ecoPETROL

ctyf@ecopetrol.com.co

EFFECT OF IMPURITIES PRESENT IN THE CRUDE GLYCEROL POLYMERIZATION REACTION TO PRODUCE POLYGLYCEROL

■ EFECTO DE LAS IMPUREZAS EN LA REACCIÓN DE POLIMERIZACIÓN DEL GLICEROL CRUDO PARA PRODUCIR POLIGLICEROL

Ardila-Suárez, Carolina[a,b] ; Rojas-Cristancho, Jeimmy[a]; Pineda- Martínez, Jennifer[a]; Ramirez-Caballero, Gustavo E.[a,b]*; Ramirez-Garcia, Álvaro[a].

ABSTRACT

Crude glycerol (CG) is a low-cost biodiesel industry co-product in a ratio of 1:10 with the main product. The large quantities of CG produced affect the biodiesel and glycerol markets. Consequently, the exploration of new applications for CG becomes crucial. As the composition of CG differs significantly from that of purified glycerol, this work was focused on studying the effect of CG impurities on its polymerization, as this process, at the same reaction conditions established for the polymerization of purified glycerol, did not result in polymeric products. To identify the reason for this result, the CG was fully characterized to identify its composition. Hence, an experimental design using simulated-CG was performed to study the effect of the most abundant impurities in the CG on the polymerization and the impurities that would persist with such reaction conditions, such as soap and sodium. The response variable for the experimental design was the hydroxyl number of the reaction products. FT-IR spectroscopy was used to analyze differences among the reaction products obtained from different treatments. The presence of soap was identified as primary inhibitory factor and the bottleneck in the formation of polyglycerol via polymerization of CG. Molecular weights of the polymerization reaction products were determined and analyzed as per the MALDI-TOF technique. The identification of the effect of impurities of CG polymerization suggests new routes for using it in the production of high value-added chemicals.

RESUMEN

El glicerol crudo es un co producto de bajo valor de la industria del biodiesel, que se produce en una relación 1:10 respecto al producto principal. Las grandes cantidades de glicerol crudo producido afectan los mercados tanto del biodiesel como del glicerol. En consecuencia, es fundamental la exploración de nuevas aplicaciones para el glicerol crudo. La composición del glicerol crudo difiere significativamente del glicerol purificado, es por esto que el presente trabajo busca estudiar el efecto de las impurezas del glicerol crudo en su polimerización ya que este proceso, a las mismas condiciones de reacción que aquellas establecidas para el glicerol purificado, no conlleva a productos poliméricos. Para identificar las razones de este resultado, el glicerol crudo fue totalmente caracterizado para identificar su composición. De acuerdo a esto, un diseño experimental usando glicerol crudo-simulado fue desarrollado para encontrar el efecto de las impurezas más abundante presenten en el glicerol crudo sobre su polimerización, además de las impurezas que permanecen a las condiciones de reacción como jabones y sodio. La variable de respuesta del diseño experimental es el índice de hidroxilo de los productos de reacción. La espectroscopia FT-IR se utilizó para analizar las diferencias entre los productos de reacción obtenidos de diferentes tratamientos. La presencia de jabón se identificó como el principal factor inhibitorio y el cuello de botella en la formación de poliglicerol mediante la polimerización de glicerol en crudo. Los pesos moleculares de los productos de reacción de polimerización se determinaron y analizaron con la técnica MALDI-TOF. La identificación del efecto de las impurezas en la polimerización del glicerol crudo abre las puertas a nuevas futas para su uso en la producción de químicos de alto valor agregado.

AFFILIATION

*[a]Grupo de Investigación en Polímeros, Escuela de Ingeniería Química, Universidad Industrial de Santander (UIS), Km 2 vía el refugio, Guatiguará, Piedecuesta, 681011, Colombia.
[b]Centro de Investigaciones en Catálisis, Escuela de Ingeniería Química, Universidad Industrial de Santander (UIS), Km 2 vía el refugio, Guatiguará, Piedecuesta, 681011, Colombia.
email: gusramca@uis.edu.co

1 INTRODUCTION

Biomass is an attractive alternative input for the production of fuels [1],[2], as well as a potential driving force for development of bio refineries [3]-[5]. The development of biomass based fuels as an alternative for fossil fuels energy has been encouraged worldwide by governmental policies, seeking to diversify energy sources and reduce environmental pollution caused by emissions from combustion of fossil fuels [6],[7]. Therefore, the production of bio-diesel via transesterification reaction of mainly vegetable oils has gained considerable attention in recent years. For example, the current biodiesel production in the European Union is approximately 11 million tonnes and forecasts suggest that in 2020 it will exceed 15 million tonnes per year [8]-[10]. However, 10% (w/w) of the total biodiesel production is CG [11],[12]. Thus, in the stoichiometry of the vegetable oils transesterification reaction, three moles of methanol react with the glycerides in three stages, in presence of a catalyst to produce methyl esters and glycerol. In the first stage, methanol reacts with triglycerides to form methyl esters and diglycerides. In the second stage, methanol reacts again, this time with diglycerides to form monoglycerides and methyl esters. Finally, in the third stage, monoglycerides react with methanol to form glycerol and methyl esters. According to the reactions described above, one mole of glycerol is produced per 3 moles of methyl esters synthesized.

CG production is exponentially increasing as a result of growth of biodiesel world production and it is forecast to reach 1.54 million tons in 2015 [13]. Oversupply of glycerol has negative environmental effects [14] as well as on the profitability of biodiesel production processes, if not properly managed. Therefore, obtaining products with high added value from glycerol contributes to sustainability and increased profitability for the biodiesel industry, as well as environmental benefits [12],[15].

Currently, glycerol used in industrial applications requires a purity of at least 85%. The purification process to bring the CG to that purity level represents approximately 14% of the total production cost [16]. The high purification costs of CG to obtain purified glycerol are associated with the requirements of separation techniques such as electrochemical [16], ion exchange [17], and vacuum distillation [18], which entail high operation and energy costs. Impurities to remove include catalyst and alcohol residues, free fatty acids, alkyl esters, mono, di and triglycerides [19].

Glycerol application fields, as it is a very versatile compound [20], are mostly related to the production of materials with applications in basic chemical industry, industrial microbiology and oxygenated fuel additives such as glycerol carbonate [21],[22]; acrolein [23],[24] and 1,2-propanediol [25],[26]. Additionally, pure glycerol has applications in the food industry, industrial microbiology, pharmacology and cosmetics; however, these applications require purity levels above 99%, which implies intensive purification procedures [11]. By contrast, the use of CG as raw material for development of industrial use products may not require high purification costs. Therefore, research work is currently focused on finding greater value- added uses for CG that would enable its use in industrial applications such as hydrogen production [27-29], production of polyhydroxyalkanoates (PHAs) [30]-[33], such as polyol in polyurethane foam production [34],[35], and biogas production [36],[37], to transform the current biodiesel industry, into bio refinery based on the oleochemical industry [38].

If glycerol produced as a by-product from the transesterification reaction is discarded as waste stream, it could threat the biodiesel production as a cost-effective process and would constitute an environmental threat. Therefore, there is a need to revaluate CG using it in industrial applications. Already known applications of CG include: hydrogen production [27]-[29], synthesis of microbial polyhydroxyalkanoates (PHAs) [30]-[33], fumaric acid production [39], synthesis of 1,3 – propanediol [40]-[42], bioconversion into ethanol [43],[44] and polyols for the production of polyurethane [34],[45].

A promising valued-added product of glycerol is polyglycerol, a high molecular weight polymer formed by an inert polyether chain with abundant pendant hydroxyl groups, which makes polyglycerol a building block for diverse polymeric complexes [46]. One of the main characteristics of polymers made out of polyglycerol is that it is biocompatible, biodegradable, and a sustainable material. However, the reported production of polyglycerol, using sulfuric acid as catalyst, comes from purified glycerol [47]. To the best of our knowledge, synthesis of polyglycerol from CG as raw material has not been reported before. The CG composition shows that 60 to 80% is glycerol and the rest are impurities, mainly classified as soap, water, methanol, catalyst residues, free fatty acids, and salts [11],[48]. The purification process of CG to obtain purified glycerol results in a three-time cost increment. The high purification cost is an economic disadvantage that discourages the industrial production of polyglycerol [16],[49].

The use of CG for polymers feedstock is a promising application, among others. For example, Luo et al. [50] found that the CG can be used as biopolyols for polyurethanes foams production. Furthermore, Godinho et al [51] synthesized a pre-polymer of poly(glycerol sebacate), an elastomer with potential biomedical applications, using lipase B as catalyst.

An attractive alternative to revaluate CG is to produce polyglycerol. Polyglycerol is a polymer composed of an inert polyether backbone and abundant highly reactive hydroxyl groups that are exposed and allow for further modification to produce a variety of related compounds [46],[52],[53]. The presence of a catalyst – either of homogeneous or heterogeneous type- which can be either acidic or basic- is required for glycerol polymerization.
Din et al [54] polymerized the CG using microwave irradiation and the soap content as the catalyst. The authors found that this process results in the formation of glycerol oligomers, from diglycerol to pentaglycerol.

Salehpour and Dubé [47] evaluated the use of sulfuric acid as a catalyst of pure glycerol polymerization reactions at reduced pressures and obtained polyglycerols of relatively high molecular weights. Polyglycerol is industrially produced by ring opening polymerization of glycidol, and polymers with narrow distribution and molecular weights in a range between 1000 and 30000 g/mol are obtained [46],[55]-[57]. Polyglycerols of higher molecular weight and branched structure, directly synthesized from glycerol, could replace hyperbranched polymers obtained from glycidol, a toxic monomer [58] opening the possibilities of application at industrial levels for the production of complex polymeric structures derived from glycerol. However, according to this study, the production of polyglycerol from CG as raw material does not occur. This research is aimed at understanding and identifying the factors that inhibit polymerization of CG using sulfuric acid as the catalyst. Therefore, a sample of CG was characterized to identify impurities. Simulated-CG

was prepared adding the impurities, previously identified as purified glycerol. The effect of each impurity on the polymerization reaction, as well as the interaction between them, was analyzed.

An experimental design was conducted to study the effect of the most abundant impurities (soap and sodium) and the concentration of catalyst (sulfuric acid) in the polymerization of CG. As a result, it was found that sulfuric acid in presence of soap produces side reactions that compete with polyglycerol synthesis. Furthermore, a statistical analysis to assess the effect of the presence and absence of impurities, soap and sodium, at a fixed concentration of catalyst, revealed that the presence of soap in CG is the main inhibitory factor of polyglycerol synthesis.

2. EXPERIMENTAL DEVELOPMENT

MATERIALS

Pure glycerol, sodium hydroxide, and sulfuric acid were obtained from Merck. CG, a by-product from the biodiesel manufacturing process, was kindly provided by BioSC S.A. (Santa Marta, Colombia), which uses palm oil as raw material for biodiesel production.

METHODS

CRUDE GLYCEROL (CG) CHARACTERIZATION

Physico-chemical characterization
Density of CG was determined using a 2 mL pycnometer. The pH of CG was measured with a digital pH meter Schott HANDYLAB 1 at room temperature ($25 \pm 1°C$).

Glycerol content in the CG sample was determined using the iodometric–periodic acid method in accordance with the AACC 58 technique. Soap content was determined according to a modified version of the AOC Cs method [59]. Ash content was determined following the ISO 2098-1972 method.

Water content was determined following the AOCS official method (Ea 8-58), using a Volumetric Karl Fischer titrator (Metrohm 870 KF Tritino plus). The presence of methanol was determined by gas chromatography with an Agilent Technologies 6890N system equipped with a flame ionization detector. The method followed was the EN14110. Metals (Ca, K, Mg and Na) were detected by inductively-coupled plasma atomic absorption spectroscopy, using a Perkin Elmer 5300 DV spectrometer. These analyses were carried out in collaboration with the Quality Inspection Coordination, ECOPETROL S.A.

Complementary characterization
A thermogravimetric analysis (TGA) was performed to determined polymer degradation as a function of temperature. A temperature range from 25 to 300°C at a heating rate of 5 °C min^{-1} was used. This analysis was performed in a TGA 2050 from TA instruments, Inc., equipped with a nitrogen purge gas system (50 cm^3 min^{-1}). Infrared spectrum was obtained in transmittance mode in a Shimadzu 8400s spectrometer. Fatty acid methyl esters (FAME) present in the CG sample were identified with a gas chromatography system (Agilent Technologies 6890 series), coupled to a FID detector, using an Agilent DB23 column and SUPELCO 38 FAMES as standards. All measurements were performed in duplicate. The mass analysis was performed by ESI-MS on a BRUKER DALTONICS INC, AMAZON X mass spectrometer. The molecular weight distributions were obtained using MAL-TOF-MS with a Bruker Reflex mass spectrometer, according to our previous work [60].

EXPERIMENTAL PROCEDURE

The polymerization reaction was carried out on a 50 mL glass reactor equipped with nitrogen inlet, catalyst feeding, thermometer inlet, and a distillation trap for continuous water removal from the reaction mixture. Temperature was maintained at 150°C, using a temperature-controlled heating bath. A vacuum pump was attached to the reactor through the condenser; in the meantime, condensation reactions were carried out at pressures below 33.86 kPa during ~ 3 h and before reaching the gel point. The soap used to simulate CG was made from palm oil saponification [61], and the metal amount was obtained from the neutralization of sodium hydroxide with sulfuric acid.

3. RESULTS ANALYSIS

Three different concentrations of sulfuric acid as catalyst, 0%, 1%, and 4.8% (% w/w), were used to carry out polymerization reactions of CG. The viscosity of CG is 0.28 Pa*s. The highest product viscosity was obtained with the reaction performed with 0% (w/w) sulfuric acid (1.63 Pa*s) compared with the viscosities obtained when using 1% and 4.8% catalyst (0.4 and 1.57 Pa*s respectively). The result can be explained by the presence of soaps in the CG sample, which catalyzes the oligomerization of glycerol increasing product viscosity [62]. Despite the increase of viscosity in the reaction products, there was not polyglycerol formation under any condition tested. The fact that polymerization of CG did not occur, even though the reaction was performed under the same conditions for which successful polymerization of purified glycerol was achieved, encouraged us to study the factors that inhibit polymerization of CG. To find the polymerization inhibitory factors present in CG, simulated-CG samples were prepared according to the composition in the characterization of CG.

CHARACTERIZATION OF CRUDE GLYCEROL (CG)

The physico-chemical characterization of CG from the hydrolysis of triglycerides in the production of biodiesel, suggests that 75% is glycerol with a pH of 6.14, and a density of 1.28 (g/cm^3). The moisture content determined was 10.5%, soaps content 13.9%, ashes 3.5%, and methanol 0.025%. The presence of metals found in the sample were mainly sodium (22850 ± 3860 mg/Kg), potassium (46.7 ± 3.54 mg/Kg), calcium (17.1 ± 1.78 mg/Kg), and magnesium (8.6 ± 0.68 mg/Kg). Moreover, the free fatty acid (FAMES) composition was formed by palmitic acid 63.3%, oleic acid 29.6%, stearic acid 5.6%, and linoleic acid 1.6%. As regards metals and FAMES composition, a considerable high amount of sodium with respect to other metals was observed; similarly, palmitic acid was found in a significantly higher proportion with respect to other free fatty acids. This increase in sodium and palmitic acid could be explained by the use of sodium
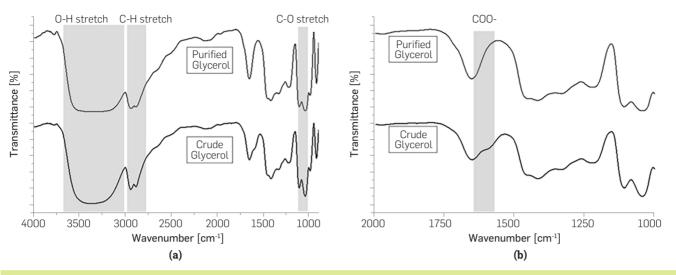
Figure 1 . FT-IR spectra of crude and purified glycerol. (a) Shows the presence of stretching bonds in the samples analyzed. (b) Shows a carboxyl (COO-) peak that appears only in the CG sample.

hydroxide or methoxide as a catalyst in the transesterification reaction; as well as African palm oil as raw material for biodiesel production.

A comparison between Fourier Transform Infra-Red (FT-IR) spectra of crude and purified glycerol is shown in **Figure 1**. The spectra shows the presence of a broad OH stretching band from 3000 cm^{-1} to 3600 cm^{-1}, C-H stretching between 2883 to 2947 cm^{-1} and C-O stretching from 1040 to 1120 cm^{-1} (**Figure 1a**). A carboxyl (COO-) peak only appears in the CG sample, see **Figure 1b**. This peak indicates that soluble soaps present in CG were removed after the acidification stage [63],[64].

The thermo-gravimetric analysis reveals a 2.45% weight loss in a temperature range between 25-37°C. This weight loss is due to the presence of volatile materials such as methanol. From 37-94°C, there is a 9.46% weight loss due to water evaporation, and between 100-200 °C, there is a significant weight loss attributed

to glycerol thermal degradation. The remnant mass observed in the thermogram after 200 °C might be explained by the presence of inorganic salts and fatty acids, as reported in previous studies [65],[66].

SIMULATION OF CRUDE GLYCEROL (CG) COMPOSITION

Based on the composition obtained from the characterization of CG, a simulated-CG sample was prepared by adding the impurities into purified glycerol. Soaps and metals were the most abundant impurities identified and, considering that at 150°C, water and methanol evaporated, the last two were not considered to affect the polymerization of CG to produce polyglycerol. The soap used to simulate CG was made from palm oil saponification [61], and the metal was sodium because in the characterization of CG, there was a significantly higher amount as compared with other metals. The simulated-CG was prepared by adding soap at 14%w/w, and sodium at 22850 mg/Kg.
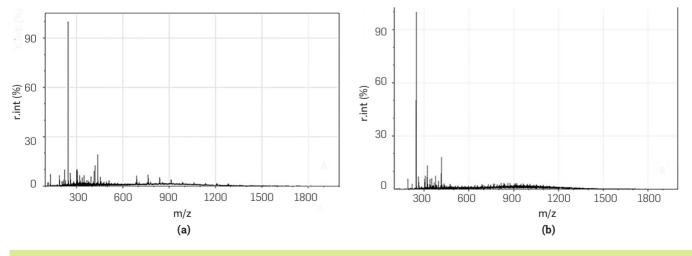

Figure 2 . Electrospray Ionization (ESI) mass spectrum comparison between the polymerization reaction products of characterized (a) and simulated (b) CG. The concentration of sulfuric acid used as catalyst was 4.8% w/w. A similar mass distribution of the two samples was observed.
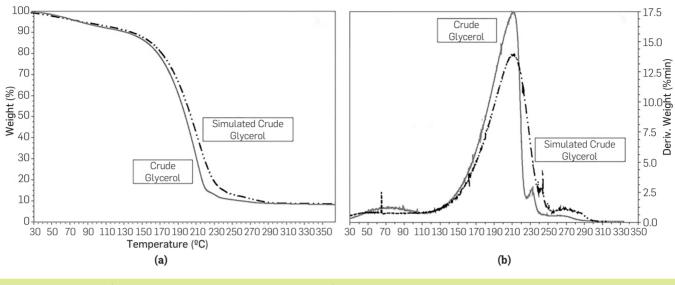
Figure 3. TGA (3A) and the first derivative of TGA curves (3B) of the reaction products from polymerization reaction of characterized and simulated-CG. Similar weight loss profile of the two samples was observed.

To confirm if the simulated CG prepared resembles the characterized one, two polymerization reactions were conducted under the same conditions using the simulated and characterized crude glycerols as raw material. The catalyst used was sulfuric acid at 4.8% w/w. Polymerization reactions were performed under conditions previously established in our previous work [60]. Hydroxyl number, mass spectroscopy, and thermogravimetry analysis were performed to compare reaction products obtained from polymerization reaction of the simulated and characterized crude glycerols. Results show a similar hydroxyl number for both glycerols used, simulated and the characterized one, which correspond to 376.25 ±6.68 and 406.76 ±7.35 mg KOH/g, respectively. Mass spectroscopy peaks for both samples were comparable (**Figure 2a-2b**). Related to ESI-MS results, it seems that the two reaction products exhibited similar mass distributions. Thus, the simulated-CG led to similar products than the original CG. This is also noticed in the TGA analysis, see **Figure 3a** and **3b**. However, the first weight loss region is related to the remaining water molecules in the final reaction product. On the other hand, the second region is associated with glycerol biodegradation that could be catalyzed due to the presence of the impurities in the two samples [67].

EFFECT OF SULFURIC ACID, SODIUM, AND/OR SOAP IN THE POLYMERIZATION REACTION OF SIMULATED-CRUDE GLYCEROL

A 2^k full factorial experimental design was performed to determine the effect of impurities on the sulfuric acid- catalyzed polymerization reaction of simulated-CG. **Table 1** summarizes the factors and levels used in the experimental design. Samples for each treatment were prepared adding the impurities corresponding to the factor levels proposed in the factorial design into purified glycerol. The reaction procedure was carried out as described in the experimental procedure section.

The hydroxyl number of the reaction products was selected as response variable, since it is an indicator of etherification or esterification reactions that may occur from different treatments. If in a treatment, an etherification or esterification reaction occurred,

Table 1. 2^k experimental design layout.

Parameter	Levels	
	Low	High
(A) Soap [%w/w]	10	14
(B) Sodium [mg/kg]	0	22850
(C) Sulfuric acid [%w/w]	0	4.8

the hydroxyl number of the product should decrease with respect to the initial hydroxyl number of glycerol, as some of the initial OH groups have reacted.

Table 2. Treatments, levels, and response variable of the 2^3-factorial design.

Treatment	Factors*			Hydroxyl number value [mg KOH/g]
	(A) Soap [%w/w]	(B) Sodium [mg/kg]	(C) Sulfuric acid [%w/w]	
(1)	10	0	0	1780.97 ± 7.01
A	14	0	0	1446.40 ± 13.01
B	10	22850	0	1728.19 ± 12.12
AB	14	22850	0	1725.86 ± 52.34
C	10	0	4.8	339.15 ± 3.15
AC	14	0	4.8	318.21 ± 4.03
BC	10	22850	4.8	725.03 ± 0.28
ABC	14	22850	4.8	376.25 ± 6.68

*Two independent samples were performed per treatment. The data reported is the average of two replicates that deviated less than 5% for treatments with 14% (w/w) soap, 22850 mg/kg sodium, and 0% sulfuric acid, and less than 1% for other treatments.

The response variable chosen may also suggest the formation of polyglycerol, as this polymerization reaction is an etherification. The hydroxyl number of the reaction products for each treatment was determined following the ASTM D 4274-11 method. The hydroxyl number of purified glycerol is 1800 [mg KOH/g] [68]. Data reported in **Table 2** is the average of two replicates which deviate less than 5% in all the treatments.
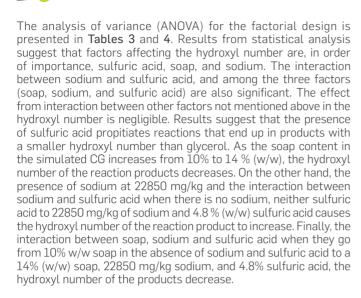
The analysis of variance (ANOVA) for the factorial design is presented in **Tables 3** and **4**. Results from statistical analysis suggest that factors affecting the hydroxyl number are, in order of importance, sulfuric acid, soap, and sodium. The interaction between sodium and sulfuric acid, and among the three factors (soap, sodium, and sulfuric acid) are also significant. The effect from interaction between other factors not mentioned above in the hydroxyl number is negligible. Results suggest that the presence of sulfuric acid propitiates reactions that end up in products with a smaller hydroxyl number than glycerol. As the soap content in the simulated CG increases from 10% to 14 % (w/w), the hydroxyl number of the reaction products decreases. On the other hand, the presence of sodium at 22850 mg/kg and the interaction between sodium and sulfuric acid when there is no sodium, neither sulfuric acid to 22850 mg/kg of sodium and 4.8 % (w/w) sulfuric acid causes the hydroxyl number of the reaction product to increase. Finally, the interaction between soap, sodium and sulfuric acid when they go from 10% w/w soap in the absence of sodium and sulfuric acid to a 14% (w/w) soap, 22850 mg/kg sodium, and 4.8% sulfuric acid, the hydroxyl number of the products decrease.

Table 3. Statistical analysis of the factors effect on the hydroxyl number of the reaction products and analysis of variance.

Factors	Effect on hydroxyl number	P − value
A	-88.33	< 0.0001*
B	83.83	< 0.0001*
C	-615.35	< 0.0001*
AB	0.55	0.9574
AC	-4.10	0.6913
BC	27.15	0.0260*
ABC	-82.51	< 0.0001*

*The factor has a significant effect on the response variable (p<0.05)

The reaction products obtained from the treatments proposed in the experimental design were analyzed with FT-IR. The spectrum obtained confirmed that the decrease in the hydroxyl number in the treatments was not due to polyglycerol formation, but due to other chemical reactions. The FT-IR spectra performed on all reaction products are presented in **Figure 4**. The spectra obtained from the reaction products formed are different from the polyglycerol spectra reported hereunder, as well as in others [47]. In the spectrum of treatment (ac), where sulfuric acid and soap factors were 4.8 % w/w and 14 % w/w respectively, there is a pronounced peak in 1735 cm^{-1}. Our hypothesis is that in these cases sulfuric acid does not act as a catalyst and becomes a reagent that forms free fatty acids with soap. These free fatty acids react with glycerol forming esters, as shown in equations 1 and 2. These chemical reactions under similar conditions have been reported to occur in previous studies [69],[70]. For treatments (a), (b) and (ab), where sulfuric acid was absent (0% w/w) in the mixture, there is a C-O-C ether stretching peak in the range between 1290 to 1100 cm-1. This result may indicate glycerol oligomerization catalyzed by soaps, as previously reported [62].

In the former experimental design, all the treatments contained soap. To study the effect of the presence and absence of soap in the simulated CG sample, another experimental design was performed, where soap and sodium were the factors. The concentration of sulfuric acid was fixed at 4.8% (w/w), as with this concentration of sulfuric acid, polyglycerol was successfully synthetized in previous works using purified glycerol [47]. **Table 4** shows the concentration of the factors analyzed (levels) and the response variable of the
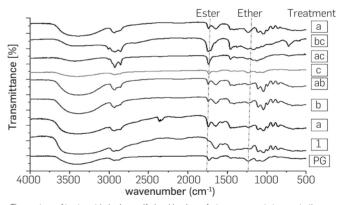
Table 4. Treatments, levels, and response variables of the 2^2 factorial design. Sulfuric acid was fixed at 4.8% w/w.

Treatment	Factors		Hydroxyl number value [mg KOH/g]
	(A) Soap [%w/w]	(B) Sodium [mg/kg]	
(1)	0	0	448.58± 11.64
A	14	0	318.21± 4.03
B	0	22850	424.36± 0.01
AB	14	22850	376.25± 6.68

The data reported is the average of two replicates which deviated less than 1% for all the treatments.

factorial design, which was again the hydroxyl number of the reaction product. The data reported is the average of two replicates that deviated less than 1%.

The analysis of variance (ANOVA) shows that the presence of soap as well the interaction between sodium and soap, affect the hydroxyl number, see **Table 5**. The increment of soap from 0% to 14% (w/w), decreases the hydroxyl number of the reaction product from 448.58±11.64 to 318.21±4.03. In the absence of soap, the effect of sodium in the hydroxyl number is negligible; however, when sodium and soap are present, the interaction between these factors causes a significant effect by increasing the hydroxyl number. The FT-IR spectra of products obtained from the reactions in the absence of soap (treatment (1) and (b) presented in **Table 4**), are similar to the reported polyglycerol spectra [47], see **Figure 5**.

The spectrum of treatment (ac), where sulfuric acid and soap factors are present at concentrations of 4.8 % and 14% w/w respectively (high levels of the factorial design), a signal in the range of 1735 to 1750 cm-1 is observed, indicating the presence of the ester functional group. The spectra of treatment (a), (b) and (ab), where sulfuric acid is absent (0% w/w) in the mixture, the presence of peaks in the range of 1290 to 1100 cm-1 indicate a C-O-C ether stretching.
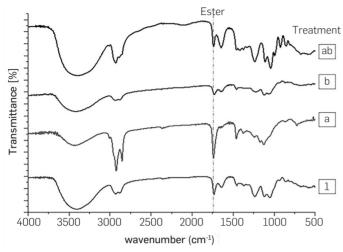
Figure 4 . FT-IR spectra of the eight treatments proposed in the 2^3 factorial design.

Table 5. Statistical analysis of the factors effect on the hydroxyl number of the reaction product.

Factors	Factor Effect	P-value
A	-44.62	0.0008*
B	8.45	0.1630
AB	20.56	0.0142*

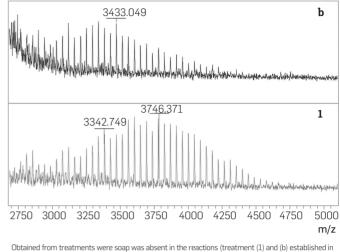* The factor has significant effect on the response variable (p<0.05)

On the other hand, as expected from the former experimental design, the FT-IR spectrum of treatments where soap was present showed an ester peak that is consistent with the explanation stemming from previous results.

FT-IR spectrum of the product obtained from the reaction in the absence of soap (treatment b) is similar to the reported polyglycerol spectrum (Salehpour & Dubé, 2011). The FT-IR spectra of treatments where soap was present show an ester peak (Treatments (a) and (ab)).

Figure 5 . FT-IR spectrum of the four treatments proposed in the 2^2 factorial design.

Based on these results, it may be concluded that in the absence of soap, the reduction in the hydroxyl number of the reaction product is caused by a polymerization reaction that forms polyglycerol. The molecular weight distributions of treatments where soap was absent in the reaction (treatment (1) and (b)) using a MALDI- TOF analysis, are shown in **Figure 6**. Polyglycerol molecular weight distribution in absence of soap and in presence of sodium (treatment (b)) ranges between 2800 to 4100 Da. Polyglycerol molecular weight distribution in absence of soap and sodium (treatment (1)) ranges between 2700 to 4400 Da. These results are consistent with the average molecular weight of polyglycerol previously reported [47]. Results from this study suggest that by removing the soap from CG and using sulfuric acid as catalyst under the reaction conditions described in the experimental procedure section, it is possible to synthesize polyglycerol. Therefore, the bottleneck for successful polymerization of CG to produce polyglycerol is soap removal.

Obtained from treatments were soap was absent in the reactions (treatment (1) and (b) established in the 22 factorial design). Thus, the removal of soap content from CG, allows polyglycerol synthesis, if sulfuric acid is used as the catalyst, following previous works [47, 60].

Figure 6. MALDI- TOF analyses of the products.

CONCLUSIONS

Soap and sodium are the most abundant impurities in CG and the impurities that affect the most polyglycerol synthesis because of reaction conditions. A statistical analysis using the simulated-CG as the starting monomer confirmed a significant effect caused by three factors: soap, sulfuric acid, and sodium, as well as the interaction between the first two and all the three factors on the hydroxyl number of the reaction product. The FT-IR analysis showed that when CG contains soap, changes in the hydroxyl number of the products formed were not due to polyglycerol. This is because of other side reactions between soaps and sulfuric acid (catalyst), which compete with the reaction where polyglycerol is synthesized. The effect of soap and sodium in the product formed revealed that soap is the main factor inhibiting polyglycerol synthesis. MALDI-TOF analysis confirmed that polymerization of CG in the absence of soap results in polyglycerol synthesis. It is worth noting that this study was focused on the CG from biodiesel with high palmitic acid content. Consequently, further work is necessary to establish the effect of other vegetable oils or renewable sources on the CG polymerization.

REFERENCES

[1]. Salvi, B.L., Subramanian, K.A., and Panwar, N.L., *Alternative fuels for transportation vehicles: A technical review.* Renewable and Sustainable Energy Reviews, 2013. 25: p. 404-419.10.1016/j.rser.2013.04.017

[2]. Sobrino, F.H., Monroy, C.R., and Pérez, J.L.H., *Critical analysis on hydrogen as an alternative to fossil fuels and biofuels for vehicles in Europe.* Renewable and Sustainable Energy Reviews, 2010. 14(2): p. 772-780.10.1016/j.rser.2009.10.021

[3]. Lanzafame, P., Centi, G., and Perathoner, S., *Evolving scenarios for biorefineries and the impact on catalysis.* Catalysis Today, 2014.10.1016/j.cattod.2014.03.022

[4]. Azapagic, A., *Sustainability considerations for integrated biorefineries.* Trends Biotechnol, 2014. 32(1): p. 1-4.10.1016/j.tibtech.2013.10.009

[5]. Thornley, P., Chong, K., and Bridgwater, T., *European biorefineries: Implications for land, trade and employment.* Environmental Science & Policy, 2014. 37: p. 255-265.10.1016/j.envsci.2013.09.004

[6]. Florin, M.J., van de Ven, G.W.J., and van Ittersum, M.K., *What drives sustainable biofuels? A review of indicator assessments of biofuel production systems involving smallholder farmers.* Environ Sci Policy, 2014. 37: p. 142-157.10.1016/j.envsci.2013.09.012

[7]. Rizzi, F., Jan van Eck, N., and Frey, M., *The production of scientific knowledge on renewable energies: Worldwide trends, dynamics and challenges and implications for management.* Renew Energ, 2014. 62: p. 657-671.10.1016/j.renene.2013.08.030

[8]. Hejna, A., Kosmela, P., Formela, K., Piszczyk, Ł., and Haponiuk, J.T., *Potential applications of crude glycerol in polymer technology–Current state and perspectives.* Renewable and Sustainable Energy Reviews, 2016. 66: p. 449-475.https://doi.org/10.1016/j.rser.2016.08.020

[9]. Kupczyk, A., et al., *Selected Aspects of Biofuels Market and the Electromobility Development in Poland: Current Trends and Forecasting Changes.* Applied Sciences, 2019. 9(2): p. 254

[10]. Bórawski, P., et al., *Development of renewable energy sources market and biofuels in The European Union.* Journal of Cleaner Production, 2019. 228: p. 467-484.https://doi.org/10.1016/j.jclepro.2019.04.242

[11]. Ayoub, M. and Abdullah, A., *Critical review on the current scenario and significance of crude glycerol resulting from biodiesel industry towards more sustainable renewable energy industry.* Renew Sust Energ Rev, 2012. 16(5): p. 2671-2686.10.1016/j.rser.2012.01.054

[12]. Zhang, Y., Dubé, M.A., McLean, D.D., and Kates, M., *Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis.* Bioresource Technology, 2003. 90(3): p. 229-240.10.1016/s0960-8524(03)00150-0

[13]. Dumeignil, B.K.S.P.V.B.-B.P.R.a.F., *Glycerol dehydration to acrolein in the context of new uses of glycerol - Critical Review* Green Chemistry, 2010. 12 p. 2079-2098.10.1039/C0GC00307G

[14]. Siegfried Warwel, F.B., Christoph Demes, Michael Kunz, Mark Rusch gen. Klaas. , *Polymers and surfactants on the basis of renewable resources.* Chemosphere, 2001. 43: p. 39-48

[15]. Ayoub, M. and Abdullah, A.Z., *Critical review on the current scenario and significance of crude glycerol resulting from biodiesel industry towards more sustainable renewable energy industry.* Renewable and Sustainable Energy Reviews, 2012. 16(5): p. 2671-2686.10.1016/j.rser.2012.01.054

[16]. Schaffner, F., Pontalier, P.-Y., Sánchez, V., Lutin F, *Bipolar electrodialysis for glycerin production from diester wastes.* Filtra Separ, 2003. 40(10): p. 35-39

[17]. Manuel Carmona, A.L., Antonio de Lucas, Angel Perez and Juan F. Rodriguez, *Purification of glycerol/water solutions from biodiesel synthesis by ion exchange: sodium and chloride removal. Part II.* Journal of Chemical Technology and Biotechnology 1130–1135, 2009. 84(8): p. 1130–1135.10.1002/jctb.2144 10.1002/jctb.2016

[18]. Yong, K.C., Ooi, T.L., Dzulkefly, K., Wan Yunus, W.M.Z., Hazimah, A.H., , *Characterization of glycerol residue from a palm kernel oil methyl ester plant* Journal of Oil Palm Research 2001. 13(2): p. 1-6

[19]. Javani, A., Hasheminejad, M., Tahvildari, K., and Tabatabaei, M., *High quality potassium phosphate production through step-by-step glycerol purification: a strategy to economize biodiesel production.* Bioresour Technol, 2012. 104: p. 788-90.10.1016/j.biortech.2011.09.134

[20]. Richter, M., Krisnandi, Y., Eckelt, R., and Martin, A., *Homogeneously catalyzed batch reactor glycerol etherification by CsHCO3.* Catalysis Communications, 2008. 9(11-12): p. 2112-2116.10.1016/j.catcom.2008.04.007

[21]. Yadav, G.D. and Chandan, P.A., *A green process for glycerol valorization to glycerol carbonate over heterogeneous hydrotalcite catalyst.* Catalysis Today, 2014.10.1016/j.cattod.2014.01.043

[22]. Tudorache, M., Negoi, A., Tudora, B., and Parvulescu, V.I., *Environmental-friendly strategy for biocatalytic conversion of waste glycerol to glycerol carbonate.* Applied Catalysis B: Environmental, 2014. 146: p. 274-278.10.1016/j.apcatb.2013.02.049

[23] de Oliveira, Aldenor, et al.,Catalytic conversion of glycerol to acrolein over modified molecular sieves: Activity and deactivation studies. Chemical Engineering Journals, 2011, 168, p. 765-774. https://doi.org/10.1016/j.cej.2010.09.029

[24]. Shen, L., et al., *Liquid phase catalytic dehydration of glycerol to acrolein over Brønsted acidic ionic liquid catalysts.* Journal of Industrial and Engineering Chemistry, 2014. 20(3): p. 759-766.10.1016/j.jiec.2013.06.004

[25]. Montes, V., et al., *Synthesis of different ZnO-supported metal systems through microemulsion technique and application to catalytic transformation of glycerol to acetol and 1,2-propanediol.* Catalysis Today, 2014. 223: p. 129-137.10.1016/j.cattod.2013.09.021

[26]. Sánchez, T., Salagre, P., Cesteros, Y., and Bueno-López, A., *Use of delaminated hectorites as supports of copper catalysts for the hydrogenolysis of glycerol to 1,2-propanediol.* Chemical Engineering Journal, 2012. 179: p. 302-311.10.1016/j.cej.2011.11.011

[27]. Sarma, S.J., et al., *Evaluation of different supplementary nutrients for enhanced biohydrogen production by Enterobacter aerogenes NRRL B 407 using waste derived crude glycerol.* Int J Hydrogen Energ, 2013. 38(5): p. 2191-2198.10.1016/j.ijhydene.2012.11.110

[28]. Chookaew, T., Prasertsan, P., and Ren, Z.J., *Two-stage conversion of crude glycerol to energy using dark fermentation linked with microbial fuel cell or microbial electrolysis cell.* N Biotechnol, 2014. 31(2): p. 179-84.10.1016/j.nbt.2013.12.004

[29]. Yung-Chung, L., Xue-Jiao, C., Chi-Yu, H., Ying-Jin, Y., Jo-Shu, C, *Dark fermentative hydrogen production with crude glycerol from biodiesel industry using indigenous hydrogen-producing bacteria.* Int J Hydrogen Energ, 2013. 38: p. 15815-15822

[30]. Shah, P., Chiu, F.S., and Lan, J.C., *Aerobic utilization of crude glycerol by recombinant Escherichia coli for simultaneous production of poly 3-hydroxybutyrate and bioethanol.* J Biosci Bioeng, 2014. 117(3): p. 343-50.10.1016/j.jbiosc.2013.08.018

[31]. Naranjo, J.M., Posada, J.A., Higuita, J.C., and Cardona, C.A., *Valorization of glycerol through the production of biopolymers: the PHB case using Bacillus megaterium.* Bioresour Technol, 2013. 133: p. 38-44.10.1016/j.biortech.2013.01.129

[32]. Garcia, I.L., et al., *Evaluation of by-products from the biodiesel industry as fermentation feedstock for poly(3-hydroxybutyrate-co-3-hydroxyvalerate) production by Cupriavidus necator.* Bioresour Technol, 2013. 130: p. 16-22.10.1016/j.biortech.2012.11.088

[33]. Hu, S., McDonald, A.G., and Coats, E.R., *Characterization of Polyhydroxybutyrate Biosynthesized from Crude Glycerol Waste Using Mixed Microbial Consortia.* J Appl Polym Sci, 2013. 129(3): p. 1314-1321.10.1002/app.38820 10.1002/APP.38820

[34]. Luo, X., Hu, S., Zhang, X., and Li, Y., *Thermochemical conversion of crude glycerol to biopolyols for the production of polyurethane foams.* Bioresour Technol, 2013. 139: p. 323-329.10.1016/j.biortech.2013.04.011

[35]. Gómez, E.F., Luo, X., Li, C., Michel, F.C., and Li, Y., *Biodegradability of crude glycerol-based polyurethane foams during composting, anaerobic digestion and soil incubation.* Polymer Degradation and Stability, 2014.10.1016/j.polymdegradstab.2014.01.008

[36]. Athanasoulia, E., Melidis, P., and Aivasidis, A., *Co-digestion of sewage sludge and crude glycerol from biodiesel production.* Renewable Energy, 2014. 62: p. 73-78.10.1016/j.renene.2013.06.040

[37]. Baba, Y., et al., *Anaerobic digestion of crude glycerol from biodiesel manufacturing using a large-scale pilot plant: methane production and application of digested sludge as fertilizer.* Bioresour Technol, 2013. 140: p. 342-8.10.1016/j.biortech.2013.04.020

[38]. Yuguo Zheng, X.C., and Yinchu Shen, *Commodity chemicals derived from glycerol, an important biorefinery feedstock.* Chemical Reviews, 2008, Vol. 108, No. 12, 2008. 108(12): p. 5253-5277.10.1021/cr100058u

[39]. Zhou, Y., et al., *Production of fumaric acid from biodiesel-derived crude glycerol by Rhizopus arrhizus.* Bioresour Technol, 2014. 163: p. 48-53.10.1016/j.biortech.2014.04.021

[40]. Casali, S., Gungormusler, M., Bertin, L., Fava, F., and Azbar, N., *Development of a biofilm technology for the production of 1,3-propanediol (1,3-PDO) from crude glycerol.* Biochem Eng J, 2012. 64: p. 84-90.10.1016/j.bej.2011.11.012

[41]. Pflugl, S., Marx, H., Mattanovich, D., and Sauer, M., *Heading for an economic industrial upgrading of crude glycerol from biodiesel production to 1,3-propanediol by Lactobacillus diolivorans.* Bioresour Technol, 2014. 152: p. 499-504.10.1016/j.biortech.2013.11.041

[42]. Szymanowska-Powałowska, D. and Leja, K., *An increasing of the efficiency of microbiological synthesis of 1,3-propanediol from crude glycerol by the concentration of biomass.* Electron J Biotechn, 2014. 17(2): p. 72-78.10.1016/j.ejbt.2013.12.010

[43]. Liu, X., Jensen, P.R., and Workman, M., *Bioconversion of crude glycerol feedstocks into ethanol by Pachysolen tannophilus.* Bioresour Technol, 2012. 104: p. 579-86.10.1016/j.biortech.2011.10.065

[44]. Suzuki, T., Nishikawa, C., Seta, K., Shigeno, T., and Nakajima-Kambe, T., *Ethanol production from glycerol-containing biodiesel waste by Klebsiella variicola shows maximum productivity under alkaline conditions.* N Biotechnol, 2014. 31(3): p. 246-53.10.1016/j.nbt.2014.03.005

[45]. Gómez, E.F., Luo, X., Li, C., Michel, F.C., and Li, Y., *Biodegradability of crude glycerol-based polyurethane foams during composting, anaerobic digestion and soil incubation.* Polym Degrad Stabil, 2014. 102: p. 195-203.10.1016/j.polymdegradstab.2014.01.008

[46].Wilms, D., Stiriba, S.-E., and and Frey, H., *Hyperbranched Polyglycerols: From the Controlled Synthesis of Biocompatible Polyether Polyols to Multipurpose Applications.* Acc Chem Res, 2010. 43(1): p. 129-141

[47].Salehpour, S. and Dubé, M.A., *Towards the Sustainable Production of Higher-Molecular-Weight Polyglycerol. Macromol Chem Phys*, 2011. 212(12): p. 1284-1293.10.1002/macp.201100064

[48].Leoneti, A.B., Aragão-Leoneti, V., and Valle Walter Borges de Oliveira, S., *Glycerol as a by-product of biodiesel production in Brazil: Alternatives for the use of unrefined glycerol.* Renew Energ, 2012. 45: p. 138-145.10.1016/j.renene.2012.02.032

[49].Vlysidis, A., Binns, M., Webb, C., and Theodoropoulos, C., *A techno-economic analysis of biodiesel biorefineries: Assessment of integrated designs for the co-production of fuels and chemicals.* Energy, 2011. 36(8): p. 4671-4683.10.1016/j.energy.2011.04.046

[50].Luo, X., Hu, S., Zhang, X., and Li, Y., *Thermochemical conversion of crude glycerol to biopolyols for the production of polyurethane foams.* Bioresource Technology, 2013. 139: p. 323-329.https://doi.org/10.1016/j.biortech.2013.04.011

[51].Godinho, B., Gama, N., Barros-Timmons, A., and Ferreira, A., *Enzymatic synthesis of poly(glycerol sebacate) pre-polymer with crude glycerol, by-product from biodiesel prodution.* AIP Conference Proceedings, 2018. 1981(1): p. 020031.10.1063/1.5045893

[52].Steinhilber, D., et al., *Hyperbranched polyglycerols on the nanometer and micrometer scale.* Biomaterials, 2011. 32(5): p. 1311-6.10.1016/j.biomaterials.2010.10.010

[53].Nieberle, J., *HYPERBRANCHED POLYGLYCEROLS AS BUILDING BLOCKS FOR COMPLEX AMPHIPHILIC STRUCTURES: SYNTHESIS, CHARACTERIZATION AND APPLICATIONS, in Fachbereich Chemie, Pharmazie und Geowissenschaften* 2008, Johannes Gutenberg-Universität: Mainz.

[54].Din, N., Idris, Z., Kian, Y.S., and Hassan, H., *Preparation of polyglycerol from palm-biodiesel crude glycerin.* Journal of Oil Palm Research, 2013. 25(3): p. 289-297

[55].Alexander Sunder, R.H., Holger Frey, and Rolf Mulhaupt, *Controlled Synthesis of Hyperbranched Polyglycerols by Ring-Opening Multibranching Polymerization.* Macromolecules, 1999. 32: p. 4240-4246

[56].R. Tokar, P.K., and S. Penczek', *Cationic Polymerization of Glycidol: Coexistence of the Activated Monomer and Active Chain End Mechanism Macromolecules,* 1994. 27: p. 320-322

[57].Wilms, D., Wurm, F., Nieberle, J., and Frey, H., *Hyperbranched Polyglycerols with Elevated Molecular Weights: A Facile Two-Step Synthesis Protocol Based on Polyglycerol Macroinitiators.* Macromolecules, 2009. 42: p. 3230-3236

[58].Rokicki, G., Rakoczy, P., Parzuchowski, P., and Sobiecki, M., *Hyperbranched aliphatic polyethers obtained from environmentally benign monomer: glycerol carbonate.* Green Chemistry, 2005. 7(7): p. 529.10.1039/b501597a

[59].Van Gerpen, J., Shanks, B., Pruszko, R., Clements, D., and Knothe, G., *Biodiesel analytical methods. National Renewable Energy Laboratory (NREL); August 2002–January 2004. [NREL/SR-510-36240].* , Energy, N.R. and [NREL/SR-510-36240]., L.N.A.-J.J., Editors. 2002: Colorado, USA. .

[60].Ardila-Suárez, C., Rojas-Avellaneda, D., and Ramirez-Caballero, G.E., *Effect of Temperature and Catalyst Concentration on Polyglycerol during Synthesis.* International Journal of Polymer Science, 2015. 2015: p. 8.10.1155/2015/910249

[61].Oluwatoyin, S.M., *Quality of Soaps using Different Oil Blends J Microbiol Biotech* Res, 2011. 1(1): p. 29-34

[62].Ahmad, S., et al., *Process of producing polyglycerol from crude glycerol* 2011: USA.

[63].Hidawati, E.N. and Sakinah, A.M.M., *Treatment of Glycerin Pitch from Biodiesel Production.* IJCEE, 2011. 2(5): p. 309-313

[64].Kongjao, S., Damronglerd, S., and Hunsom, M., *Purification of crude glycerol derived from waste used-oil methyl ester plant.* Korean J Chem Eng, 2010. 27(3): p. 944-949.10.1007/s11814-010-0148-0

[65].Dou, B., Dupont, V., Williams, P.T., Chen, H., and Ding, Y., *Thermogravimetric kinetics of crude glycerol.* Bioresour Technol, 2009. 100(9): p. 2613-20.10.1016/j.biortech.2008.11.037

[66].Koch, C., et al., *Determination of activation energy for animal fat and crude glycerol using thermogravimetric analysis, in 13th Brazilian Congress of Thermal Sciences and Engineering* 2010, Proceedings of ENCIT 2010 Copyright by ABCM: Uberlandia, MG, Brazil.

[67].Almazrouei, M., Samad, T.E., and Janajreh, I., *Thermogravimetric Kinetics and High Fidelity Analysis of Crude Glycerol.* Energy Procedia, 2017. 142: p. 1699-1705. https://doi.org/10.1016/j.egypro.2017.12.552

[68].Maminski, M.L., Szymanski, R., Parzuchowski, P., Antczak, A., and Szymona, K., *Hyperbranched Polyglycerols with bisphenol A core as glycerol-derived components of polyurethane wood adhesives. .* BioResources, 2012. 72(2): p. 1440-1451

[69].Boucher, M.B., et al., *Variables affecting homogeneous acid catalyst recoverability and reuse after esterification of concentrated omega-9 polyunsaturated fatty acids in vegetable oil triglycerides.* Green Chem, 2008. 10(12): p. 1331.10.1039/b810225b

[70].Sari, A., Bicer, A., Karaipekli, A., Alkan, C., and Karadag, A., S*ynthesis, thermal energy storage properties and hemral reliability of some fatty acid esters with glycerol as novel soli-liquid phase change materials* Sol Energ Mat Sol, 2010. 94: p. 1711-1715

Ecopetrol, being aware of the importance of science and technology in the oil industry, has increased in recent years its cooperation with the national science and technology system. As a result from this effort, the alliance with the Universidad Industrial de Santander (UIS) was established, focusing on exploratory risk reduction, increase in the recovery factor of the oil production fields, environmental sustainability, production of cleaner fuels, and heavy crude production and transport.

- Over COP$ 54.368 billion have been invested in R&D activities in a single site.
- Four applications for invention patents have been filed.
- Twelve copyright records have been granted by the
- Superintendence of Industry and Commerce.
- 11 PhDs graduate, 73 professors, 15 specialists, 369 students and 690 co-researchers have participated in joint projects.
- Over 120 seminars, 73 scientific articles, and 52 presentations at various technical and scientific events have been conducted with the aim of sharing the knowledge acquired.
- 31 research groups from 15 schools and 4 UIS faculties have contributed to the development of solutions and research works.

Universidad Industrial de Santander