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Improvement of the Crude Glycerol Purification Process Derived from Biodiesel Production Waste Sources through Computational Modeling

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Abstract: Considering waste as a possible new resource for useful purposes is one of the strategies included in the circular economy principles. In fact, industrial processes are seen as great contributors to the formation of waste streams. With the aim to attain more sustainable and resilient systems, in this study, a process flow chart was elaborated in an Aspen Plus computer simulator, to obtain the production of pure glycerol from crude glycerol (a by-product of biodiesel production). This process occurs through fractional vacuum distillation, the methanol recovery route in the deacidification process and the removal of methanol from the reaction medium. The separation stages of the crude glycerol implemented enabled a degree of purification of 99.77%, meeting the specifications of the pharmaceutical use. The developed model allowed for the optimization of the purification process, raising by 40% the mass flow rate of pure glycerol. A conclusion could be drawn that the use of crude glycerol is an excellent option for the development of new products with greater added-value, contributing to the zero waste principles and to the circular economy.

Keywords: glycerol; biodiesel wastes; purification process modeling; Aspen Plus

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1. Introduction

The main factor in decreasing the availability of natural resources is disorderly population growth, associated with economic development, which in turn encourages overconsumption, exceeds the limits of the availability of natural resources and affects the balance of the ecosystem [1]. In the last few decades, however, reducing environmental pollution has become a global objective. The social-political-environmental scenario has been stimulating the replacement of the fossil fuel matrix with fuels from renewable sources, in order to reduce the emission of various greenhouse gases (GHG) that cause the greenhouse effect [2–4]. Improving environmental conditions, especially in large metropolitan centers, also means reducing government health costs for citizens. Environmental concerns about the use of fossils began to mark history with important events, such as the following: Toronto Conference on the Changing Atmosphere in 1988, IPCC's First Assessment Report in 1990 and ECO-92, culminating in the Kyoto Protocol in 1997 [5]. In addition, the adoption of environmental agreements makes it possible to plan international financing under favorable conditions, in the carbon credit market, under the mechanism of clean development.

In this context, biodiesel is considered as a potential and promising alternative to replace fossil fuels and its production has been growing worldwide [6–8]. Bearing in mind that fossil fuel reserves are not renewable, there are uncertainties regarding the market in the

future, in addition to the availability of the resource [5]. Therefore, the paradigm between development and sustainability becomes a fertile environment to promote technological development, namely for the production of chemicals from renewable resources, such as biomass [6]. Bio-renewables in chemical commodities, including environmentally friendly biofuels, are mobilizing scientists from industries and universities around the world [9]. Biodiesel has emerged as a sustainable alternative to diesel, and its use has been encouraged by many countries, representing an economic, social, and environmental strategy [7,10].

The increase in biodiesel production has generated a surplus of crude glycerol in the market, which represents a major bottleneck in the biodiesel production chain and creates new challenges for its sustainable use; therefore, new technologies are required for the treatment of abundant residual glycerol that has great potential to be an important raw material, for the production of products with high added-value [7,8,11,12]. This residue cannot be deposited in landfills and the industries that use it as raw material will not be able to absorb this excess produced [8,13]. Therefore, finding new uses for glycerol is very important to ensure the sustainability of the global production of biodiesel.

Biodiesel refers to fuel formed by esters of fatty acids, methyl, ethyl or propyl esters of long chain carboxylic acids. It is a renewable and biodegradable fuel, commonly obtained from the chemical reaction of lipids, oils or fats, of animal or vegetable origin, with an alcohol in the presence of a catalyst (reaction known as transesterification) [1,12]. There are also several biodiesel production processes from renewable sources, such as agricultural products and microalgae, in the presence of a suitable catalyst. Numerous studies are available on the production of microalgae-based biodiesel [14,15], as well as through the thermal cracking reactions and esterification processes. This work addresses the purification of glycerol from production by transesterification, one of the main production routes for biodiesel in the world. In fact, it has lower energetic requirements, needs less time, and less quantities of alcohol for the reaction to occur [7,8,12,16]. Even with a higher water content, the proposed process presents satisfactory results, milder conditions being considered the most usual.

The products of oil and fats transesterification are esters of fatty acids (80–90%) and glycerol (10–20%, by-product of biodiesel production) [3,7,8,17]. The biodiesel production process is composed of the following steps: preparation of the raw material, transesterification reaction, phase separation, recovery and dehydration, alcohol distillation, glycerol distillation and purification of this renewable fuel, as well as the purification of water as a residue [12]. For every 100 liters of biodiesel, 10 kilograms of crude glycerol are produced, generating an average of 60 liters of waste water [18]. There are several options for purification procedures, such as treatment with ethanol and activated carbon, pH adjustment, solvent extraction, and precipitation of the fatty acids with calcium, ion exchange resins, membrane separation and distillation [19,20]. The process using ion exchange resins becomes unfeasible when the crude glycerin has a high content of dissolved salts. Distillation and membrane separation are used to obtain glycerol with a high degree of purity, the first process being the most effective. A highly employed process is vacuum distillation in an inert atmosphere, providing 99% content in glycerol [19]. Other processes can also be applied, such as neutralization, drying, saponification, polar solvent extraction and adsorption [21]. Purification with adsorbent materials has become an interesting alternative, as it eliminates the need to use water in the process. Another advantage is the avoidance of liquid effluents and the ability to reuse some adsorbents [22].

In many countries, including Brazil, one of the largest biodiesel producers in the world, most large-scale industrial biodiesel plants still do not effectively value glycerol. According to Freitas [23], the crude glycerol produced in the country is sold to refineries, and around 50% is exported to China. To comply with the pharmaceutical and food industry requirements, glycerol needs to undergo purification processes to obtain more competitive purity grades or valuable by-products [11,24]. Glycerol is a compound of extreme technical versatility. Due to its unique combination of properties, glycerol is used in many areas of the industry. Glycerol is an alcohol and viscous liquid, soluble in water, practically colorless,

odorless, hygroscopic, virtually non-toxic to humans and nature, with a high boiling point (ebullition temperature of 290 °C) [5]. Due to this unusual combination of physical and chemical properties, glycerol has more than 2000 known end applications, including several large-scale applications [5,7,16]. A great diversity of research is being developed to reduce the impact of this waste on the environment, adding value to the production of biodiesel. Therefore, means of purification and transformation of glycerol are required in order to avoid future problems due to its accumulation, as well as to advance biodiesel production techniques, enabling higher competitiveness and viability [6]. The biodiesel industry was responsible for about 68% of glycerol produced worldwide in 2015 and glycerol production by transesterification is expected to grow about 6.8% by 2022 [25]. Thus, a technology that contributes to the storage or use of glycerol, giving value to this by-product, will also contribute to the production of biodiesel and renewable energies.

In this context, the present work aimed to evaluate glycerol's purification process, using computational modeling and simulation in Aspen Plus. The use of computational tools makes the analysis of quality, demand and cost easier and faster, with good accuracy [26,27]. Regarding simulators, the product portfolio of Aspen Technology Inc. has the optimal solution and process optimization tools on the market. These are based on mathematical and thermodynamic models, based on the basic principles of transport phenomena [28]. Scientific computational modeling applies computing to areas of knowledge in which it is impossible, or very expensive, to carry out experimental tests to analyze possible solutions for some processes, starting from experimental models or analytical solutions. Therefore, the development of existing processes is relevant and of interest, as it can help to identify previous problems and estimate whether what is being proposed is economically viable [29].

In this way, using Aspen Plus, it was possible to perform the chemical and thermodynamic modeling of the purification of glycerol from the biodiesel production co-product. The study of this process, through the Aspen Plus platform, allowed for analysis regarding the variables; the tempering and concentration of reagents in the process parameters that need to be optimized.

2. Materials and Methods

2.1. Glycerol Transesterification

Transesterification by basic catalysis is one of the main production routes for biodiesel in the world, among the countless ways of production [7,8,12,16,30]. Other production routes are, for example, acid catalysis [31], heterogeneous or enzymatic catalysis [32], ultrasonic radiation [33], or even thermal decomposition of the catalyzed oil [34,35]. Of these, transesterification by basic catalysis is the most used in commercial production, probably due to its high conversion rate of oil (triglycerides) into biodiesel (methyl esters), in a simple, short-term chemical reaction, presenting fewer problems related to equipment corrosion [36].

The methodology followed in this research addresses the purification of glycerol produced by transesterification by basic catalysis [7,8,12,16,30]. Commercially available purified common glycerol is manufactured to meet the requirements of the United States Pharmacopeia (USP) and the Food Chemicals Codex (FCC). Figure 1 shows the transesterification reaction.

Glycerol is normally classified in three categories, according to its purity, as seen in Table 1. Crude glycerol presents purity ranging between 40–88%. Glycerol with purity levels above this may be used in the transformation of products or chemical intermediates [7]. Technical glycerol, with purity greater than 96%, is used in industry to produce chemical compounds. Pharmaceutical glycerol shows purity levels higher than 99.7% and is used in the food and pharmaceutical industry, research and other high standard applications [37,38]. In practice, the glycerol obtained in the transesterification process also contains various impurities, such as methyl ester (ME), triglycerides, free fatty acids (FFA), methanol, water, inorganic salts, and other contaminating organic matter. The composition

and, consequently, the properties of the crude glycerol obtained depend strongly on the type of process used and the quality of the raw material [8]. Thus, according to the combination of the process and the raw material used, crude glycerol, as a by-product from the transesterification of biodiesel production, can be considered to have a content between 30% and 60%. In the case studied, the glycerol had a low initial purity of 50% [37,38].

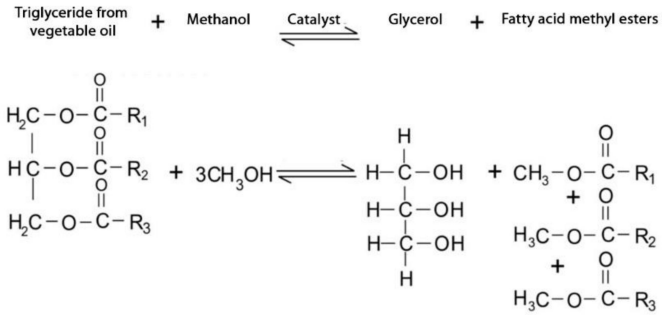

Figure 1. Transesterification Reaction by Catalysis.

Table 1. Specifications of Glycerol as to its Purity [37].

Degree	Degree I	Degree II	Degree III
Purity	~99.5% (Technical degree)	96-99.5% (USP * degree)	99.5-99.7% (Kosher or USP/FCC **)
Manufacturing and Use	Prepared by synthetic process and used in chemical industry, but not applicable to food or drug formulation.	Prepared from sources of animal fat or vegetable oil, suitable for food, pharmaceutical and cosmetic products.	Prepared from vegetable oil sources, suitable for use in kosher food and beverages.

* USP—United States Pharmacopeia, ** FCC—Food Chemicals Codex.

Table 2 shows a typical composition of crude glycerol derived from the biodiesel production used in this study [38]. The purity of the glycerol produced from the synthesis of biodiesel is of crucial importance as it increases the added-value of the product. Ashes are composed of dissolved inorganic species, formed mostly by sodium ions (due to the excess of catalyst in the production of biodiesel), chlorides and other species present in used oils. Non-glycerol organic matter (NGOM) in this case is represented by a mixture of many organic compounds such as free fatty acids, unconverted glycerides and other residual organic compounds present in the raw material [5].

Table 2. Composition of Crude Glycerol [38].

Component	Wt. (%)
Glycerol	50
Methanol	35
Potassium hydroxide	10
Methyl oleate	5
Sulfuric acid	0
Water	0

The use of modeling and simulation stands out as process improvement, since the use of computational tools makes quality analysis simpler, faster and with good accuracy. Therefore, the study of improvements through operational models is original and of relevant interest, as it can help to optimize the process, identifying problems and estimating economic viability. The use of modeling from the experimental data obtained for the esterification stage, allows us to predict the trend of the reaction behavior. Using the Aspen

Plus software, it was possible to model the reaction kinetics, in addition to the simulation of the fractional distillation process, being important for the analysis of the variables involved such as concentration, temperature and pressure, establishing the necessary conditions, demands, equipment and results.

For the purification of crude glycerol, a vacuum distillation method was used, which can be divided into several stages, as seen in Figure 2.

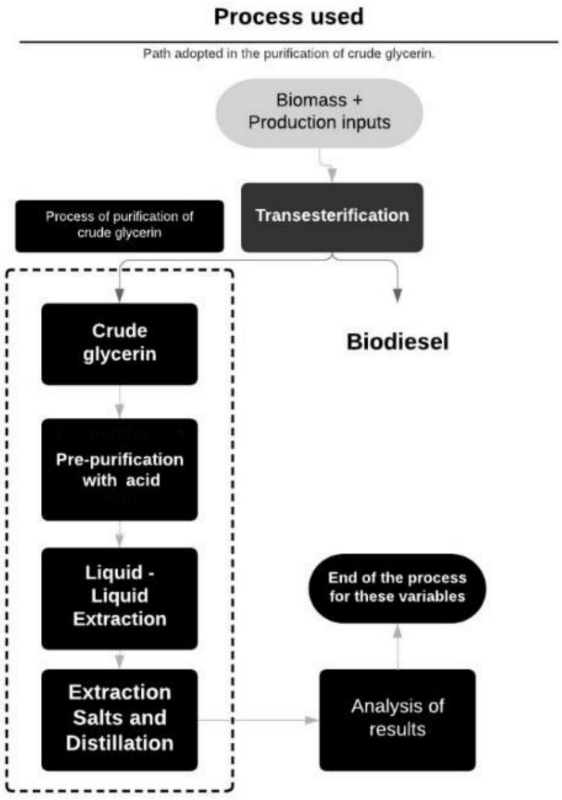

Figure 2. Vacuum Glycerol Purification Process.

Neutralization of the concentrated solution (potassium hydroxide) occurs through the addition of a strong acid, sulfuric acid (H_2SO_4). The mass flow was designed so that all the base present in the crude glycerol oil was consumed, forming a mixture of salt and water. The commercial software Aspen Plus allows changes in different variables; temperature and concentration of reagents, improving the efficiency of the process. The main parameters were the temperature and the reagent concentration. In this way, the minimum and maximum values were defined to obtain a sensitive variation, in order to avoid the degradation or polymerization of glycerol into polyglycerol, occurring at high temperatures [8].

2.2. Aspen Plus Model

In the present study, the modeling process was performed using Aspen Plus, and can be seen in Figure 3.

Maintaining a fixed feed flow, simulations were carried out involving variations in the flow of the distiller. At each interaction the feed flow rate remained constant, for each variation presented, the simulator automatically recalculated the flow rate of the bottom product.

The properties of all components were taken from the Aspen Plus library. As with the base model, the simulation involves ionic species (potassium hydroxide and sulfuric acid) and polar components (glycerol and methanol). As such, the thermodynamic model chosen for the purification processing was electrolyte non–random two liquid (ENRTL).

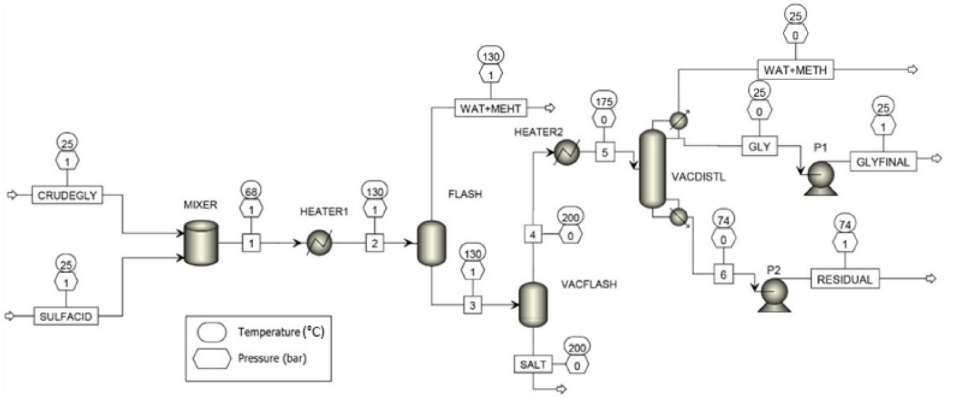

Figure 3. Process Flow Diagram of The Glycerol Treatment, in Aspen Plus Model.

This is a vacuum distillation process, where the potassium hydroxide is neutralized using sulfuric acid and the methanol is removed in a vacuum (flash) separator. The description of this initial stage of the process is in Figure 4.

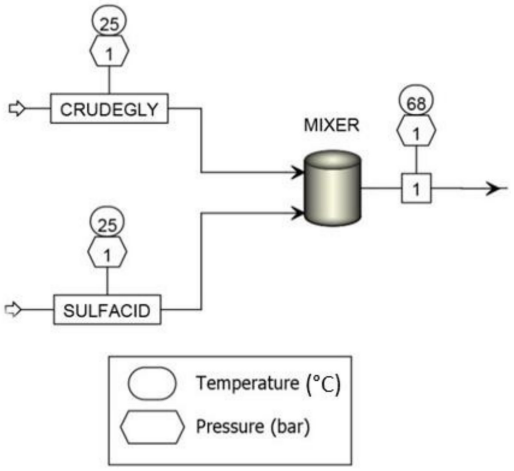

Figure 4. Mixing Tank.

Crude glycerol (CRUDEGLY) and sulfuric acid (SULFACID) enter the process at atmospheric pressure and at room temperature and are neutralized in the mixing tank (MIXER). Their compositions can be seen in Table 3 while the resulting flow is shown in Table 4.

Table 3. Properties and Composition of the Mixing Process Inlet Streams.

Property	Crude Glycerol	Sulfuric Acid
Temperature (°C)	25	25
Pressure (kPa)	101.325	101.325
Molar flow (kmol/h)	24.10	10.99
Mass flow (kg/h)	1200	283.78
Component Mass Fraction (%)		
Glycerol	50.0	0.0
Methanol	35.0	0.0
Potassium hydroxide	10.0	0.0
Methyl oleate	5.0	0.0
Sulfuric acid	0.0	37.0
Water	0.0	63.0

Table 4. Composition of the Mixing Process Outlet Streams.

Component	Mass Fraction (%)
Glycerol	2.22
Methanol	41.39
Potassium hydroxide	0.0
Methyl oleate	4.34×10^{-6}
Sulfuric acid	9.88×10^{-4}
Water	56.38

The mixture resulting from the reaction first stage of the process (1), is then heated to 130 °C by a heat exchanger (HEATER1) and goes to the separator (FLASH), seen in Figure 5.

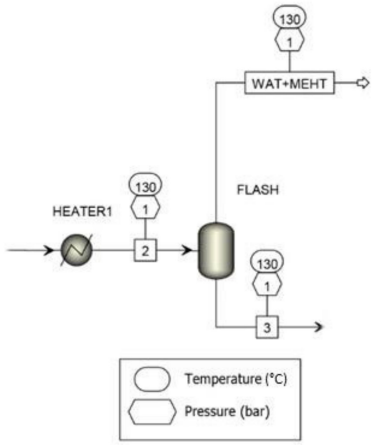

Figure 5. Heating and Separation Stage Stream (METH + WAT).

Methanol and water are separated in the stream (METH + WAT) and the main mixture flows through flow (3) to the vacuum separator (VACFLASH). In this component there is the separation of potassium hydroxide from the mixture. Some operational obstacles arose during the dimensioning of the temperature in this separator, which did not allow a resulting flow for temperatures below 310 °C. The temperature established for the separation was 200 °C. Figure 6 shows the resulting streams from the process of salt separation.

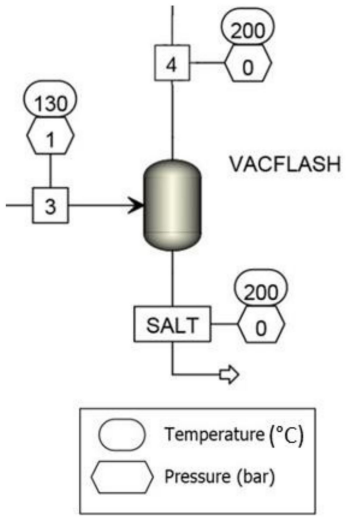

Figure 6. Flash for Salt Separation.

The resulting mixture was then sent to the final stage of the purification process in the vacuum distillation column (VACDISTL), after passing through a heat exchanger (HEATER2) that decreased its temperature to 200 °C. In the distillation column we had three products, two in liquid state and one in steam state. Figure 7 depicts a product (WAT + METH) consisting practically of water and methanol, another one (RESIDUAL) that presents residual material, but that is of interest for reuse to generate more purified glycerol, and finally the desired product, glycerol with 99.77% purity (GLYFINAL) as expressed in Table 5.

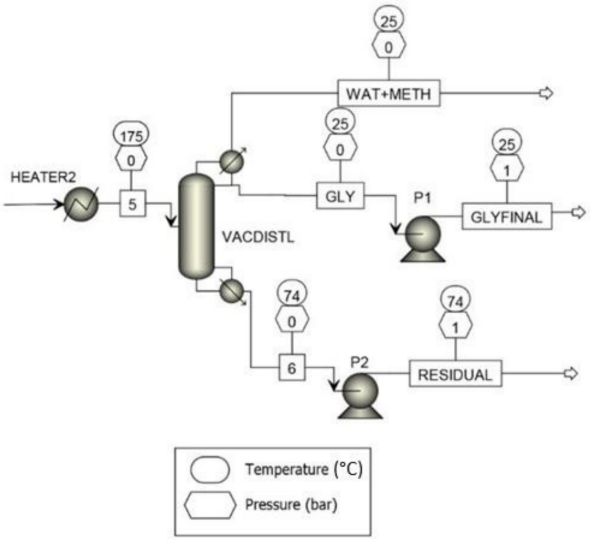

Figure 7. Vacuum Distillation Stage.

Table 5. Properties and Composition of the Outlet Streams.

Property	Glycerol	Residual	Wat + Meth
Molar flow (kmol/h)	6.69	2.70	3.30
Mass flow (kg/h)	616.53	867.25	84.20
Component Mass Fraction (%)			
Glycerol	99.768	20.64	2.22
Methanol	2.47×10^{-3}	1.56×10^{-3}	41.39
Potassium hydroxide	0.0	0.0	0.0
Methyl oleate	5.17×10^{-3}	23.82	23.82×10^{-10}
Sulfuric acid	0.206	55.53	4.33×10^{-10}
Water	0.018	8.23×10^{-5}	56.38

3. Results and Discussion

The purification process in the distillation column was accomplished in several stages. The simulation results have shown that the process is sensitive to only five levels, since in additional levels, the degree of purification was inexpressive, as shown in Figure 8.

Through these procedures, a purification level of 99.77% was reached, as shown in Table 6. In this study, an improved process is suggested, with the addition of a heat exchanger after the distillation column, following the main line, to avoid the presence of vapors in the pump. Results may be seen in Table 6.

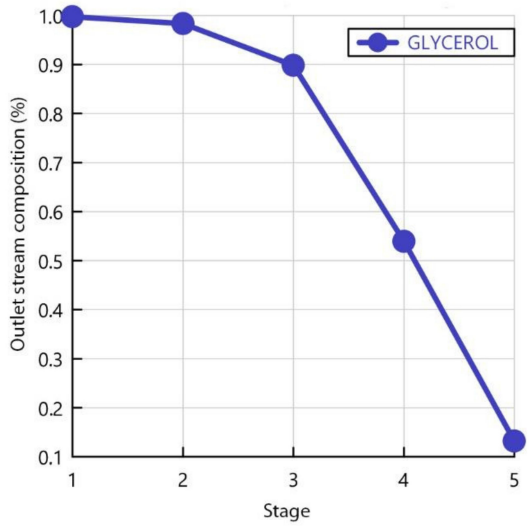

Figure 8. Composition and Stage of the Vacuum Distillation Process.

Table 6. Composition of the Outlet Streams in Each Stage of the Vacuum Distillation Process.

Stage	Glycerol (%)	Sulfuric Acid (%)	Methyl Oleate (%)	Methanol (%)	Potassium Hydroxide (%)	Water (%)
1	13.19	37.79	49.01	3.46×10^{-6}	4.83×10^{-6}	1.03×10^{-5}
2	53.95	26.19	19.86	6.43×10^{-6}	3.65×10^{-18}	2.01×10^{-5}
3	89.80	7.44	2.75	8.43×10^{-6}	0.0	2.69×10^{-5}
4	98.37	1.39	0.24	9.44×10^{-6}	0.0	3.04×10^{-5}
5	99.77	0.21	0.01	8.59×10^{-4}	0.0	3.46×10^{-3}

The present model was based on the model of Arora et al. [38], in which the authors performed simulations to obtain a flow of glycerol with a purity content of 99%. Seeking to maintain the separation conditions, such as number of stages and column sizing, a sensitivity analysis in the operational variables and the addition of a heat exchanger that provides a substantial additional income is proposed. Table 7 shows a comparison of the results of the product glycerol obtained in this study and Arora's [38].

Table 7. Comparison Between the Obtained Results and Literature Results.

Property	Arora et al. [38]	This Work
Glycerol (%)	99	99.77
Methanol (%)	0.047	2.47×10^{-3}
Potassium hydroxide (%)	0.0	0.0
Methyl oleate (%)	3.61×10^{-6}	5.17×10^{-3}
Sulfuric acid (%)	3.60×10^{-6}	0.206
Water (%)	0.072	0.018
Mass flow (kg/h)	436.90	616.53
Molar flow (kmol/h)	4.76	6.69

The mass fraction of the six components in the product glycerol is very similar. The purity of the glycerol is 99% in the Arora [38] study and 99.77% in the current study. The most relevant result of this comparison is the 40% increase in mass and molar flow, which can be justified by the improvement of the process promoted in this study, by the inclusion of an additional heat exchanger in the vacuum separator component or in the distillation column. These values depend on the temperature in the separator, as well as the required flow in the distillation column and its reflux degree. The higher the applied temperature, the greater the separation and, consequently, the greater the flow. In this way, the separator

is the equipment most sensitive to temperature variations. Future works may provide further knowledge in reducing the energy requirements, using pinch analysis of the heat exchangers network, and optimization of the operating conditions.

4. Conclusions

In this study, a numerical methodology for the improvement of the purification process of the biodiesel by-product glycerol was developed in the Aspen Plus process simulator. It was shown that glycerol can be produced from the crude glycerol by-products of biodiesel, with a theoretical purity level of 99.77%. The developed model allows the improvement of the purification process of glycerol by the vacuum distillation route, by the inclusion of an additional heat exchanger, leading to around 40% higher mass of glycerol, in relation to the reference case study. This study demonstrates that the use of crude glycerol, as a by-product of biodiesel production, is an excellent option for the development of new products, with greater added-value and a consequent decrease in the production cost of the main product, contributing to the zero waste principles and circular economy. This result is even more relevant in the actual and future scenario of the biodiesel and glycerol market. These markets are expected to grow significantly in the years to come, which presents good business opportunities for the related companies. A cost analysis is envisioned for the next steps, as a follow-up study, to assess the viability of the proposed improvements.

Author Contributions: Conceptualization, M.O. and A.R. (Abel Rouboa); methodology, M.O. and A.R. (Abel Rouboa); software, M.O.; validation, A.R. (Abel Rouboa), E.M. and A.R. (Ana Ramos); formal analysis, M.O. and E.M.; investigation, M.O.; resources, M.O. and A.R. (Abel Rouboa); data curation, E.M.; writing—original draft preparation, M.O.; writing—review and editing, E.M. and A.R. (Ana Ramos); visualization, A.R. (Ana Ramos); supervision, A.R (Abel Rouboa).; project administration, A.R. (Abel Rouboa); funding acquisition, A.R. (Abel Rouboa) and E.M. All authors have read and agreed to the published version of the manuscript.

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