CIEEMAT`19

The 5th Ibero-American Congress on Entrepreneurship, Energy, Environment and Technology

PROCEEDINGS

POLITÉCNICO DE PORTALEGRE

5th Ibero-American Congress on

Entrepreneurship, Energy, Environment and Technology

11th – 13th September 2019

Portalegre, Portugal

ISBN 978-84-17934-30-9

Portugal, September 2019

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Valorization of acidic waste oils through conversion to biodiesed catalysed by an acidic ionic liquid

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***Abstract*—Biodiesel is an alternative diesel fuel which is industrially produced from vegetable oils and animal fats. Currently most commercial biodiesel is produced from oils, using alkaline catalysts. However, conventional mineral acid catalysts like sulfuric acid, are commonly used to catalyze esterification reactions of fatty acids which also produce biodiesel. Ionic Liquids (ILs) offer an alternative solution to classical homogeneous catalysts, because it can be recycled and reused in subsequent runs after a few recovery steps. In this study, a Brønsted acidic IL, 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM]HSO_4) was used as a catalyst in the conversion of a simulated acidic waste oil, based in mixtures of a waste cooking oil and oleic acid, into biodiesel by esterification/ transesterification reactions. The kinetic studies showed that the esterification reaction can be modeled as a third order reaction with an activation energy of 52.2 kJ/mol, and was significantly influenced by the temperature and molar ratio of oil/alcohol. The methodology proposed for recovery of the IL is adequate because it has the capacity to recover the IL with high purity. After five reaction/recovery cycles, the conversion efficiency falls from 93.4% to 86.9% and the FAME content decreases from 18.4%wt to 11.5%wt. The IL [BMIM]HSO_4 was not able to promote the transesterification reaction of the simulated oil but presented promising results for the esterification reaction and for a treatment of oils with high acidity.**

Keywords*— *biodiesel, esterification, ionic liquids

VI. INTRODUCTION

A. Biodiesel

Biodiesel is a biodegradable, renewable, non-toxic, sulfur-free, and environmentally clean alternative diesel fuel, which is composed by fatty acid alkyl esters, produced from renewable resources, such as vegetable oils, animal fats, and waste restaurant greases. One of the attractive characteristics of biodiesel is that its use does not require any significant modifications to diesel engines [1]. Comparing to diesel fuels, biodiesel fuels show advantages in terms of sulfur content, flash point, aromatic content and biodegradability. Biodiesel contributes also with lower emissions than petroleum diesel, and does not add to a rise of the net concentration of carbon dioxide in the atmosphere, leading to a decreasing in greenhouse effects intensity in global climate [2].

Biodiesel is usually produced by a transesterification reaction, by which the triglycerides present in the fat materials react with alcohols, in the presence of a catalyst, to produce fatty acid alkyl esters. Glycerol is produced as a byproduct of this transesterification process. The most common alcohol used in biodiesel production is methanol (MeOH). So, biodiesel is typically constituted by a mix of fatty acid methyl esters (FAME) [3].

However for highly acidic vegetable oils, namely waste vegetable oils (WVOs), it is required to treat the raw materials in order to diminish its excessive acidity, which may introduce severe operational problems in the downstream processes. Thus, a previous esterification step of the free fatty acids (FFA) present in the oils is required, which is usually catalyzed by conventional mineral acids, such as sulfuric acid. An esterification reaction occurs when a carboxylic acid (the fatty acid) reacts with an alcohol (usually methanol) to produce an ester (biodiesel) and water.

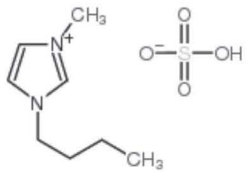
B. Ionic Liquids

Ionic liquids (ILs) are defined as liquid state molten salts at low temperatures (below 100°C), which are

composed of organic cations and either organic or inorganic anions, and are used as solvents/catalyst for several reactions [4]. It is important to emphasize that while these compounds may actually be solid at room temperature, they are typically referred to as liquids because they have a melting point below 100°C [5].

ILs exhibit general properties such as: very low relative volatility (i.e., close to zero), wide liquid temperature range and significantly less toxicity compared to organic solvents. Additionally, they can be colorless, non-flammable, and show high catalytic activity, low viscosity, potential recyclability, being easily manipulated and environmentally friendly. Furthermore, they can be made miscible or immiscible with organic solvents and water. ILs are generally regarded as green solvents, receiving worldwide attention in several application fields including catalysis, electrochemistry, separation, and inorganic nanomaterials [6]. Besides the use as solvents, ILs can also be used as sole catalysts in biodiesel production processes [7-8], either by esterification or transesterification paths. For these applications, Brønsted acidic ILs reveal to be highly efficient catalysts. Imidazolium based ILs, due to its inherent ionic patterns, low pressure and ability of self-organization in different states, are the most studied IL species. This type of ILs have been progressively used as green solvents to replace the volatile and relatively toxic organic solvents, in homogeneous and heterogeneous catalysis, materials science, nanomaterials, lithium ion batteries, and separation technology [9-11].

Hence, the main objective of this study was the production of biodiesel through the reactions of esterification /transesterification of a simulated oil, based in mixtures of a waste cooking oil and oleic acid (OA), catalyzed by the ionic liquid 1-butyl-3-methylimidazolium hydrogen sulfate, [BMIM]HSO_4, whose chemical structure is presented in Fig. 1.



Brønsted acidic IL, 1-butyl-3-methylimidazolium hydrogen sulfate, [BMIM]HSO_4, chemical structure.

VII. Materials And Methods

A. Materials

The feedstocks used were a waste cooking oil sample, collected in restaurants from the region of Bragança, Portugal, oleic acid (OA), tech 90%, obtained from ThermoFisher. IL 1-butyl-3-methylimidazolium hydrogen sulfate was obtained from Sigma Aldrich. Other materials used were n-heptane (99%), anhydrous absolute ethanol and sodium sulfate anhydrous (Carlo Erba), diethyl ether, methanol, potassium hydroxide, borax and methyl red indicator (Riedel-de-Haën), concentrated sulfuric acid and boron trifluoride-methanol(Sigma Aldrich), and hydrochloric acid (37%) (Fisher Chemical). The 37 FAME mixture was purchased from Sigma Aldrich and the standard methyl heptadecanoate (97%) was purchased from Tokyo Chemical. The phenolphthalein indicator (99%) was obtained from Panreac. All materials were used without further purification.

B. Characterization of the Feedstocks

To a 20 mL volumetric flask, 25 mg of the biodiesel sample and 2.5 mL of methanolic KOH solution (0.5 mol/L) were added. Then, the flask was closed and submitted to a drying process in an oven at 90 °C for 10 min. After this time, it was removed from the oven and allowed to cool to room temperature, and 2 mL of BF_3 in methanol solution (10%, v/v) was added. The flask was again closed and placed in the oven at 90 °C for more 30 min, then was removed from the oven and allowed to cool to room temperature. Latter, 3 mL of methyl heptadecanoate solution was added and the solution was agitated using a vortex apparatus. Saturated sodium chloride, NaCl, solution (2 mL) was added and the solution was again subjected to the same homogenization procedure. The sample was centrifuged for 5 min at 3000 rpm for total separation of the two phases. After centrifugation, 2 mL of the upper phase was withdrawn and added to a 4 mL flask. Anhydrous sodium sulfate was added in sufficient quantity to remove all moisture present. Gas chromatography analysis was then performed for fatty acids characterization present in the sample.

C. Reactions

Ionic liquid, oleic acid, waste cooking oil and methanol were added, using this order and in different previously defined proportions, to a 100 mL reaction vessel. Then, the reaction vessel was immersed in a paraffin bath, coupled to a reflux condenser and placed over an automatic heating plate with agitation and automatic temperature control. An extra thermometer was used to confirm the temperature inside the reaction vessel. When the predetermined reaction time was reached, the vessel was removed from the bath and immersed in cold water to stop the reaction. The mixture was transferred to centrifuge tubes and then stored in a refrigerator (4 °C) for a period of 60 h, then subjected to 20 min centrifugation (3000 rpm). Using this procedure, the final product of the reaction reached a level of complete separation of phases which could now be completely splitted. Both phases (organic and aqueous) were stored in flasks and kept in a fridge for further analysis.

The kinetic study assays were carried out with a similar procedure. Throughout the reaction and at predetermined times (0, 15, 30, 60, 90, 120, 180, 240, 300, 360, 420 and 480 min), 1 mL of sample was removed from the reaction vessel using a micropipette and stored in a 2 mL vial. After cooling, the acidity decrease was measured to determine the conversion.

D. Reaction Yield

The standard method to measure the acid value of biodiesel is a volumetric titration (acidity is expressed in mg KOH/g oil) using standard solution of KOH with concentration of 0.1 mol/L (EN 14104:2008 [12]). A solution of 1:1 diethyl ether/ethanol (v/v) was used as the solvent for volumetric titration, and phenolphthalein was used as the indicator.

The acid value (AV) of biodiesel was calculated by:

$$AV = \frac{V \times C_{KOH} \times M_W}{m_{biodiesel}} \quad (1)$$

where,

V – Volume of KOH standard solution needed to titrate biodiesel sample (mL);

C_{KOH} – concentration of potassium hydroxide (KOH) standard solution (mol/L);

M_W – molecular weight of KOH (56.1 g/mol);

$m_{biodiesel}$ – mass of biodiesel sample (g).

The biodiesel conversion was estimated using the equation:

$$\text{Production Yield, Y(\%)} = \frac{AV_i - AV_f}{AV_i} \times 100 \quad (2)$$

$$\alpha + \beta = \chi. \quad (1)$$

(1)

where,

AV_i – acidity of oleic acid (initial) ($mg_{KOH}/g_{oleic\ acid}$);

AV_f – acidity of sample (after reaction) ($mg_{KOH}/g_{biodiesel}$).

E. Gas Chromatography

Gas Chromatography with a Flame Ionization Detector (GC-FID) was used to measure the FAME content in biodiesel samples, in compliance with the European Standard EN14103/2003 [13]. All analyses were carried out on a Varian 3800 GC equipment, equipped with a Supelcowax 10 column (30m×0.25mm×0.25μm). The GC analysis was carried out using the following operating conditions: helium flow-rate of 1 mL/min, initial oven temperature of 50 °C maintained for 1 min, then a temperature ramp from 25 °C/min to 200 °C, and then a second ramp temperature at 3 °C/min until 230 °C. The final temperature was maintained for 23 min, for a total running time of 40 min. The injector was operated with a temperature of 250 °C and a split ratio of 1:25. The detector temperature was 250 °C.

The identification of each FAME was done by comparing the retention times of the Supelco 37 FAME compound mix analysis obtained in the GC Shimadzu system with the retention times in two other analysis of FAMEs mixtures published by two different manufacturers. The first one is a 16 FAME mix analysis published by Macherey-Nagel using the same column OPTIMA BioDiesel Fand, and the second one is a 37 FAME compound mix analysis published by Supelco [14] using a DB-Wax column. After identification of all 37 compounds, the individual and the total chromatographic areas of FAMEs were used to quantify the FAME content present in biodiesel using equation (3), according to EN14104 [12].

$$C(\%) = \frac{(\sum A_{FAME} - A_{IS})}{A_{IS}} \cdot \frac{m_{IS}}{m_{biodiesel}} \quad (3)$$

where ΣA_{FAME} is the sum of the areas of all FAMEs (from C4:0 to C22:0), A_{IS} is the area of the internal standard (heptadecanoate methyl ester), m_{IS} is the mass of the internal standard and $m_{biodiesel}$ is the mass of the biodiesel sample.

Similarly, the contribution of each FAME compound to the total FAMEs content was calculated using equation:

$$C_n(\%) = \frac{A_{FAME(n)}}{A_{IS}} \cdot \frac{m_{IS}}{m_{biodiesel}} \quad (4)$$

where C_n (%), is the contribution, in percentage, of FAME n in the sample, expressed in mass fraction and $A_{FAME(n)}$ is the area of the compound n. Solely the methyl esters which showed a contribution to the total content higher than 1% were considered.

F. Ionic Liquid Recovery

The vials of the aqueous phase were submitted to a drying process using an oven at 110 °C for 5 h. The dried samples were washed with distillated water (1:3 wt/wt ratio) and the same drying procedure was repeated. At the end of this procedure all samples were analyzed by FTIR (Fourier Transform Infrared Spectroscopy) to measure the correlation with the pure sample of [BMIM]HSO_4 and the effectiveness of the procedure.

G. FTIR Analysis

The spectra were emitted between the wavenumber of 400 to 4500 cm^{-1} in a resolution of 4 cm^{-1} and 4 cumulative scans, using a PerkinElmer FT-IR, model Spectrum Two, spectrometry equipment.

VIII. Results

A. Characterization of the Feedstocks

The waste cooking oil (WCO) and oleic acid 90% (OA) were characterized by determination of the acid value (AV) and identification of the fatty acid profile followed by verification of the composition. The acidity value found for the studied WCO sample was 4.78 mg_{KOH}/g_{oil} and for the OA sample, the acid value determined was 177.04 mg_{KOH}/g_{OA}.

The fatty acid profile in both samples of the feedstock was identified through the derivatization of the Fatty Acid Methyl Esters by BF_3, followed by GC analysis. This analysis was performed in duplicate. Tables I and II present the qualitative and quantitative characterization of each FAME in relation to the waste cooking oil and the OA, respectively.

Characterization of FAME in waste cooking oil.

Peak name	Peak ID	Content (%)
Myristoleic acd methyl ester	C14:1	1.0
Pentadecanoic acid methyl ester	C15:0	0.7
cis-10-Pentadecanoic acid methyl ester	C15:1	0.6
Palmitic acid methyl ester	C16:0	8.0
Stearic acid methyl ester	C18:0	2.6
Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	29.3
Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	34.2
gamma-Linolenic acid methyl ester	C18:3n6	0.3
Linolenic acid methyl ester	C18:3n3	2.1
TOTAL		**78.7**

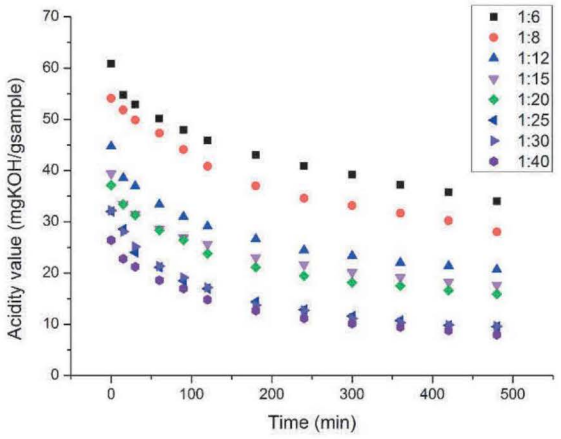
Characterization of FAME in OA.

Peak name	Peak ID	Content (%)
Palmitic acid methyl ester	C16:0	1.7
Stearic acid methyl ester	C18:0	2.9
Oleic acid methyl ester, Elaidic acid methyl ester	C18:1(c+t)	87.3
Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2(c+t)	4.5
TOTAL		**96.4**

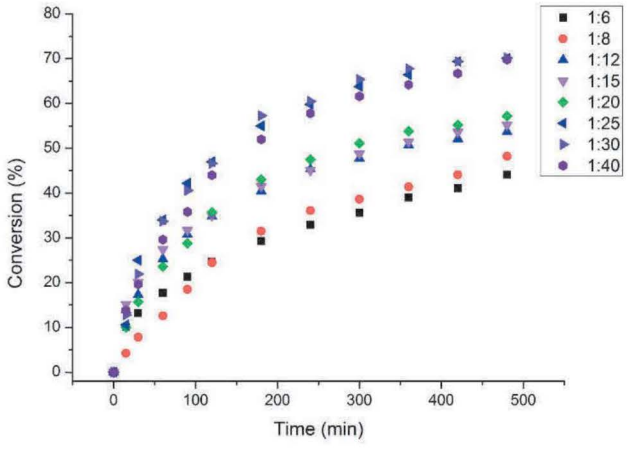
B. Kinetic Study

The kinetic study was performed for different oil:methanol molar ratios (1:6; 1:8; 1:12; 1:15; 1:20; 1:25; 1:30 and 1:40), using a catalyst load of 10 %wt, 20% incorporation of OA acid and a reaction temperature of 65 °C. In a second experimental step, the determination of the activation energy for the reaction was conducted for different temperatures (50; 55; 60 and 65 °C) using the most promising molar ratio of oil/MeOH.

Fig.s 2 and 3 exhibit the results for the acidity value and consequent conversion throughout the reaction for all tests. It is evident that by increasing the molar ratio of oil/alcohol added to the reaction, the acid value decreases and the conversion increases. For a reaction time of 8 h the conversion reaches a limit of 70% with a ratio of 1:25 oil/MeOH, repeating this result for the ratios of 1:30 and 1:40.



Reduction of acidity value for different molar ratios oil/MeOH.



Conversion for different molar ratios oil/MeOH.

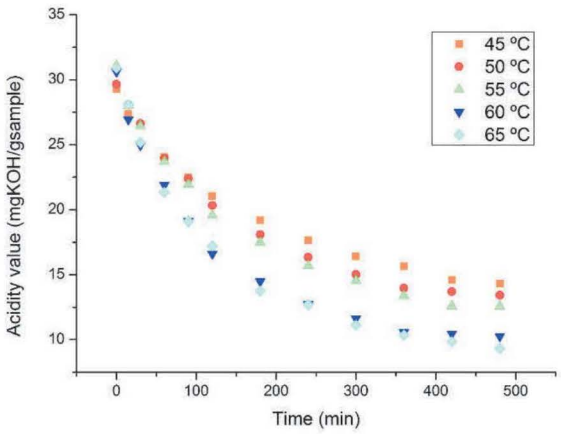
In order to determine the order of reaction in relation to OA, the Integral Method was used, applied to 0^{th}, 1^{st}, 2^{nd} and 3^{rd} order kinetic models, for all oil/methanol molar

ratio tests implemented. The data were then plotted for each order of reaction, and the coefficient of determination (R^2) was used to determine the apparent order of the reaction. The highest coefficient of determination in all cases corresponded to the third order reaction in relation to the OA reactant.

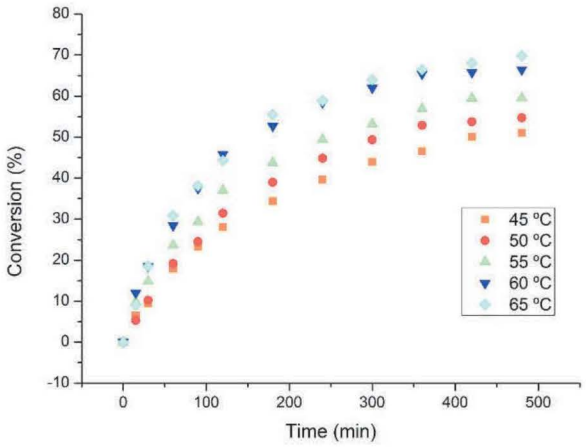
Therefore, assuming a third order esterification reaction of oleic acid, it was possible to estimate the activation energy of this reaction. For this reason, the molar ratio oil/MeOH of 1:30 was chosen, since a conversion of 70% was obtained after 8 h of reaction was obtained in these conditions. The reaction tests were carried out with a temperature variation (45, 50, 55, 60, 65 °C), setting all other operational conditions and using the procedure described above.

In these tests, acidity reduction and conversion plots were also obtained (see Fig.s 4 and 5). It is easy to notice that with the increase in temperature, the acidity values assume lower values while the conversion reaches higher values.

For a reaction time of 8 h, a conversion of 51% was achieved at a temperature of 45 °C, while 55% conversion was reached for a temperature of 50 °C. At a temperature of 55 °C it was obtained 60% conversion, and 66% conversion was attained for a temperature of 60 °C. Finally, a 70% conversion was reached for the temperature of 65 °C.



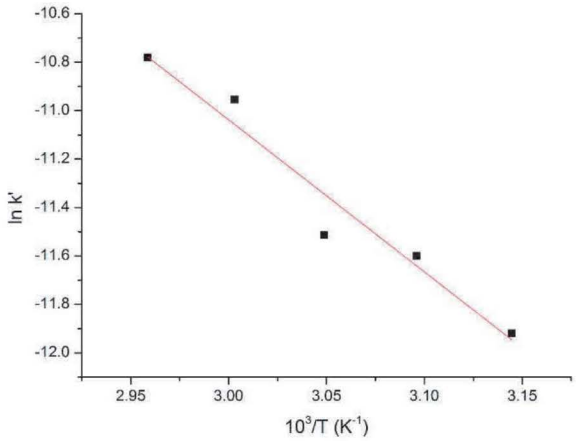
Reduction of acidity value for all temperature conditions.



Conversion for all temperature conditions.

Now, it is possible to estimate the value of the kinetic constant for each temperature assuming a third order esterification reaction. Through the application of the Arrhenius equation, the plotting of the inverse of the temperature in K and the natural logarithm of the kinetic constant at each temperature, made possible the estimation of the activation energy for the reaction. Hence, the Arrhenius plot is shown in Fig. 6.

A determination coefficient of $R^2 = 0.9536$ was obtained. The pre-exponential factor (k_0) was estimated at 2.46×10^3 $L^2.mol^{-2}s^{-1}$ and the activation energy (E_a) as 52.2 kJ/mol. This considerable activation energy indicates a dependence on temperature, being highly influenced by it.



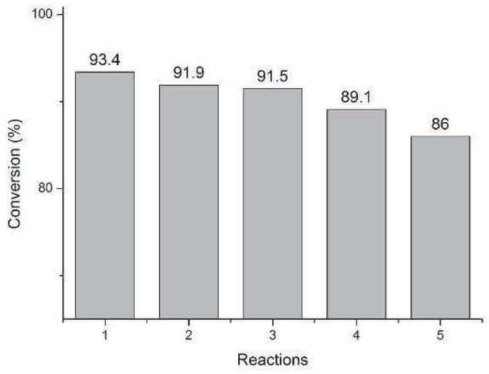
Arrhenius plot for the experimental data.

C. Recovery of Ionic Liquid

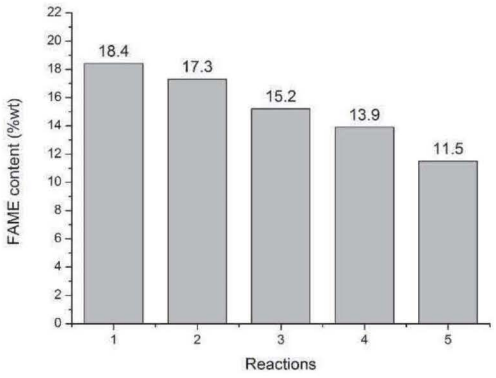
The recovery of the ionic liquid was studied by measuring the number of times that the catalyst could be re-used without a significant decrease in its catalytic activity. The experimental conditions consisted of 40% incorporation of OA, an oil/MeOH molar ratio of 1:20, a reaction temperature of 65 °C and reaction time of 4 h. The ionic liquid was recovered and then submitted to new

reactions of biodiesel production with the same referred experimental reaction conditions to access its catalytic capacity. For this determination, the responses analyzed were the conversion estimated by the decrease in acidity and the increase in content of FAMEs.

It is necessary to point out that for each of the tests performed the mass of catalyst used at the beginning of the reaction corresponded to approximately 10%wt. of the feedstock used, being indispensable to consider the gradual reduction of the mass of the simulated oil used in each reaction cycle. Acidity reduction analysis for conversion estimation and FAME content were performed on the biodiesel produced in each of the five reactions. The results are shown in Fig.s 7 and 8.



Conversion variation during the IL recovery cycles.



FAME content variation during the IL recovery cycles.

It is possible to observe that in the first three cycles the conversion decreased smoothly. However it is also noticeable the occurrence of more abrupt decreases for the 4th and 5th cycle. When compared to the first cycle, the following cycles show decreases of 1.5%; 2.0%; 4.6% and 7.9%, respectively.

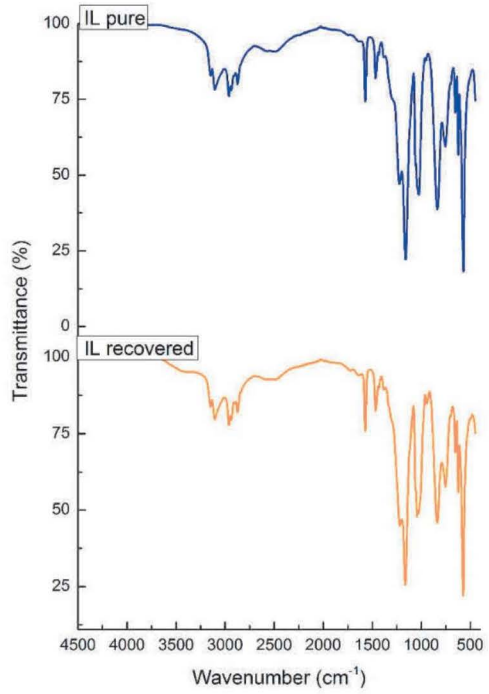
In the same way as the conversion calculated through the reduction of acidity, the FAME content in each of the tests has decreased, and the largest reduction was observed in the last one. When compared to the first cycle, the others had a decrease of 6.0%; 17.4%; 24.4% and 37.5%, respectively, which is a noticeable progression. This large decrease in FAME content is, also, due to the fact that at each cycle the mass of the feedstock used was reduced, relative to the mass of catalyst lost, thus having a constant catalyst dosage of 10 %wt.

After the fifth cycle, the recovered ionic liquid was subjected to FT-IR analysis to determine its purity and correlation with a sample of the ionic liquid not yet used. A 96.8% correlation was obtained between the samples, and it is possible to verify that after five reactions of biodiesel production the [BMIM]HSO_4 still has high purity. Fig. 9 shows the spectra with the unused IL and the recovered IL after the fifth reaction cycle.

IX. Conclusions

The objective of this study was the production of biodiesel through the reaction of esterification/transesterification of a simulated oil, based in mixtures of WCO and OA, catalyzed by the ionic liquid 1-butyl-3-methylimidazolium hydrogen sulfate, [BMIM]HSO_4.

It is known that the reuse of WCO for the production of biodiesel has the potential to reduce the cost associated with the product, which makes it competitive with the petrochemical market. The characterization of the oil used in this study showed that it is similar to a sunflower oil, mainly composed of 43.4% of C18:2 (linoleic acid methyl ester), 37.2% of C18:1 (oleic acid methyl ester), 10% of C16:0 (palmitic acid methyl ester), 2.7% of C18:3n3 (linolenic acid methyl ester) and 1% of C18:0 (stearic acid methyl ester), in a weight basis.



Comparison of spectra for the unused IL and the recovered IL.

The IL showed promising results for the production of biodiesel by the esterification reaction of the incorporated oleic acid, but it was not able to induce the transesterification reaction of triglycerides. Therefore, it is a valid alternative for the treatment of waste oils, by reducing their level of acidity and adding value to this product. The kinetic study allowed to evaluate the influence of the molar ratio of oil on the esterification reaction, showing that above a ratio of 1:25 the conversion remains unchanged for a period of 8 h. For molar ratios of 1:25; 1:30 and 1:40, 70% conversion was reached for the pre-determined time in all the experiments.

Then, it was possible to measure the activation energy of the esterification reaction catalyzed by IL 1-butyl-3-methylimidazolium hydrogen sulfate by changing the reaction temperature, reaching a value of 52.2 kJ/mol. This activation energy value means that the reaction is influenced by the temperature, which reinforces the fact that the maximum conversion is reached for a reaction time of 8 h and decrease as the temperature decreased, obtaining a maximum value of 70% for the temperature of 65 °C and 51% for 45 °C .

The proposed methodology for the recovery of the ionic liquid was efficient, being feasible until five consecutive cycles of reuse, leading to a decrease in conversion from 93.4 % to 86.9 % and the content of FAMEs initially measured in 18.4 %wt decreased to 11.5 %wt.

[BMIM]HSO_4, was not able to promote the transesterification reaction, but presented excellent results as a catalyst for the esterification reaction. Its use can be applied as a preliminary treatment for non-edible commercial oils with high FFA content, that is, acid oils. The preliminary treatment may increase the cost of biodiesel production, but recovery of ionic liquid is an advantage to reduce process costs.

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