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Research Article

Improving Glycerol Conversion by Implementing Recycle Streams and Reducing Distillation Steps in Glycerol Carbonate Production

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Abstract

The rising surplus of glycerol from biodiesel production drives the need for its valorization into high-value compounds such as glycerol carbonate (GC). This study proposes a process intensification strategy to enhance glycerol conversion efficiency through transesterification with dimethyl carbonate (DMC). The modification involves incorporating a recycle stream for unreacted DMC and reducing one distillation column to minimize energy consumption and thermal degradation. Simulations were conducted using Aspen HYSYS® v11, modeling a CSTR operating at 95 °C and 1 atm with a DMC:glycerol molar ratio of 3:1. Process modification resulted in complete DMC utilization and a shift in separation strategy, with simulated glycerol conversion increasing from 91% to 99.98%. These findings demonstrate the trade-offs between energy efficiency and conversion performance in process redesign, offering valuable insights into more sustainable GC production.

Keywords: Glycerol; Glycerol Carbonate; Transesterification; Recycle Stream; Distillation Reduction

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1. Introduction

The increasing demand for biodiesel has led to a significant surplus of glycerol, a by-product generated in large quantities during transesterification. Although glycerol is a valuable chemical intermediate, its oversupply has depressed its market value, urging the need for effective conversion routes into high-value derivatives [6]. One such promising route is the production of glycerol carbonate (GC), an environmentally benign compound with applications in polymers, solvents, and electrolytes [7].

Conventional processes for GC synthesis, such as transesterification of glycerol with dimethyl carbonate (DMC), often involve multiple separation and purification steps, particularly energy-intensive distillation. Additionally, the process suffers from incomplete glycerol conversion and low carbon atom efficiency due to undesired by-products and unutilized reactants [5].

To improve sustainability and economic performance, integrating recycle streams of unconverted reactants and minimizing the number of distillation steps have emerged as viable process intensification strategies. Recycle can boost reactant utilization, while reduced distillation can lower energy consumption and simplify process design [15]. This study aims to evaluate the impact of these modifications on glycerol conversion efficiency, glycerol carbonate yield, and overall process energy demand, using simulation-based analysis.

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2. Methods

2.1 Transesterification Process of Glycerol with Dimethyl Carbonate to Glycerol Carbonate

Synthesis of glycerol carbonate can be achieved through various chemical routes, including the transesterification reaction of glycerol with dimethyl carbonate (DMC), carbon monoxide (CO), carbon dioxide (CO_2), phosgene, or urea [10]. However, several challenges and limitations are associated with these routes. A promising pathway involves the transesterification reaction of glycerol with DMC using either homogeneous or heterogeneous catalyst. This pathway is advantageous due to its mild reaction conditions and the ease of product separation [14].

The basic process design was adapted from [1], incorporating a transesterification reaction followed by a three-step distillation process. In the production of glycerol carbonate, the use of three distillation columns is essential to achieve high conversion of product separation. The first column (T-100) separate methanol and unreacted DMC (overhead stream) from glycerol carbonate and unreacted glycerol (bottom stream). The second column (T-102) separate methanol (overhead stream) from unreacted DMC (bottom stream). The third column (T-101) purifies the glycerol carbonate by eliminating the remaining impurities, ensuring the final product meets high-purity specifications [1].

The reaction between glycerol and dimethyl carbonate (DMC) was modeled using a CSTR reactor (R-100). Operating at 95 °C and 1 atm, the reactor achieved a glycerol conversion rate of 91% with a DMC-to-glycerol molar ratio of 3:1. Due to the mildly exothermic nature of the reaction, temperature control was maintained by circulating cooling water at 298 K [4]. According to Yu *et al.* [12], the main reaction of glycerol carbonate production from glycerol with DMC defined as:

$$C_3H_8O_3 + C_3H_6O_3 \rightarrow C_4H_6O_4 + 2\ CH_3OH \qquad \Delta H^\circ_{298K} = -356.7\ \text{kJ/mol} \tag{1}$$

2.2 Process Modification

The process of glycerol carbonate production was enhanced by incorporating a recycle stream and eliminating one of the distillation columns. In this modified system, the reactor outlet contains unreacted dimethyl carbonate (DMC), which is separated and returned to the feed stream for further reaction. This recycling strategy ensures that nearly all of the DMC is utilized, minimizing raw material loss and increasing overall process efficiency.

In addition to implementing the recycle loop, increasing the molar ratio of DMC to glycerol within the reactor is essential to drive the reaction equilibrium toward glycerol carbonate formation. Introducing DMC in excess reduces the amount of unreacted glycerol in the reactor effluent, resulting in a significant improvement in glycerol conversion. A molar ratio of dimethyl carbonate (DMC) to glycerol of 1:8 was applied in the simulation.

As a result, the reactor output consists primarily of unreacted DMC, methanol, and glycerol carbonate. These components are then separated based on their boiling points using two distillation columns. The use of only two columns is made possible by the high glycerol conversion achieved, which leaves a negligible amount of unreacted glycerol, thus eliminating the need for a third separation unit. The first column (T-100) separates the most volatile component, methanol, as the overhead product, while unreacted DMC and glycerol carbonate remain in the bottom stream. The second column (T-101) further separates unreacted DMC as the overhead product while glycerol carbonate in the bottom stream, enabling the recovery and reuse of DMC in the process. The modified process was simulated in Aspen HYSYS v11, aiming to improve glycerol conversion efficiency.

Glycerol conversion can be calculated as follow:

$$\text{Glycerol Conversion} = (\text{Reacted Glycerol}) / (\text{Glycerol Input}) \times 100\% \tag{2}$$

3. Results and Discussion

3.1 Process Flow Diagram of Transesterification Glycerol to Glycerol Carbonate

Before starting the simulation, the chemical components, their properties, the thermodynamic model, the kinetics of the reactions involved, and the conditions under which the raw materials enter the process had to be defined. All of the chemicals required for the simulation are available in the Aspen HYSYS® v11 simulator database. However, the hydrogen reagent for the acrolein production process and the dimethyl carbonate (DMC) reagent and glycerol carbonate (GLC) product for the glycerol carbonate production process were not as desired. The hydrogen in the acrolein production process comes from the Lewis acid site of the acid catalyst and the coke species. Even though this substance is available in the Aspen HYSYS® v11 database, we decided to consider it as a hypothetical substance so that it could react according to the kinetics proposed for the process, without associating it with the UNIFAC structure. The DMC and GLC of the glycerol carbonate production process were considered hypothetical substances and were created using the UNIFAC Component Builder tool. The process of making glycerol carbonate from glycerol is modified using ASPEN HYSYS, where mixer, reactor, heat exchanger, and distillation column were added.

The glycerol carbonate process flowsheet after modified can be seen in Figure 3. Since the reactor used in this process is a CSTR, the conversion rate obtained by Esteban *et al.* [4] was used to determine the reactor volume; to be consistent with the results of the study by Xu and Xu [5], the catalyst volume was calculated for the economic analysis even though it was not considered in the simulations. Based on the 5% m/m value used in the experiments of Kaur and Ali [9], a catalyst load of 53.5 kg/h was calculated in this study; using the CSTR feed stream conditions obtained in Aspen HYSYS® v11 and the desired glycerol conversion, a 0.1925 m3 reactor volume was obtained. The reactor size was calculated from the kinetic parameters of the selected catalyst and the expected yield. However, since the experiments from which the kinetic parameters were derived were performed on a laboratory scale, scaling up could ultimately affect the performance of the catalyst and thus the reactor size. Thus, although the calculated reactor volume appears to be quite small, it could eventually be larger if it becomes reality, but at this point it is only a conjecture. In this process, there are three heat exchangers. The first heat exchanger (E-100) heats the reactor feed stream. The second heat exchanger (E-101) cools the glycerol stream and introduces it into the first distillation column (T-100).

For the heat exchangers, following the recommendations of Seider et al [3], the thermal utilities available in Aspen HYSYS® v11 were considered, and those containing process streams with temperatures above 240 °C were fired with heaters; the condensers and reboilers in the distillation columns operated below 240 °C were considered as general heat exchangers considered. Reactor temperatures are maintained by stainless steel coils.

Heat transfer coefficients were obtained directly from the simulator. The global heat transfer coefficient depends on the chemical species involved in the heat exchange and was extracted from Seider *et al.* [3] and Towler and Sinnot [8].

Low pressure saturated vapor (LP vapor) is flowed at 408 kg/h with the Aspen HYSYS® v11 utility used in the E-100 heat exchanger. In the second and third heat exchangers, water (referred to as cooling water in the simulator) is selected for cooling, flowing at 12,190 kg/h and 7182 kg/h, respectively, into the equipment at 25 ◦C and out of the equipment at 50 ◦C. In the initial analysis, a minimum approach temperature of 10 ◦C was adopted to avoid an excessively large heat exchange area.

To begin the product separation process, the initial column design proposed by Xu and Xu was used as a reference. However, the simulation revealed that the reboiler generated excessively high temperatures, prompting a shift from atmospheric to vacuum pressure operation. This adjustment was necessary to prevent the degradation of residual glycerol, which can occur at temperatures above 200 °C. To mitigate this risk, it was decided that this column, along with the subsequent ones, should operate under vacuum conditions. Despite this change, the reboiler temperature still exceeded 200 °C. As a result, a cooler was installed immediately after the column to lower the temperature of the glycerol stream upon exit, thereby reducing the potential for thermal degradation [13].

In addition, the separation results from the simulated column differed from those reported, which served as the basis for the column design. Rather than producing a distillate stream consisting solely of methanol, the simulation yielded a mixture of methanol and dimethyl carbonate (DMC) [11]. This discrepancy is likely due to the use of different thermodynamic models in the two studies. Since the simulation results differed from those of the original study used to design the first column, the subsequent columns were designed using the simulator's Shortcut Column tool, applying the same heuristic approach used in acrolein production. Based on the obtained parameter values, the column configurations shown in in Figure 1 were refined and process flow diagram of glycerol carbonate production shown in Figure 2 were also refined. In column T-102, methanol and dimethyl carbonate (DMC) were separated to allow for the potential recycling of DMC within the process, as well as methanol in a possible integrated biodiesel production system. Column T-101 was used to adjust the purity of the stream containing glycerol carbonate and unreacted glycerol, aiming to produce the final product. Despite operating under vacuum, high reboiler temperatures were still required, making it necessary to install a cooler immediately after this column to lower the temperature and prevent degradation.

3.2 Mass and Energy Balances

The results of mass and energy balances of glycerol carbonate of unmodified process through the transesterification process can be seen in Tables S1 and S2 (Supporting Information).

3.3 Thermodynamics Consideration

Transesterification reaction is as follow:

$$C_3H_8O_{3(l)} + C_3H_6O_{3(l)} \rightarrow C_4H_6O_{4(l)} + 2CH_3OH_{(l)} \quad (2)$$

For the determination of the reaction and the direction of the reaction, it is necessary to calculate the standard heat of formation at 1 bar and 368 K of the reactants and products. The value of ΔH_f° and ΔG_f° can be seen in Table 1.

Standard heat of reaction (ΔH_R°) calculation:

$\Delta H_R^\circ = \sum \Delta H_f^\circ{}_{\text{product}} - \sum \Delta H_f^\circ{}_{\text{reactant}}$

$\Delta H_R^\circ = (\Delta H_f^\circ\ C_4H_6O_4 + \Delta H_f^\circ\ 2CH_3OH) - (\Delta H_f^\circ\ C_3H_8O_3 + \Delta H_f^\circ\ C_3H_6O_3)$

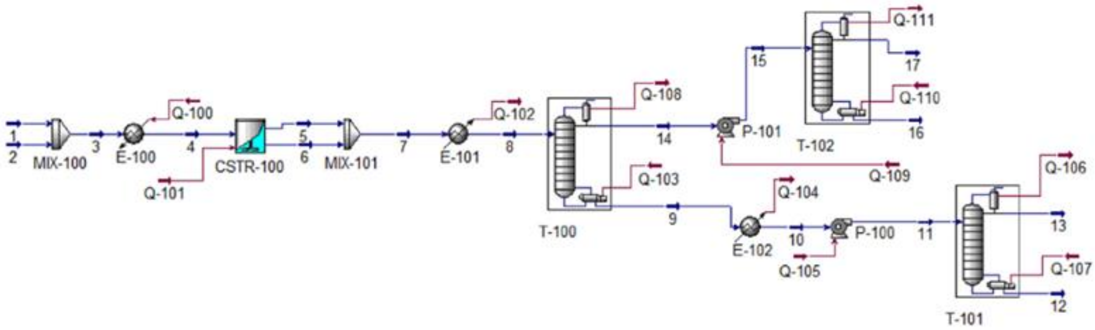

Figure 1. Simulation of glycerol carbonate production before modified with Aspen HYSYS V11.

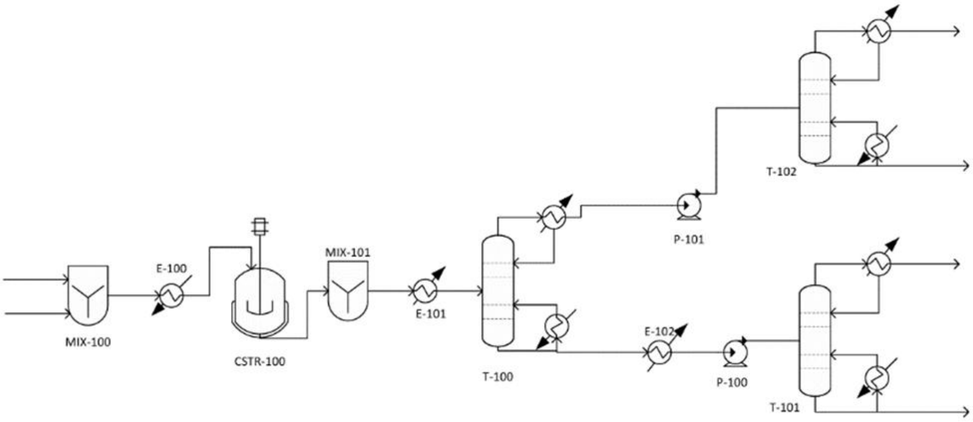

Figure 2. Process flow diagram of glycerol carbonate production before modified.

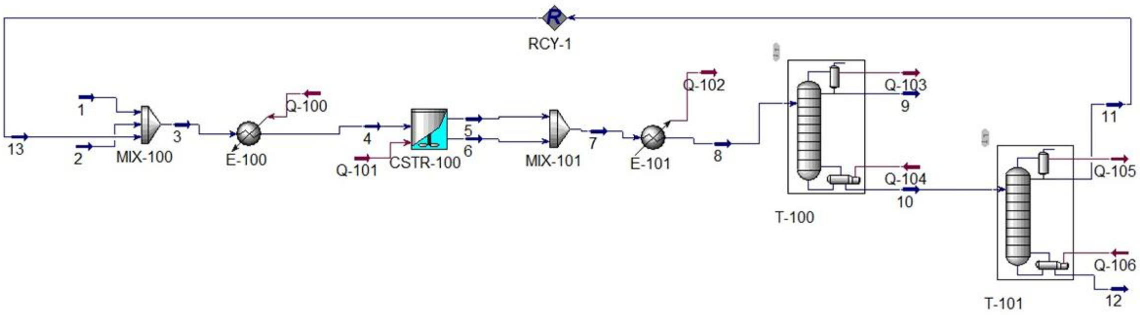

Figure 3. Simulation of glycerol carbonate production after modified with Aspen HYSYS V12

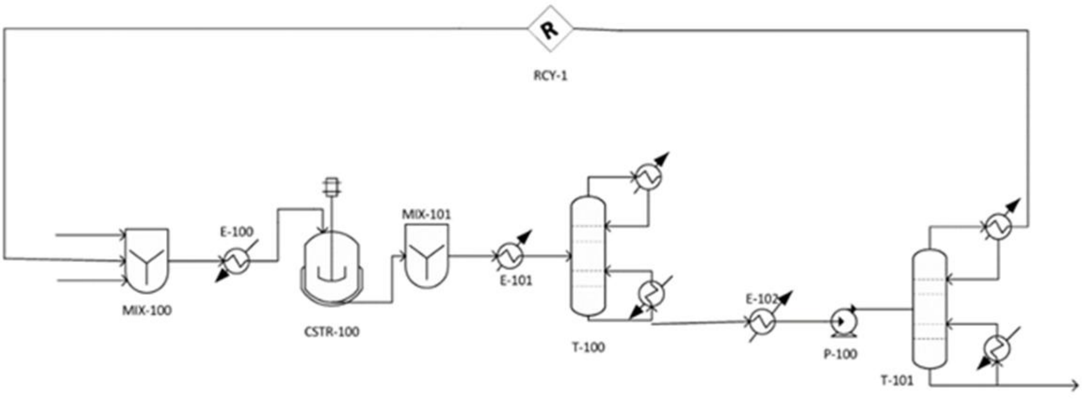

Figure 4. Process flow diagram of glycerol carbonate production after modified.

$\Delta H_R° = -356.7$ kJ/mol = -356,700 J/mol

Based on the above calculation, the value $\Delta H_R° = -356{,}700$ J/mol (negative value). So, it can be concluded that the reaction is going under exothermic reaction.

Gibbs free energy ($\Delta G_f°$) calculation:
$\Delta G_f° = \sum \Delta G_f°{}_{\text{product}} - \sum \Delta G_f°{}_{\text{reactant}}$
$\Delta G_f° = (\Delta G_f°\ C_4H_6O_4 + \Delta G_f°\ 2CH_3OH) - (\Delta G_f°\ C_3H_8O_3 + \Delta G_f°\ C_3H_6O_3)$
$\Delta G_f° = -84.4$ kJ/mol = -84,400 J/mol

Equilibrium constant (K_{298}) in the standard state is as follow:

$$\Delta G_{298} = -RT \ln K_{298}$$
$$\ln K_{298} = -\frac{\Delta G_{298}}{RT}$$
$$\ln K_{298} = -\frac{-84400\ \text{J/mol}}{8.314\frac{\text{J}}{\text{mol}} \cdot \text{K} \times 298\ \text{K}}$$

$K_{298} = 6.2302 \times 10^{14}$
At operating temperature 368.15 K:

$$\ln\frac{K_{368.15}}{K_{298}} = -\frac{(-\Delta HR°\ 298\ \text{K})}{R} \times \left(\frac{1}{T} - \frac{1}{298\ \text{K}}\right)$$
$$\ln\frac{K_{368.15}}{6.2302 \times 10^{14}} = -\frac{(-(-356700\ \ \text{J/mol}))}{8.314\frac{\text{J}}{\text{mol}}\text{K}} \times \left(\frac{1}{368.15\ \text{K}} - \frac{1}{298\ \text{K}}\right)$$

$K_{368.15} = 5.11302 \times 10^{26}$
Because the value of $K_{368.15} > 1$, thus, the main reaction is irreversible.

3.4 Process Modification for Increasing Conversion of Glycerol

To improve conversion of glycerol, the process was modified by adding recycle stream and eliminating a distillation column. First, the reactant input will enter the CSTR-100 (Reactor) to react and form glycerol carbonate. The product exiting the reactor is still in the form of a mixture consisting of glycerol carbonate, methanol (as a by-product), and unreacted dimethyl carbonate (DMC). Then proceeds to the separation process via the distillation column (T-100). In this distillation column, glycerol carbonate is separated from methanol, with the top product being methanol and the bottom product consisting of glycerol carbonate and DMC. Next, the bottom product is pumped into the distillation column (T-101). In this column, glycerol carbonate is separated from DMC, where the bottom product is the main product, glycerol carbonate, and the top product is DMC.

The unreacted DMC is then recycled through the recycle stream (RCY-1) and mixed with the main reactants before entering the reactor. The presence of a recycle stream for DMC increases the conversion of the glycerol reactant, as DMC is made in excess, there by reducing the production of unreacted glycerol from the reactor. The calculation of glycerol conversion can be obtained from the data on the moles of glycerol that react with to the initial moles of glycerol in the reactor, specifically from the reactor input (stream 4) and outputs (stream 5 and stream 6). Additionally, the molar flow rate and mole fraction of glycerol for each reactor input and output are also used to calculate the moles of glycerol.

Table 1. The value of $\Delta H_f°$ and $\Delta G_f°$ of compounds.

Compounds	Molecular Formula	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)
Glycerol	$C_3H_8O_3$	-669.3	-447
Dimethyl Carbonate	$C_3H_6O_3$	-397.4	-395
Glycerol Carbonate	$C_4H_6O_4$	-946	-623.2
Methanol	CH_3OH	-238.7	-166.6

4. Conclusion

Improvements were made in the production of glycerol carbonate from glycerol with dimethyl carbonate to improve glycerol conversion. ASPEN HYSYS V.12 was used to model and simulate the process of producing glycerol carbonate from dimethyl carbonate and glycerol via a transesterification process. To improve conversion of glycerol, the process was modified by adding recycle stream and eliminating a distillation column. The conversion of glycerol before modification process is 91%, so a modification was necessary to increase the conversion of the reactant. By performing two distillations and adding recycle stream, the conversion of the glycerol reached 99.98%.

Credit Author Statement

Author Contributions: D. P. Wilujeng: Conceptualization, Writing, Software, Review and Editing; K. C. Kollelsy: Writing, Software, Review and Editing; D. P. Prathista: Writing, Review and Editing, Resources, Investigation; S. Dwitasari: Conceptualization, Writing, Methodology, Review

Table 2. Conversion of glycerol to glycerol carbonate before and after process modification.

Process Type	Glycerol Conversion
Before Modification	91%
After Modification	99.98%

and Editing. All authors have read and agreed to the published version of the manuscript.

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