycerol can be recycled which still has high purity, and adding valves and coolers to adjust the operating conditions of recycled glycerol with feed glycerol. The process design can significantly increase the mass flowrate and yield of propylene glycol.

Aspen HYSYS used to simulate production of propylene glycol. Aspen HYSYS can observe the influence of operating parameters and provide a good analysis of chemical and physical phenomena in chemical industrial processes, allowing the optimization process to take place efficiently [10]. In this context, this work aims to develop a preliminary conceptual design to assess the potential of glycerol transformation to propylene glycol with hydrogenolysis reaction through process simulation, in order to obtain the main process parameters, such as material and energy balances [11]. Many studies have explored the optimization of the propylene glycol production process using HYSYS software. Jiménez et al. [6] employed HYSYS to evaluate production costs and assess the consumption of raw materials and utilities in a propylene glycol facility. Janoovsk *et al.* [12] applied HYSYS to identify potential hazards in the plant caused by variations in process parameters.

The purpose of this research is to enhancing mass and yield efficiency as an innovative perspective compared to previous research. In addition, recycle was added to the glycerol and the separation sequence in the distillation column was adjusted.

2. Methods

2.1 Hydrogenolysis

The production of propylene glycol through glycerol hydrogenolysis represents one of the most promising technologies for chemicals [13]. According to Liu *et al.* [14], the main reactions of glycerol hydrogenolysis to propylene glycol defined as:

$$C_3H_8O_{3(l)}+H_{2(g)} \rightarrow C_3H_8O_{2(l)}+H_2O_{(g)} \quad \Delta H^o_{298K} = -80.5 \text{ kJ/mol} \quad (1)$$

The hydrogenolysis reaction breaking the C-O bonds in glycerol that leads to the glycols formation such as propylene glycol [15].

Hydrogen, unreacted glycerol, propylene glycol, and byproducts make up the majority of the reactor effluent. In order to guarantee a 5:1 M ratio of hydrogen to glycerol at the process inlet, excess hydrogen is recovered in a tee valve, recycled, and combined with pure hydrogen in the mixing section [6]. Excess moles of hydrogen are employed at the start of the process. Because of the high material needs, production costs will rise if hydrogen is not used at the end of the process [16].

2.2 Methods to Increase Mass Efficiency of Propylene Glycol

The production propylene glycol from glycerol is modified, where valve, cooler, mixer to recycle the glycerol. In addition, changes were also made to the separation sequence by distillation to obtain higher purity propylene glycol. We have refined the production process for propylene glycol by implementing modifications based on established research [17]. The improvement focuses on the increase mass flow of glycerol to propylene glycol via hydrogenolysis, designed to achieve an annual production capacity of 10.000 tons.

When the sequence of separation process between propylene glycol is changed, the first distillation column (COL-01) will produce propylene glycol and water as the top product and glycerol as the bottom product with high purity. The bottom product will be recycle and the top product will go to the second distillation column

(COL-02) to separate propylene glycol and water to get high purity propylene glycol product. In the previous research, the remaining unconverted glycerol was not used and only became a side-product. Therefore, in this study, glycerol is reused through a recycle process to increase the amount of reactants used. The side product of glycerol will be reduced pressure through Valve-01 [18] and then cooled using Cooler-01 [19] to change the phase of glycerol from gas to liquid to adjust the feed conditions of glycerol in Mix-04. When the reactants increase in size, the amount of product produced is also large. The increase in the amount of product directly increases the amount of yield produced [20].

2.3 Calculation Yield of Propylene Glycol

The process modification results indicate an increase in propylene glycol yield by recycling the output from the distillation column (COL-01). The yield of propylene glycol can be determined using Equation (2) [21]:

$$Yield\ of\ Propylene\ Glycol\ (\%) = \frac{Mol\ of\ propylene\ glycol}{mol\ of\ glycerol} \times 100\% \qquad (2)$$

3. Result and Discussion

3.1 Basic Process Flow Diagram of Propylene Glycol Production

Basic (unmodified) process flow diagram of propylene glycol is depicted in Figure 1 and Table S1 for material balance and composition of process before modification, while the Aspen HYSYS V11 simulation of the basic process is depicted in Figure 2. In the initial stage, glycerol and hydrogen are fed into the mixer (Mix-02) with a molar ratio of hydrogen to glycerol of 5:1. Excess hydrogen is added to inhibit side reactions and increase the selectivity of the conversion of glycerol to propylene glycol. The output from the mixer (Mix-02) is then fed into the conversion reactor, which operates at a temperature of 490.75 K and a pressure of 4000 kPa, with the hydrogenolysis process taking place under controlled conditions to maximize efficiency.

The reactor output, which consists of two phases, passes through a separator (Sep-01) to separate excess hydrogen. Hydrogen for recycling is removed and released as purge gas, which can be used as fuel if it meets the standards [22]. The bottom output from the separator is processed through two distillation columns. The first distillation column (COL-01) produces air as the top product, while the bottom product containing glycerol and propylene glycol is flowed to the second distillation column (COL-02) to remove propylene glycol as top product and glycerol as bottom product.

3.2 Thermodynamic Review

For the determination of the nature of the reaction (exothermic/endothermic) and the direction of the reaction (reversible/ irreversible), it is necessary to calculate the standard heat of reaction (ΔH_{298K}) at 1 bar and 298 K based of standard heat of formation of the reactants and products [23].

Chemical reaction:

$C_3H_8O_{3(l)} + H_{2(g)} \rightarrow C_3H_8O_{2(l)} + H_2O_{(g)}$

$\Delta H_{f298} = [(\Delta H_{f298}\ C_3H_8O2_{(l)} + \Delta H_{f298}\ H_2O_{(g)}) - (\Delta H_{f298}\ C_3H_8O_{3(l)} + \Delta H_{f298}\ H_{2(g)})]$ J/mol

$\Delta H_{f298} = [(-421500 + (-241800)) - (-582800 + 0)]$ J/mol

$\Delta H_{f298} = -80500$ J/mol

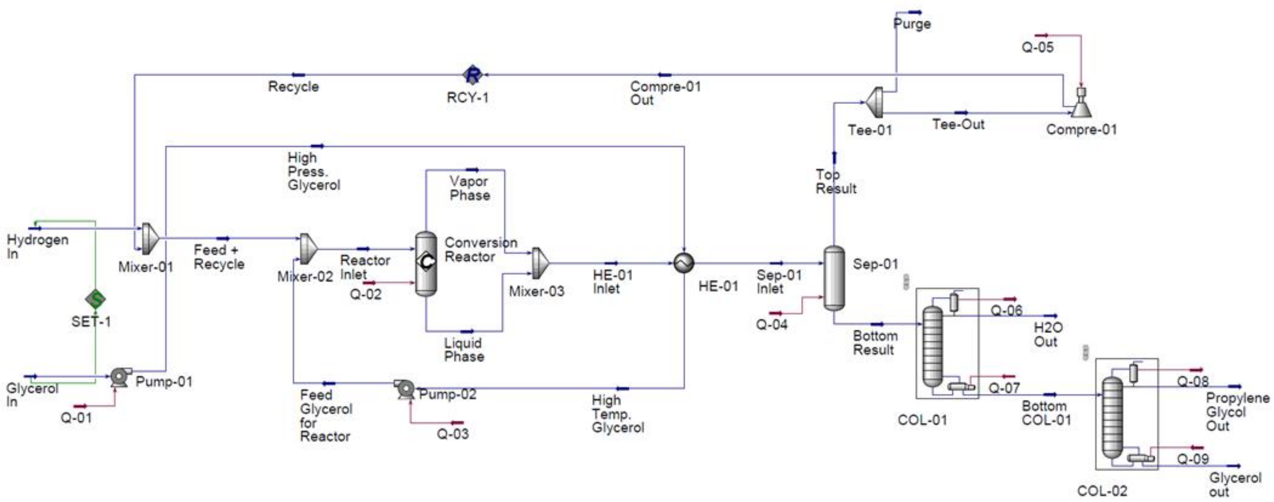

Figure 1. Aspen HYSYS simulation of propylene glycol production before modification

From the above calculations, the values of ΔH_{f298} are −80500 J/mol. Thus, it can be concluded that the occurring reaction is exothermic.

Calculation of Gibbs Free Energy at operating temperature (298 K):

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

$$\Delta G_{f298} = [(-304480 + (-228600)) - (-448490 + 0)]\ \text{J/mol}$$

$$\Delta G_{f298} = -84590\ \text{J/mol}$$

Calculation of reaction equilibrium constant at operating temperature (298 K):

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

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

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

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

Calculation of reaction equilibrium constant at reactor temperature (490.75 K):

$$\ln\frac{K_{490.75}}{K_{298}} = \frac{(-\Delta Hr_{\ 298\ K})}{R} \times \left(\frac{1}{490.75\ K} - \frac{1}{298\ K}\right)$$

$$\ln\frac{K_{490.75}}{6.7268 \times 10^{14}} = \frac{\left(-\left(-80500\frac{\text{J}}{\text{mol}}\right)\right)}{8.314\frac{\text{J}}{\text{mol}}\text{K}} \times \left(\frac{1}{490.75\ K} - \frac{1}{298\ K}\right)$$

$$K_{490.75} = 1.929 \times 10^{9}$$

The obtained value of $K_{490,75K}$ for this side reaction is 1.929×10^{9}. Due the large equilibrium constant value, the reaction irreversible.

3.2 Process Modification: Increase Mass Flow of Propylene Glycol

Modified process and its Aspen HYSYS V11 simulation are depicted in Figure 3 and 4, respectively, while Table S2 presents material balance and composition of process after modification. In order to increase mass flow (feed amount) can be done by recycling the main raw materials of propylene glycol production by hydrogenolysis process, namely glycerol. Recycle glycerol is obtained from the bottom product of COL-01. These results are presented in Table 2. Based on the Table 2, recycle of glycerol system maximize the mass flow of propylene glycol produced. With the same feed, there is increase 2708 ton/year of mass flow. This mean, it increase 1.3× than before. The feed amount of hydrogen also increases due to the change in feed amount of glycerol.

From the modification results, several internal modifications were obtained in the process, component have the same composition so that pure glycerol is obtained for recycling, and it

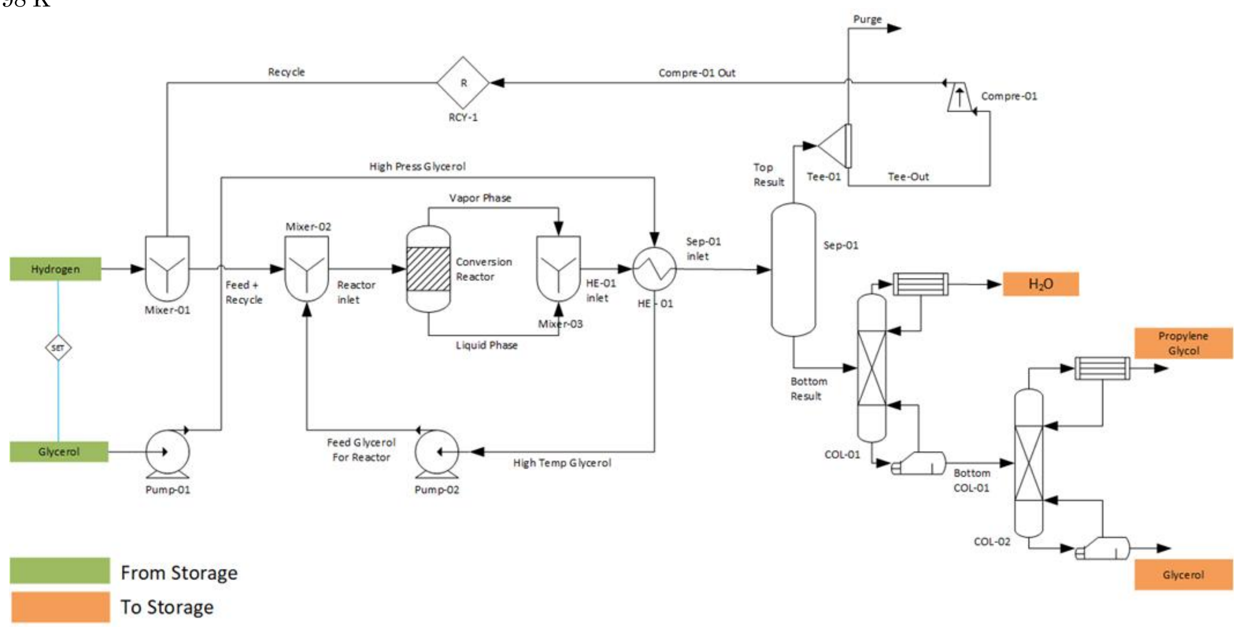

Figure 2. Process flow diagram of propylene glycol production before modification

Table 2. Mass flow of propylene glycol production before and after modification

Treatment	Feed amount (ton/year)		Mass flow of propylene glycol (ton/year)
	Hydrogen	Glycerol	
Before modification	14,050	12,500	7,304
After modification	15,470	15,310	10,012

reduce costs production by reusing glycerol at the end of the process [24].

3.3 Process Modification: Increase Yield of Propylene Glycol

The results of the process modification show an increase in propylene glycol yield by recycling the bottom product from Sep-01 containing glycerol back to the glycerol feed in mix-04. The process modification applied to the propylene glycol production simulation involves the addition of one glycerol recycle flow and adjustment of the distillation separation sequence from the basic process flow diagram. The simulation results using Aspen HYSYS V11, obtained the yield of Propylene glycol production before and after modification. These results are presented in Table 3 which illustrates that modifying the process for propylene glycol production increases the yield from 70% to 98%. One common modification to achieve such improvements is the change in the distillation sequence by separating glycerol in COL-01 to separate high purity glycerol so that it can be recycled back into the system as part of the glycerol feed. The second distillation column (COL-02) focuses on separating water from

Table 3. Yield of propylene glycol production before and after modification

Process	Propylene glycol yield (%)
Before modification	70
After modification	98

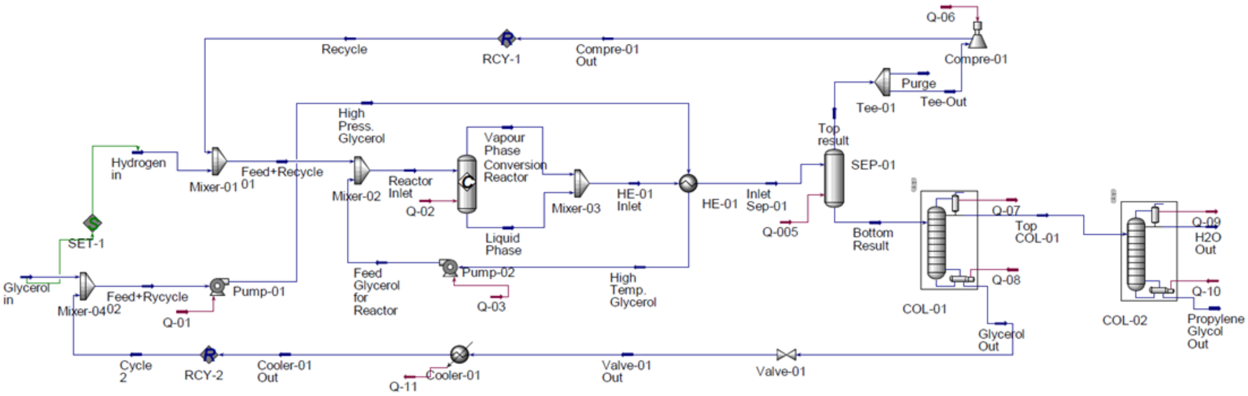

Figure 3. Aspen HYSYS simulation of propylene glycol production after modification

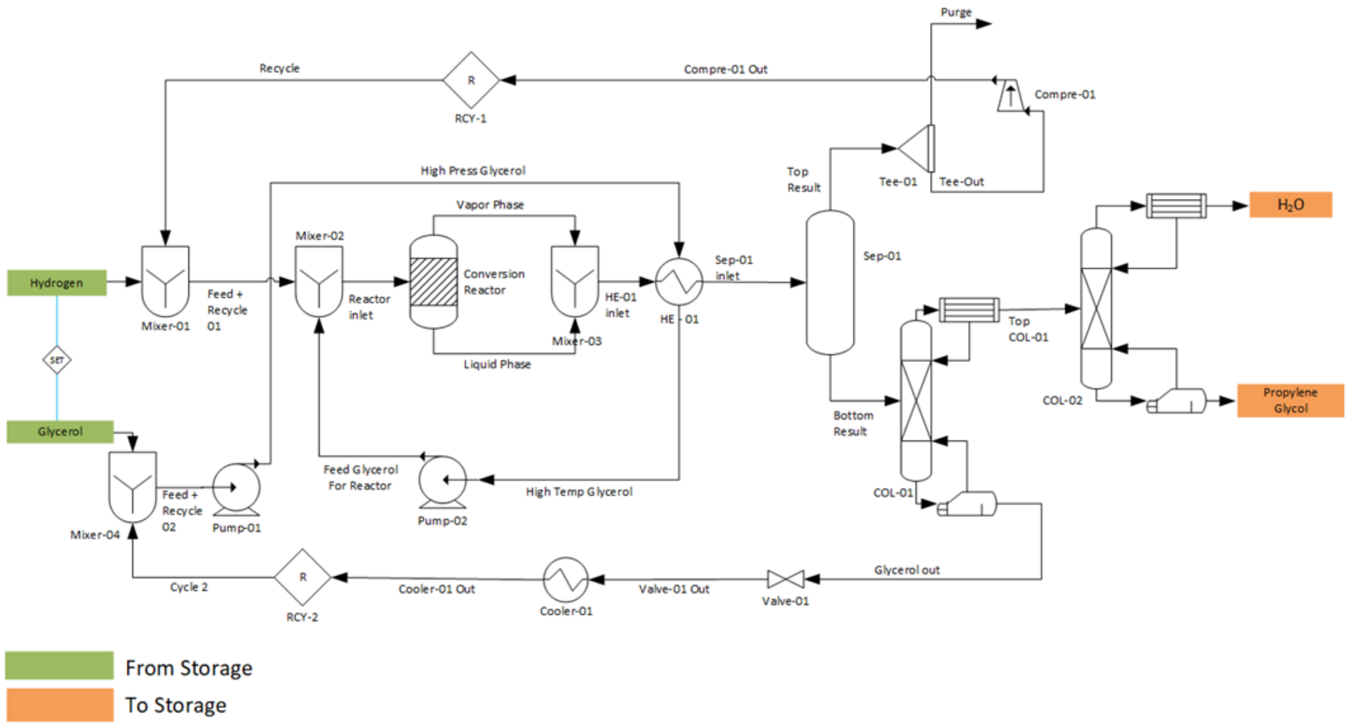

Figure 4. Process flow diagram of propylene glycol production after modification

propylene glycol, ensuring a higher purity product that meets industrial specifications. These improvements demonstrate the importance of integrating efficient separation processes and recycling strategies to achieve higher yields, greater resource efficiency, and more sustainable chemical production [25].

4. Conclusions

The process of producing propylene glycol from glycerol has been modified by incorporating a recycle, valve, cooler, mixer and change the sequence of distilation column. Recycling glycerol can increase the mass flow rate production of propylene glycol from 7304 ton/year to 10012 ton/year and the percentage yield of propylene glycol in the final product increasing from 70% to 98% with the same feed amount. The modifications applied to the production process of propylene glycol through glycerol hydrogenolysis have proven to be highly effective in optimizing both yield and production capacity. By implementing a glycerol recycle system and change in the distillation sequence, the process not only maximizes the utilization of raw materials but also minimizes waste, making it more cost-effective and sustainable. Such advancements pave the way for more sustainable and scalable operations in industrial applications, making it crucial to conduct a comprehensive techno-economic analysis to evaluate the feasibility of large-scale implementation, identify key cost drivers, and explore potential areas for cost reduction

CRediT Author Statement

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