

Chemical Recycling: Comparative Study about the Depolymerization of PET Waste-Bottles to Obtain Terephthalic Acid [†]

Samir Cavalcante ¹, Daniel Vieira ² and Isis Melo ^{2,*}

¹ Instituto de Defesa Química, Biológica, Radiológica e Nuclear (IDQBRN), Centro Tecnológico do Exército (CTEx), Guaratiba, Rio de Janeiro, RJ 23020-470, Brazil; samir.cavalcante@eb.mil.br

² Instituto Federal do Rio de Janeiro, Maracanã, Rio de Janeiro, RJ 20270-021, Brazil; daniel.vieira@ifrj.edu.br

* Correspondence: isis.costamelo@gmail.com; Tel.: +55-21-97497-3174

[†] Presented at the 23rd International Electronic Conference on Synthetic Organic Chemistry, 15 November–15 December 2019.

Published: 15 November 2019

Abstract: Currently, the plastic packaging industry in Brazil is the second largest producer in the packaging sector, with approximately 35% of the total packaging produced per year. Out of this total, 572 thousand tons are composed of polyethylene terephthalate plastic bottles (PET). In the ranking of the main materials discarded in the country, plastic occupies the third position and, in most cases, inadequately. Objectifying minimizes the amount of PET packaging improperly discarded and to instigate the industrial interest in the subject, our work pursued a viable path, as clean as possible in the principles of Green Chemistry, to depolymerize it. Obtaining the terephthalic acid as the main product, which is commercially obtained by oil sources and using salts and oxide of zinc as catalyzers in water as solvent, besides using inorganic bases as catalyzers in alcohols as solvent, including glycerol, which is a sub product of Biodiesel Industries. The reactions were made by refluxing (traditional way) and by microwave, where was used the reactor Biotage Initiator Plus. The products were characterized by Fourier Transformed Infrared Spectroscopy (FTIR of Bruker) and Ultra Performance Liquid Chromatography with Mass Spectrometer with Electrospray Ionization (UPLC-ESI/MS), where the results were better while using zinc sulfate as catalyzer in water and potassium hydroxide as catalyzer in pentan-1-ol.

Keywords: green chemistry; chemical recycling; sustainability; microwave; glycerol

1. Introduction

Polyethylene terephthalate (PET) is a widely used polyester industrially, mainly in the food industries as packaging, as it has the following properties: mechanical resistance, chemical resistance, difficult gas and odor permeability, transparency, gloss and easy recyclability. This polymer can be obtained from three commercial routes: by the esterification reaction of terephthalic acid with ethylene glycol, by the transesterification reaction of dimethyl terephthalate with ethylene glycol and terephthaloyl chloride with ethylene glycol [1]. Ethylene glycol and terephthalic acid, as well as the terephthalic acid derivatives, are derived from first generation products of the petrochemical industry: ethylene and para-xylene, respectively. In addition to the problem of using a non-renewable source of raw material, PET is highly resistant to degradation and can remain in the environment for over 500 years [2].

Aiming at reducing the production of PET bottle waste in the environment, this work tried to meet the concepts of Green Chemistry, where one of the categories that a “chemically green” or

technologically clean industry would be inserted is using sources of recycled raw materials. This concept has been disseminated since the 1990s, in order to promote less polluting or non-polluting alternatives when chemical processes are used in both industrial and academic atmospheres [3].

2. Materials and Methods

2.1. Conventional Depolymerization

The methodology used in the reflux reaction was the same as that adopted by VIEIRA, D. P. P. et al., 2018 [4].

PET bottles were collected in trash cans, labels and lids were removed and bottles were cleaned and dried. After that, they were ground into pieces of approximately 1×1 cm.

The crushed material was weighed and transferred to a reaction flask next to ethylene glycol and potassium hydroxide, where they were heated at reflux for one and a half hours.

Then the product obtained was acidified with a solution of sulfuric acid 5 mol/L and the precipitate was vacuum filtered.

The filtered material was oven dried and characterized by Fourier Transform Infrared Spectroscopy (FTIR).

The product was reacted with refluxing thionyl chloride to give terephthaloyl chloride, as it is highly reactive and more easily employed in the production of other molecules. However, this methodology was discarded for deviating from the principles of Green Chemistry, because it uses hazardous solvents and generates a lot of waste.

2.2. Microwave Assisted Reactions

The methodologies used were adaptations of the methodologies of TANG, 2011 [5] and NIKJE, 2007 [6], where the first uses zinc salts with 0.41% in molar fraction of zinc as depolymerization catalysts and water as solvent and the second uses potassium hydroxide as catalyst and pentan-1-ol as solvent.

After the reactions, the products were characterized by Ultra-Efficient Liquid Chromatography coupled to the Electrospray Ionization Mass Spectrometer (UPLC-ESI/MS).

Adapting to Nikje's 2007 methodology, a glycerol and water mixture was used as a solvent to replace pentan-1-ol.

Prior to solvent adaptation, the ideal temperature, pressure and power conditions were studied by varying the proportions between glycerol and water: 25% glycerol and 75% water, 50% glycerol and 50% water, 75% glycerol and 25% water and also only glycerol (100%).

Using the best performance mixture relative to the maximum pressure supported by the equipment, the inorganic bases used as catalysts were varied, namely: potassium hydroxide, sodium hydroxide, calcium hydroxide and barium hydroxide. The products are still awaiting characterization by Ultra-Efficient Liquid Chromatography coupled with the Eletrospray Ionization Mass Spectrometer (UPLC-ESI/MS).

3. Results and Discussion

3.1. Conventional Reaction

The reaction product was characterized via FTIR and compared to the standard spectrum of TPA, as shown in the figure below (Figure 1).

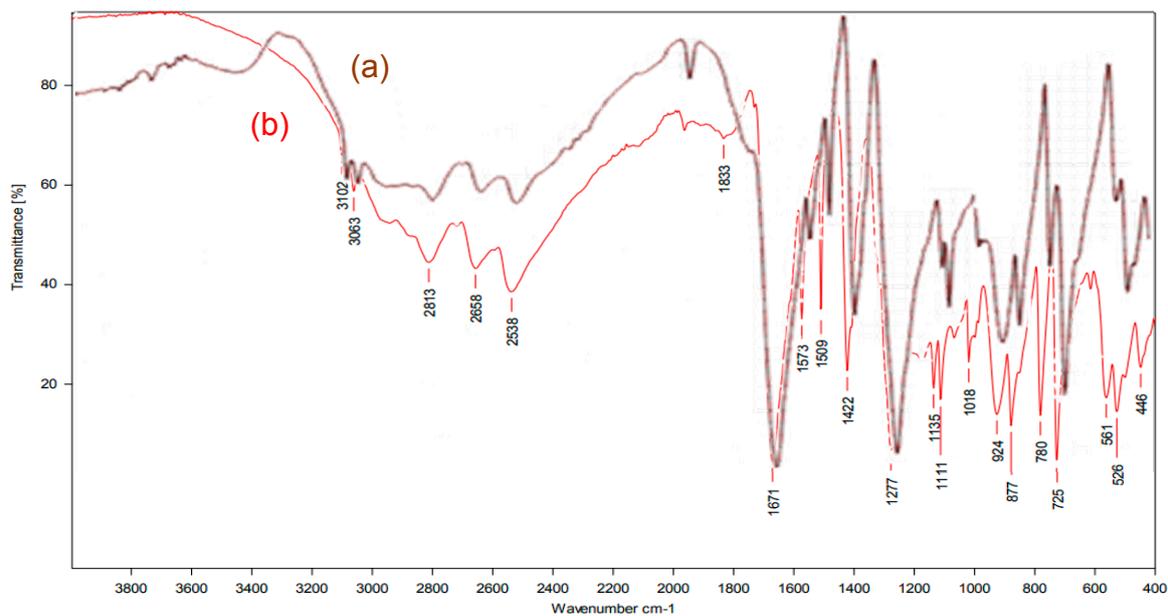


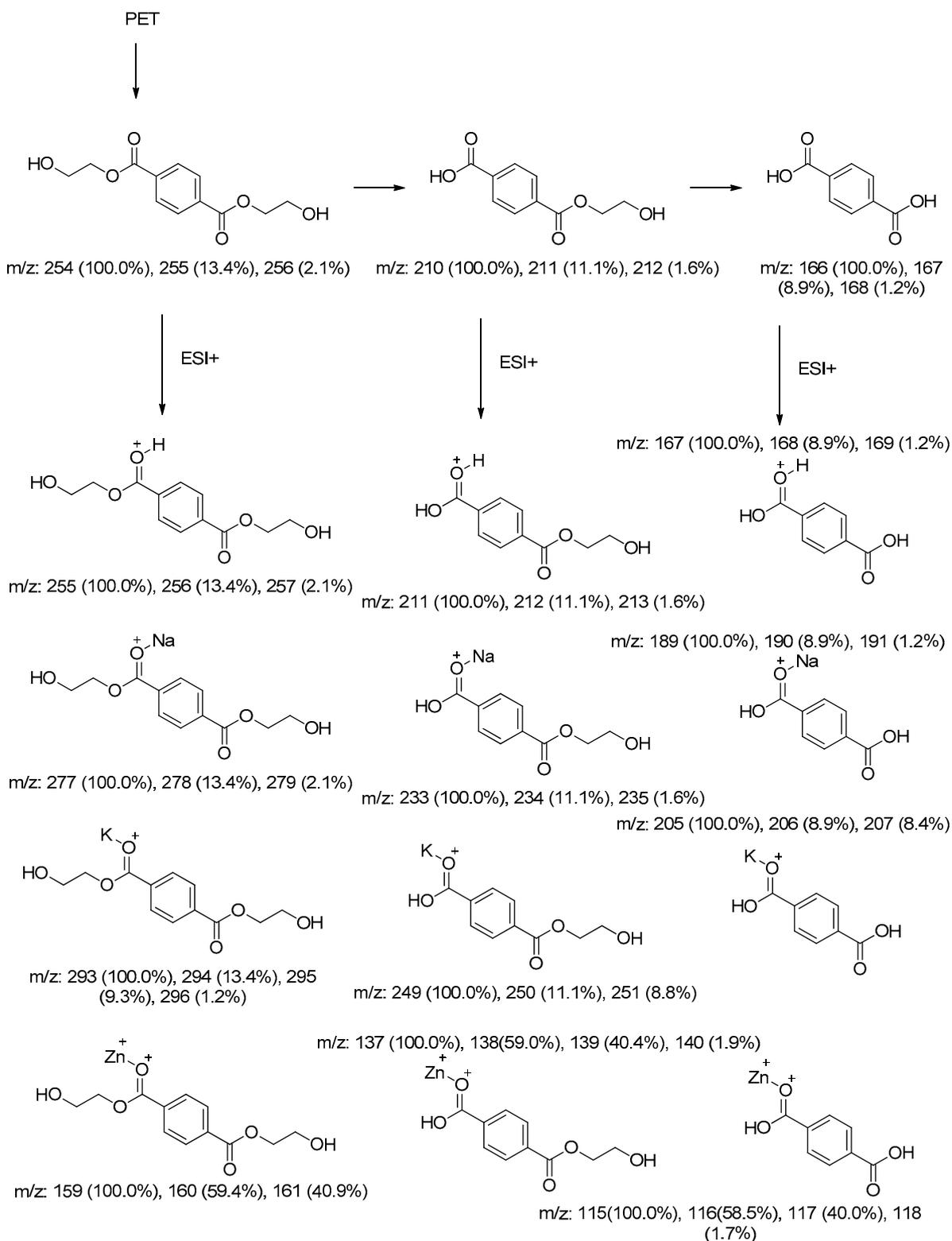
Figure 1. Comparison between the standard (a) and the product of the reaction (b) spectra.

By the similarity between the two spectra, it can be previously stated that terephthalic acid was obtained.

3.2. Microwave Assisted Reactions

For the characterization of the microwave reaction products, ultra-efficient liquid chromatography coupled to the electrospray ionization mass spectrometer, which relates the mass by the ion charge and does not fragment the sample, being very useful for identification of product formation.

Schemes 1 and 2 show the anionic and cationic species, respectively, to be observed and their mass relations per charge (m/z), as well as the abundance of each species, in parentheses.



Scheme 2. Cationic species (ESI (+)) expected from PET depolymerization.

Reactions using zinc sources as catalyst were performed at 150 °C for 30 min at 300 W power, adapting the methodology used by Tang, 2011. All reactions used 3 g of crushed transparent PET bottles, 20 mL of distilled water and 0.41 molar zinc, varying only the source of zinc in each reaction, as shown in the table below:

Table 1. Reaction versus source of zinc.

Reaction	Zinc Source
1	Zinc Sulfate
2	Zinc Acetate
3	Zinc Oxide
4	Zinc Chloride

Figure 2 shows the cell containing the reaction reagents and products using zinc sulfate and it is noticeable the formation of a white solid as a product, which may be TPA.

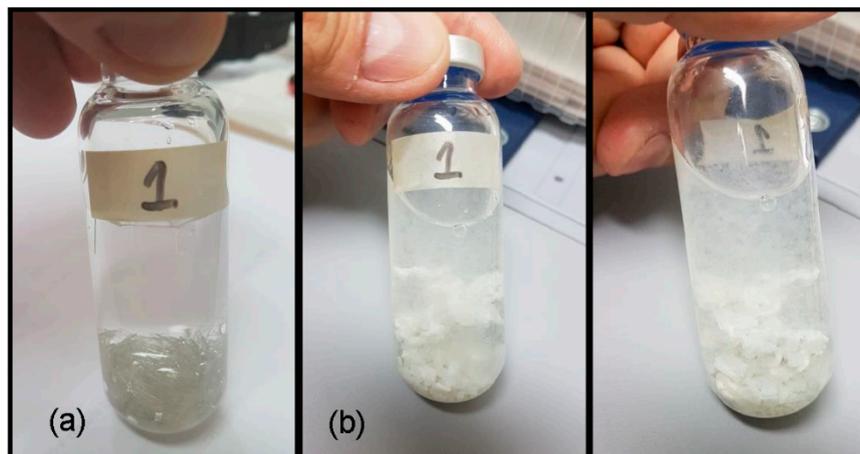


Figure 2. Cell before (a) and after (b) reaction with zinc sulfate as catalyst.

With the spectrum obtained from ESI (-) (Figure 3), it is possible to confirm the formation of TPA in reaction 1, since a small peak is observed at 165, as expected for deprotonated TPA in one of the carboxyl groups.

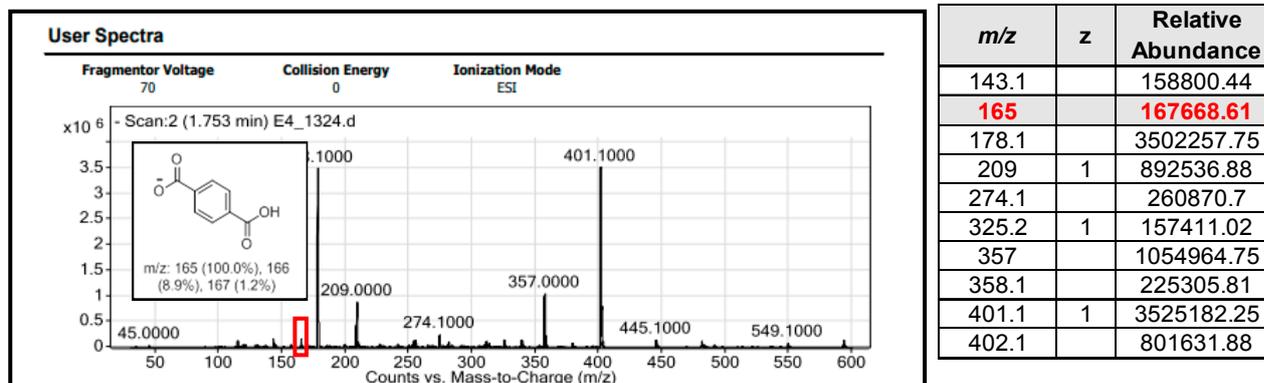


Figure 3. ESI (-) spectrum for reaction 1.

In reactions using other sources of zinc as catalyst, no peak indicating the formation of the desired product was observed.

Reactions using different alcohols as solvents and potassium hydroxide as catalyst were carried out at 150 °C for 30 min at 300 W power—where “a” reactions were at over 200 °C for 5 min at 300 W power and reactions “b” were adapting the methodology used by Nikje, 2007. All reactions used 1 g of crushed transparent PET bottles, 8 mL of alcohol and 0.69 g of potassium hydroxide, where the variables are in the table below.

Table 2. Reaction versus variables.

Reaction	Temperature	Time	Solvent
11a	>200 °C	5 min	Pentan-1-ol
11b	150 °C	30 min	Pentan-1-ol
12a	>200 °C	5 min	Propan-1-ol
12b	150 °C	30 min	Propan-1-ol
13a	>200 °C	5 min	Propan-2-ol
13b	150 °C	30 min	Propan-2-ol

Reactions “a”, as they are at very high temperatures, reached the limit pressure of the equipment and could not be completed. In reactions “b” it was only possible to observe the formation of terephthalic acid when using pentan-1-ol as solvent. Showing that it is possible to adapt the Nikje methodology, where a more powerful reactor was used.

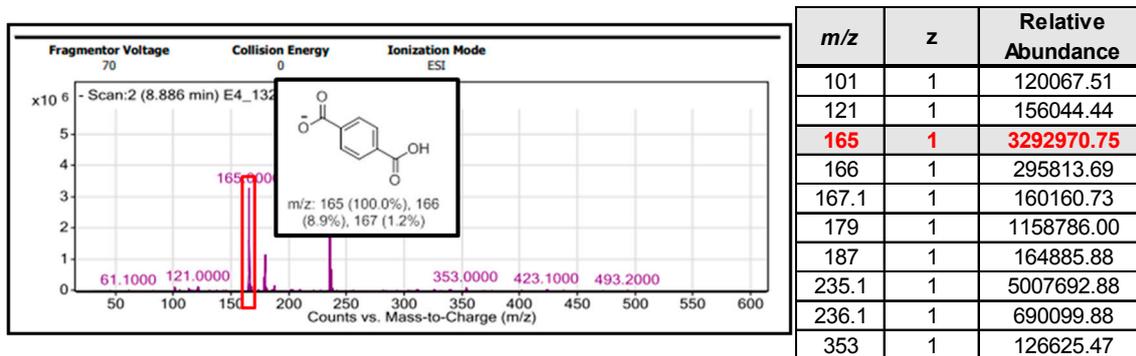


Figure 4. ESI (-) spectrum for reaction 11b.

From the results obtained, we departed to studies where pentan-1-ol was replaced by a greener alcohol, as glycerol (propantriol) which is obtained as residue from biodiesel industries. Since the vapor pressure of glycerol is lower than that of pentan-1-ol (<0.001 hPa and 2.0 hPa at 20 °C, respectively), in addition to being a greener solvent, it is also a more efficient solvent, because the lower the pressure within the reaction cell, the higher the temperature reached and, consequently, the faster is the conversion of reagents into products.

The glycerol mixtures in water were submitted to the microwave reactor where only the power was set at 300 W, changing the temperature until the limit pressure of the equipment was reached, seeking to find a maximum reaction temperature without exceeding this pressure. The results showed that a higher glycerol concentration (75%) guaranteed a higher temperature within the working pressure range (Figure 4).

It is observed that the 25% glycerol in water mixture reached a higher temperature, however, since most of the mixture is water (vapor pressure is 23 hPa at 20 °C), the limit pressure was reached and the equipment did not proceed with the analysis. In the proportion of 75% a temperature above 250 °C was obtained without reaching the maximum pressure of the equipment, stabilizing at 25 bar.

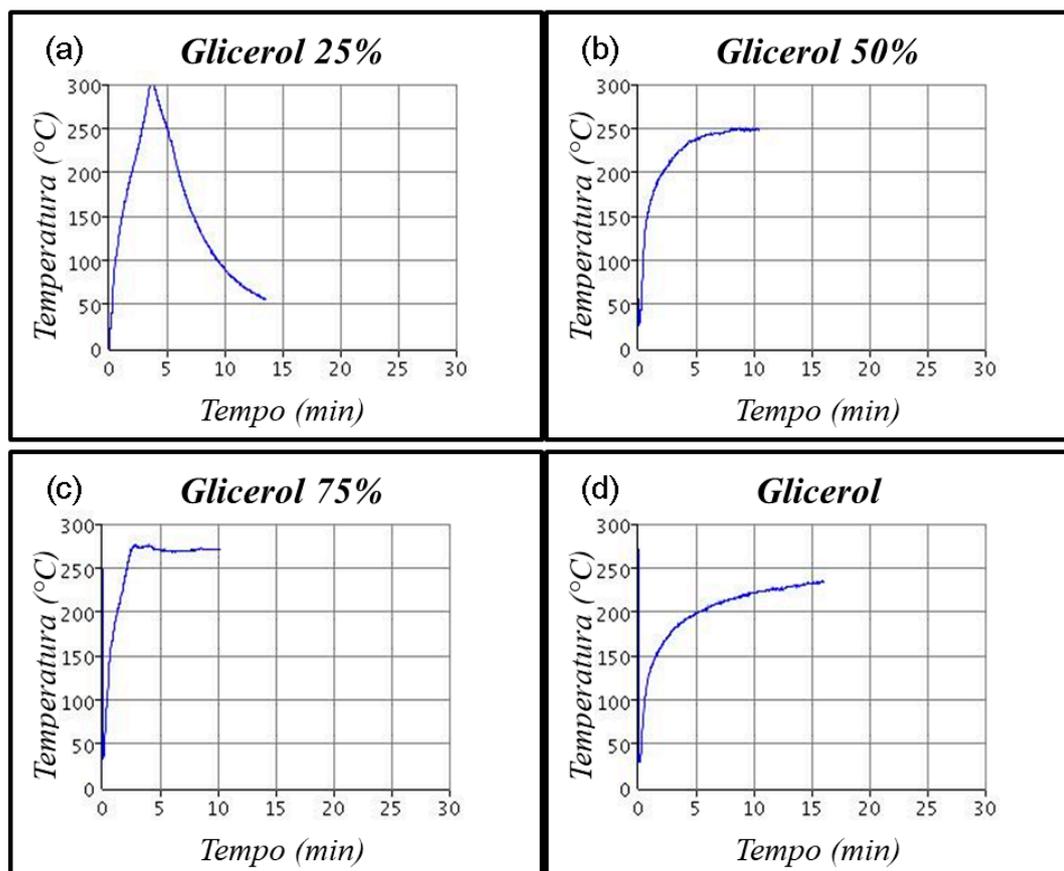


Figure 4. Glycerol in water ratios versus temperature, where: (a) is the 25% glycerol in water mixture, (b) is the 50% glycerol in water mixture, (c) is the 75% mixture of glycerol in water and (d) is only glycerol (100%).

4. Conclusions

The study showed that using a greener solvent is more efficient and clean process, by the improve of the work pressure and, consequently, the improve of conversion in a lower time. We still are waiting for the results of UPLC using the glycerol mixture and a non-toxic catalyzer, as inorganic hydroxides, we are confident that the results will be favorable.

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