EFFECTS OF THE ADDITION OF [2HEA][HX] ON BIODIESEL SYNTHESIS USING METHANOL AND METHANOL/ETHANOL MIXTURE

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Received: 19.03.2019 / Revised: 04.06.2019 / Accepted: 19.06.2019 / Published on line: 08.10.2019

ABSTRACT

Currently, the use of ionic liquids (ILs), such as catalysts and co-solvents, in the production of biodiesel commonly demands extreme operating conditions (especially temperature and / or time). Besides the environmental benefits, these compounds have versatile physical and chemical properties. Some of these compounds also possess amphiphilic features that allow them to act as surfactants and, in this case, when employed as additives in transesterification reactions, they can overcome mass transfer limitations and, consequently, the reaction rate. This work aims at studying the effects of protic ionic liquid (PIL) 2-hydroxyethylammonium hexanoate [2HEA][Hx] in the alkaline transesterification of soybean oil using methanol and a methanol/ethanol mixture. The reaction conditions were alcohol/oil molar ratio of 6:1, 1.5% (%wt/wt) KOH as the catalyst, 2% (%wt/wt) PIL as the additive, 60 °C, and 30 min reaction time. The highest mass yield was 92.72% for both pure methanol and methanol/ethanol mixture (molar ratios 5:1), since the mean was not statistically different for those two ratios.

KEYWORDS

biodiesel; transesterification; methanol/ethanol mixture; protic ionic liquid; co-solvent

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doi:10.5419/bjpg2019-0015

1. INTRODUCTION

Biofuels are alternative energy sources with the potential to meet energy needs in the field of fuels (Guimarães et al., 2018; Ullah et al., 2018). Biodiesel, which belongs the family of biofuels, is obtained from vegetable oils, animal fats, algae lipids, waste oils, and hydrogenated fats. For this reason, it is considered a clean, renewable, biodegradable, and nontoxic alternative to fossil fuels (Moro et al., 2017; Verma & Sharma, 2016). It can be used either to replace diesel or as an additive, reducing the emission of greenhouse gases and sulfur oxides, thus, improving gas combustion emission profile (Khudhair et al., 2018; Ullah et al., 2018).

Fatty acids alkyl esters (biodiesel), as a final product, and glycerol, as co-product, are obtained mostly through the transesterification (reversible chemical reaction) of triglycerides, which react with an excessive amount of alcohol in the presence of a catalyst (Feng et al., 2017; Guimarães et al., 2018; Keera et al., 2011; Verma & Sharma, 2016).

Both methanol and ethanol have been used successfully in the production of biodiesel (Ma et al., 2015). Methanol is the often the first choice due to its physical and chemical properties. However, is not considered a completely eco-friendly alternative, whereas ethanol is. Additionally, it has greater solubility in oils than methanol. Nevertheless, ethanol can produce steric and emulsification effects after transesterification, which difficult the purification of biodiesel and compromises the yield of the process (Khudhair et al., 2018; Li et al., 2013; Ma et al., 2015; Verma & Sharma, 2016).

The type of alcohol and the molar ratios influence biodiesel yield and its properties. Studies using the methanol/ethanol mixtures have been conducted in an attempt to benefit from the synergistic effect and the specific properties of homogeneous and heterogeneous catalysts (Khudhair et al., 2018; Lam & Li, 2011; Ma et al., 2015; Ma et al., 2016).

The catalysts used in the transesterification reaction can be homogeneous, heterogeneous, or enzymatic (Verma & Sharma, 2016). Alkaline catalysts are used more commonly (Simonelli et al., 2018) due to their intense activity in mild operating conditions (Issariyakul & Dalai, 2014). In

this regard, ionic liquids have also been used as catalysts in the synthesis of biodiesel.

Ionic liquids (ILs) are organic salts in the liquid state below 100 °C, produced by cation (organic compound) and anion (organic and inorganic compound) combinations, with either hydrophobic or hydrophilic nature. These solvents have been used in several applications, such as in the synthesis of biodiesel, acting as catalysts, co-solvents; and as extraction agents in the purification process (Álvarez et al., 2010; Fauzi & Amin, 2012; Troter et al., 2016).

ILs present important physical and chemical properties, which include biodegradability, negligible vapor pressure, high miscibility in organic and inorganic solvents, high ionic conductivity, remarkable catalyst activity, high thermal and chemical stability, and the possibility of setting up their properties, being projectable (Camargo et al., 2016., Feng et al., 2017; Muhammad et al., 2015). They can be protic (PIL) and aprotic (AIL) (Camargo et al., 2016).

PILs have low production costs and are easily synthesized by protons transfer from an acid to a Brønsted base, in which the cation has an interchangeable proton that allows the formation of hydrogen bonds with the anion (Muhammad et al., 2015; Shmukler et al., 2018).

Studies using ILs in biodiesel production, in their vast majority, have reported demanding operating conditions, environmental benefits, and process improvements. Their use as catalysts (homogeneous, heterogeneous, or self-supported) shows good potential to improve the synthesis process but, demands, among other variables, higher process temperatures compared to the use of traditional homogeneous or heterogeneous catalysts. In these studies, the aprotic ionic liquids are the most assessed (Fauzi & Amin, 2012; Feng et al., 2017; Ullah et al., 2018; Zanin et al., 2013). As co-solvents, ILs have been used mostly in enzymatic catalysis (Fan et al., 2018; Troter et al., 2016). Basically, two types of ILs have been studied. The first type, ILs with a more hydrophobic nature, which has shown good performance, increasing the catalytic activity and reaction rate. In addition, they improve oil transesterification and favor the biodiesel separation. The second type, ILs with hydrophilic features that are capable of promoting enzyme dissolution or denaturing,

showing lowest yields (**Muhammad et al., 2015; Troter et al., 2016**).

Some ILs have surfactant features due to their amphiphilic properties. Even in low concentrations, they can reduce interfacial tension in aqueous solutions and form micelles. In this regard, the interfacial behavior of some protic ILs have been explored. For instance, **Santos et al. (2014)** proved that ILs based on a 2-hydroxyethylammonium cation, bis (2-hydroxyethylammonium), and stearate anion in aqueous solutions formed micelles. In a previous work from our group, **Trindade et al. (2019)** studied the action of a PIL, also designed from an amine and carboxylic acid (diethylenetriammonium hexanoate), in the reaction medium via homogeneous catalysis. The PIL showed good performance and promising results.

The interfacial behavior of some substances has already been employed to overcome common mass transfer restrictions in transesterification. In some studies, organic surfactants and co-solvents, (e.g., acetone, esters, tetrahydrofuran, and hexane) have been used as additive to increase mixture efficiency, contact and mutual solubility between the immiscible phases and, consequently, improve the reaction rate in the transesterification and yield in biodiesel. These organic co-solvents generally are used in high amounts 14.5%-25% (%wt/wt) with reference to the oil mass, additionally, they are toxic, volatile, and generate wastes that are difficult to separate and discard (**Alhassan et al., 2014; Encinar et al., 2016; Fadhil et al., 2015; Simonelli et al., 2018; Wu et al., 2016**).

This study employs the PIL 2-hydroxyethyl ammonium hexanoate ([2HEA][Hx]), with potential to develop interfacial activity. The anion group is hexanoate [Hx], the same as that used by **Trindade et al. (2019)**, [DETA][Hx]. This anion was chosen because it has the polar carboxyl and apolar carbon chain, similar to the stearic one proposed by **Santos et al. (2014)**, but with a lower carbonic chain and lower viscosity. These domains in the anion chain suggest that they could exhibit surfactant behavior necessary to promote the formation of micelles. The cation 2-hydroxyethylammonium [2HEA] was chosen due to the presence of hydroxyl group on the chemical structure and the structural similarity with the solvent medium. Considering the excess of alcohol

used in the transesterification, this group could facilitate the solubility in the reaction medium, contributing to the increase of the effect surfactant of [2HEA][Hx]. Additionally, the base used (ethanolamine) is inexpensive, and equal amounts of both the acid and the base are required to synthesize it.

Departing from the application of ILs as both catalysts and co-solvents, this work seeks to explore whether the surfactant potential of [2HEA][Hx] is sufficient to allow an increase in the miscibility, and if this is would be possible using a low amount of PIL in such a way that it could be applied as an additive in biodiesel production.

Previous research has not explored the use of this PIL in the production of biodiesel, employing the reactional medium of transesterification alkaline. Additionally, there have been few studies that touch upon the application of the ILs as an additive in homogenous catalysis.

This work studies the alkaline transesterification of soybean oil using methanol and a methanol/ethanol mixture combined with the effect the PIL [2HEA][Hx]. To this end, we evaluated the effect of PIL [2HEA][Hx] at different proportions of alcohols and determined how the additive influences biodiesel yield. Temperature, time, amount of KOH, and the alcohol-oil molar ratio were kept fixed.

2. MATERIALS AND METHODS

This study employed soybean oil (Soya[®] brand), methanol (Synth, 99.8% pure), ethanol (Synth, 99.5% pure), potassium hydroxide- KOH (Sigma-Aldrich VetecTM, 85% pure), ethanolamine $\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$ (CAS Registry N. 141-43-5), and hexanoic acid $\text{CH}_3(\text{CH}_2)_4\text{COOH}$ (CAS Registry No. 142-62-1).

2.1 Characterization of the soybean oil

The physical characterization of the raw material comprised four tests. The acidity index (**ABNT NBR 11115, 2014**) was determined by titrimetric analysis. The water content was determined using the gravimetric method in accordance with the procedure defined in the ANVISA 2008 standard (**ANVISA, 2008**). Density at

20 °C (ASTM D 4052-16, 2016) was measured using an Anton Paar DSA 5000 density meter.

Finally, the kinematic viscosity (ν_{sample}), at 40 °C (ASTM D 445-17a, 2017) was calculated based on the absolute viscosity of soybean oil at 40 °C (μ_{sample}) which, in turn, was measured with an Anton Paar MCR 501 rheometer and, then, related to the density (ρ_{sample}) of soybean oil, by Equation 1. All tests were done in triplicate.

$$\nu_{\text{sample}} = \frac{\mu_{\text{sample}}}{\rho_{\text{sample}}} \quad (1)$$

2.2 Synthesis and characterization of the protic ionic liquid

The 2-hydroxyethyl ammonium hexanoate ([2HEA] [Hx]) was synthesized via a stoichiometric neutralization reaction between ethanolamine and hexanoic acid. The acid was slowly added to the base, dropwise, under slow mechanical stirring, at 40 °C. Since the reaction is exothermic, a slight increase in temperature improves the miscibility between the reagents (Camargo et al., 2016; Pinto et al., 2015). The process results in an ammonium salt, being water its main impurity. Some studies have reported the presence water in protic ionic liquids as a result of the neutralization by ammonia, due to the hygroscopic features (Álvarez et al., 2010; Pinto et al., 2015). Figure 1 shows the combination reaction.

The formation of [2HEA] [Hx] was confirmed and its chemical structure was characterized through carbon and hydrogen analysis, using FT-IR and NMR techniques. Additionally, humidity (% H₂O) was determined using the Karl Fisher method (Álvarez et al., 2010; Fauzi & Amin, 2012; Penttilä et al., 2014)

The FT-IR spectra were obtained using a Shimadzu IR Prestige 21 spectrophotometer. The NMR spectra for hydrogen (¹H) and carbon (¹³C) were recorded with a Bruker DRX 400

spectrometer at 9.39 tesla and 400 MHz, using the spectra processing software Mestre Nova 11.0. CDCl₃ was used as solvent for the proton spectrum and as a reference for the carbon spectrum, where the capillary tube was coaxially inserted in the NMR tube. Deuterated 3- (trimethylsilyl) propanoic acid (TSP) was used to calibrate the signal in ~0 ppm. Humidity (%H₂O) of the IL was measured using a Mettler Toledo V20 volumetric Karl Fisher titrator. The use of ¹H NMR technique to determine the presence and amount of water in the sample presents some limitations (Penttilä et al., 2014), since some impurity identification peaks, such as water, overlap the spectra and cannot be quantified. Therefore, more specific methods should be employed to achieve more accurate results.

2.3 Biodiesel production

Biodiesel was synthesized through a batch process using alkaline transesterification. During the synthesis, the following process variables were kept fixed: alcohol-oil molar ratio (6:1), catalyst 1.5% (% wt/wt), PIL [2HEA][Hx] 2 % (% wt/wt), time (30 min), temperature (60 °C), methanol (molar ratio 6:0), and a methanol/ethanol mixture (molar ratios 4:2, 5:1, 6:0) the latter two were used as transesterification agents. Tests in the presence and absence of PIL were performed in triplicate. For each test, 100 g soybean oil were placed in a flat bottom flask. Then, the amount of KOH was measured and added to the transesterification agent (departing from pure methanol) under magnetic stirring to homogenize them and, finally, the PIL [2HEA][Hx] was added (under the same conditions). The resulting mixture was, then, added to the oil in the flat bottom flask and put on a magnetic stirrer (600 rpm) heating plate (Ika® C-MAG HS 7) (Simonelli et al., 2018). The system was attached to a condenser associated with an ultrathermostatic bath device (Quimis® Q214M2), which was set to 15 °C, thus, keeping the alcohol vapors in the system. After the reaction completion

Figure 1. Neutralization reaction of [2HEA][Hx].

Table 1. Physical and chemical characterization of soybean oil.

Properties (Unit)	Value	References		
		Simonelli et al. 2018	Cintra et al. 2017	Keera et al. 2011
Acidity index (mg KOH.g ⁻¹)	0.30 ± 0.05	0.59 ± 0.03	0.091	0.42
Water Content (%)	0.07 ± 0.04	0.1032 ± 0.0008	0.103	*
Density at 20 °C (g.cm ⁻³)	0.916 ± 0.004	0.920 ± 0.001	*	0.933
Kinematic viscosity at 40 °C (mm ² .s ⁻¹)	27.3563 ± 0.0002	30.61 ± 0.03	*	*

* Value was not reported

time, the biodiesel – glycerol mixture was transferred to a separation funnel and left to decant for 24 h. Once the grosser phases were removed, the raw biodiesel went through a washing process using distilled water at 80 °C (Ma et al., 2015), and this process was repeated four times. The purified biodiesel was then taken to a stove for drying at 105 °C for three hours to be dehydrated. Finally, the biodiesel sample had its weight measured to determine the biodiesel weight yield (%wt) by means of Equation 2, which considers the weight of purified biodiesel (g) and the weight of raw material (g), based on the gravimetric method (Fadhil et al., 2015; Moro et al., 2017; Simonelli et al., 2018).

$$\%Yield = \frac{Weight_{purifiedbiodiesel}}{Weight_{rawmaterial}} * 100 \quad (2)$$

2.4 Comparative analysis of means

Tukey's HSD (honestly significant difference) test was performed. This test is based on the range of distribution and consisted in a multiple comparison analysis between each pair of means (in the presence of PIL) using the molar ratios 4:2, 5:1, and 6:0 (methanol only) with 95% adjustment. The test determined which means were statically different in the set.

2.5 Characterization of biodiesel

The resulting biodiesel was characterized focusing on the conditions that led to the highest weight yield. The goal was to assess whether the quality specifications demanded by Brazilian National Petroleum, Natural Gas, and Biofuels Agency, ANP's resolution 45/2014 (ANP, 2014) were met. The acidity index was determined by titration, in triplicate, using isopropyl alcohol,

heptane, and fenoltaleine. The flash point (ASTM D 93-18, 2016) was found using a semiautomatic Petrotest PM4 device. Density at 20 °C (ASTM D 4052-16, 2016) was measured using an Anton Paar DSA 5000 density meter. Kinematic viscosity at 40 °C (ASTM D 445-17a, 2017) was obtained by Equation 1, which establishes a relationship between absolute viscosity (measured in an Anton Paar MCR 501 rheometer) and density.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of soybean oil

Table 1 shows the mean values found for the main properties assessed, as well as their standard deviations.

The values of the acidity index and water content were lower than 1 mg KOH/g and 0.06% (%m/m), respectively, confirming the good quality of the raw material, and, therefore, making the oil pre-treatment unnecessary (Wu et al., 2016). The control of properties such as water content and acidity index are fundamental in alkaline homogeneous catalysis.

The water content must be as low as possible so that hydrolysis and saponification reactions are not favored (Issariyakul & Dalai, 2014; Wu et al., 2016). These reactions reduce the catalyst activity, make separation difficult, and, consequently, lead to lower yields (Encinar et al., 2016). A low acidity value suggests a low amount of free fatty acids (Moro et al., 2017). A high value decreases the rate and yield (Issariyakul & Dalai, 2014) and influences fuel ageing because acidity increases over time (Alhassan et al., 2014).

Figure 2. FT-IR spectra for the IL [2HEA][Hx].

3.2 Characterization of the ionic structure of the PIL [2HEA][Hx]

FT-IR, NMR and %H₂O analyses confirmed the formation of all feature peaks of the structure and gave information about compositions of the PIL [2HEA][Hx]. Figure 2 shows the FT-IR spectra in the region from 400 cm⁻¹ to 4000 cm⁻¹. The formation is confirmed by the presence of feature bands

belonging to the bond vibrations N-H (deformation), O-H (stretching, deformation), C-H SP³ (symmetric and asymmetric stretching of CH₂), C-H (bond -CH₂), C-N (stretching), C=O (stretching of carboxylic acid groups), C-O (hydroxyl group).

Álvarez et al. (2010) and Camargo et al. (2016), in their studies, found two bands that are characteristic of an ammonia structure. One band between 3500 -2400 cm⁻¹ produced by the

Figure 3. ¹H NMR spectra for [2HEA][Hx]. S: Solvent peak.

Figure 4. ^{13}C NMR spectra for [2HEA][Hx]. S: Solvent peak.

stretching vibration O-H, and another broader band centered in 1500 cm^{-1} , resulting from the band combination of the carbonyl stretching and the N-H plane bending vibrations.

This study verified the formation of structures in the referenced spectra, with one strong stretching vibration band O-H at 3300 cm^{-1} , and another band at 1580 cm^{-1} , corresponding to the formation of the N-H bond primary amine adsorption band.

The NMR analysis showed the chemical shifts that refer to the structural arrangement and the bonds between carbon and hydrogen atoms contained in the PIL.

The NMR results proved the correspondence of all hydrogen and carbon peaks in the chemical structure (Figures 3 and 4 and Table 2). Therefore, there was a chemical shift of the anion's proton and a protonation of the cation's hydrogen.

The water content ($\%\text{H}_2\text{O}$) in the sample was $0.769 \pm 0.071\%$.

3.3 Effect of the addition of PIL [2HEA][Hx] to methanol and methanol/ethanol mixture

Figure 5 shows the mean weight yield (%) as a function of each molar ratio among alcohols, both in presence and absence of [2HEA][Hx].

A clear increase of the weight yield by adding PIL for molar ratios 6:0 (methanol only) and 5:1, of 3.39% and 2.20%, respectively, was observed in comparison to the tests without PIL. For the molar ratio 4:2, the PIL did not show any effect on the weight yield. Even though a significant dispersion was observed, the yield was similar, with and without the PIL. This behavior could be explained by the fact that the PIL reached a limit beyond which it could not continue facilitating the mass transfer for this ethanol concentration in the mixture. As a consequence, the weight yield also

Table 2. ^1H and ^{13}C chemical shift of [2HEA][Hx].

Peaks	Chemical shift (ppm)	
	^1H	^{13}C
A,h	7.22	-
A	-	181.76
D	2.13	37.91
B	-	31.83
E	1.52	26.08
F	1.28	22.52
G	0.88	14.00
B	3.76	58.54
C	2.99	41.86

Figure 5. Influence of the addition of [2HEA][Hx] on the biodiesel weight yield.

decreased by 11.59% with respect to the test with pure methanol (6:0).

Ma et al. (2015) studied the synergistic effect of methanol/ethanol in acid homogeneous catalysis. They reported that the steric hindrance prevailed over the synergy for ethanol proportions greater than 30%, decreasing the process yield. This is similar to the effect observed in this study, although the catalysis was alkaline.

Some studies have reported better reactions and more efficient separations using ILs since they have good solubility with reagents and very low solubility with the final products. Besides, it is also possible that IL provides energy to push out the biodiesel of the phase glycerol and waste at the end of the reaction (**Fauzi & Amin, 2012; Muhammad et al., 2015; Ullah et al., 2018**).

The statistical significance of the results obtained in presence of PIL was proved using the confidence intervals in terms of multiples comparisons between pairs of groups and by the difference between mean values by Tukey test. In the 95% confidence interval, the statistical mean for pairs of groups 5:1 and 4:2, 6:0 and 4:2 were different statically in intervals [3.31 – 11.34], [5.62 – 13.65] and had a p-value of 0.003 and 0.001, respectively. For comparison of pairs of groups 6:0 and 5:1, the Tukey test indicated that mean yields were not statically different within the intervals [-

1.71 – 6.33], and had a p-value of 0.26, using a significance level $p < 0.05$. Figure 6 shows the comparison of pairs of groups.

When ILs are used as catalysts in the transesterification process, they require a high alcohol-oil ratio, high temperature, and long time. **Feng et al. (2017)** used a low amount of Brønsted acid AIL, based on quaternary ammonium cation ([CyN1,1PrSO₃H][p-TSA], 3.0% (%wt/wt) as catalyst to oil, palm oil, and methanol, getting a yield of 98.4 %. However, the process variables (24:1 molar ratio, 120 °C, and 150 min) had high values. **Zanin et al. (2013)** used soybean oil and ethanol and achieved conversions above 70% for 10% mol/mol with respect to oil of Brønsted acid ionic PIL, based on the imidazole type (N-methyl-2-pyrrolidonium methyl sulfonate), in worse processes conditions (78 °C, 8 h).

The results found in this work with the addition of PIL [2HEA][Hx] show that it is possible to produce biodiesel with high weight yields in mild process conditions using low amounts of methanol (2% (%m/m)). Similar results were reported by **Trindade et al. (2019)**, yield in mass around 96% with only 3% (%wt/wt) of PIL [DETA][Hx], molar ratios alcohol to oil 9:1, at 60 °C and 60 min, and using KOH catalyst as well. Both results proved the good performance of the LIPs as additive (based on hexanoate anion and cation difference) in transesterification via alkaline catalysis.

Figure 6. Mean difference of weight yield with [2HEA][Hx] for methanol and methanol/ethanol mixture in the biodiesel production.

Scientific interest in using traditional organic co-solvents and surfactant is due to the fact that they produce high yields in short period of time and at mild temperatures, even room temperature. Basically, they are intended to reduce the interfacial tension in the mixture (Wu et al., 2016; Simonelli et al., 2018).

The effect of the [2HEA][Hx] in the reaction medium can be explained by its good solubility and amphiphilic features. It improves the contact between alcohol/oil phases, thus, allowing the interactions to occur at a molecular level, instead of occurring at the interface. The hydrophobic part of the chain of the PIL [2HEA][Hx] could interact with the alkyl chains of fatty acid molecules forming emulsions (surrounded for the polar molecules) while the polar part formed hydrogen bonds with the methanol or both methanol and

ethanol in the interface. The thermodynamic effects of micellization have as consequence the reduction of the interfacial tension, increasing the miscibility between phases and, consequently, the yield.

3.4 Characterization of biodiesel

Table 3 shows some quality parameters of biodiesel produced with the addition of the PIL [2HEA][Hx], considering the highest weight yield conditions. Since the mean of 6:0 (methanol only) and methanol/ethanol mixture (molar ratios 5:1) were not significantly different, only the sample (6:0) was characterized. The results show that the properties meet the ANP's specifications, thus, attesting the quality of the product.

Table 3. Biodiesel Properties using [2HEA][Hx].

Properties	Value	ANP 45/2014
Kinematic viscosity at 40 °Cmm ² .s ⁻¹	4.3239	3.0-6.0
Density at 20 °C (kg/m ³)	882.690000 ± 0.000001	850-900
Acidity index (mgKOH/g)	0.18 ± 0.06	< 0.5mgKOH/g
Flash point (°C)	186	minimum 100

4. CONCLUSIONS

Because of the known mass transfer restrictions in transesterification reaction, generally, it is necessary to increase the process variables to improve reaction rate, and yield. This research sought to improve the miscibility between oil and alcohol, without relying on increasing the quantities of the process variables. The addition of PIL [2HEA][Hx], which has a surfactant effect, in a low quantity, enhanced the miscibility in the reaction, in a manner similar to organic co-solvents, but under much milder conditions. PIL is also much less harmful both to operators and to the environment than organic co-solvents.

The PIL [2HEA][Hx] showed good performance in the reaction medium when added in small amounts and under mild process conditions (temperature and time). It favored the surfactant effect, improving the interaction between alcohol and oil phases, separation (biodiesel – glycerol), and weight yield.

The highest weight yield achieved by adding PIL to [2HEA][Hx] at 2% (% m/m) was 92.72%. This value was achieved with both the use of pure methanol and with the methanol/ethanol mixture (molar ratios 5:1), considering that mean values were not statistically different. The process conditions were 6:1 alcohol / oil molar ratio, 1.5% (%wt/wt) KOH, 60 °C, and 30 min.

When the amount of methanol decreases in the reaction and the ethanol increases in the lowest molar ratio assessed (4:2), the weight yields were similar both in presence and absence of PIL, therefore, not justifying an increase in the amount of ethanol for higher molar ratios.

ACKNOWLEDGMENTS

This study was financed in part by *Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brazil (CAPES)* – Finance Code 001. S. Mattedi acknowledges CNPq (Grant 306640/2016) and FAPESB/SECTI (Project APP0075/2016).

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