Optimization of a reactive distillation process to produce propylene glycol as a high value-added glycerol derivative.

Jahaziel Alberto Sánchez-Gómeza\*, Fernando Israel Gómez-Castroa, Salvador Hernándeza.

aDepartmento de Ingeniería Química, División de Ciencias Naturales y Exactas, Campus Guanajuato, Universidad de Guanajuato, Noria Alta S/N, Guanajuato, Gto. 36050, Mexico. [fgomez@ugto.mx](mailto:fgomez@ugto.mx)

Abstract

Glycerol is a key component that is currently obtained in significant volumes as a by-product in the production of biodiesel. Due to this increase on its production, the prize of crude glycerol has become lower. Moreover, its availability has triggered its potential to be used as a platform molecule for the generation of high value-added chemical products. In the present work, process intensification and optimization techniques are applied to the production of propylene glycol (PG) from glycerol. The design parameters of the reactive distillation scheme are adjusted by rigorous simulation and optimization using genetic algorithms through a link between Python and the Aspen Plus process simulator. The TAC value obtained for the reactive distillation scheme is 16.279×105 USD/y, with operation and capital costs of 8.711 ×105 USD/y and 37.838 ×105 USD, respectively.

**Keywords**: reactive distillation, crude glycerol valorization, process simulation, process optimization, propylene glycol production.

* 1. Introduction

Renewable glycerol is a by-product generated in the biodiesel production process by transesterification of triglycerides. Unlike fossil fuels, biodiesel is a renewable resource since it can be obtained from biomass. Moreover, it can reduce greenhouse gas emissions, being an environmentally friendly alternative (Rasrendra et al., 2023). The increase in global biodiesel production has led to an increase in glycerol generation. In 2020, the production of more than 4.6 billion liters of crude glycerol derived from biodiesel industry has been reported (REN 21, 2021). Due to this increase on its production, glycerol is considered a financial and environmental problem for the biodiesel industry, and the need arises to look for alternatives to take advantage of glycerol as a renewable and abundant source of carbon to obtain high value-added chemical products.

Propylene glycol (PG) is an important chemical used as antifreeze, humectant, solvent, and preservative. It is usually obtained by hydrolysis of propylene oxide, which is generated from petrochemicals. Alternatively, PG can be produced by a more environmentally friendly route by using renewable glycerol as a carbon and hydrogen source. Although cost competitiveness remains a major constraint, the conversion of glycerol to PG is a promising route. An approach to improve economic and energy indicators in the renewable PG production process involves applying process intensification (PI) strategies. The goal of PI is to achieve technological improvement in chemical processes to make them more efficient, reducing the size of equipment and/or the number of basic process operations by using multifunctional equipment (Devaraja and Kiss, 2022). Furthermore, there are few precedents in the literature on the design of intensified processes for the valorization of glycerol.

This work presents the intensification of the conventional process to produce propylene glycol from renewable glycerol. The intensified process includes the implementation of a reactive distillation system. Given the large number of decision variables involved in the reactive distillation scheme, as well as the non-linearity of the model that represents this type of system, its optimization is carried out by coupling the Aspen Plus simulation software with a genetic algorithm coded in Python, with the objective of minimizing the total annual cost.

* 1. Methodology
     1. Process design

Considering the pressure conditions used in the process and the presence of organic mixtures with a large amount of water, the UNIQUAC model was selected as the thermodynamic model for the simulation of the process. This model has been previously used to describe satisfactorily the phase equilibrium in similar systems (Jimenez et al., 2020). The binary interaction parameters for the thermodynamic model were obtained from the Aspen Plus database.

The production of PG (C3H8O2) from glycerol (C3H8O3) has as by-products ethylene glycol (C2H6O2), methanol (CH3OH) and water (H2O). The reactions involved in the generation of PG are shown in Eqs. (1) and (2). The hydrodeoxygenation of glycerol to produce PG occurs in the liquid phase, using Cu/ZrO2 as catalyst. For this catalyst reaction, the power-law first-order kinetic model developed by Gabrysch et al. (2019) has been used. The dependence of the kinetic constant (*kI*) on temperature is given by the Eq. (3), where is the pre-exponential factor, and *EA,I* is the activation energy. The parameters required for the calculation of reaction rates are summarized in Table 1.

|  |  |
| --- | --- |
|  | (1) |
|  | (2) |
|  | (3) |

**Table 1.-** Pre-exponential factor and activation energy for reactions.

|  |  |  |
| --- | --- | --- |
| **I** |  | **(kJ/mol)** |
| 1 | 2 x 1010 L mol-1 s-1 | 106 |
| 2 | 9 x 107 L mol-1 s-1 | 97 |

The conventional process (CS) for PG production is shown in Figure 1. The simulation of the conventional process is adapted from the work of Jimenez et al. (2020), in which the technical and economic evaluation of a PG production process using glycerol as raw material was performed. In this CS a plug flow reactor is employed for carrying out the glycerol hydrodeoxygenation reaction, followed by two distillation columns for the separation and recovery of PG with a purity of 99 mol%. In the bottom of Figure 1, the reactive distillation scheme (RDS) proposed for PG production is presented (Sánchez-Gómez et al., 2023). It consists of a reactive distillation column where the glycerol hydrodeoxygenation takes place, followed by a distillation column for the purification of PG. The aqueous glycerol and hydrogen feed streams have flowrates of 100 kmol/h and 16.4 kmol/h, respectively (1:1 by weight). In the simulation of these schemes, the RadFrac module of the commercial simulator Aspen Plus has been used. A total pressure drop of 10 psia has been assumed for each distillation column.

Diagrama

Descripción generada automáticamente

**Figure 1.-** Conventional scheme (CS) and reactive distillation scheme (RDS) for propylene glycol production.

* + 1. Process optimization

In process optimization, it is necessary to select appropriate criteria to determine the potential of each processing scheme. Among these performance criteria, one of the most widely used is the total annual cost (TAC), which considers the capital and operating costs required in the process, Eq. (4). Operation cost (OC) includes those derived from the use of utilities, which are steam, cooling water, electricity, and catalysts. The operation time of the plant is 8600 hours per year. The unitary costs considered for these services are 12.247 USD/GJ for HP steam, 0.354 USD/GJ for cooling water, 0.0775 USD/kW for electricity and 143.87 USD/kg for catalyst (Atsbha, et al., 2021).

|  |  |
| --- | --- |
|  | (4) |

The capital cost (CC) considers the cost of distillation columns, trays, reactor, reboiler, condenser, pumps, and compressors. In the evaluation of these costs, the methodology proposed by Guthrie (Turton et al., 2003) was used, with the expressions updated to 2022. This methodology was used for coding mathematical functions in the Python programming language, which will be used later for the evaluation of the objective function in the optimization process. The design parameters of the process scheme will be adjusted by rigorous optimization using genetic algorithms (GA) and data transfer between Python and Aspen Plus. The GA method was implemented using the freely available Pymoo library (Blank et al., 2020). The objective function and constraints for the optimization are show in Eq. (5). The design variables and their ranges used in the optimization of the RDS are detailed in Table 2.

|  |  |
| --- | --- |
|  | (5) |

**Table 2.-** Design variables and their search ranges used in the optimization process.

|  |  |  |  |
| --- | --- | --- | --- |
| **Unit operation** | **Variable, ID** | **Type** | **Search range** |
| Reactive distillation column (I) | Number of stages, NI | Discrete | 10-50 |
| Reflux ratio, RRI | Continue | 0.2-5.0 |
| Bottoms flow, BFI | Continue | 15-17, kmol/h |
| Reactive stage, Nrea | Discrete | 5-45 |
| Holdup, H | Continue | 0.01-0.9, m3 |
| Distillation column (II) | Number of stages, NII | Discrete | 10-100 |
| Reflux ratio, RRII | Continue | 0.2-20.0 |
| Distillate flow, DFII | Continue | 15-17, kmol/h |

* 1. Results and discussion

The optimized diagram of the reactive distillation scheme (RDS) is show in Figure 2. In Column I, with 29 stages, glycerol and hydrogen feed streams are introduced in stages 23 and 28, respectively. These compounds are transformed into PG in the reactive zone between stages 24 to 27. After removing the water in the top of the column, the PG produced is obtained with a mole fraction of 0.967 in the bottoms stream. Then, this PG is depressurized and sent to the Column II. In Column II, with 51 stages, the PG is fed to middle of the column (stage 25). At the bottom of the column, ethylene glycol and glycerol are found, while PG is obtained as top product with a purity of 99 mol%. Additionally, the reboiler duty of the Column I represent the highest energy consumption (1364 kW), because of the large volume of water present in the feed mixture and the pressure conditions required in the reactive distillation process.

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**Figure 2.-** Optimized RDS for propylene glycol production.

The TAC obtained for the RDS is 16.279×105 USD/y, with OC and CC of 8.711 ×105 USD/y and 37.838 ×105 USD, respectively. The comparation of RDS and the CS is shown in Table 2. Compared with the CS, the TAC increased by 10.19 % because of the increased operating conditions of the reactive distillation process. However, due to the combination of reaction and separation processes in a single process unit, the operating costs decreased from 11.40×105 USD/y for the CS to 8.71×105 USD/y for the RDS. In this sense, although the RDS is associated to a higher TAC, the implementation of this scheme allows a higher energy efficiency, which is also present in the reduction of 28.9 % of the energy requirements. Although it is not estimated here, this has a direct impact on the carbon dioxide emissions associated to the production process.

**Table 2.-** Comparison of the intensified and conventional processes for PG production.

|  |  |  |
| --- | --- | --- |
| **Parameters, unit** | **CS** | **RDS** |
| **TAC, 105 USD/y** | **14.77** | **16.27** |
| **OC, 105 USD/y** | **11.40** | **8.71** |
| Steam, 105 USD/y | 9.35 | 6.65 |
| Cooling water, 105 USD /y | 0.3 | 0.22 |
| Electricity, 105 USD /y | 0.6 | 0.61 |
| Catalyst, 105 USD /y | 1.15 | 1.23 |
| **CC, 105 USD** | **16.82** | **37.83** |
| Vessel | 1.91 | 2.62 |
| Trays | 1.09 | 1.49 |
| Reboiler | 5.25 | 27.14 |
| Condenser | 5.94 | 3.91 |
| Compressor | 2.38 | 2.38 |
| Bomb | 0.25 | 0.25 |
| Total Cooling Duty, kW | 2789.31 | 2011.63 |
| Total Heating Duty, kW | 2467.69 | 1757.38 |
| **Energy Intensity, kW/kg of PG** | **2.07** | **1.47** |

Table 2 shows that heating and the catalyst account for more than 70 % and 10 % of the operating costs, respectively, in both schemes. Additionally, it can be observed that the capital cost of the heating system (reboiler) increases from 5.25×105 USD in the CS to 27.14×105 USD in the RDS because the reactive distillation column (Column I) operates at a pressure of 25 bar, which is necessary for the glycerol hydrodeoxygenation reaction, generating considerably high temperatures at the bottom of the column.

* 1. Conclusions

A novel intensified process to produce renewable propylene glycol has been proposed, and its performance has been analysed. The optimal design and operating conditions for the RDS have been obtained by rigorous optimization using genetic algorithms. The intensified process has been contrasted with a conventional scheme. It has been shown that an increase in the TAC (10.19 %) occurs because of the pressure conditions required in the RDS. However, this scheme allowed the reduction of 28.9% of the energy consumption. As future work, it is proposed to compare these results with the other proposed intensified process schemes as thermally coupled distillation systems.

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