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Polymerization of purified residual glycerol from biodiesel production

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Abstract: In the face of climate change and the increasing frequency of climate-related disasters, there is a growing emphasis on renewable fuel sources to mitigate greenhouse gas emissions. Biodiesel, produced from crude or residual vegetable oils and animal fats, represents a significant biofuel option. Its production process involves transesterifying triglycerides with short-chain alcohols, resulting in biodiesel and low-purity glycerol as byproducts. This study explores the polymerization of residual glycerol as a sustainable strategy to enhance its value, particularly in light of the rising biodiesel production rates, which generate approximately 10% residual glycerol. The research focuses on synthesizing polymers from glycerol and highlights its potential as a method to repurpose a byproduct of biodiesel production. Experimental tests were conducted in a batch reactor, utilizing glycerol and adipic acid polycondensation in ratios of 1:0.75, 1:1, 1:1.5, and 1:2 to produce adipic polyglycerol. The reactions were carried out at 160 ºC with stirring at 60 RPM, using dibutyl phthalate as a catalyst, and monitored for water accumulation. Both partially purified and commercially bi-distilled glycerol were employed in the experiments. Infrared spectrophotometry analysis revealed significant molecular transformations in the polymers synthesized under varying reaction conditions. These findings provide promising prospects for utilizing this material in the production of polymers with the potential to serve as robust alternatives to petroleum-based plastics.

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This study concludes that residual glycerol from biodiesel production can be effectively utilized as a raw material for polymer synthesis, offering considerable potential to replace fossil-based polymers and significantly reduce environmental impact.

Keywords: Biodiesel, Glycerol, Polycondensation, Polyglycerol, Transesterification

1. Introduction

The glycerol residue generated during the biodiesel production process via transesterification exhibits low purity, with its quality varying based on the conversion methods, type of alcohol, and catalyst employed. This residue typically contains excess alcohol, residual catalysts, and soaps formed as byproducts of parallel chemical reactions occurring during transesterification. These impurities significantly reduce the commercial value of residual glycerol and limit its potential applications. As a result, such residues are often discarded in biodiesel production processes due to the aforementioned limitations (Domingos et al., 2019; Attarbachi et al., 2023; Aziz et al., 2018; Kalvelage et al., 2017; Kumar et al., 2019; Nasir et al., 2017; Barros et al., 2008; Cai et al., 2013; Chol et al., 2018; Colombo et al., 2017; Colombo et al., 2019; Silva et al., 2021; Rahman et al., 2022; Oliveira et al., 2020; Gupta et al., 2023; Santos et al., 2021).

In biodiesel production processes, glycerol has been produced in significant volumes, primarily because biodiesel is used as an additive to fossil fuels. Therefore, in recent decades, with the advent of biodiesel production, residual glycerol with a low degree of purity has been generated in the ratio of 1 mole of glycerol for every 3 moles of methyl or ethyl esters (biodiesel) produced, corresponding to approximately 10% by weight of the total mass of the products of the transesterification reaction (Kumar et al., 2019; Nasir et al., 2017; Barros et al., 2008; Colombo et al., 2017; Colombo et al., 2019; Zeleme and Barros, 2022; Barros, 2022, Silva et al., 2021; Rahman et al., 2022; Oliveira et al., 2020; Gupta et al., 2023; Santos et al., 2021, Calderon et al., 2023).

In this context, Domingos et al. (2019) and Al-Haimi et al (2024) conducted studies on glycerol purification and optimization of crude glycerol purification, respectively, to enhance the commercial value of this product. The methodologies developed aimed to define a route for the purification of crude glycerol to yield a higher purity product, involving the following steps: a) neutralization of residual glycerol with phosphoric acid; b) vacuum filtration; and c) adsorption onto activated carbon heated to 60 °C to reduce its viscosity. The combination of these steps aimed to produce glycerol of higher purity, which would be more suitable for commercial applications. This purification route could potentially increase the economic value of crude glycerol, a by-product of biodiesel production, by making it usable in more demanding industries such as pharmaceuticals, cosmetics, and food.

A study conducted by Aziz et al. (2018) showed that the glycerol generated as a byproduct in biodiesel production from waste cooking oil has low purity. The crude glycerol sample contained impurities such as methanol, catalyst, soap, and water, with analysis revealing 67.7% water, 16.7% ash, and a density of 1.1217 g/mL. The impurities were adsorbed onto bentonite that had been activated in 1.5 M sulfuric acid and characterized by SEM-EDX. After treatment with bentonite at 60 °C for 75 minutes, the purified glycerol sample contained 89.5% glycerol, 4.3% water, and 3.6% ash, with a density of 1.2212 g/mL. The cited authors concluded that activated bentonite could be used for the adsorption and removal of impurities from waste cooking oil.

Raman et al. (2019) utilized crude glycerol from biodiesel production to produce high-purity glycerol

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through neutralization, ultrafiltration, ion exchange resins, and vacuum distillation operations. The results verified that high-purity glycerol could be produced by combining these techniques.

Aziz et al. (2018) and Nanda et al. (2014) purified crude glycerol obtained from biodiesel production through acidification using sulfuric, hydrochloric, or phosphoric acids, and the results were compared. The effects of pH on the purification efficiency were also investigated, and both the crude glycerol and the purified products were characterized. The authors concluded that phosphoric acid was a better purifying agent than the other acids.

Statistics from the European Biodiesel Board (EBB, 2023a) indicate that the European Union (EU) continues to be a major producer of biodiesel, with an annual production exceeding 13.7 million tons in 2022. This large-scale production generates a significant amount of crude glycerol as a by-product, estimated at approximately 1,37 million tons per year (assuming a 10% glycerol yield from biodiesel production). The oversupply of glycerol has further intensified market challenges, driving down prices and creating economic and environmental pressures.

Statistics show that the European market produces more than 13.7 million tons of biodiesel per year EBB (2023a), and the residual glycerol from this process drives down the price of industrial glycerol in the international market and contributes to observed environmental impacts (Tomatis, Zilli, & Pavan, 2024).

However, the advancement in biodiesel production rates has had worldwide repercussions. In 2023, Brazil's biodiesel production reached approximately 7.5 million cubic meters (7.5 billion liters), marking a significant increase from the previous year, while in the same year, the European Union produced approximately 19.02 million metric tons of biodiesel, marking a decrease from the previous year. In Asia, Indonesia led biodiesel production with an estimated 13.57 billion liters in 2023, a 25% increase from 2022. Malaysia and Thailand's specific biodiesel production figures for 2023 are not readily available in the provided sources. Collectively, these countries significantly contribute to global biodiesel production, with Indonesia alone accounting for a substantial portion (Rahmanulloh and Osinski, 2023).

Therefore, statistics indicate that in 2023, the leading countries in biodiesel production and usage produced, approximately, 35 million tons of biodiesel, which, in relation to the glycerol fraction described in this work, represents approximately 3.5 million tons of glycerol (EBB, 2023b; OECD/FAO, 2023a; IEA, 2023a).

Glycerol is a colorless, odorless, viscous chemical component used in pharmaceutical formulations, the food industry, and explosives. It is an alcohol designated by IUPAC as 1,2,3-propanetriol, known for its high-water solubility and hygroscopic nature, comprising three hydroxyl groups. Commercial production of glycerol can also be achieved through microbial fermentation or chemical synthesis from petrochemical products. Alternatively, it can be obtained from soap production or as a byproduct of fat hydrolysis (da Silva et al., 2009; Dhabhai et al., 2016; Gabriel et al., 2019; Gabriel et al., 2015; Habaki et al., 2019).

Therefore, new applications for glycerol have emerged in the international market, particularly in the food industry, where it is utilized as a humectant, solvent, softener, sweetener, and lubricant in industrial equipment. In the medical and pharmaceutical industries, glycerol is used in ointments, syrups, cosmetics, toothpaste, and as a drug delivery agent (Gerpen, 2005; Wolfson et

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al., 2009; Ciriminna et al., 2014; OECD/FAO, 2023b).

In the chemical industry, glycerol serves as a fiber softener and is incorporated into the composition of special papers, providing greater flexibility and tenacity. Additionally, it is applied as an antifreeze agent, in paint formulations, and as a precursor for bio-based polymers (Gerpen, 2005; Wolfson et al., 2009; Yang et al., 2012; Mota et al., 2017).

Glycerol is also widely used in chemical syntheses, particularly in the production of dendrimers, polyethers, and hyperbranched polyesters, which possess a large surface area and significant amounts of functional groups. It can be catalytically hydrogenated to produce propylene glycol, especially 1,3-propanediol, a high-value component for polyester synthesis. These processes require high-purity glycerol (Wolfson et al., 2009; Quispe et al., 2013; Ciriminna et al., 2014).

Wolfson et al. (2009) conducted alternative studies on using crude residual glycerol as a reaction medium for chemical synthesis. Similarly, Mota et al. (2009) researched the production of ethers, acetals, and esters from crude glycerol derived from biodiesel production. Recent studies have expanded these applications, exploring the use of glycerol in bio-based plastics, lubricants, and renewable fuels (Mota et al., 2017; OECD/FAO, 2023b; IEA, 2023b).

In this context, the prospect of depleting oil reserves and the ecological pressures resulting from the use of petroleum derivatives, combined with the geopolitical instabilities of oil-producing countries, have driven industrial and governmental efforts to develop scientific and technological research. These efforts aim to propose new renewable inputs for the chemical industry, replacing petrochemical feedstocks with sustainable alternatives like glycerol (Gerpen, 2005; Ciriminna et al., 2014; OECD/FAO, 2023a).

Recent research indicates that alcohol chemistry has developed over the last decade as a precursor to the petrochemical industry. Jewur (1984) highlighted the catalytic reactions of ethanol to produce ethylene, propylene, and acetylene, among other products. More recent studies, such as those by Zhang et al. (2020), have expanded on these findings, exploring advanced catalytic processes and the use of renewable alcohols like ethanol and butanol in the production of bio-based chemicals, further bridging the gap between renewable feedstocks and the petrochemical industry.

Additionally, the text notes that Dutch chemists had already produced gas from ethanol catalyzed by alumina, with the ethanol dehydration reaction being conducted on a mixed oxide of silica and alumina. Recent advancements, such as those by Shinde et al. (2021), have explored enhanced catalysts for ethanol dehydration, increasing efficiency and selectivity in producing biofuels and olefins, demonstrating the continued evolution of alcohol chemistry in industrial applications.

Biopolymerization processes, commonly used in scientific literature, refer to natural polymers obtained and used in their natural state, sometimes modified by unique processes or biosynthesized. Examples include animal skins, vegetable fibers, plant resins, and latex, commonly known as biopolymers. Synthetic polymers derived from natural sources, however, rely on chemical synthesis to achieve the desired physicochemical properties (Andrade et al., 2001; Pitt et al., 2011). Recent studies, such as those by Wu et al. (2022), have explored the functionalization of biopolymers with synthetic modifications to enhance properties like biodegradability, mechanical strength, and processability, making them more competitive with traditional synthetic polymers.

https://doi.org/10.55343/CogSust.137

This research investigates the potential of producing polymers from industrial process residues, specifically glycerol residues generated during the transesterification of oils and fats in biodiesel production. This residue, after purification, can be polymerized to yield polyglycerol, a product that can compete with synthetic polyglycerol derived from petrochemicals. Polyglycerol, as the first hyperbranched polymer produced through controlled synthesis, exhibits a unique combination of stability, biocompatibility, high functionality of terminal groups, and compactness, referred to as dendrimer architecture (Frey and Haag, 2002). Wu et al. (2020) have also explored polyglycerol derivatives for drug delivery systems, showcasing their versatility beyond traditional polymer applications.

Garti et al. (1981) explored the possibility of producing polyglycerol by polymerizing PA glycerol through a chemical reaction within a temperature range of 260–280 °C under an inert atmosphere, using 2.5 mol% of NaOH as a catalyst. The author investigated the influence of temperature, catalyst type, and catalyst mass. The glycerol used had a purity level of 99%, and the reaction progress was monitored by measuring the volume of water produced. More recent studies, such as those by Zhang et al. (2023), have optimized glycerol polymerization under green chemistry conditions, using alternative, more sustainable catalysts and solvents, thereby improving yield and reducing environmental impact.

Brioude et al. (2007) conducted the esterification reaction of glycerol with adipic acid using molar ratios of 1:1, 1:1.5, and 1:2 of glycerol to adipic acid, employing 10% by weight of dibutyltin dilaurate as a catalyst in hexane. The reaction was performed under stirring conditions, maintaining a temperature of 100 °C for sufficient time to ensure complete homogenization. Subsequently, the temperature was increased to 150 °C to facilitate the glycerol and adipic acid reaction. The reaction progress was monitored by measuring the amount of condensed water recovered. In this context, this study enabled the evaluation of appropriate conditions for utilizing the potential of residual glycerol to produce polymers capable of replacing petroleum-derived polymers. These polymers offer reduced environmental impact and high biodegradation rates. Liu et al. (2023) has further refined esterification processes for glycerol-based polyesters, enhancing their mechanical properties and biodegradability, thereby increasing their competitiveness with traditional petrochemical plastics.

For other hand, the environmental impact assessment focuses on key sustainability categories, particularly the use of residual glycerol as a renewable raw material, which results in a significantly lower carbon footprint compared to petroleum-derived polymers. The potential CO_2 emissions associated with energy consumption during the polymerization process can be further minimized by utilizing renewable energy sources, such as solar or wind energy. Additionally, the substitution of fossil-based raw materials with residual glycerol reduces the overall carbon footprint of the final product, aligning with sustainable development goals (Zoldy et al., 2022; Virt and Arnold, 2022; Zöldy and Baranyai, 2023; Silva et al., 2025).

Residual glycerol is derived from biomass, a renewable source, which reduces reliance on non-renewable resources such as oil and natural gas. This shift contributes to the mitigation of non-renewable resource depletion. Furthermore, the adoption of greener technologies and the use of less harmful catalysts in the polymerization process help minimize environmental impacts. However, emissions of compounds such as NOx and SOx, generated from the combustion of fossil fuels for energy production, can contribute to the eutrophication of water bodies and the acidification of soil

https://doi.org/10.55343/CogSust.137

and water. Therefore, reducing fossil fuel consumption in the polymer production process is critical to mitigating these adverse environmental effects (Zoldy et al., 2022; Virt and Arnold, 2022; Zöldy and Baranyai, 2023; Goldbach et al., 2022).

Thus, the goal of this paper is to explore the polymerization of residual glycerol as a sustainable strategy to enhance its value, particularly in light of the rising biodiesel production rates, which generate approximately 10% residual glycerol as a by-product. The study focuses on synthesizing polymers from glycerol, emphasizing its potential as a method to repurpose this by-product of biodiesel production. By transforming residual glycerol into high-value polymers, this research aims to address the economic and environmental challenges associated with glycerol oversupply, reduce reliance on fossil-based raw materials, and contribute to the development of sustainable materials with a lower carbon footprint.

2. Material and Methods

The characterization of glycerol and the produced polymer involved the use of a Shimadzu TCC240A spectrophotometer with the UVprobe 2.21 program for data collection, a gas chromatograph with a flame ionization detector Varian, model GC-450, and a Nicolet 4700 FT-IR infrared spectrometer.

The materials utilized included purified glycerol and bi-distilled glycerin from Quimidrol Com. Ind. Imp. Ltda with a molecular mass of 92.09 g/mol and highly pure adipic acid 1,4-Butanedioic Acid ($C_6H_{10}O_4$), from Vetec Química Fina Ltda. Additionally, dibutyl phthalate from Vetec Química Fina Ltda was used.

The glycerol used in the process was purified following the method by Domingos (2019), which involved neutralizing residual glycerol with phosphoric acid, vacuum filtration, and adsorption onto activated carbon heated to 60 °C to reduce its viscosity.

The polymerization reactions were carried out in a 0.750-liter stainless steel batch chemical reactor (Figure 1), heated by a 1,000 W electric resistance, controlled with a PID controller that receives temperature information from inside the reactor through a PT-100 sensor and a solid-state relay.

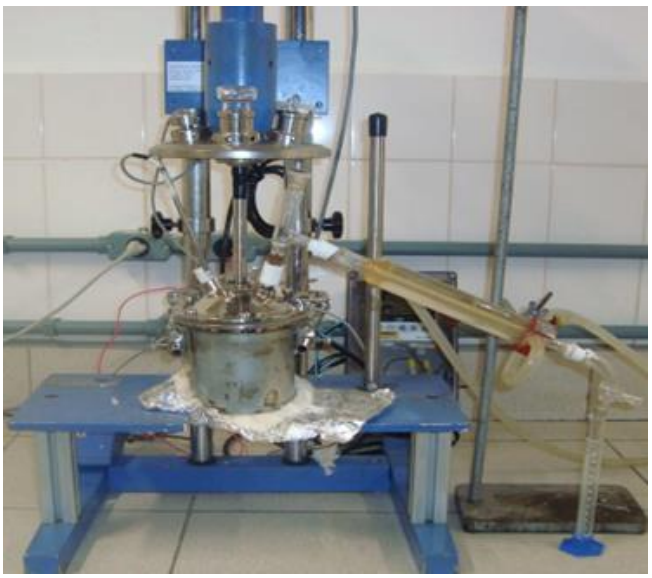

Figure 1: The polymerization reactor used in this study

https://doi.org/10.55343/CogSust.137

The reactor was coupled with an agitation system with rotation control and a torque meter, and it was also insulated using a thermal insulation blanket. Purified glycerol and adipic acid were added to the reactor in the molar ratio given in Table 1. The reactor was sealed with screws, fixed to the support of the mechanical stirrer, and thermally insulated. The mechanical stirrer was set to a low rotation speed, and heating was initiated. When the reactor's internal temperature reached 100 °C, the agitation was increased to 60 rpm for 30 minutes to ensure complete homogenization of the reagents. Upon completing this stage, the catalyst (dibutyl phthalate) was added to the glycerol/adipic acid mixture, and the condenser assembly was attached to the reactor. These apparatuses were used to recover the water resulting from the polycondensation reaction conducted in the reactor. At this stage, the temperature was increased to 160 °C and maintained constant until the end of the reaction.

In all tests, a catalyst loading of 2% dibutyl phthalate (relative to the mass of glycerol) was used. The reaction was conducted at a constant temperature of 160 °C and an agitation rate of 60 rpm. The progress of the polycondensation reaction was monitored by tracking the accumulation of water produced, with time zero defined as the collection of the first drop of liquid. The reaction was considered complete when water condensation ceased, indicated by stability or a plateau in the accumulated water volume, which was monitored using PID controller.

Table 1. Polymerization test with different glycerols and varied molar ratio.

Glycerol	**Glycerol/Acid Ratio**	**Agitation (rpm)**	**Temperature (ºC)**
Adsorbed	1:0.76	60	160
	1:1.0		
	1:1.5		
	1:2.		
Standard	1:0.76		
	1:2		
Adsorbed	1:2		
Distilled	1:2		
Filtered	1:2		

The produced polymer was characterized using a Thermo Fischer Scientific Nicolet 4700 FT-IR infrared spectrometer, with a scanning range of 400–4000 cm^{-1}, a resolution of 4, and 32 scans in ATR mode with a germanium crystal.

https://doi.org/10.55343/CogSust.137

3. Results and Discussion

The progress of the reaction was monitored by tracking the volume of water condensed (Figure 2), with time zero defined as the moment the first drop of liquid was collected. The polymerization tests followed the experimental plan outlined in Table 1, making it possible to assess the influence of glycerol quality on the polymerization process.

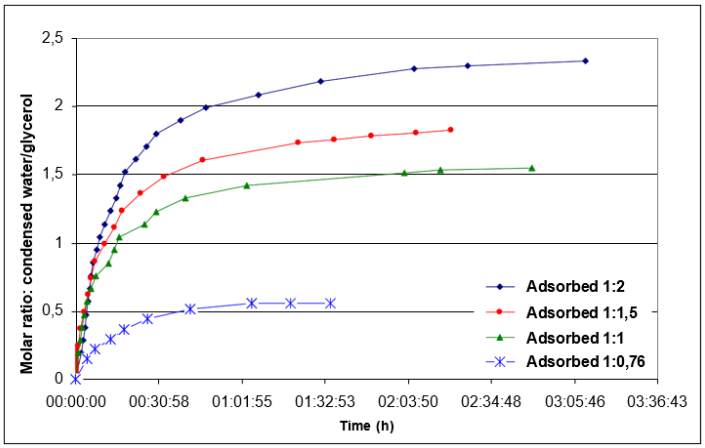

Figure 2. Reaction evolution as a function of the molar ratio of condensed water relative to the glycerol added to the reactor (Adsorbed Glycerol)

3.1. Evolution of Polymerization

The data collected during the polymerization tests revealed the relationship between glycerol volume and recovered water volume, as depicted in Figures 2, 3 and 4. These figures highlight the influence of the adsorbed glycerol to adipic acid ratio on the polymerization process. Figure 2 demonstrates the impact of this ratio, showing the importance of adipic acid in water recovery and, consequently, in improving polymerization performance.

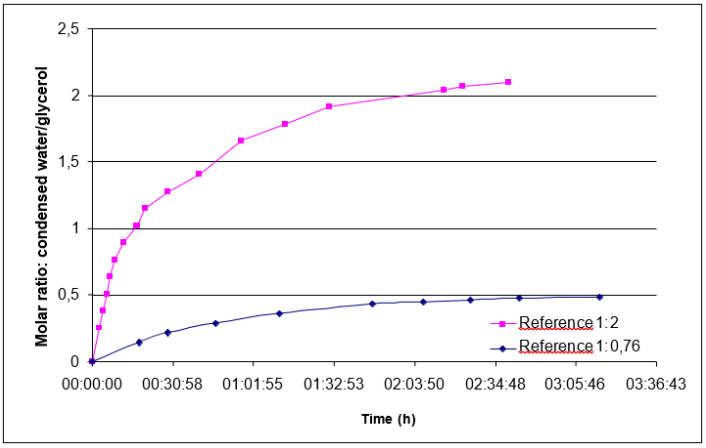

Figure 3. Reaction evolution as a function of the molar ratio of condensed water relative to the glycerol added to the reactor

The results indicate that a lower mass of adipic acid leads to a smaller volume of accumulated water and, consequently, lower process performance. The 1:2 ratio exhibited a more pronounced increase in polymerization water volume during the first hour of the reaction, after which the process stabilized and continued until the third hour. Lower ratios of adipic acid to glycerol resulted in decreased performances, directly proportional to the increase in adipic acid mass in the reaction mixture.

https://doi.org/10.55343/CogSust.137

To confirm the influence of the glycerol-to-adipic-acid ratio, experimental tests were conducted using reference glycerol, observing the same behavior described in Figure 2. This indicates that increasing the mass of adipic acid in glycerol during the polymerization reaction increases the volume of polymerization water recovered by condensation (Figure 3).

Given the optimal performance based on the glycerol-to-adipic-acid ratio, the polymerization performance for different types of glycerol was evaluated based on the purification stages involved. Figure 4 shows three curves of polymerization progression involving the reactions of adsorbed, reference, and distilled glycerol with adipic acid in a molar ratio of 1:2. While all three types of glycerol exhibited similar polymerization performance, adsorbed glycerol consistently outperformed both distilled and reference glycerol.

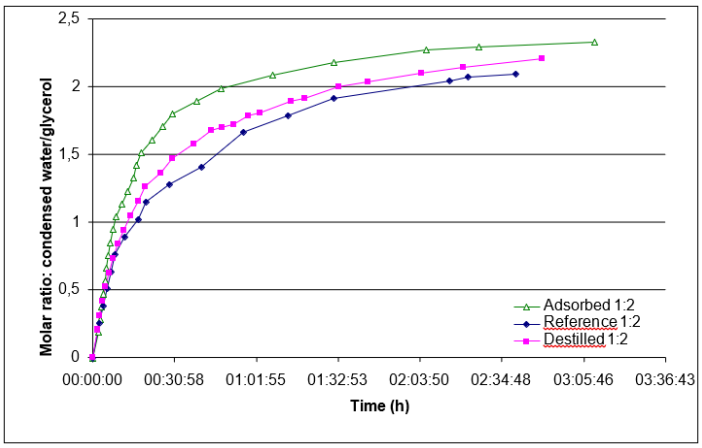

Figure 4. Reaction evolution as a function of the molar ratio of condensed water relative to the glycerol added to the reactor (Glycerol/Adipic Acid molar ratio of 1:2)

Domingos et al. (2019) conducted absorbance tests to assess the quality of the glycerol used, based on the attenuation of a light beam passing through a quartz filter. The glycerol samples were diluted in anhydrous ethanol and analyzed using a spectrophotometer. The measurements demonstrated that each stage of purification significantly influences the quality of the purified glycerol. The absorbance curves obtained from the analysis of the purified glycerol samples (adsorbed, neutralized, and crude glycerol) exhibited qualitative behavior similar to the reference glycerol curve (Figure 5). However, a marked deviation was observed, attributable to the presence of a high content of impurities. This distinction underscores the impact of residual contaminants on the optical properties of the glycerol samples.

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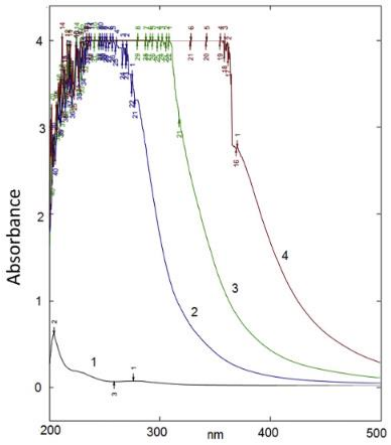

Figure 5: Absorbance spectra from 200 to 500 nm for: 1) reference glycerol, 2) adsorbed glycerol, 3) neutralized glycerol, and 4) crude glycerol (Domingos et al., 2019).

This approximation suggests that the purified glycerol contains residual impurities, primarily evidenced by the yellowish coloration of the final product (Domingos et al., 2019). The presence of these impurities likely accounts for the higher recovery of water observed during the polymerization of adsorbed, distilled, and reference glycerol, in a 1:2 ratio (Figure 4). This correlation highlights the influence of impurity levels on the reaction dynamics and water yield during the polymerization process.

Therefore, the water produced during the reaction results from the aggregation of glycerol and adipic acid monomers, which involves the breaking of hydroxyl (OH^-) and hydrogen (H^+) radicals, leading to the formation of water upon their combination. These findings align with those reported in the literature by Garti et al. (1981) and Brioude et al. (2007), as well as more recent studies by Zhang et al. (2018) and Kumar et al. (2021), who investigated polymer production from glycerol and evaluated reaction conversions based on the volume of condensed water recovered.

Furthermore, the analysis of Figures 2, 3, and 4 allows us to conclude that the mass ratio between glycerol and the reagent (adipic acid) significantly influences the quality of the produced polymers. Higher volumes of recovered water indicate a more extensive aggregation of monomers within the polymer's molecular structure, as illustrated in Figure 6. This relationship underscores the critical role of stoichiometric ratios in optimizing polymerization efficiency and polymer quality, as highlighted by recent advancements in polymerization techniques and reaction kinetics (Silva et al., 2020; Li et al., 2022).

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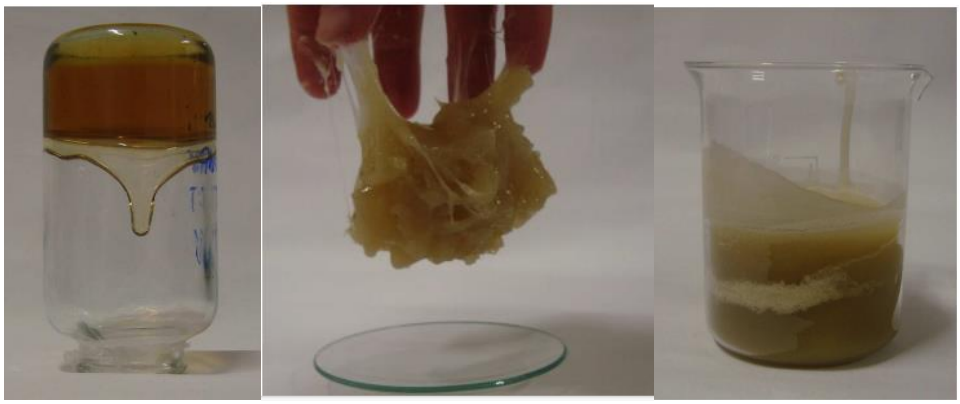

Figure 6. Polymer produced with adsorbed glycerol at the ratio: a) 1:1, b) 1:1.5, and c) 1:2

The results presented in Figure 6 show an increase in the viscosity of the produced glycerol with a decrease in the molar ratio between glycerol and adipic acid, forming a polymer with high resistance and strong adhesion to the surface of the conditioning container.

3.2. Characterization of the Produced Polymer

The polymers produced in the experimental tests, as depicted in Figures 2, 3, and 4, were characterized using infrared spectroscopy (Figure 7) within the 400–4000 cm^{-1} range to identify the functional groups present. Figure 7 shows the spectra of adsorbed glycerol and the polymers produced with adsorbed glycerol under four different scenarios. These scenarios correspond to glycerol-to-adipic acid molar ratios of 1:0.75, 1:1, 1:1.5, and 1:2, respectively. The analysis of these spectra provides insights into the structural changes and functional group interactions that occur during polymerization, highlighting the influence of stoichiometric ratios on the final polymer properties.

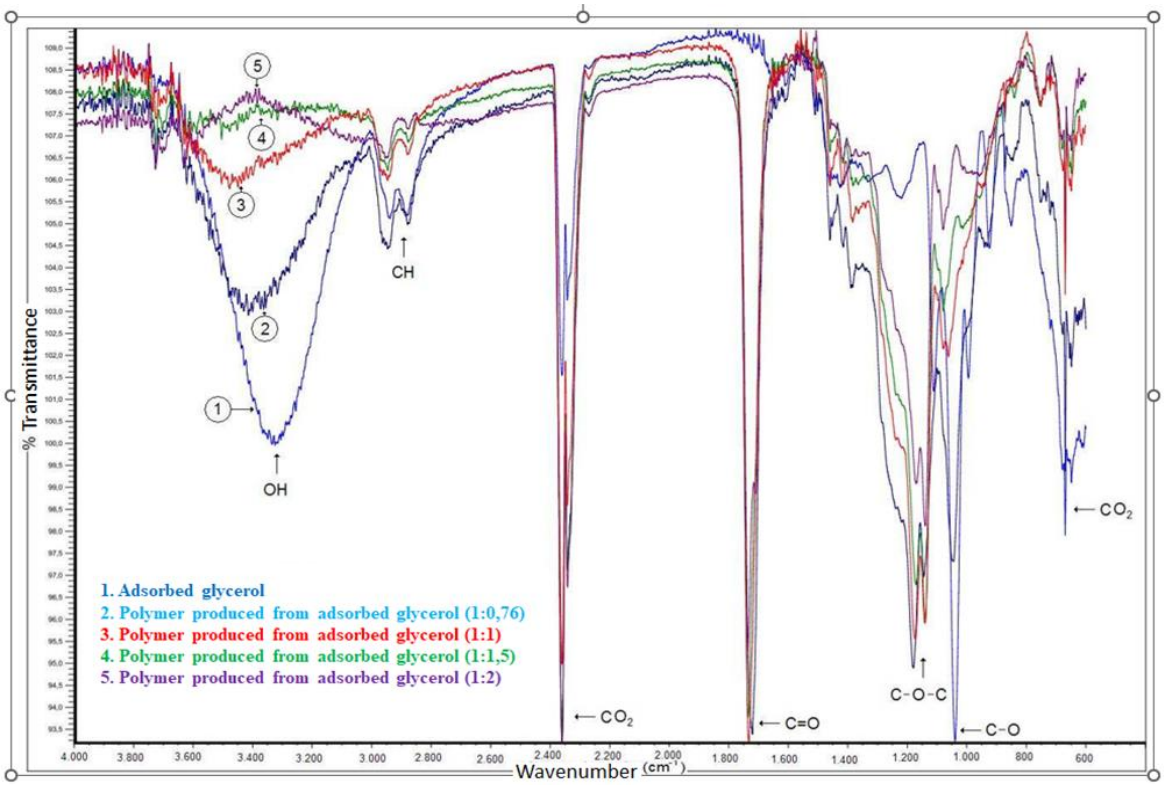

Figure 7. Infrared scan spectrum of adsorbed glycerol compared with the produced polymer

https://doi.org/10.55343/CogSust.137

The evidence of polymer formation by polycondensation is identified by the band of the consumed hydroxyl group, which leads to the formation of water during polymerization, with an increase in the molar ratio of adsorbed glycerol to adipic acid and the consequent formation of the ester group. Additionally, there is an increase in the bands at the wavelengths corresponding to C=O, C–O–C, and C–H, characteristic of esters that constitute the polymers obtained from biomass (glycerol from biodiesel production).

These results are consistent with the findings of Zhang et al. (2018) and Kumar et al. (2021), who synthesized a polyester from glycerol and phthalic acid using glycerol-to-phthalic acid molar ratios of 1:1, 1:1.5, and 1:2. These ratios correspond to OH-to-COOH molar ratios of 1.5:1, 1:1, and 0.75:1, respectively. A decrease in the molar ratios results in a reduction of unreacted hydroxyl (OH) groups and an increase in unreacted carboxyl (COOH) groups, reflecting the stoichiometric influence on the polymerization process. Zhang et al. (2018) and Kumar et al. (2021) have further validated these findings, emphasizing the critical role of stoichiometric control in optimizing polymerization efficiency and polymer properties.

Additionally, two bands unrelated to any functional group were observed in the spectra. These bands are attributed to interference caused by dissolved carbon dioxide in the material, with approximate bands appearing between 2325 cm^{-1} and 2360 cm^{-1}, as well as a distinct signal at 667 cm^{-1}. These artifacts are common in infrared spectroscopy and do not correspond to the chemical structure of the polymer. Recent advancements in spectroscopic analysis, as highlighted by Zhang et al. (2018) and Kumar et al. (2021), have improved the identification and interpretation of such spectral interferences, ensuring more accurate characterization of polymer structures. Furthermore, studies by Silva et al. (2020) have demonstrated the application of advanced spectroscopic techniques to minimize these interferences, enhancing the reliability of polymer characterization in complex systems.

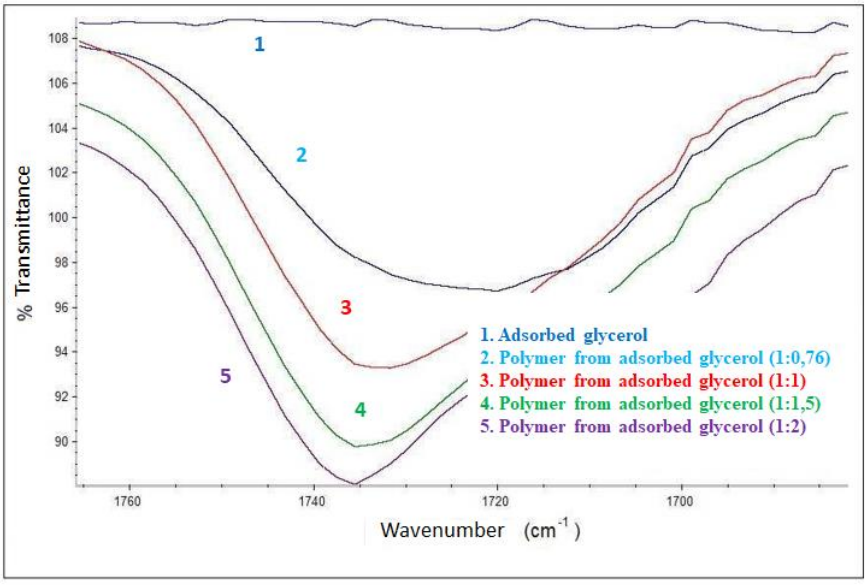

Figure 8. Highlight of the IR spectrum in the ester group band (1670–1760 cm^{-1})

According to Calderon et al. (2023), the main characteristic of polyglycerol adipic is forming ester bonds from the reaction of alcohol and carboxylic acid groups. The carbonyl group of the ester bonds can be identified by the absorption at 1730–1720 cm^{-1}. The remaining alcohol groups can be observed

https://doi.org/10.55343/CogSust.137

at the absorption at 3600–3000 cm^{-1}, confirming the increased formation of ester bonds at higher reaction temperatures and supporting the observed OH number, acid number, and viscosity behaviors. The authors confirm that increasing O–H transmittance and decreasing phthalic acid C–H transmittance occur as the OH molar ratio increases. This observation aligns with the behavior of the OH number and acid number as the OH ratio increases. The decrease in phthalic acid C–H transmittance is due to the lower acid content as the OH ratio increases, showing a decrease in transmittance as the OH molar ratio increases, confirming that lowering the available acid groups for the reaction reduces the formation of ester bonds.

3.3. Life Cycle Assessment of Residual Glycerol

The use of residual glycerol as a raw material for polymer production is an environmentally sustainable alternative when analyzed in comparison to fossil-derived polymers, especially considering the increasing biodiesel production rates, which generate a significant amount of residual glycerol. Based on this principle, it is possible to quantify and compare the environmental impacts associated with using residual glycerol from biodiesel production for polymer synthesis, in comparison to conventional fossil-based polymers such as polyethylene and polypropylene. This allows for the establishment of a scientific foundation for adopting residual glycerol as a raw material, with the potential to reduce the environmental impacts of the polymer industry.

For this analysis, the functional unit adopted is the production of 1 kg of polymer from residual glycerol, considering the environmental impact throughout the entire life cycle, from raw material extraction to final polymer production. The system boundaries include all stages of the product's life cycle, such as obtaining residual glycerol as a byproduct of biodiesel production, transportation to the polymerization unit, the polymerization process itself, energy usage in the process, and the necessary auxiliary materials such as catalysts and solvents. The life cycle of the produced polymer is considered up to the production of the final product. The disposal or recycling of the polymer is not addressed in this evaluation.

Thus, the compilation of a Life Cycle Inventory (LCI) is an essential stage that involves quantifying the inputs and outputs of the process, encompassing raw materials, energy flows, and waste generated. The LCI incorporates the analysis of typical processes used to produce polymers from residual glycerol.

Approximately, 1 kg of residual glycerol generates 0.9 kg of polymer, considering 0.1 kg of process losses and byproducts, as the polymerization process involves dibutyl phthalate as catalysts and adipic acid as a reagent, and the conversion is not complete. The use of dibutyl phthalate as a catalyst and adipic acid as a non-toxic solvent helps minimize environmental impacts. In this process, both electrical and thermal energies are consumed, as the reactor operates at temperatures above 160 °C, with energy efficiency considered a crucial factor in determining the environmental impact.

The transportation of residual glycerol from biodiesel production facilities to processing units, along with the associated CO_2 emissions from transport, is considered. The polymerization of residual glycerol involves chemical reactions to form polymer chains, with energy consumption (thermal or electrical) and the generation of byproducts such as wastewater and gaseous effluents. CO_2 emissions resulting from the consumption of electrical and thermal energy during the polymerization process are quantified based on the energy sources used. Process waste includes non-recoverable solvents,

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contaminated catalysts, and liquid effluents, and the proper management of such waste is essential to minimize environmental impacts.

The results show that the use of residual glycerol as a raw material for polymer production is an environmentally favorable alternative compared to fossil-derived polymers, especially in terms of reducing carbon footprint and using renewable resources. However, impacts related to energy consumption and chemical waste management require more in-depth critical analyses, as using residual glycerol and adopting more efficient polymerization processes and renewable energy sources can significantly reduce global environmental impacts. To achieve this, the implementation of cleaner technologies and improvements in energy efficiency are essential steps to maximize environmental benefits. Additionally, a circular economy model, where residual glycerol is efficiently utilized to generate value and mitigate the environmental impacts associated with its disposal, is an opportunity for further exploration. Sustainable catalysts and solvents, as well as polymer recycling, are areas that demand more research and development.

Therefore, the life cycle assessment of using residual glycerol for polymer production presents significant potential for reducing environmental impacts, especially by replacing fossil-derived polymers. The adoption of greener processes, renewable energy sources, and less toxic catalysts are crucial conditions to maximize environmental benefits and ensure that polymer production from residual glycerol is truly sustainable.

4. Conclusions

Based on the analysis of the results presented in this work, it is possible to conclude that:

i. Purified glycerol can be characterized by spectrophotometry and chromatography, and used for the production of polymers, whose characteristics were evaluated in this work;

ii. The methodology of polycondensation polymerization of purified glycerol represents a significant advancement for harnessing the potential of glycerol residues produced in biodiesel production units;

iii. The polymers produced from reference, adsorbed, and distilled glycerol in different molar ratios of glycerol/adipic acid show adequate quality and potential for scaling up this process, utilizing the potential of these residues for the chemical industry;

iv. Characterizing the polymers by infrared spectroscopy in the wavelength range of 400–4000 cm^{-1} confirms the formation of functional groups related to the poly (adipic polyglycerol) polymer formed.

Competing Interest Statement

The authors declare that there are no competing interests related to the research, authorship, or publication of this manuscript. No financial, personal, or professional relationships, whether direct or indirect, exist that could inappropriately influence the work presented in this study. The authors further confirm that they have adhered to ethical guidelines in conducting and presenting the research, ensuring that the results and conclusions drawn are unbiased and free from any conflict of interest.

Author Contributions

The authors of this article contributed proportionally to the development of this work, with the first and last authors assuming greater responsibility in the proposed studies, conducted within the scope

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