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Article

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Abstract: The objective of this work was to investigate the deacidification of bio-oils (BOs) from triglyceride-based biomass through the application of liquid-liquid extraction (LLE) in a simple stage, using methanol and water as a binary solvent and feed/solvent ratio of 1/1. For this, the effects of process parameters such as the water content present in the solvent, the content of carboxylic acids present in the bio-oil, and the extraction temperature on the deacidification process through the efficiency and distribution coefficient were evaluated, as well as the effects of such parameters on the quality of deacidified bio-oils through physical-chemical analyzes and GC-MS analysis. The results show that such process parameters significantly affect the quality of deacidified bio-oils. The ideal condition to have the highest acid removal, i.e., the highest deacidification efficiency (72.65%), is the one in which the deacidification process is performed with aqueous methanol (5% water) at 35 °C and for BOs that have a total acid number (TAN) equal to 24.38 mg KOH/g. Therefore, the process of deacidification by LLE using aqueous methanol is a promising alternative for removing carboxylic acids and other oxygenated compounds, contributing significantly to the upgrading or improving biofuels produced by catalytic thermal cracking.

Keywords: solvent extraction; biofuel; pyrolysis oil; carboxylic acids; oxygenated compounds

1. Introduction

Currently, with increasing environmental concerns and, unlike other renewable energy sources that generate only heat and power, biomass has a promising potential to be converted into heat, energy (for example, alternative liquid biofuels), and value-added chemicals due to its abundant chemical composition and resources worldwide [1]. Sources of biomass (material consisting mainly of carbon, hydrogen, oxygen, and nitrogen, although sulfur is also present in smaller proportions) encompass various natural materials and their derivatives. In such a way, it is possible to divide them into two main groups to produce liquid biofuels: lignocellulose (LC) and triacylglycerol (TAG)

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sources. The latter are the main components of vegetable oils and animal fats. One of the technologies that can convert lignocellulose-based or triacylglycerol-based biomass into biofuels and other chemicals is pyrolysis. The liquid fraction obtained from the pyrolysis of both biomasses is called bio-oil, but the products have differences in their physical properties and chemical composition [2]. For this reason, this study focused on bio-oils from TAG-based biomass pyrolysis.

Pyrolysis or thermal cracking, as it is also known, is a process of thermochemical conversion of biomass, which works at 350-650 °C in the absence of oxygen and, in some cases, in the presence of a catalyst (catalytic cracking), to produce solid, liquid (bio-oil) and gaseous biofuels [2–4]. Bio-oils, also known as biomass pyrolysis oil, pyrolysis oil, or bio-crude, have been considered promising candidates to replace petroleum-derived products regarding power generation, heat, and the extraction of valuable chemicals [1,2,5].

During the pyrolysis process, different reactions occur that depend on the TAG-based biomass [6,7] and other variables used in pyrolysis such as reaction temperature [8,9], residence time/spatial velocity [10], and type of catalyst [11], resulting in a complex variation in the composition and properties of the bio-oils produced [7], which, in general, presents almost black, dark reddish brown or dark green color [12]. Therefore, bio-oil is a complex mixture consisting of hydrocarbons (linear and cyclic paraffins, olefins) and oxygenated compounds (aldehydes, ketones, and carboxylic acids) [2,4,13]. The catalytic cracking of TAG-based biomass consists of the following steps: (1) primary cracking, in which the decomposition of triacylglycerol molecules produces acidic species; (2) secondary cracking, which involves the formation of hydrocarbons by the degradation of acids from primary cracking [10,14,15].

There is an impediment to the direct substitution of petroleum-derived fuels and chemical products by bio-oil due mainly to its low calorific value and high oxygen content, resulting in its instability, high corrosiveness [1–3,16], and high acid value (with an average of 82.03 mg KOH/g), as the breakdown of triglycerides generates free carboxylic acids [2]. Therefore, bio-oil must be processed, refined, or upgraded to usable transportation fuels and value-added chemicals [1,3,16–21], aiming to improve some of their properties or comply with the standards established for such products, mainly in terms of olefin content and acid value [2]. Although the complexity of bio-oil composition hinders such procedures [2,18], bio-oil refining/upgrading is possible due to the employment of specific customized separation technologies and processes [1].

Several research studies in the form of reviews on upgrading bio-oil address the various technologies developed for this purpose [12,18,22,23]. Among the technologies that have been addressed are catalytic cracking, hydrotreatment, esterification and stabilization of physical-chemical properties of bio-oil [24–26]. However, there is a gap regarding the fractionation/extraction of bio-oil via separation techniques such as supercritical fluid extraction, adsorption, membrane, electrosorption and ionic liquid extraction [1], column chromatography, distillation, solvent extraction, in particular, liquid-liquid extraction (organic solvent extraction, water extraction) [1,16], which can also provide efficient separation of bio-oil, laying a solid foundation for its improvement [16].

Regarding liquid-liquid extraction, few researchers have used organic solvents to extract bio-oil components [1,3,27,28], much less for bio-oil from TAG biomass, to say the least, aiming at its upgrading. In addition, the few studies that use liquid-liquid extraction with organic solvents to separate oxygenated compounds use it to purify the aqueous phase, not the crude bio-oil itself.

Liquid-liquid extraction separates the components of a liquid (the feed) by contact with a second liquid phase (the solvent). The separation process is based on differences in the chemical properties of the feed components, such as polarity differences and hydrophobic/hydrophilic character. To be more precise, a deviation from thermodynamic equilibrium drives the transfer of components from one phase to the other, and the state of equilibrium depends on the nature of the interactions between the components of the feed and the solvent phase. Differences in these interactions determine the potential for the separation of feed components. In this way, a liquid-liquid extraction process produces a solvent-rich stream called an “extract” that contains a portion of the feed and a feed stream without the extracted components called a “raffinate” [29].

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Therefore, in bio-oil extraction using organic solvent, it is essential to understand the compatibility and solubility of bio-oil species or compounds in such solvent. In parallel, the solubility of bio-oil compounds in the organic solvent is strongly influenced by the polarity of solutes and solvents. The complex chemical composition of bio-oil is another factor that affects the distribution of solutes in the bio-oil (raffinate) and organic solvent (extract) phase due to concentration gradients [1].

The extraction and fractionation of bio-oil through liquid-liquid extraction has been widely studied and reported using water [30–33] and organic solvents [34–41], aiming mainly to study the feasibility of extraction regarding the solvent used and the optimization of extraction conditions [1]. Thus, research that applies liquid-liquid extraction as a process of separation of different classes of chemical compounds, such as oxygenated compounds, investigates the efficiency of extraction and recovery through parameters such as: 1) bio-oil/solvent ratio [38]; (2) addition of co-solvent or modifier [35]; (3) extraction temperatures [35,37]; and (4) reaction time [35].

Oxygenated compounds such as acids and other organic acid components present in bio-oils have been related to the corrosion of metals and instability in their storage when applied as fuels. In such a way, bio-oil's corrosiveness is more severe when the water content is high and when used at high temperatures. Therefore, removing the acids can be a valuable technique to reduce corrosiveness [41]. The most widely used and effective process to eliminate naphthenic acids from petroleum is liquid-liquid extraction, especially when using ammonia or alkaline alcohol solutions. However, these systems usually form stable emulsions [42]. Therefore, several proposals for liquid-liquid extraction use different solvent systems [43–47]. In the oils and fats industry, one of the deacidification methods for oils with high acidity is liquid-liquid extraction, which is based on the different solubilities of free fatty acids (FFA) and triglycerides in various organic solvents. The deacidification of oils by LLE has been evaluated by several researchers, and ethanol, methanol and acetone have been emphasized as solvents for FFA extraction. Even though a large number of organic solvents are consumed during the LLE process, by selecting appropriate solvents for the extraction of the desired products, a good separation of the components present in the bio-oil can be achieved [16].

In this context, the main objective of this work was to investigate the deacidification of bio-oil from triglyceride-based biomass through the application of liquid-liquid extraction as a separation process, using methanol and water as a binary solvent. For this, and as specific objectives, the following effects were evaluated:

(1) water content in the combined organic solvent on the deacidification process and the quality of the raffinate streams (deacidified BO);
(2) content of carboxylic acids in the feed (bio-oil) on the deacidification process and the quality of the raffinate streams;
(3) temperature on the deacidification process and the quality of the raffinate streams;
(4) water content in the solvents on the distribution of hydrocarbons versus the distribution of oxygenated compounds in both the raffinate and the extract;
(5) water content in the solvents on the distribution of the classes of oxygenated compounds in both the raffinate and the extract;
(6) water content in the solvents in the distribution of free fatty acids in both raffinate and extract.

2. Materials and Methods

2.1. Materials

To carry out the deacidification experiments of crude biofuels by liquid-liquid extraction, four bio-oils with high content of carboxylic acids (free fatty acids), i.e., high acidity, were selected, as shown in **Table 1**. These free fatty acids were the target components for extraction in the present study. All bio-oils were obtained via triglyceride cracking under different operating conditions in a pilot cracking unit, as described in detail by Mota et al. [48]. The aqueous methanol (5, 10, 15, 20 and 25% by mass of water) used as a solvent for liquid-liquid extraction was prepared by mixing absolute alcohol with different masses of deionized water to obtain the desired water content. The

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pre-established amount of water was added to the methanol to increase their specific gravity and, thus, favor the formation of phases, which is fundamental in liquid-liquid extraction.

Table 1. Physical-chemical properties of the bio-oils used in the present study to evaluate deacidification by liquid-liquid extraction.

Physical-chemical property	Test Method	Feedstock (Bio-oils)			
		BO_1	**BO_2**	**BO_3**	**BO_4**
Specific gravity at 20 °C (kg/m³)	ASTM D4052	815.00	826.00	848.56	860.00
Viscosity at 40 °C cSt (mm²/s)	ASTM D445	4.65	5.21	6.5885	5.51
Corrosiveness to copper, 3 h at 50 °C	ASTM D130	1A	First	1A	1A
TAN (mg KOH/g)	ASTM D974	24.38	33.21	51.5600	73.77
Saponification value (mg KOH/g)	AOCS Cd 3-25	48.23	67.00	70.9480	108.54
Ester content (mg KOH/g)	Paquot [49]	23.85	34.79	19.388	34.77
Refractive index	AOCS Cc 7-25	1.457	1.458	1.4580	1.457

2.2. Preliminary Tests

The study of any liquid-liquid extraction process only becomes relevant if the systems have limited solubility, in other words, if, at some point, the formation of at least two liquid phases occurs [50]. Therefore, preliminary tests were carried out with five different water contents in methanol to define the water contents that should compose the aqueous methanol solutions, and the feed/solvent ratio of 1/1 remained constant.

To carry out the preliminary tests, a mass of approximately 5 g of bio-oil and methanol with 5% by weight of water was used as a basis. Once weighed, the bio-oil and aqueous methanol were added to a 20 ml test tube, and the system (bio-oil/aqueous methanol) was shaken manually for thirty seconds and remained at rest for 24 hours. After the rest period, it was verified which preliminary trials formed at least two phases. The same procedure was performed for methanol with 10, 15, 20 and 25% by mass of water.

From the results of the preliminary tests, it was determined which water contents should be used in the preparation of the aqueous methanol solutions. However, in larger quantities to carry out the experiments themselves, once aliquots of extract and, mainly, raffinate should be removed to perform various physical-chemical and composition analyses, as described in the following sections. As the five water contents in methanol allowed the formation of at least two phases, it was established that these contents would be part of the list of variables investigated in deacidifying bio-oils via liquid-liquid extraction.

2.3. Experimental Procedure

In this step, the deacidification of bio-oil by liquid-liquid extraction was investigated through the following variables: (1) water content in methanol (5, 10, 15, 20 and 25% by water mass); (2) carboxylic acid (FFA) content in the feed, indicated by the acid value of the bio-oil, as shown in **Table 1** and, (3) extraction temperature (25 and 35 °C). At the same time, the effect of the deacidification of bio-oils by liquid-liquid extraction on the quality of the raffinate streams, i.e., of the deacidified bio-oil, was investigated, evaluating the following physical-chemical properties: specific gravity at 20 °C, kinematic viscosity at 40 °C, corrosiveness to copper, saponification value, ester value and refractive index. The following two sections describe the experimental procedure for conducting such an investigation.

2.3.1. Deacidification of BOs by LLE (Group of Experiments I)

The group of experiments I is characterized by a set of experiments developed to investigate the effect of the water content in the methanol and the effect of the content of free fatty acids present in the feed on the deacidification of bio-oil by liquid-liquid extraction through the following experimental procedure: approximately 100 g of BO_1 and approximately 100 g of solvent (aqueous

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methanol with 5% by mass of water) were weighed to maintain the feed/solvent mass ratio constant and equal to 1/1 in all experiments. In a separation funnel with a capacity of 500 mL, the bio-oil was first added, and then the solvent was added. Then, the materials added to the separation funnel were vigorously stirred for 30 seconds so that the solvent had adequate contact with the feed. After the end of the stirring, the mixture rested for 24 hours at room temperature to ensure total separation of the phases. After the resting period and with the two phases formed, the raffinate phase (organic phase) at the top of the funnels was carefully separated from the extract phase (aqueous phase), in which the extract phase is characterized by the presence of solvent and acidic compounds extracted from the bio-oil and the raffinate phase consists of deacidified bio-oil. Then, both phases were collected (**Figure 1**) and weighed. Finally, this group of experiments' raffinate stream was subjected to a series of physical-chemical and spectroscopic analyses with Fourier Transform Infrared (FTIR), described in Section 2.4.

Figure 1. Extract phase and raffinate phase obtained in the bio-oil deacidification process by LLE.

As described above, the LLE process was repeated for the deacidification of BO_1, adding methanol with 10, 15, 20, and 25% by mass of water. The same experimental procedure was used to deacidify BO_2 and BO_4, totaling 15 experiments for Group I.

2.3.2. Deacidification of BOs by LLE (Group of Experiments II)

Group of Experiments II is characterized by a set of experiments developed to investigate the effect of temperature on the deacidification of bio-oils by liquid-liquid extraction through the following experimental procedure: approximately 100 g of BO_3 and approximately 100 g of solvent (aqueous methanol with 5% by mass of water) were weighed to keep the feed/solvent mass ratio constant and equal to 1/1 in all experiments. In parallel, a 1 L capacity stainless steel stirred and jacketed vessel coupled to a temperature-controlled ultra thermostatic bath was programmed to operate at 25 °C. Once the established temperature was reached, the bio-oil and solvent were added. Then, the materials added to the vessel were vigorously stirred for 60 minutes so that the solvent had adequate contact with the feed. After the stirring, the mixture was transferred to a separation hopper, resting for 24 hours at room temperature to ensure total separation of the phases. After the resting period and with the two phases formed, the raffinate phase (organic phase) at the top of the funnels was carefully separated from the extract phase (aqueous phase). Both phases were collected, weighed and analyzed, as described in Section 2.3.1.

As described above, the extraction process was repeated to deacidify BO_3 with added methanol of 10, 15, 20, and 25% by mass of water. In addition, the same experimental procedure was used for BO_3 deacidification at 35 °C, totaling ten experiments for Group of Experiments II.

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2.4. Analytical Methods

2.4.1. Physical-Chemical Analysis

The physical-chemical properties of the BOs and their respective raffinate phases were determined following the AOCS and ASTM Standard Methods: specific gravity at 20 °C (AOCS Cc 10c-95), kinematic viscosity at 40 °C (ASTM D 445), corrosiveness to copper (ASTM D130), total acid number (TAN) or acid value (ASTM D974), saponification value (AOCS Cd 3-25), refractive index (AOCS Cc 7-25), and ester value, which is the difference between the saponification value and the acid value, as described by Paquot [49].

2.4.2. FTIR Analysis

Spectroscopic analyses of bio-oils using Fourier Transform Infrared were performed using an FTIR spectrometer (Shimadzu, Model Prestige 21). The absorbance spectra were obtained within the interval 4000–400 cm^{-1} and a resolution of 16 cm^{-1} with the aid of a KBr Window. Thus, the bio-oil samples were placed on the KBr surfaces using micropipettes to spread the liquid, producing a uniform layer.

2.4.3. Chemical Derivatization

Before carrying out the analysis of gas chromatography coupled to mass spectrometry (GC-MS), the samples of BO_3, raffinate streams and extract streams were pre-treated through chemical derivatization, aiming to identify and correctly quantify the compounds polar organic compounds, mainly carboxylic acids in the form of free fatty acids. This way, an aliquot of 20.0 µL of BO_3 was transferred to a vial, and 100 µL of N-methyl (trimethylsilyl) trifluoroacetamide (MSTFA) was added. The mixture was homogenized and heated at 60 °C for 30 min using an orbital shaker. After dilution in 880 µL of CH_2Cl_2 solvent, the homogeneous liquid phase was ready to be injected into the GC–MS apparatus, as described by Mancio et al. [51]. The same procedure was performed for the raffinate and extract streams.

2.4.4. GC-MS Analysis

Derivatized samples were subjected to GC-MS analysis as described in the literature [51]. Thus, a gas chromatograph coupled to a mass spectrometer (Shimadzu, Model: GCMS-2010) and QP2010 interface was used for that analysis. The column was an RTX-5MS with a length of 30 m and a diameter of 0.25 mm. Helium was used as a carrier gas with a 1 mL/min flow rate and a split ratio of 1/100. The following temperature schedule was used: the oven temperature was increased by 15 °C/min to 150 °C, then by 8 °C/min to 200 °C and 2 °C/min to 240 °C. This temperature was maintained for 4 min before heating the oven at 15 °C/min to 300 °C. The injector and detector temperature were 280 °C. The chemical compounds in BO_3, raffinate, and extract streams were identified by comparison with the NIST05s.LIB library, considering those that showed a high similarity index.

2.5. Determination of LLE Process Parameters

The distribution coefficient and extraction efficiency were used to evaluate the three variables in the deacidification of BO_3 via LLE with aqueous methanol. The distribution coefficient can be determined directly by measuring the solute concentration in the extract and the raffinate. When an adequate analytical method is available only for the feed phase, as is the case in the present study, the distribution coefficient can be determined by measuring the solute concentration in the feed (BO_3) and raffinate (BO_3 deacidified after application of LLE with aqueous methanol) and calculating the distribution coefficient from the material balance. When the initial solute concentration in the extraction solvent is equal to zero (before extraction), the distribution coefficient expressed in terms of mass fractions is given by

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$$K'' = \frac{Y_e''}{X_r''} = \frac{M_r}{M_e}\left(\frac{M_f}{M_r}\cdot\frac{X_f''}{X_r''} - 1\right) \quad (1)$$

where, K'' is the mass fraction of the solute in the extract divided by the mass fraction of the solute in the raffinate, M_f is the total mass of feed added to the vial, M_s is the total mass of extraction solvent before extraction, M_r is the mass of raffinate after extraction, M_e is the mass of extract after extraction, X_f'' is the mass fraction of solute in the feed before extraction, X_r'' is the mass fraction of solute in the raffinate, in equilibrium and, Y_e'' is the mass fraction of solute in the extract, in equilibrium.

The efficiency of deacidification of bio-oils by liquid-liquid extraction using aqueous methanol as solvent was evaluated as a function of the percentage of removal of carboxylic acids, mainly free fatty acids, calculated by the following equation:

$$\eta_{FFA} = \frac{C_{FFA_0} - C_{FFA_R}}{C_{FFA_0}} \times 100 \quad (2)$$

where, η_{FFA} is the efficiency of deacidification of bio-oils by liquid-liquid extraction, C_{FFA0} is the free fatty acid content of the bio-oil before extraction, and C_{FFAR} is the free fatty acid content of the bio-oil after extraction, i.e., it is the free fatty acid content of the raffinate. As the acidic components of bio-oils, in particular, carboxylic acids in the form of free fatty acids are related to the total acid number (TAN), which indicates the acid value of the samples [52,53], this physical-chemical property was used to calculate the deacidification efficiency through the following equation:

$$\eta_{FFA} = \frac{TAN_0 - TAN_R}{TAN_0} \times 100 \quad (3)$$

where TAN_0 is the total acid number of the bio-oil before extraction, and TAN_R is the total acid number of the raffinate.

3. Results and Discussion

3.1. Deacidification of BOs by LLE (Experiment Group I)

3.1.1. Effect of BO Deacidification by LLE on the Quality of Raffinates

To evaluate the effect of BO deacidification by LLE using aqueous methanol as extraction solvent on the quality of raffinate streams (deacidified BO), the effect of water content in methanol and carboxylic acid content in feed (original bio-oil) on the following physical-chemical properties was investigated: specific gravity at 20 °C, kinematic viscosity at 40 °C, saponification value, ester value, refractive index and corrosiveness to copper. The results of this investigation are presented in **Figures 2–6**. The results for corrosiveness to copper are available in **Table S1** of the **Supplementary Materials**.

According to **Figures 2–6**, BO deacidification by LLE using aqueous methanol significantly affects the quality of deacidified bio-oils. In such a way, both the water content in the methanol and the content of carboxylic acids present in the original bio-oil significantly modify most of the physical-chemical properties, indicating that the LLE process changed the chemical composition of the bio-oil. Such a result is expected once the objective of this study is to remove carboxylic acids. According to Santos et al. [54] and Buzetzki et al. [55], the physical-chemical properties strongly depend on bio-oil composition, which justifies the results obtained here. In addition, the results show a non-linear trend, either of decrease or increase, of the physical-chemical properties of deacidified bio-oils as there is an increase in the water content in methanol.

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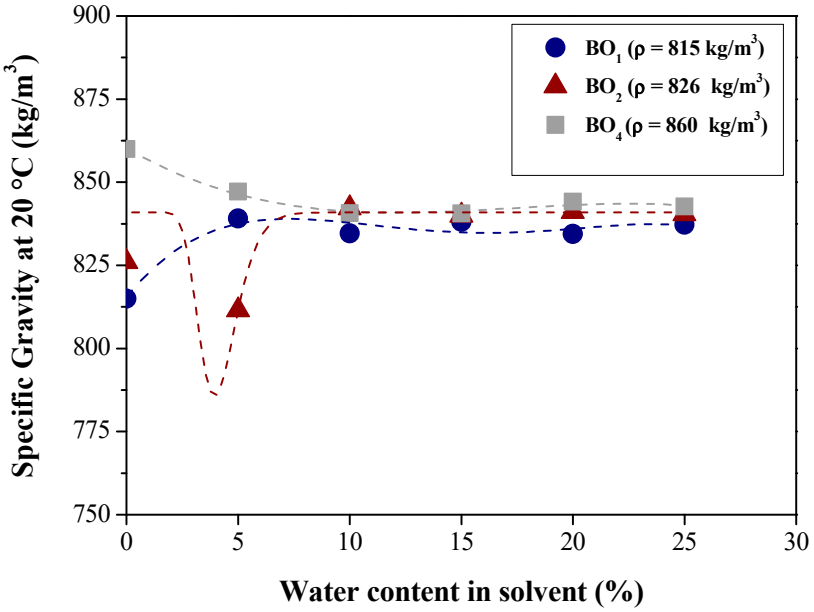

Figure 2. Effect of water content in methanol and different starting bio-oils on the specific gravity values of raffinate streams (deacidified BOs).

Figure 2 shows a significant change in the specific gravity values of the raffinate streams when LLE is performed with methanol containing 5% water. As the amount of water in methanol increased from 10 to 25%, there was slight variation in the specific gravity values, which remained in the range of 834 to 844 kg/m^3, regardless of the content of carboxylic acids in the feed. BO_1 showed an increase in specific gravity values (5% of water), which remained practically constant at 10% of water. BO_2 first showed a reduction (5% of water) and then increased specific gravity values, remaining essentially constant from 10% of water. BO_4 showed a decrease in specific gravity values, remaining almost constant from 10% of water. This result can be attributed to the effect of deacidification by LLE on the levels of hydrocarbons (reduction or increase of light or heavy fractions) and oxygenated compounds, which can be confirmed by GC-MS analysis.

Figure 3 shows that the kinematic viscosity values of all raffinate streams are higher than those obtained for the original bio-oils. Secondly, the values referring to this property are significantly altered with the addition of water to methanol and with the content of carboxylic acids in the feed, indicating a higher concentration of hydrocarbons with long chains. Santos et al. [54] reported in their study that BOs containing long-chain hydrocarbons result in higher viscosity values.

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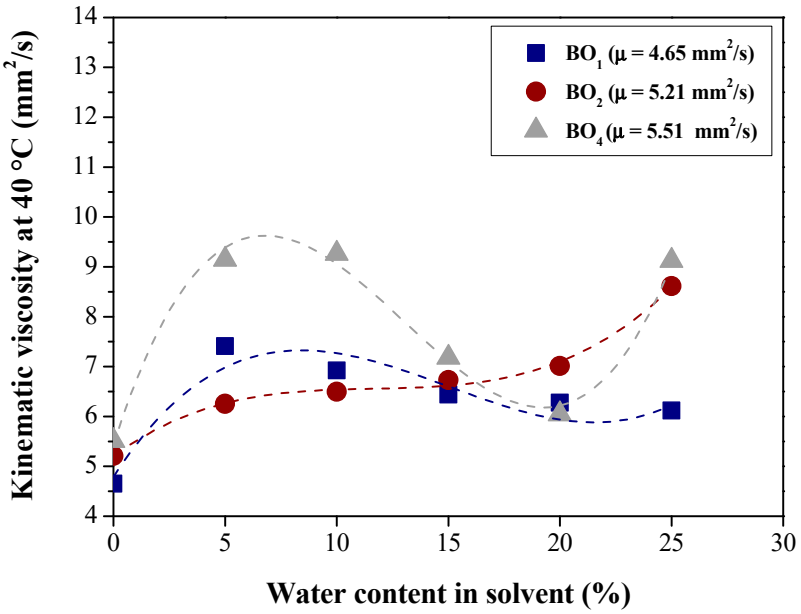

Figure 3. Effect of water content in methanol and different starting bio-oils on kinematic viscosity values of raffinate streams (deacidified BOs).

Figure 4 shows that the raffinate streams' saponification values are lower than those of the original bio-oils. This fact is directly linked to removing carboxylic acids by the liquid-liquid extraction process, which is indicated by the TAN values. Therefore, the saponification value is another parameter that confirms the removal of oxygenated compounds, especially carboxylic acids, characterizing the deacidification process. Secondly, **Figure 4** shows that the saponification values are significantly altered as water to methanol increases due to different levels of carboxylic acids in the original bio-oils. However, none of the three trend curves show similar behavior for the data obtained. This can be expected since, although the study was conducted with real BO from triglyceride-based biomass, they all have different compositions in both hydrocarbons and oxygenated compounds. In such a way that this will affect, to a lesser or greater degree, the physical-chemical properties investigated in the present study. According to Haas [56] and Gunstone [57], the higher the saponification value, the shorter the chain length of carboxylic acids. Therefore, knowing that the BOs have levels of oxygenated compounds, including the size of the chain, it is possible to have different behaviors for the saponification values from different BOs, which justifies the results obtained.

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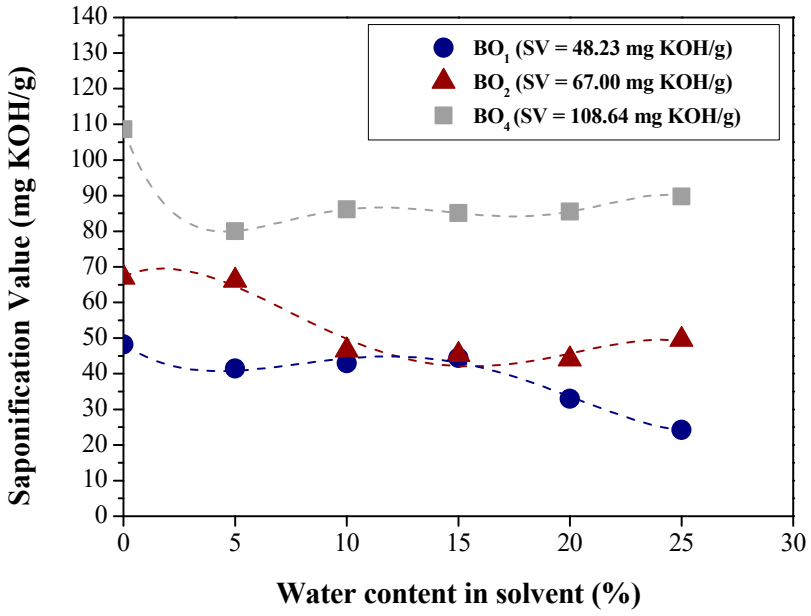

Figure 4. The effect of water content at methanol and different starting bio-oils on the saponification values of raffinate streams (deacidified BOs).

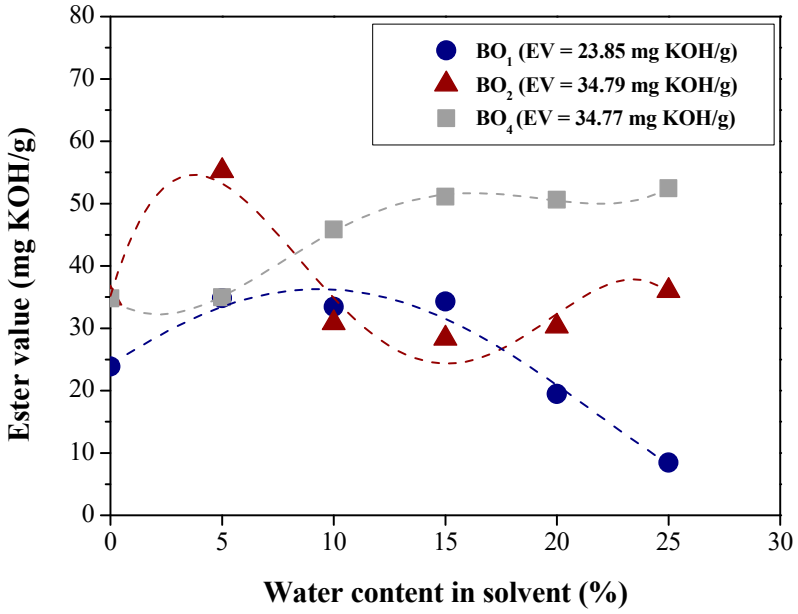

Figure 5. The effect of water content in methanol and different starting bio-oils on the ester values of raffinate streams (deacidified BOs).

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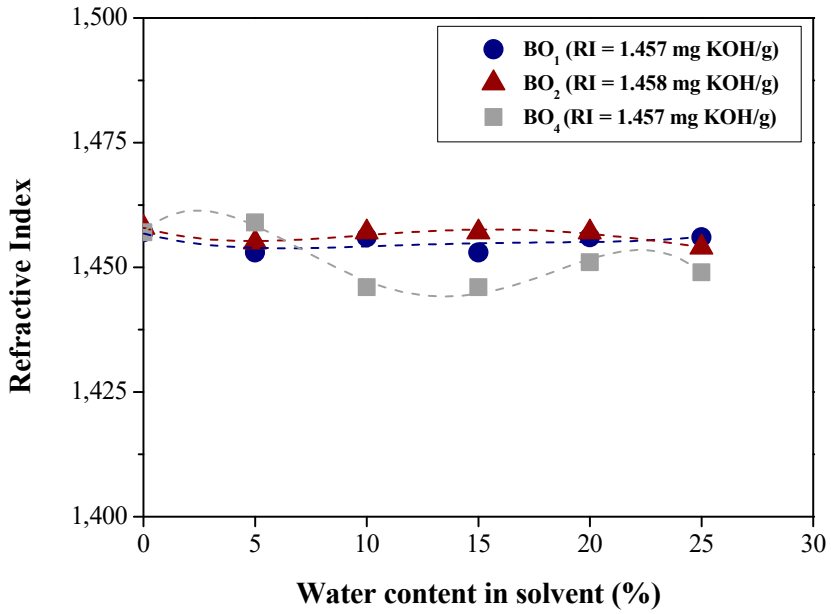

Figure 6. Effect of water content in methanol and different starting bio-oils on the refractive index values of raffinate streams (deacidified BOs).

3.1.2. Efficiency of LLE Deacidification

Effect of Water Content on Deacidification

According to **Figure 7**, an increase in the water content in methanol promoted a significant reduction in the efficiency of deacidification by liquid-liquid extraction of BO_1 and BO_2. These results agree with the results obtained by Wu et al. [58], who found that in a system of free fatty acids and triglycerides, the deacidification capacity of methanol decreases with the increase in the concentration of water present in the alcohol. On the other hand, an increase in the water content in the methanol promoted an increase in the efficiency of BO_4 deacidification, reaching its maximum capacity when methanol with 25% water was used. Reipert [59] reported the same behavior in his study on the process of deacidification of cottonseed oil by liquid-liquid extraction at 30 °C and with aqueous ethanol (10.45% water) by increasing the concentration of linoleic acid in the vegetable oil.

Figure 8 shows that the distribution coefficient decreases as the water content increases regarding BO_1 and BO_2, which have the lowest levels of carboxylic acids, as indicated by the TAN values (**Table S2** of the **Supplementary Materials).** On the other hand, for BO_4, which has an acid value of 73.77 mg KOH/g, the opposite behavior was observed. In addition, it is possible to observe that the distribution coefficient values for all water contents reported in Figure 8 are relatively low. According to Green et al. [29], distribution coefficients equal to or greater than ten are desired for a cost-effective process, as they allow operation with minimal amounts of solvent and produce higher solute concentrations in the extract. The mass balance performed to obtain the results in Figure 8 is in **Table S2** of the **Supplementary Materials**.

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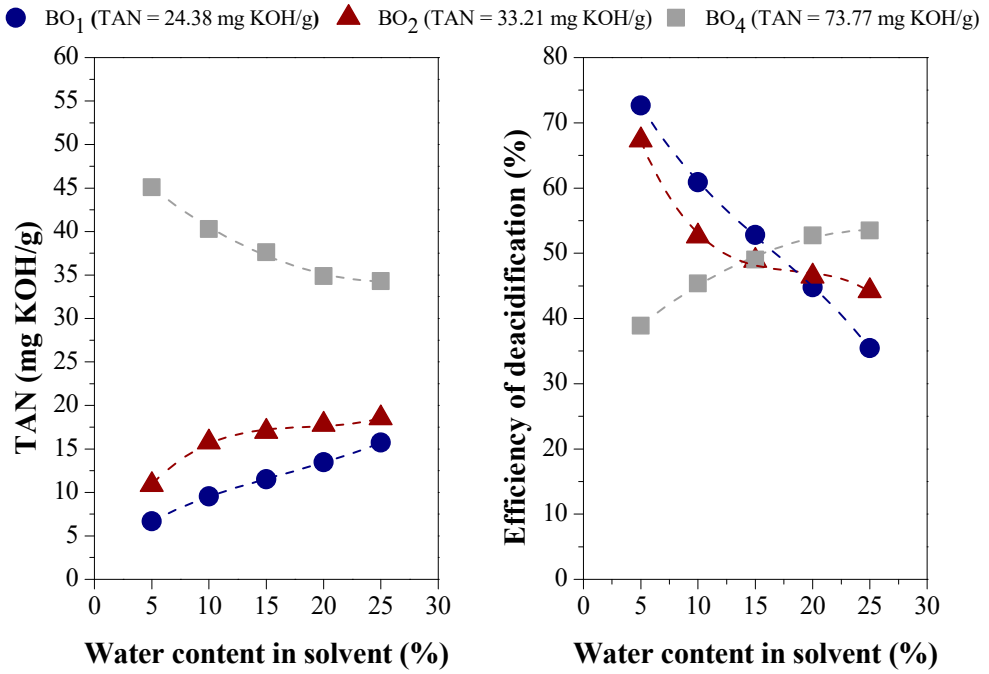

Figure 7. Effect of water content in methanol and carboxylic acid content in original bio-oils on the efficiency of deacidification by LLE.

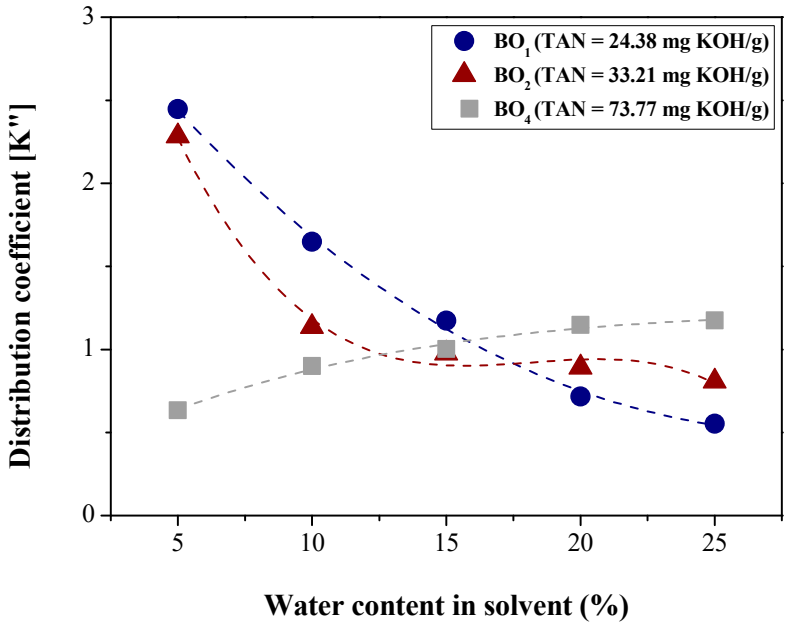

Figure 8. Effect of water content in methanol and carboxylic acid content in original bio-oils on distribution coefficient.

Effect of Acid Content in the Feedstock on Deacidification

Figure 7 also shows that the content of carboxylic acids present in the feed, indicated here by the TAN, significantly influences the efficiency of the solvent. The best results concerning the deacidification of the BOs are obtained for the feed that has the lowest acid content and the lowest water content in methanol, i.e., 24.38 mg KOH/g and 5% water, respectively, resulting in 72.65% of the acids removed. Therefore, the acid content in the feed negatively affects the deacidification process, as was already expected due to the limited capacity of the solvent caused by its saturation at high solute concentrations [60].

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3.1.3. FTIR Analysis of Original Bio-Oils and Raffinate Streams

From **Figures 9–11**, it was observed that the FTIR spectra of BO_1, BO_2 and BO_4 and their respective raffinate streams indicate the presence of bands between 3,000 and 2,840 cm^{-1}, which correspond to alkanes-type hydrocarbons that, associated with the presence of absorption bands close to 1375 cm^{-1}, a band related to the deformation vibration of the methyl groups (CH_3) [48,61,62], confirm the presence of the saturated alkanes in the original bio-oils and their raffinate streams. In addition, it is possible to infer that these saturated alkanes are long-chain due to absorption bands at about 720 cm^{-1}, associated with four or more CH_2 groups in an open chain, according to the specific literature [61,62]. The presence of absorption bands in 1715, 1719 and 1705 cm^{-1} was also verified [61,62], as illustrated by **Figures 9–11**, respectively, and that, according to Mota et al. [48], Pavia et al. [61] and Silverstein et al. [62] correspond to the carbonyl group, which associated with the wide absorption band of 3151-2650 cm^{-1} indicate the presence of carboxylic acids in the original bio-oils and their raffinate streams after the LLE process.

The results of the FTIR analysis for the extract streams are available in **Figures S1–S3** of the **Supplementary Materials**.

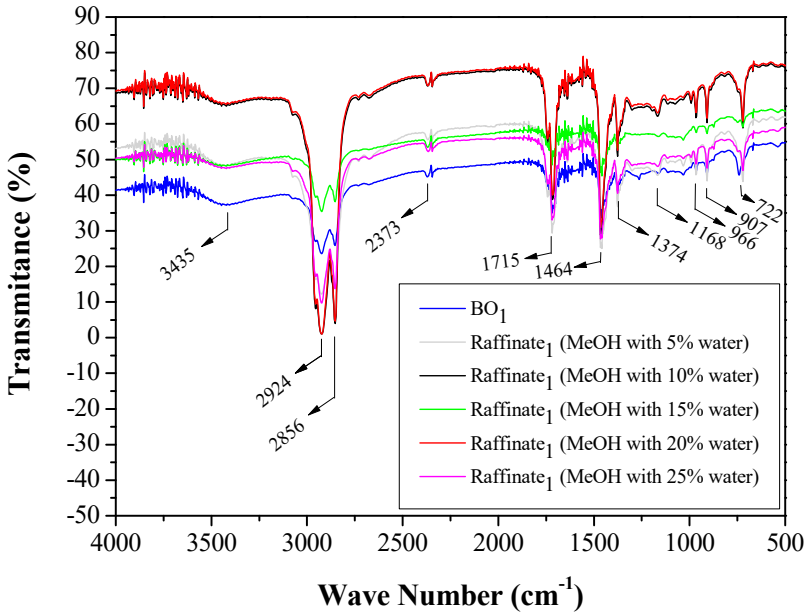

Figure 9. FTIR spectrum of the raffinate streams referring to the deacidification of BO_1 using different water contents in the methanol.

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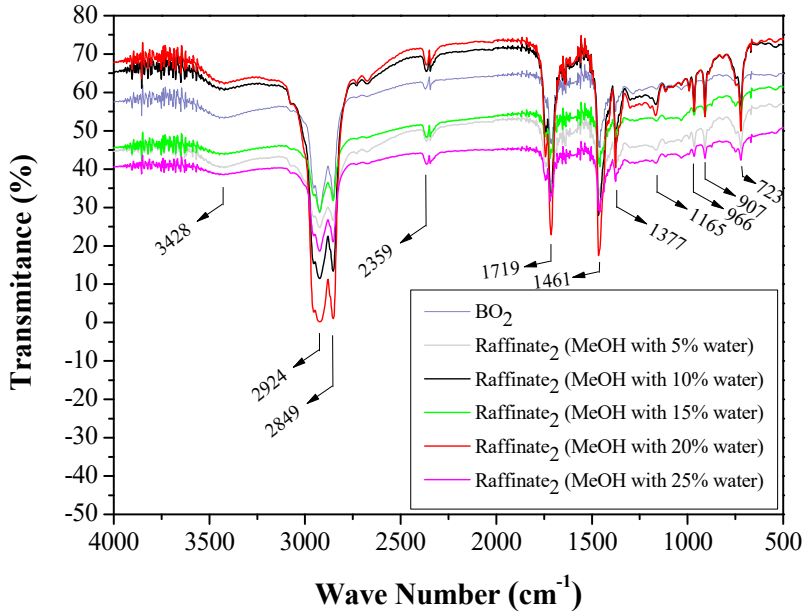

Figure 10. FTIR spectrum of the raffinate streams referring to the deacidification of BO_2 using different water contents in the methanol.

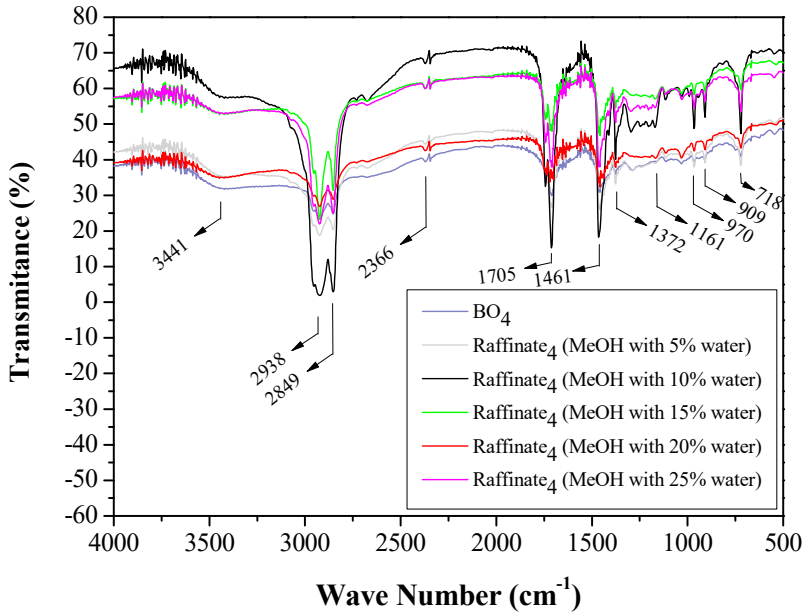

Figure 11. FTIR spectrum of the raffinate streams referring to the deacidification of BO_4 using different water contents in the methanol.

3.2. Deacidification of BOs by LLE (Experiment Group II)

3.2.1. Effect of BO Deacidification on the Quality of Raffinates

To evaluate the effect of BO_3 deacidification by LLE using aqueous methanol as extraction solvent on the quality of raffinate streams (deacidified BO_3), the effect of water content in methanol, carboxylic acid content in feed (BO_3) and mainly, temperature on the specific gravity at 20 °C, kinematic viscosity at 40 °C, saponification value, ester value, refractive index and corrosiveness to

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copper was investigated. The results of this sequence of experiments are presented in **Figures 12–16**. Results for corrosiveness to copper using different water contents in methanol at 25 °C and 35 °C are available in **Table S3** of **Supplementary Materials**.

According to **Figures 12–16**, a behavior similar to that observed for *Experiment Group I* was observed, in which there is a significant effect of BO_3 deacidification by LLE using aqueous methanol on the quality of the deacidified bio-oil. Therefore**, Figures 12–16** show that the water content present in the methanol, the content of carboxylic acids present in the original bio-oil and the operating temperature of the LLE significantly modify most of the physical-chemical properties, indicating that the LLE process changed the chemical composition of the bio-oils. As reported in Section 3.1.1, this result was expected, as the main objective of this study is to remove carboxylic acids (FFA). According to Santos et al. [54] and Buzetzki et al. [55], the physical-chemical properties of bio-oils are profoundly dependent on their composition, justifying the results obtained in the present study.

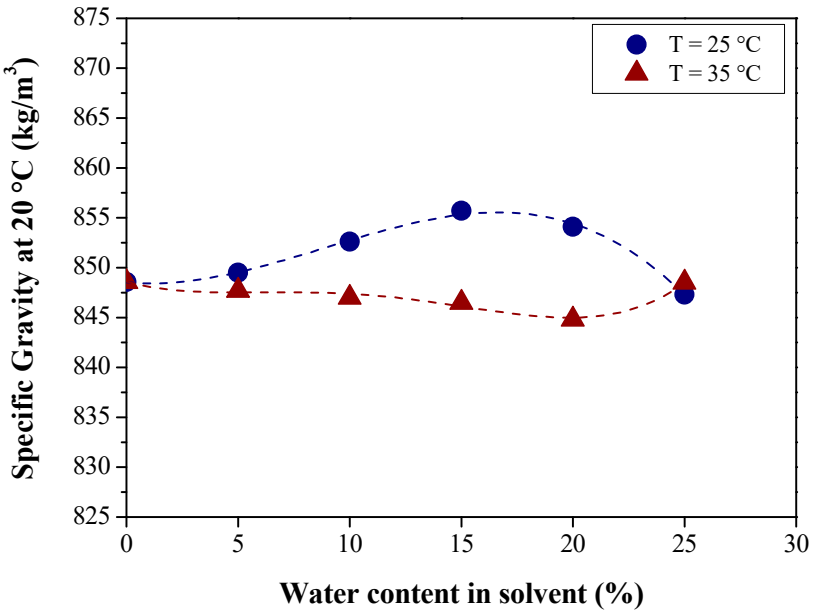

Figure 12. Specific gravity values of the raffinate streams (deacidified BO_3) for different water contents in methanol at 25 °C and 35 °C.

Another point that should be highlighted is that the results shown in **Figures 12–16** show that there is a non-linear trend, either of decrease or increase, of the physical-chemical properties of the deacidified bio-oils as there is an increase in the water content in the methanol, for both operating temperatures. This result is due to the effect of deacidification, in particular the solubility of the solvent used, on the levels of hydrocarbons (reduction or increase of light or heavy fractions) and oxygenated compounds, which can be confirmed by GC-MS analysis (Section 2.3.2). **Figure 12** also shows a significant increase in the specific gravity values of the raffinate streams when LLE is performed at 25 °C and with methanol containing 10, 15 and 20% water. This behavior is repeated for kinematic viscosity and refractive index. Therefore, there was a similarity regarding the behavior of the results obtained for the properties of specific gravity, kinematic viscosity, and refractive index, as illustrated in **Figures 12**, **13** and **16**, indicating that there is a direct correlation between these properties, as reported by Santos et al. [54].

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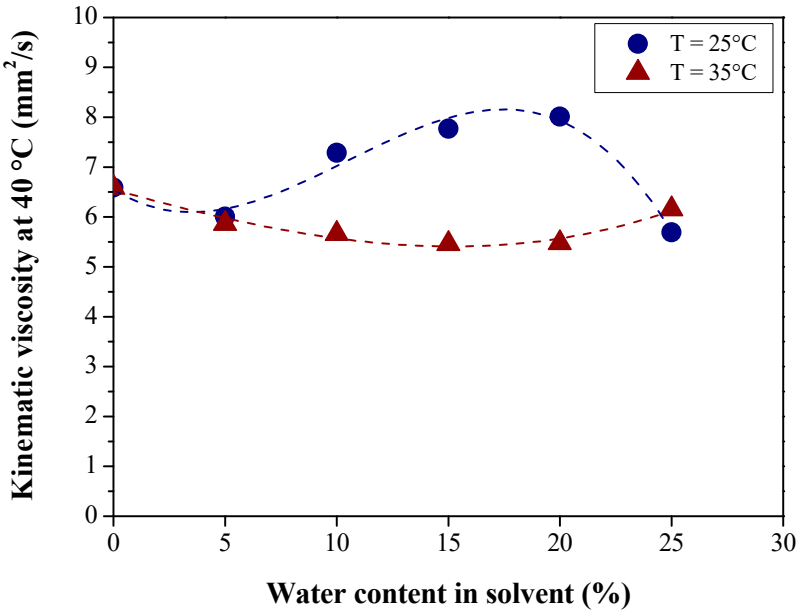

Figure 13. Kinematic viscosity values of raffinate streams (deacidified BO_3) for different water contents in methanol at 25 °C and 35 °C.

Figure **14** shows that an increase in the extraction temperature causes a reduction in the values of the BO saponification value. This result is consistent with the literature because, according to Haas [56] and Gunstone [57], the lower the saponification value, the longer the carboxylic acid chain. In this study, it was found that the carboxylic acids (palmitic acid and oleic acid) that have a relatively long chain are the acids that are extracted from BO_3 (see **Figure 25**), mainly at 35 °C, resulting in lower levels of this chemical group when compared to those obtained at 25 °C. Therefore, this fact results in a reduction in the saponification values when there is an increase in the extraction temperature.

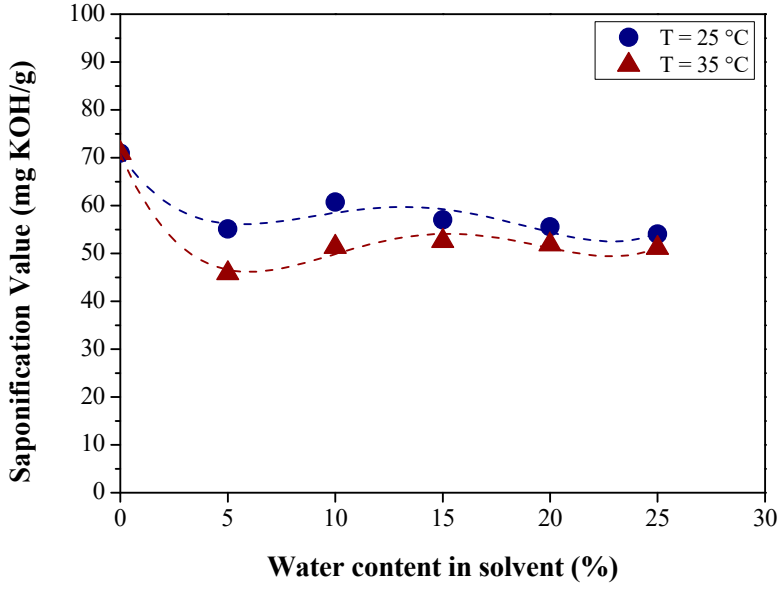

Figure 14. Saponification values of raffinate streams (deacidified BO_3) for different water contents in methanol at 25 °C and 35 °C.

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Figure 15 shows that adding water to methanol and the extraction temperature change the ester values. In addition, it was found that the ester value when 5% of water was added to methanol was higher than that obtained for the original bio-oil. This is due to the conversion of a portion of carboxylic acids into methyl esters, mainly when 5% water is used in the solvent; the highest deacidification efficiency is obtained under the conditions used in the present study. Then, it was found that there is a tendency of the ester values to reduce from 10% of water and 15% of water to the extraction temperatures of 25 °C and 35 °C, respectively, due to the reduction of the solubility of the binary solvent before the esters as there is an increase of water to the solvent, as shown in **Figure 25**.

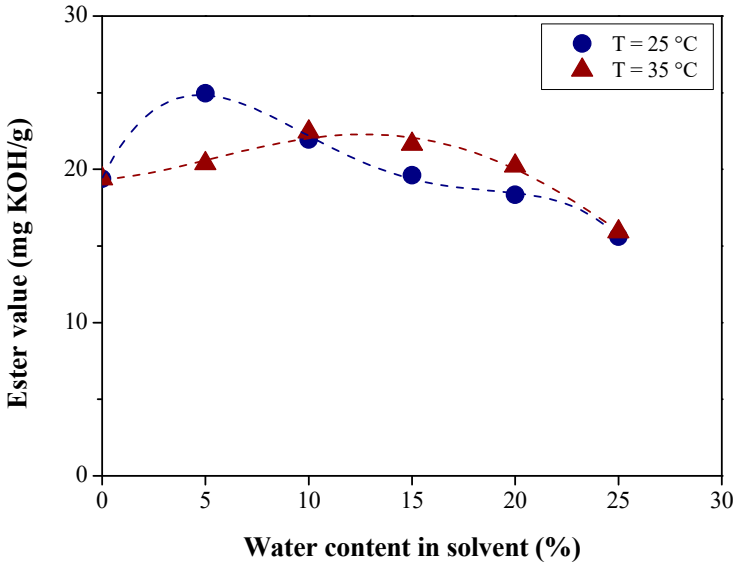

Figure 15. Ester values of raffinate streams (deacidified BO_3) for different water contents in methanol at 25 °C and 35 °C.

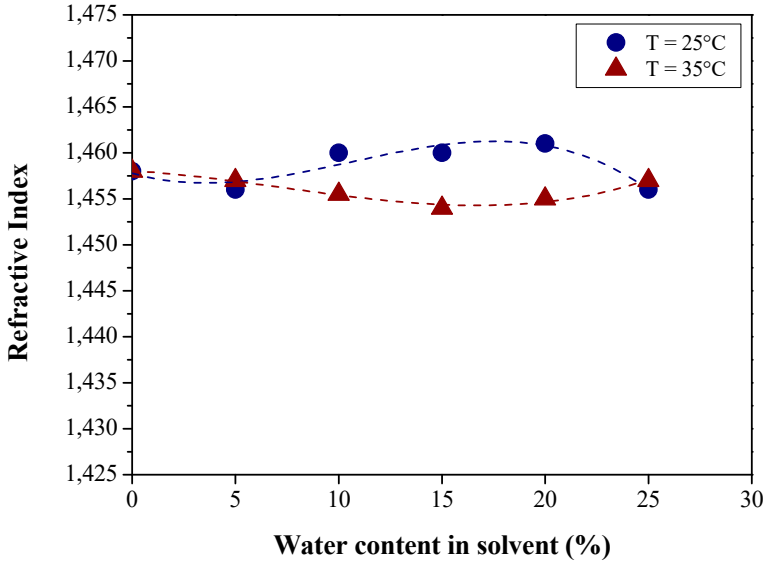

Figure 16. Refractive index values of raffinate streams (deacidified BO_3) for different water contents in methanol at 25 °C and 35 °C.

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3.2.2. Efficiency of LLE Deacidification

3.2.2.1. Effect of Temperature on Deacidification

According to **Figure 17**, the increase in temperature from 25 °C to 35 °C promoted an increase in the efficiency of BO deacidification by liquid-liquid extraction, indicating an increase in the solubility of free fatty acids in aqueous methanol. Therefore, among the two temperatures investigated, 35 °C is the best condition to promote the most significant removal of FFA when aqueous methanol is applied as an extraction solvent.

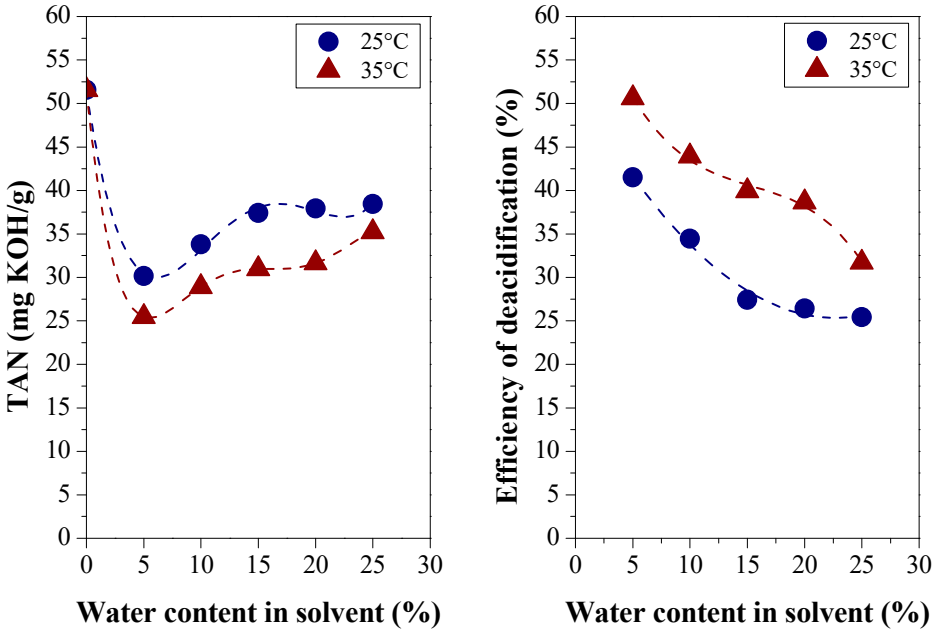

Figure 17. The effect of methanol's water content at different temperatures on the efficiency of deacidification of the BO_3 by liquid-liquid extraction.

Figure 18 shows that the distribution coefficient values decrease as the water content increases in the binary solvent. However, its value increases when there is an increase in the extraction temperature from 25 to 35 °C for any of the five water contents used in this study. In addition, it is possible to observe that the distribution coefficient values for all the water contents reported in Figure 18 are relatively low. In such a way that, according to Green et al. [29], distribution coefficients equal to or greater than ten are desired for an economical process, as they allow operation with minimal amounts of solvent and the production of higher solute concentrations in the extract. Ren et al. [63] studied the separation of chemical groups of the aqueous extract of the bio-oil using sequential extractions with four organic solvents (hexane, petroleum ether, chloroform and ethyl acetate) with different polarities. The results of this study show that ethyl acetate showed a high efficiency of organic acid extraction. In such a way, the maximum efficiency (55%) was achieved by using a solvent/feed ratio of 2:1, resulting in a distribution coefficient for the acids equivalent to 0.67. Therefore, considering that in the present study, a simple extraction was performed using a solvent/feed ratio of 1/1, aqueous methanol is an excellent solvent to altogether remove the carboxylic acids present in the bio-oil, as it promotes a deacidification process with relatively high efficiency (50.61% at 35 °C) and distribution coefficient (K'' = 1.15 at 35 °C) when compared to those values available in the literature. Considering deacidification by LLE at room temperature of a bio-oil with a TAN value lower than BO_3 (TAN = 51.60 mg KOH/g), as is the case of BO_1 (TAN = 24.38 mg KOH/g), the potential of aqueous methanol as an extractor solvent increases considerably, since the deacidification efficiency and distribution coefficient reach 72, 65% and 2.45, respectively, as shown in **Figures 7** and **8**

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The mass balance performed to obtain the results in Figure 18 is in **Table S4** of the **Supplementary Materials**.

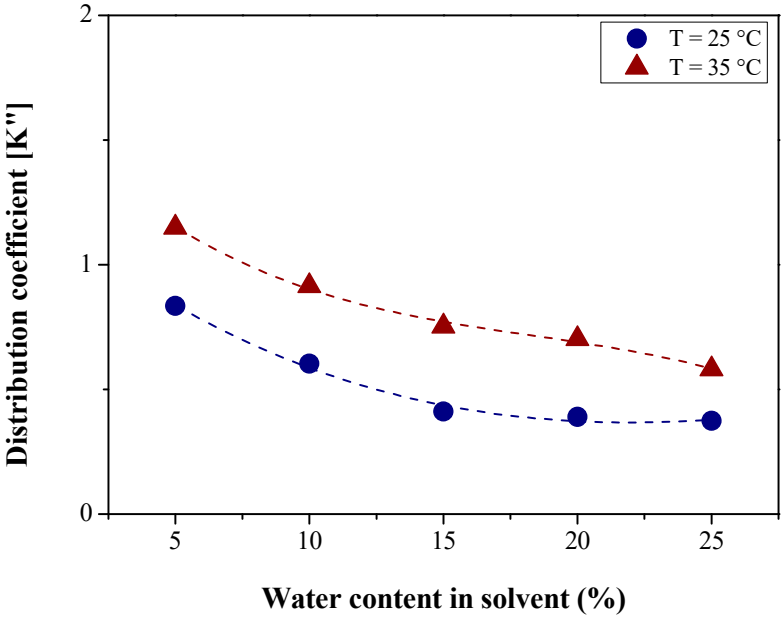

Figure 18. The effect of methanol's water content at different temperatures on the distribution coefficient.

3.2.3. Chemical Composition

In the **Supplementary Materials, Figures S4–S7** present the chromatograms and **Tables S5** to **S25** present the retention times, relative contents and identification (Molecular Formula and Compound name) of the prominent peaks obtained by GC-MS analysis of BO_3, which was taken as feed, and from the streams of raffinate and extract obtained after deacidification by liquid-liquid extraction of BO_3 at 25 °C and 35 °C, using methanol with different water contents as solvent.

The results in Figures S4–S7 and Tables S5 to S25 of the Supplementary Materials show that 30 to 70 components with a high similarity index were detected in BO3 and the extract and raffinate streams. These components were classified into two major groups: hydrocarbons (normal paraffinic, branched paraffinic, olefinic, naphthenic and aromatic) and oxygenated compounds (carboxylic acids, alcohols, aldehydes, ketones, esters, and others). Therefore, the results presented in **Figures 19–26** represent the sum of the areas of GC-MS peaks of the total number of compounds of various chemical classes detected in the respective BO_3 and extract and raffinate streams from the LLE. The values are presented as percentages and show the relative content of aqueous methanol with these classes.

Based on the analysis of **Figure 19**, it was found that BO_3 consists of 50.55% hydrocarbons and 49.45% oxygenated compounds. In the hydrocarbon group, it was possible to identify three distinct classes: normal paraffinic (19.15%), olefinic (25.58%) and naphthenic (5.82%), as shown in **Table S5** and shown in **Figure 21**. The oxygenated compounds consisted of carboxylic acids (42.35%), alcohols (2.21%), ketones (3.73%) and esters (1.16%). The analysis of the chromatograms referring to the five raffinate streams obtained after the LLE of BO_3 showed the presence of the same substances, although with different contents concerning hydrocarbons and oxygenated compounds. In such a way that the levels of oxygenated compounds of all raffinate streams, obtained from the LLE process at 25 °C and 35 °C, are lower than the content of oxygenated compounds of BO_3, indicating that the aqueous methanol can remove the oxygenated compounds present in the original bio-oil, reflecting in the reduction of TAN and, consequently, in the efficiency of deacidification, as noted in Section 3.2.2.1.

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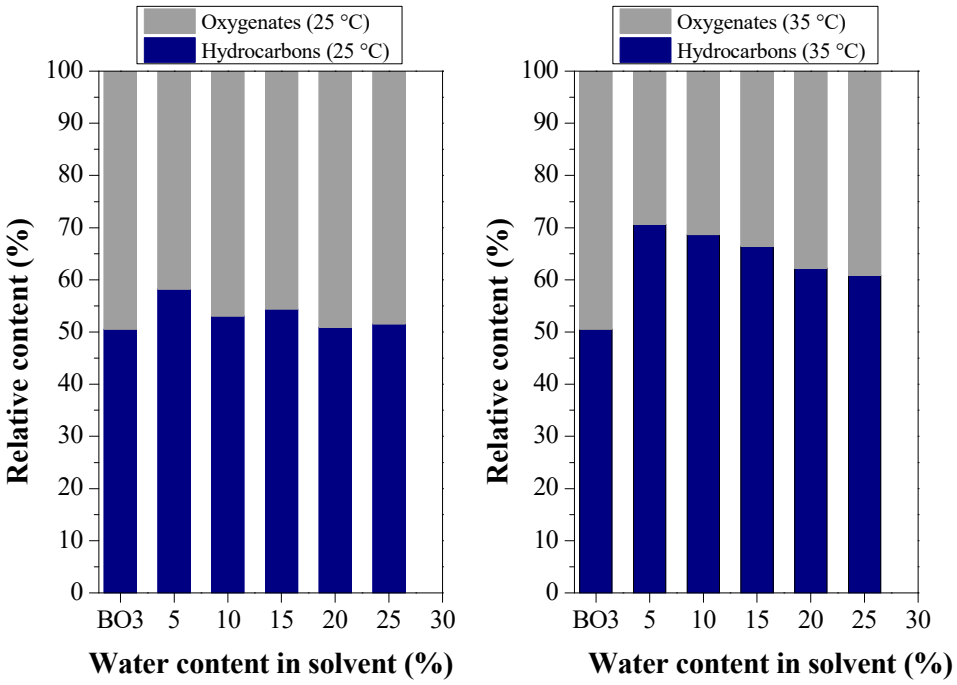

Figure 19. The effect of methanol's water content on the distribution of hydrocarbons and oxygenated compounds in raffinate streams (deacidified BO_3).

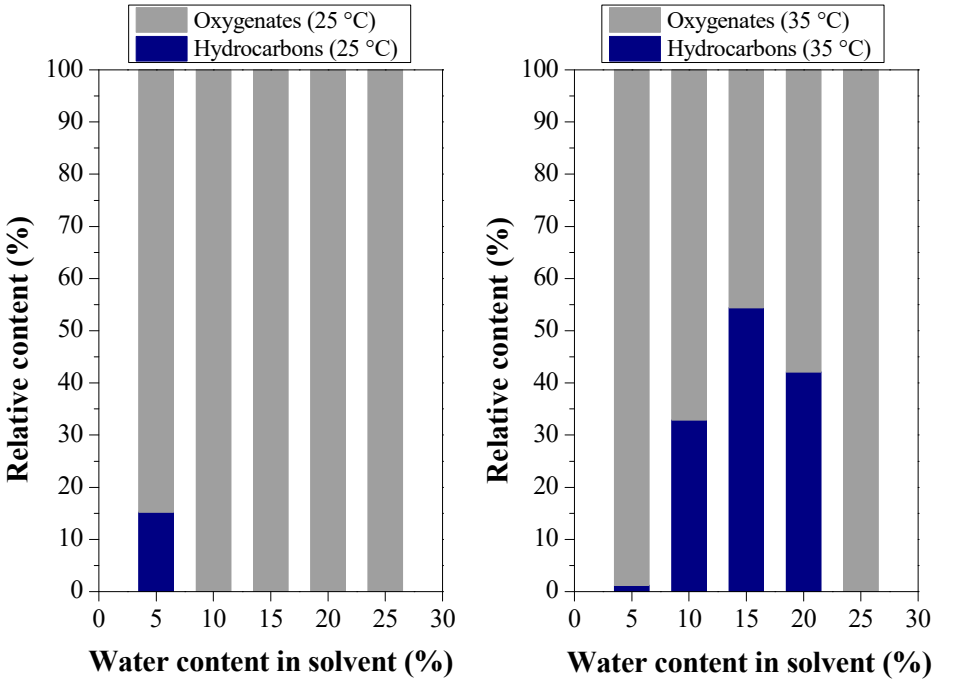

Figure 20. The effect of methanol's water content on the distribution of hydrocarbons and oxygenated compounds in extract streams.

Therefore, it was confirmed that deacidification by liquid-liquid extraction with aqueous methanol, in addition to extracting oxygenated compounds, especially carboxylic acids, also promotes an increase in the concentration of hydrocarbons, mainly when extraction occurs at 35 °C, as shown in **Figure 19**. Thus, some water contents had a relatively small loss of hydrocarbons (basically normal paraffin) to the extract streams. In others, the absence of hydrocarbons was verified, indicating no losses to the extract stream, as illustrated in **Figures 20** and **22**. The absence or low content of hydrocarbons in the extract indicates its slight solubility in aqueous methanol,

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probably due to hydrophobic interactions, especially at low temperatures. Kanaujia et al. [34] describe similar behavior when reporting a low concentration of hydrocarbons in the aqueous phase compared to the content of hydrocarbons found in the organic phase (bio-oil).

Figure 19 also shows that the water content hurt the deacidification process by LLE with aqueous methanol because while the hydrocarbon content decreases as there is an increase in the water content, the content of oxygenated compounds increases, confirming the findings made about the efficiency of deacidification from the results of TAN values presented in the previous sections. According to Kanaujia et al. [34], most of the solvent-analyte interactions in LLE are based mainly on polar-polar and hydrophobic interactions, which justifies the results obtained in the present study as there is an increase in water content.

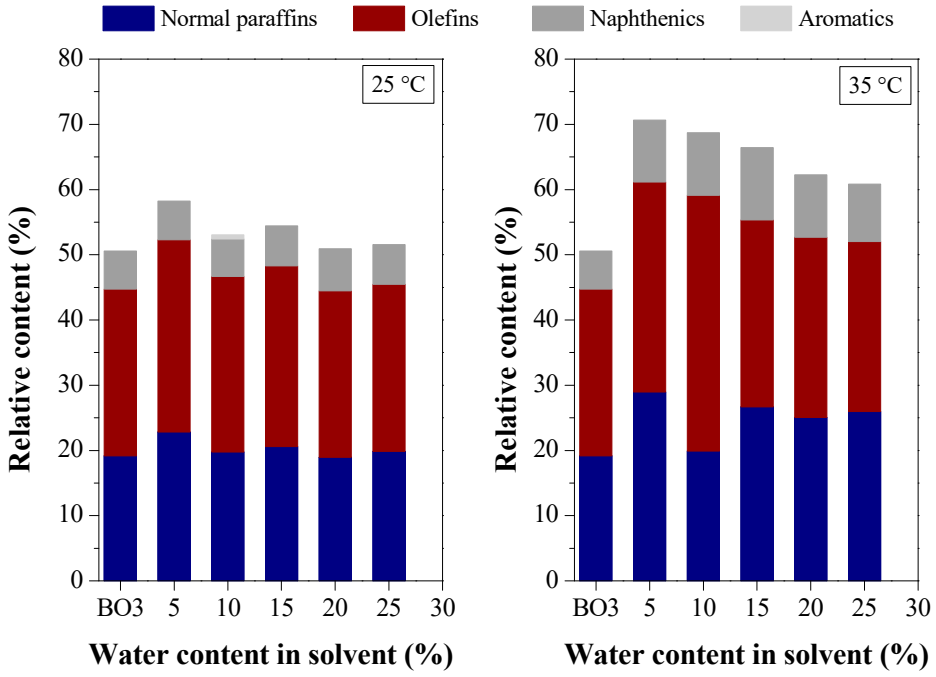

Figure 21. The effect of methanol's water content on the distribution of hydrocarbon classes in raffinate streams (deacidified BO_3).

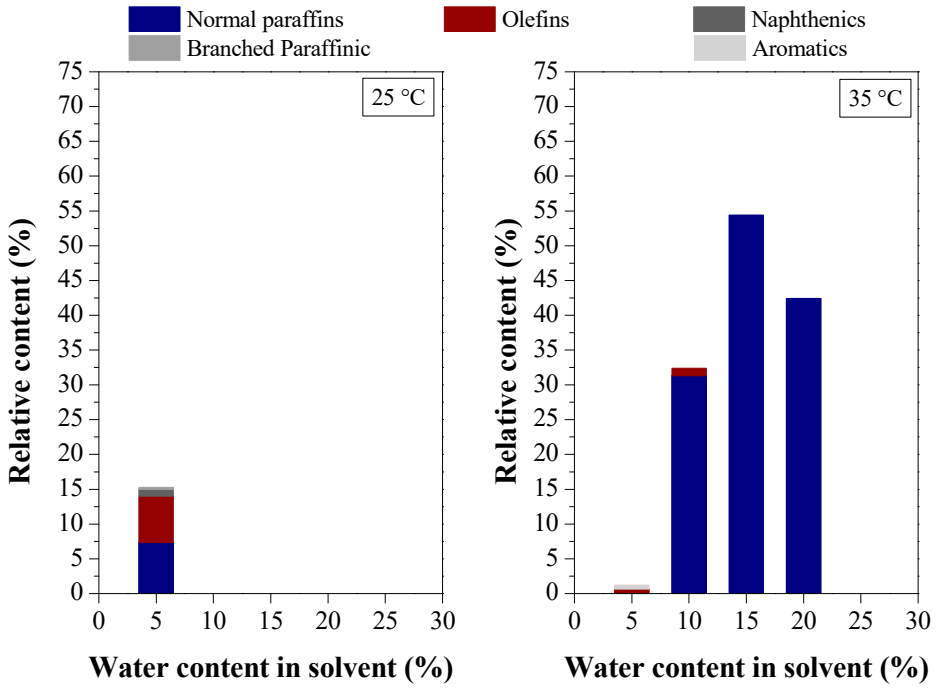

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Figure 22. The effect of methanol's water content on the distribution of hydrocarbon classes in extract streams.

In this context, the results presented in Figures 19–22 demonstrate that an increase in the temperature of the extraction process allows a more significant removal of oxygenated compounds when compared to the results obtained for the same water content. This makes it clear that while the temperature favors reducing the oxygenated compound content, water content is a detrimental factor.

To evaluate the effect of water content on the distribution of oxygen classes, we plotted the graph presented in **Figure 23**, which shows that as the water content increases, there is a tendency to increase the concentration of carboxylic acids both at 25 °C and 35 °C. Therefore, although the contents of oxygenated compounds as a whole and, specifically, of carboxylic acids are lower than those of BO_3 for all water contents and for both extraction temperatures, it was observed that an increase in the water content causes a reduction in the ability of the solvent to extract carboxylic acids. In addition, it was possible to observe that the concentration of oxygenated compounds such as alcohols and ketones changes very little with the increase of water content, indicating that the binary solvent presents more excellent selectivity for the compounds of interest in the present work, which are carboxylic acids. Oliveira et al. [60] investigated the liquid-liquid equilibrium of systems composed of rice bran oil, free fatty acids, ethanol, and water at temperatures ranging from 10 to 60 °C. The results of the study conducted by Oliveira et al. [60] indicated that the mutual solubility of compounds, including carboxylic acids (FFA), decreased with an increase in the water content of the solvent and a decrease in the extraction temperature. Therefore, the results obtained in the present study are consistent with those reported in the literature.

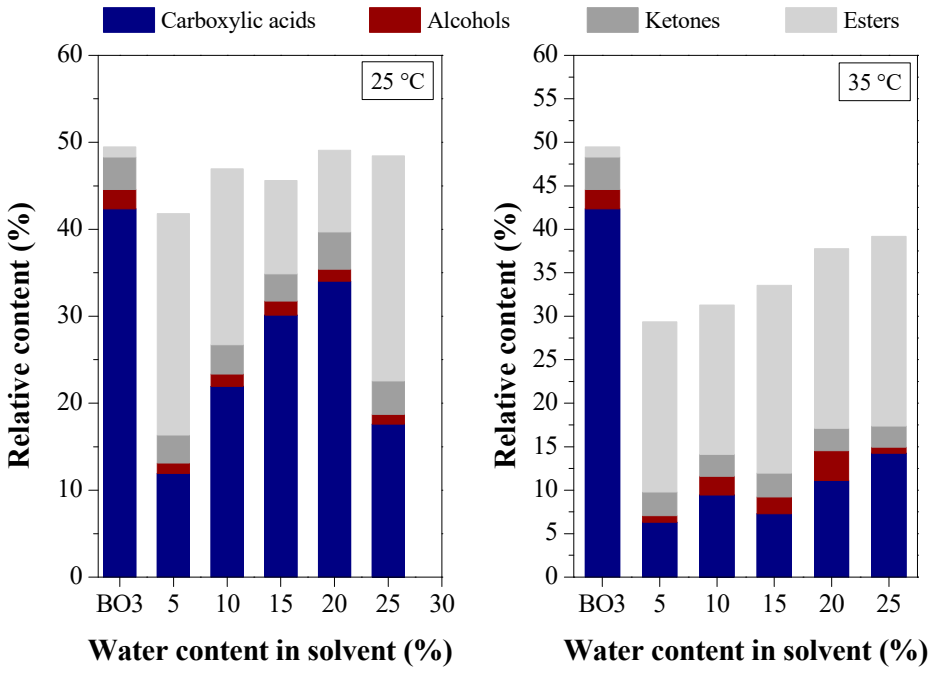

Figure 23. The effect of methanol's water content on the distribution of classes of oxygenated compounds in raffinate streams (deacidified BO_3).

Figure 23 also shows that the ester content in the raffinate streams is higher than that found in BO_3 for all water contents and both extraction temperatures, indicating that part of the carboxylic acids present in the original bio-oil was esterified when subjected to deacidification by LLE. This fact, in principle, is not a problem since it can be seen from **Figure 24** that esters are the class of oxygenated compounds that are in the highest concentration in the extract streams, followed by carboxylic acids, indicating that they are extracted by aqueous methanol. However, not in its

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entirety. This suggests that more than one extraction step is required to remove oxygenated compounds, especially carboxylic acids and esters formed during deacidification.

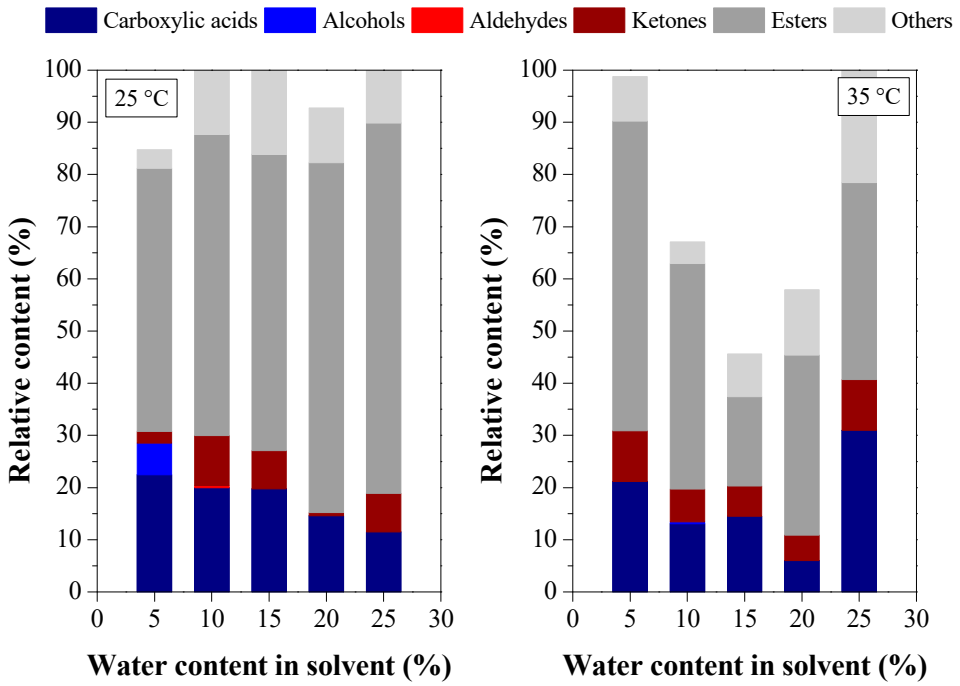
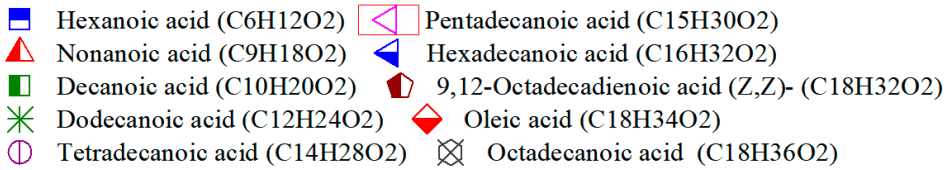


Figure 24. The effect of methanol's water content on the distribution of classes of oxygenated compounds in extract streams.

Carboxylic acids and esters are the two main chemical groups extracted from BO_3 by aqueous methanol. Palmitic acid, oleic acid and decanoic acid were detected in higher relative content, totaling 8-24% and 5-13% when extraction is performed at 25 °C and 35 °C, respectively, as shown in **Figure 25.** In addition, the analysis of **Figure 25** also indicates that carboxylic acids such as hexadecanoic acid (palmitic acid), oleic acid, and decanoic acid are the ones that are in higher concentration in BO_3 and that, after the LLE process, these acids are the ones that are extracted due to a significant reduction in their contents, mainly when methanol is used with 5% water, promoting the reduction of TAN values for the raffinate streams, as observed in Section 3.2.2.1. **Figure 25** also shows that the water content and extraction temperature have a significant effect on the contents of hexadecanoic acid (palmitic acid), oleic acid, and decanoic acid in such a way that there was little change in the levels of the other FFAs present in the original bio-oil, remaining practically constant.



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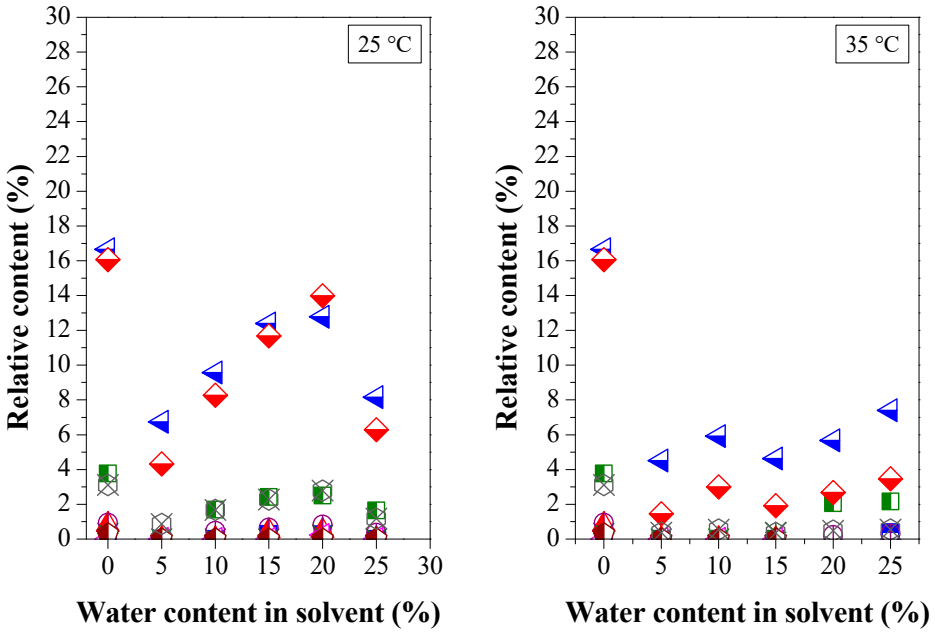

Figure 25. The effect of methanol's water content on the distribution of carboxylic acids present in raffinate streams (deacidified BO_3).

It was expected that hexadecanoic acid, oleic acid, and decanoic acid would present relatively high levels in the extract streams compared to the other FFAs. However, this result was obtained only for decanoic acid, as illustrated in **Figure 26**. The explanation for this result is that most of the hexadecanoic acid and oleic acid are esterified during the LLE process, being removed in the form of esters such as hexadecanoic acid, methyl ester and 9-octadecenoic acid (Z)-, methyl ester, respectively. This result can be seen in **Tables S11–S15** and **S21–S25** of the **Supplementary Materials**, confirming what was previously reported regarding converting a large part of the carboxylic acids into fatty acid methyl esters during the deacidification process by LLE. According to Lee et al. [64], adding methanol increases the selectivity of esters because the acidic compounds in the bio-oil, such as carboxylic acids, can engage in an esterification reaction with methanol. Therefore, the results obtained are consistent with the literature.

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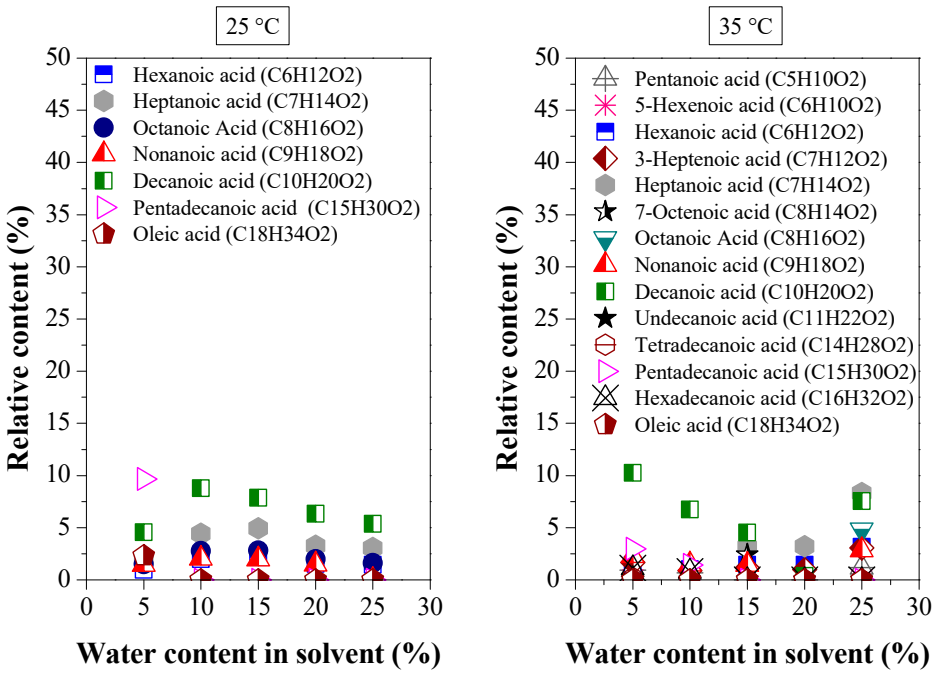

Figure 26. The effect of methanol's water content on the distribution of carboxylic acids (free fatty acids) in extract streams.

Bio-oil produced from the thermochemical route of triglyceride-based biomass is increasingly recognized as a potentially abundant source of renewable fuels and chemicals. Carboxylic acids, mainly free fatty acids, are significant constituent groups in bio-oil and end products or intermediate substances. Therefore, upgrading bio-oil through deacidification by liquid-liquid extraction is a relatively new proposition that can be employed to provide renewable chemistries.

4. Conclusions

In this study, we investigated the application of liquid-liquid extraction as a deacidification process of organic liquid products, which are biofuels produced by catalytic thermal cracking. Therefore, the effect of some process parameters (water content present in the solvents, free fatty acid content of the feed and extraction temperature) on the deacidification process by liquid-liquid extraction was evaluated.

The increase in the concentration of water in the solvent causes a decrease in the partition coefficients of carboxylic acids, so the greater the amount of water in the system, the lower the ability of the solvent to extract free fatty acids. Regarding the FFA content present in the feed, it was concluded that the increase of this parameter negatively affects the deacidification process, as was already expected due to the limited capacity of the solvent caused by its saturation in high solute concentrations.

Regarding the effect of temperature on the deacidification process, it was found that aqueous methanol showed an increase in its FFA removal capacity when the process temperature increased from 25 to 35 °C, increasing the distribution coefficient values.

Considering the best results obtained, the ideal condition to have the highest FFA removal is the one in which the deacidification process is performed with aqueous methanol (5% water) at 35°C and with BOs that have an acid value equal to or less than 24.38 mg KOH/g.

In this context, it was concluded that methanol was not only selective for carboxylic acids (palmitic acid, oleic acid and decanoic acid, the most representative in terms of quantity in BO_3) and can promote the deacidification of bio-oil through the removal of esters, since these compounds are also responsible for the acidity of biofuels. Therefore, the deacidification process by liquid-liquid extraction using aqueous methanol as an extractor solvent is shown to be a promising alternative for

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the removal of FFA and other oxygenated compounds, contributing significantly to the upgrading or improvement of biofuels produced by catalytic thermal cracking.

Supplementary Materials: Supplementary material associated with this article can be found in Appendix A.

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