

## Use of residual glycerin and glycerol in biopolymer preparation

### Uso de glicerina residual e glicerol na preparação de biopolímero

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#### Resumo

A glicerina loira, um coproduto obtido na produção do biodiesel pela reação de transesterificação, tem sido gerado na última década, em grandes quantidades cada vez maiores, devido ao aumento na produção desse biocombustível. Dessa forma, tornam-se importantes pesquisas relacionadas ao desenvolvimento de materiais e produtos que agreguem valor e destino ecologicamente adequado à esse resíduo. Nesse contexto, o presente estudo trata do reaproveitamento da glicerina loira na síntese de um biopolímero biodegradável, o poli(citrato de glicerol). As polimerizações foram estudadas empregando-se ácido cítrico/glicerina loira e  $ZnCl_2$  como catalisador. Obtiveram-se conversões de 58,2 % em 120 min de reação, usando-se a glicerina loira, sem tratamento prévio. Tais dados indicam a viabilidade do reuso da glicerina loira, sem pré-tratamentos, na preparação do respectivo biopolímero, um material com valor agregado e vantajoso ambientalmente.

**Palavras-chave:** Glicerina loira; Biopolímero; Reações de polimerização

#### Abstract

Residual glycerin, a co-product obtained in the biodiesel production by transesterification reaction, has been generated in great quantities in the last decade due to the increase in the demand of this biofuel. Therefore, researches related to the production of high added value and environmental friendly materials using residual glycerin are fundamental for an appropriate destination of this waste. In this context, the present study aims on the reuse of the glycerin co-product in the synthesis of poly(glycerol citrate) biopolymer. Polymerization reactions were studied using citric acid, residual glycerin without pre-treatment and  $ZnCl_2$  as catalyst. Conversion rates of 58.2 % were obtained in 120 min of reaction time, such results shows a promising potential in producing a biodegradable biopolymer using low cost raw material.

**Keywords:** Residual glycerin; Biopolymer; Polymerization reactions

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## 1 Introduction

In recent decades technologies were developed and deployed for renewable energy production using various alternative sources such as Sun, tides, wind and biomass. Such studies were driven mainly by environmental pollution arising, directly or indirectly, from the intensive use of oil and its derivatives. In Brazil, biodiesel, whose production was encouraged after the Federal Government established, by law n° 9,478, that the percentage of addition to common diesel should be elevated from 7 % to 8 % in 2017. That same year the national biodiesel production was 4.2 billion liters and there is a forecast of 1 % increase each year until 2020 (CASTILHO, 2017).

This biofuel in generally, is synthesized by the established method of transesterification, in which vegetable fats and/or oils react with an alcohol (methanol or ethanol) to obtain biodiesel, a mixture of methyl or ethyl esters, and glycerin. Currently, Brazil generates a significant amount of biodiesel, and consequently significant amounts of residual glycerin, justifying the necessity of developing experimental studies aiming in producing a high added value and biodegradable materials from this residue (DI BITONTO et al., 2016).

Other harmful residues are plastics. These are polymers produced on a large scale using petrochemical derivatives and consumed worldwide in expressive quantities (LOKENS GARD, 2013). As a result, large amounts of polymer wastes are generated and when discarded improperly, they become responsible for serious environmental problems, on the basis of their extended degradation period. Thus, researchers and industries seek alternative means to minimize this environmental impact. One of the solutions adopted recently is the production of biodegradable biopolymers, whose technical viability and economic feasibility shows a great potential for expansion (FABER and FERREIRA-PIGLET, 2016).

The biopolymers are produced using renewable raw materials, such as corn, sugar cane, cellulose, chitin, and other (ABNT 15448-1, 2008; ASTM D833, 2008). Such polymers can suffer degradation, in weeks or months, by microbiological action of bacteria, fungi and algae (ABNT 15448-2, 2008; ASTM D6400, 2004) and can be derived from plant origin (corn, pulp, potatoes and sugar cane) and animal origin (chitin, Chitosan or proteins) (MOHANTY et al., 2005; RAY and BOUSMINA, 2005; BELGACEM and GANDINI, 2008), or even synthesized by bacteria from organic molecules such as butyric and valeric acids (BASHIR et al., 2011; UMPIERRE and AXE, 2013).

The biodegradation process is the result of the presence of polar functional groups in the polymer structure, susceptible to hydrolytic cleavage or microbiological (BRUICE, 2006). These functional groups are often esters, however the literature also reports, the biodegradability of polymers containing other functional groups such as imines, amides and anhydrides (WISKUR et al., 2004; HOLLAND et al., 2006).

Polyesters contain ester bonds, formed by condensation of di or polycarboxylic acids and/or anhydrides and

polyfunctional alcohols (polyols). Polymers are widely used in the industries of plastic, biomedicine, agriculture, textile, paints, varnishes and adhesives (PAI, 2013; ZHANG and GRINSTAFF, 2014; PIRES et al., 2015). Example of these polymers are, poly (glycolic acid) (PGA), poly (lactic acid) (PLA), poly ( $\epsilon$ -caprolactone) and poly (*L*-lactic acid-co-glycolic) (PLGA) and the combination of citric acid and/or glycerol to other compounds, for example, as in the case of poly (glycerol sebacate), poly (octanodiol citrate) and poly (citrate co-sebacato octanodiol) (ORTEGA-TORO et al., 2016)

This work presents a preliminarily study on the reuse of crude glycerin, a co-product of biodiesel production by transesterification, for the synthesis of a biodegradable biopolymer poly(glycerol citrate), using citric acid as well as sulfuric acid and zinc chloride as catalysts.

## 2 Material and Methods

### 2.1. Preparation of the biopolymer

Polyesterification was conducted for 2 h in a reflux system consisting of a 100 ml three-necked flask, fitted with a ball condenser, under refrigeration, and desiccant tube, kept under heating bath and under stirring. A thermometer was coupled to control the reaction temperature (115 °C). Reactions were performed in different proportions of citric acid:commercial glycerol and catalysts ( $H_2SO_4$  (97 %, Merck) or  $ZnCl_2 \cdot 2H_2O$  (97 %, Neon)), according to the experimental procedure presented in Table 1. When the reaction temperature reached the value the catalyst was added. This was considered the initial reaction time. Using the same conditions were conducted tests using crude glycerin resulted from the production of biodiesel by Petrobrás Biodiesel Unit in Montes Claros/MG. Samples of residual glycerol used did not undergo any type of physical-chemical treatment and presented approximately 50.0% of glycerol. This percentage was considered and corrected in the tests maintaining the same proportions of reagents, previously adopted. The polymerization was performed in triplicate. (CABRAL and LOFRANO, 2016).

### 2.2. Determination of acid value and conversion rate

The polymerization was monitored by the Acidity index (AI) during 120 min and every 20 min aliquots were removed from the reaction system. These were then titrated using standardized aqueous solution 1.0 mol L<sup>-1</sup> sodium hydroxide (98 %, Merck). Aqueous solution of phenolphthalein (98 %, Neon) was used as indicator in case of reactions which uses  $H_2SO_4$  as a catalyst, and the indicator bromothymol blue (97.5 %/Vetec) for reactions using anhydrous  $ZnCl_2$ . The volume of the basic solution was determined in each titration and used in the calculation of the medium conversion rate of the citric acid in the reaction product (CABRAL and LOFRANO, 2016).

### 2.3. Identification of the ester link by hydroxamic acid

Aliquots of 1.0 mL of the reaction medium were taken every 20 min and transferred to a test tube. Then they were added 4 drops of ethanolic solution (anhydrous ethanol 99 %, Synth) of hydroxylamine hydrochloride (99 %, Sigma Aldrich) (5 % m/m) and 5 drops of aqueous solution of potassium hydroxide (97 %, Merck) (5 % m/m). The resulting mixture was heated in a water bath (Novatecnica NT 268) to 60 °C for 1 min. Then this was cooled in ice bath. Then were added 4 drops of HCl (37 %, chemical/Vetec) (5 % v/v) and 4 drops of FeCl<sub>3</sub> (95 %, Sigma Aldrich) (1 % m/m). For a positive result for presence of organic ester function (-COO-) in the reaction medium, the solution should be present an intense violet color. In the absence of the organic function the solution should keep its original color (ENGEL et al., 2012).

## 3 Results

The stoichiometric ratio citric acid:commercial glycerol 1:5 was chosen as the most promising in preparing the biopolymer by polyesterification. Adopting

this proportion, studies were carried out regarding the solubility of tricarboxylic acid in glycerol at different temperatures (25, 60, 100, 110 and 120 °C). The obtained results demonstrated that only at 110 °C it was possible to solubilize the mixture citric acid/glycerol in the chosen proportion. Thus, it was decided to set the temperature at 115 °C as ideal to be employed in the polymerization reactions, ensuring that all the citric acid was soluble in commercial glycerol.

The following are images of the material obtained in the conversion of citric acid:commercial glycerol 1:5 to 115 °C and after 120 min of reaction. To examining them, it is seen that the material achieved has polymeric characteristics, such as adhesion to the surface of the reaction flask rather than flow. And since the viscosity can be defined as the flow resistance, it can be stated that the respective material is extremely viscous. These results confirm that the product resulting from the reaction between citric acid and commercial glycerol is polymeric (Figure 1).

The data presented in Table 1 shows that by using 4.7 % of the catalyst H<sub>2</sub>SO<sub>4</sub> a 91.5 % conversion rate was attained, while the use of 4.7 % of the catalyst ZnCl<sub>2</sub>, promoted a 78.6 % conversion rate. It can be also observed that the conversion rate of citric acid in poly(glycerol

Figure 1- Illustrative images of the polymer obtained using citric acid:commercial glycerol 1:5 to 115 °C and after 120 min of reaction



Table 1 - Reaction conditions employed, their respective normal conversion rates and results obtained in the tests with ferric hydroxamate

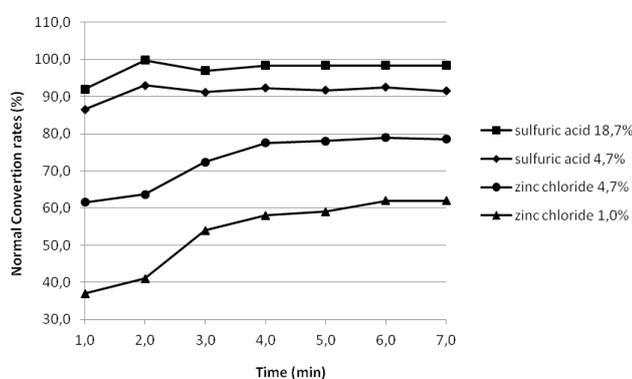
Stoichiometric ratios citric acid/commercial glycerol	Catalysts	Quantities of catalysts (%)*	Normal conversion rates (%)	Hidroxamic acid test
1:5	H <sub>2</sub> SO <sub>4</sub>	18.7	98.4	Positive
1:5	H <sub>2</sub> SO <sub>4</sub>	4.7	91.5	Positive
1:5	ZnCl <sub>2</sub>	1.0	62.0	Positive
1:5	ZnCl <sub>2</sub>	4.7	78.6	Positive

\*Percentage values related to the number of moles of citric acid

citrate) was positively influenced by the increase in the concentration of both catalysts used in the polymerization reactions. On the other hand, it is important to point out that by employing a low concentration of 1% of  $ZnCl_2$ , a conversion rate of 62.0% was achieved (Table 1).

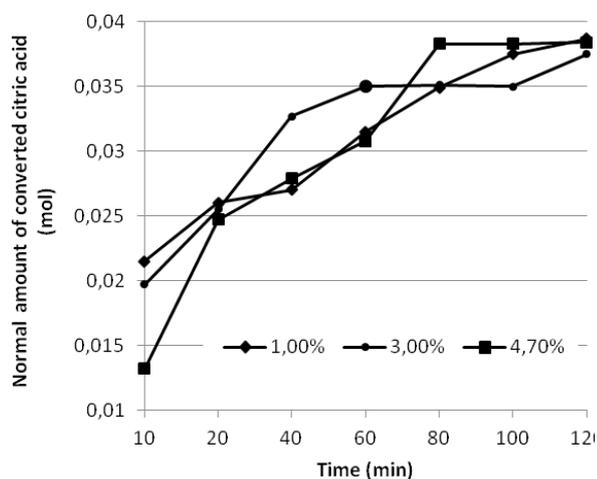
Analyzing Figure 2, it was possible to verify that the polyesterification reactions obtained by using  $H_2SO_4$  as catalyst, reached after only 20 min their maximum values of conversion rates, while in the polymerization reactions employing the  $ZnCl_2$  there has been a gradual increase in the conversion of reactants.

Figure 2 – Normal conversion rates values versus reaction time using  $H_2SO_4$  and  $ZnCl_2$  in different percentages.



According to Figure 3, it was observed that the three different concentrations of the catalyst  $ZnCl_2$  showed a similar reaction profile, with gradual conversions of the reagents (citric acid and commercial glycerol) in product. In all cases, similar amounts of citric acid were converted after 120 min of reaction time. On the other hand, high conversion values of citric acid were observed after 80 min of reaction time when 4.7% of  $ZnCl_2$  was used (Figure 4).

Figure 3 – Normal values of molar amounts of citric acid converted versus time using different percentages of the  $ZnCl_2$  catalyst.

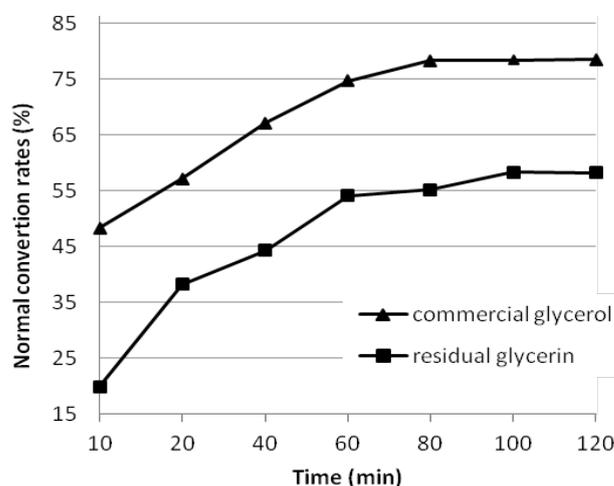


In all trials, in the different evaluated conditions, positive results were obtained in the tests of hydroxamic acid.

After the improvement of reaction conditions and applying qualitative methodology characterization by the method of hydroxamic acid, polymerization reaction using crude glycerin were carried out under the same conditions, previously studied (citric acid:commercial glycerol 1:5 the 115°C and 120 min of reaction).

Figure 4 presents the behavior of commercial glycerol and crude residual glycerin, whose conversion rates were 78.6% and 58.2% respectively. In both cases were recorded positive results in tests of hydroxamic acid, indicating the presence of the ester function in polymeric obtained biopolymer.

Figure 4 – Normal values of conversion rates versus time using commercial glycerol and crude residual glycerin.



## 4. Discussion

In esterification reactions alcohols, in general, are used as a solvent in excess in order to increase the efficiency of the reversible reaction. Such choice is made due to its lower boiling in comparison with carboxylic acids, which facilitates alcohol elimination (MORRISON and BOYD, 2005). This information associated to the literature data (VUKOVIC et al., 2006; BRIOUDE et al., 2011; MOURA et al., 2012), subsidized the use of glycerol (triol) as excess reagent and solvent. According to the obtained results, the optimal conditions for the biopolymer production by polyesterification were a molar mixture of citric acid:commercial glycerol 1:5 at 115 °C for 120 min.

Sulfuric acid ( $H_2SO_4$ ) is commonly used in polyesterification, however this is a potentially toxic compound and highly corrosive (McMURRY, 2011). Then were decided to also evaluate the performance of the catalyst  $ZnCl_2$  (Lewis acid) in the reactions. Its use can also be sustained by its low cost, non-corrosive nature and less toxic behavior. According to Cardoso (2011)  $ZnCl_2$  has proved to be an effective catalyst for liquid phase homogeneous esterification of fatty acids.

The polyesterification reactions were monitored by acidity index (AI). This method allows quantifying the

remaining carboxyl groups at the end of these reactions in which the formation of ester groups (-COOR) presents in the polymeric structure. Therefore, the reaction conversion rate percentage can be calculated (Table 1) (DHEVI et al., 2013; MIRANDA et al., 2015).

The performance of  $ZnCl_2$  (Figure 3) is in accordance with a possible transition state, formed in slow step of the reaction and resulting from the acid citric carboxyl groups coordinated the free valences  $Zn^{2+}$ . This tetra-coordinated complex formed is certainly responsible for increasing the polarization of the carbonyl, which intensifies its electrophilicity index, making it more attractive to the nucleophilic attack of alcohol (glycerol). It is necessary to consider orientation and proximity still related to this complex carboxyl- $Zn^{2+}$ -hydroxyl, can also facilitate the formation of ester linkage (CARDOSO, 2008). Similar results were obtained in studies regarding the acetylation of alcohols using  $Co^{2+}$  as a catalyst (CARDOSO, 2011).

Such behavior is probably due to  $H_2SO_4$  being a dehydrating agent, while  $ZnCl_2$  acts as an electron pair (Lewis acid) acceptor. Thus, in reactions catalyzed by  $H_2SO_4$ , it was observed that the reaction medium assumed a yellowish color, possibly resulting from the oxidation of organic compounds used in the reaction. Thus, in spite of the lower values of conversion rates obtained for the  $ZnCl_2$  catalyst, this was evaluated in different amounts using the commercial citric acid: glycerol ratio 1:5. The results indicated a gradual increase in the average conversion rate as the  $ZnCl_2$  concentration increases, 1.0; 3.7 and 4.7 %, resulting in mean conversion rates of 62.0, 68.5 and 78.6 %, respectively (Figure 3).

The hydroxamic acid test is an analytical methodology of chromogenic nature used to determine the presence of the ester functional group (-COOR) in the reaction medium. Its application is simple, fast and low cost with high sensitivity and specificity. Identification results from the reaction of ester groups with hydroxylamine hydrochloride in alkaline medium transforming them into hydroxamic acid salts reactive in ferric chloride solution, forming colored complexes from red to purple (ENGEL et al., 2012).

After the improvement of the polymerization conditions using the glycerol, reactions were carried out using residual glycerin under the same conditions previously studied. Figure 5 presented the mean percentage conversion rates of glycerol and residual glycerin, both reactions occurring in a gradual and similar manner, but with a lower value, in the case of residual glycerin (58.2 %) compared to glycerol (78,6 %). This fact probably results from the effect of contaminants present in the residual glycerin such as salts and other organic compounds which may have impaired the formation of the tetravalent carboxyl- $Zn^{2+}$ -hydroxyl complex and consequently a decrease in its average conversion rate. These results are in line with studies by Drumond and Wang (2004), Brioude et al. (2011), Anderson et al. (2016) and Jayachandran et al. (2016).

## 5 Conclusions

Through experimental assays it was found that the reaction between citric acid and commercial glycerol catalyzed by  $ZnCl_2$  is viable, since the obtained conversion rates were above 60 % after 120 min of reaction time, under all studied conditions. Moreover, hydroxamic acid verification test, methodology chosen by the authors, for the identification of organic ester function and therefore in monitoring and evaluation of the effectiveness of the conversion of the citric acid and commercial glycerol in the formation of the biodegradable biopolymer poly(glycerol citrate). Conforming the obtained results, it was concluded that the use, of crude residual glycerin without any prior treatment, in the polyesterification reactions proved promising, since the difference in the conversion rates were in the order of only 20 % lower than when commercial glycerol was used in obtaining a material with high added value, as the biopolymer here studied. In addition, the reuse of crude glycerin can avoid its inadequate discard in the environment. Thus, the present study brings a preliminary contribution concerning the production of an ecologically correct biopolymer using a residual crude glycerin from biodiesel production by transesterification.

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