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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Optimization of reaction conditions for biodiesel synthesis from a waste cooking oil using [HMIM]HSO_4 ionic liquid as catalyst

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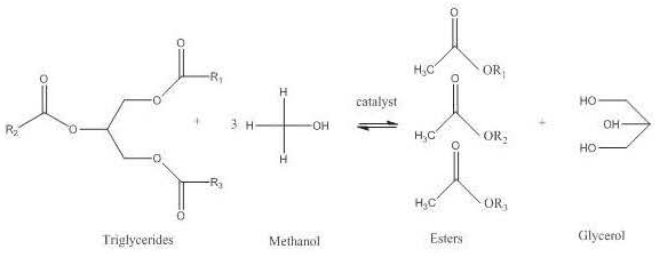
***Abstract*— The objective of this work is to study the influence of applying 1-methylimidazolium hydrogen sulfate [HMIM]HSO_4 ionic liquid on the catalysis of esterification/transesterification reactions of an acidic waste cooking oil (WCO). Samples of simulated oils with variable acidity were used as raw material. The samples were prepared by the incorporation of diverse contents of oleic acid in a qualitatively and quantitatively characterized WCO. An experimental design based on a total factorial was generated with three parameters at two levels (2^3) in duplicate: A - incorporated oleic acid (%wt.), B - methanol/ simulated oil molar ratio, and C - reaction time. Two responses were evaluated: the reaction conversion of the simulated oil, measured according to the procedure described in the European Standard EN14104/2008, and the produced biodiesel FAME content, estimated by GC-FID, according to the procedure established in the European Standard EN 14103/2003. The fixed reaction parameters were: temperature, 90°C, and catalyst charge, 10% wt, and the statistical analysis was carried out with Design Expert 11 software. The influence of the factors for the conversion response was C>B>A, and the optimal conditions were: 20% (A), 1:40 (B), and 8h (C), reaching a maximum conversion of 96.6%. On the other hand, regarding the FAME content response, the influence of factors was A>C>B, and the optimal conditions were, 40% (A), 1:20 (B), and 8h (C), for a maximum FAME content of 36.5%. It is concluded that the studied IL promoted mainly the esterification of the free fatty acids in the WCO samples, and apparently had little influence in promoting transesterification reactions.**

***Keywords*— biodiesel, optimization, full factorial, ionic liquids**

X. Introduction

Historically, economic growth was always dependent on energy generation, causing pressure on fossil energy sources. In this context, alternative renewable energy sources have been extensively studied. Therefore, biodiesel, a biofuel obtained from renewable biomass for internal combustion engines or energy generation, exhibits potential to replace partially or totally fossil fuels.

Biodiesel is chemically composed of FAMEs (fatty acid methyl esters), that can be obtained from the chemical reaction of triglycerides with an alcohol, in the presence of a catalyst. Different raw materials can be used to produce biodiesel, such as edible vegetable oils (soybean oil, rapeseed oil) or inedible oils (jatropha oil, castor oil), animal fats, waste cooking oils and oils extracted from algae [1]. Acid and basic catalysts are applied to increase the reaction rate. For transesterification reactions (see Fig. 1), basic catalysts (NaOH or KOH) are the most commonly used. Alternative options for these catalysts are ionic liquids (ILs), which are being studied in recent years since they enable a more environmentally sustainable biodiesel production process. Such compounds have potential for recyclability, high catalytic activity, simple operating conditions and high conversion rates with short reaction times [2].

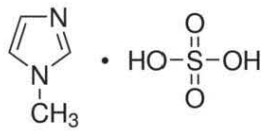


Biodiesel synthesis by transesterification process from vegetable oils with methanol [3].

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

Nevertheless, ILs can also be used as sole catalysts in biodiesel production processes [2, 4], either by esterification or transesterification paths. For these applications, Brønsted acidic ILs reveal to be highly efficient catalysts. In this framework, 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 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 [5-7].

Hence, the objective of this work is to study the influence of applying 1-methylimidazolium hydrogen sulfate, $[HMIM]HSO_4$, IL on the catalysis of esterification/ transesterification reactions of an acidic WCO, in order to assess the viability of the use of acidic imidazolium based ILs as catalysts in biodiesel production processes. Therefore, samples of simulated oils with variable acidity were used as raw material. These samples were prepared by the incorporation of different contents of oleic acid (tech. 90%) in a previously qualitatively and quantitatively characterized WCO. For the reaction, methanol was used and IL $[HMIM]HSO_4$, whose chemical structure is presented in Fig. 2, was applied as the catalyst..



Brønsted acidic IL, 1-methylimidazolium hydrogen sulfate, $[HMIM]HSO_4$, chemical structure.

XI. Materials and Methods

A. Materials

The feedstocks used were a waste cooking oil (WCO) sample, oleic acid (OA), tech 90%, obtained from ThermoFisher. IL 1-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

The derivatization of fatty acid methyl esters with BF_3 was used to determine the distribution of the fatty acids present in the raw materials for the production of biodiesel. First, there was a derivatization, i.e. the transformation of triglycerides and fatty acids present in the sample in methyl esters and subsequent identification of these compounds by gas chromatography (GC).

In a 20 mL flask, it was added 50 mg of sample and 2.5 mL of KOH methanolic solution (0.5 M). Later, the flask was closed and placed in an oven at 90 °C for 10 min. After this period, it was withdrawn from the oven and let to cool. Then, in the flask at room temperature, 2 mL of BF_3 in methanol solution (14%) was added. The flask was again closed and placed in an oven at 90 °C for 30 min. After that period, it was withdrawn from the oven and let to cool to room temperature. Then, 3 mL of internal standard (methyl heptadecanoate) was added under a vortex for homogenization. Afterwards, 2 mL of a saturated solution of sodium chloride (NaCl) was added under vortex again. Subsequently, the sample was centrifuged for 5 min at 3000 rpm for the total separation of the phases. After centrifugation, it was withdrawn 2 mL of the upper stage and added to a 4 mL vial. It was added anhydrous sodium sulfate in enough quantity to remove all moisture GC analysis was then performed for fatty acids characterization present in the sample.

C. Reaction

Ionic liquid, oleic acid, waste cooking oil and methanol were added, 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 stirring and automatic temperature control, and a 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 at 4 °C for a period of 20 h, and then subjected to centrifugation at 3000 rpm for 20 min. until a complete separation of phases is reached. Both splitted phases were stored in flasks and kept in a fridge for further analysis.

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 [8]). 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 following equation:

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

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 FAMEs (Fatty Acid Methyl Esters) content in biodiesel samples, in compliance with the European Standard EN14103/2003 [9]. All analyses were carried out on a Varian 3800 GC, equipped with a Supelcowax 10 column (30m×0.25mm×0.25µm). The GC analysis were performed 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 till 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 a 37 FAME compound mix analysis obtained in the GC Shimadzu system with the retention times of a 37 FAME compound mix analysis published by Supelco [10] 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 [8].

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

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. Only the methyl esters which showed a contribution to the total content higher than 1% were considered.

F. Experimental Design

In order to optimize the process and determine the levels of the factors that present the best performance for the response variables, it was adopted a response surface methodology (RSM). This methodology is based on mathematical and statistical techniques for the polynomial fit of the experimental data and so describes the behavior of factors and allows the establishment of statistical predictions [11].

For the application of RSM, an experimental design was generated to represent a set of experiments through the construction of a matrix of different combinations between the levels of the studied factors. The chosen Full Factorial Design 2^3, shows three factors with two levels and in duplicate: percentage of oleic acid incorporated (20% and 40%wt.), molar ratio oil/methanol (1:20 and 1:40) and reaction time (4 h e 8 h), as presented in Table I.

FACTORS AND LEVELS FOR THE FACTORIAL DESIGN.

Factor	Code	Level	
		-1	+1
incorporated oleic acid	A	20%	40%
molar ratio oil/methanol	B	1:20	1:40
reaction time	C	4 h	8 h

Thus, it was determined a combination matrix with 16 experiments. Table II describes the chosen parameters, the code applied and the respective levels, and the actual experimental values.

GENERAL DATA REGARDING THE FACTORIAL DESIGN.

Order	Code			Real values		
	A	B	C	incorporation of oleic acid (%)	molar ratio oil/methanol (mol/mol)	reaction time (h)
1	1	1	1	40	1:40	8
2	-1	-1	1	20	1:20	8
3	1	-1	-1	40	1:20	4
4	1	-1	-1	40	1:20	4
5	-1	1	1	20	1:40	8
6	1	-1	1	40	1:20	8
7	-1	-1	-1	20	1:20	4
8	-1	-1	-1	20	1:20	4
9	-1	-1	1	20	1:20	8
10	-1	1	-1	20	1:40	4
11	1	1	-1	40	1:40	4
12	1	1	-1	40	1:40	4
13	1	-1	1	40	1:20	8
14	-1	1	1	20	1:40	8
15	1	1	1	40	1:40	8
16	-1	1	-1	20	1:40	4

Each test was performed according to the generic procedure referred to in the *Reaction* section. Two responses were evaluated: the reaction conversion of the simulated oil, and the content in FAMEs of the produced biodiesel.

XII. 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 estimation of the composition. The acidity value obtained for the studied WCO sample was 1.56 mg_{KOH}/g_{oil} and for the OA sample, the acid value calculated 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 III and IV present the qualitative and quantitative characterization of each FAME relatively to the WCO and the OA, respectively. The FAME profile obtained for the WCO is consistent with the fatty acid profile typical of a sunflower oil. According to [12], the main fatty acids present in an oil of this type are C16:0 (5-8%), C18:0 (2-6%), C18:1 (15-40%) and C18:2 (30-70%).

CHARACTERIZATION OF FAME IN WASTE COOKING OIL.

Peak ID	Content (%)
C14:0	0.2
C15:0	0.1
C16:0	9.0
C16:1	0.1
C18:0	3.0
C18:1	27.4
C18:2	37.7
C18:3n6	0.4
C18:3n3	0.4
C20:0	0.2
C20:1	0.2
C20:5n3 + C22:0	0.5
C22:1	0.1
TOTAL	**79.3**

CHARACTERIZATION OF FAME IN OA.

Peak ID	Content (%)
C15:1	0.2
C16:0	1.7
C18:0	2.9
C18:1	87.3
C18:2	4.5
C18:3n6	0.8
C18:3n3	0.2

C20:1	0.4
TOTAL	**98.0**

B. Experimental Design

Table V presents the conditions applied to each test, specifying the design matrix, and the results obtained for the response variables. For each response, a different model was developed. The conversion (R_1) was determined by the drop between the initial acidity of the raw material (simulated oil) and the final acidity of biodiesel produced in accordance with the procedure described in section *Reaction Yield*. The FAME content (R_2) was determined by GC analysis of biodiesel produced in accordance with the procedure in section *Gas Chromatography*.

EXPERIMENTAL DESIGN, AND EXPERIMENTAL RESPONSES.

Order	Code			Experimental Response	
	A	B	C	Conversion (%)	FAME content (%)
1	1	1	1	93.96	32.8
2	-1	-1	1	90.85	17.9
3	1	-1	-1	74.89	29.1
4	1	-1	-1	76.87	30.9
5	-1	1	1	96.92	17.5
6	1	-1	1	87.09	36.7
7	-1	-1	-1	79.86	16.5
8	-1	-1	-1	81.51	15.2
9	-1	-1	1	93.91	18.2
10	-1	1	-1	89.34	14.9
11	1	1	-1	88.55	29.2
12	1	1	-1	87.76	29.8
13	1	-1	1	88.83	36.9
14	-1	1	1	96.41	16.9
15	1	1	1	96.80	34.8
16	-1	1	-1	89.41	14.8

The analysis of variance (ANOVA) makes it possible to compare the combination of factors with the variation of random errors associated with the generated responses. From this comparison it is possible to evaluate the significance of the proposed regression, considering the sources of imprecision and experimental inaccuracy [11]. The ANOVA results, presented in Table VI for the conversion response, was developed using the software Experimental Design 11.

ANOVA FOR THE CONVERSION RESPONSE WITH $\alpha = 0.05$.

Variation	Square Sum	DF	Average Squares	F_{calc}	F_{tab}	p-value
Model	700.43	6	116.74	74.63	3.37	3.65959×10^{-7}
A	34.42	1	34.42	22.00	5.12	0.0011
B	266.64	1	266.64	170.47	5.12	3.74136×10^{-7}
C	366.56	1	366.56	234.35	5.12	9.451448×10^{-8}
AB	11.32	1	11.32	7.23	5.12	0.0248
AC	0.0256	1	0.0256	0.0164	5.12	0.9010
BC	21.48	1	21.48	13.73	5.12	0.0049
Residual	14.08	9	1.56			
Lack of fit	0.0512	1	0.0512	0.0292	5.32	0.8686
Pure error	14.03	8	1.75			
Total	714.51	15				

DF – degrees of freedom

The significance of the regression is evaluated by the Fisher test (F test), which consists in the comparison between the F_{calc} and F_{tab}. If F_{calc} is greater than F_{tab}, there is significant difference between treatments in relation to the error level (α) applied. If F_{calc} is lower than F_{tab}, it is concluded that there are no significant differences between the treatments. Another possibility is the comparison of the p-value with α. If the p-value is lower than α, there is significant difference between the treatments, and if the p-value is greater than α, it is concluded that there are no significant differences between the treatments.

According to ANOVA for the conversion response, the model is significant, because the value of F_{calc} (74.63) is greater than the F_{tab} (3.37). The regression is statistically significant and, therefore, the model is well fitted to the data, with a confidence level of 95% ($\alpha = 0.05$). Regarding the lack of fit, the comparison between the F_{tab} (5.32) and the F_{calc} (0.0292) indicates the non-significance of the factor, because $F_{tab} > F_{calc}$, i.e. the model errors are due to random errors and are inherent in the system, and not a problem with the adjustment of data. So, the model is significant, while the lack of fit is not.

The significant factors are A, B, C, and interactions AB and BC. AC interaction is not significant.

The p-value determines the order of significance of the factors, that is, the smaller the p-value, the greater the influence of the factor on the outcome of the conversion response [1]. In this way, the descending order of significance of the factors is C (reaction time), B (molar

ration oil/methanol), A (incorporation of oleic acid), interaction BC, AB and AC (not significant).

The mathematical model (see equation 5) estimated to determine the relationship between the conversion response (R_1) of the esterification reaction and the studied factors obtained a coefficient of determination (R^2) of 0.9803, which represents a good fit to the statistical model.

$$R_1 = 88.31 - 1.47A + 4.08B + 4.79C + 0.8410AB + 0.0400AC - 1.16BC \quad (5)$$

From the equation one can observe that factor A shows a negative effect on the response, while factors B and C exhibit positive effects, represented by negative and positive signals assigned to each factor. The descending order of influence of factors is described as C > B > A, represented by the respective multiplicative coefficients for each factor. AC interaction has a non-significant influence in the response, represented by the corresponding low coefficient observed in the equation. On the other hand, interaction BC, with a negative effect, shows greater influence in the response than the positive effect AB interaction.

Considering the studied conditions, the factors and their respective levels, the best settings for the conversion response were determined. These optimal conditions with coded and real values are presented in Table VII.

OPTIMAL CONDITIONS FOR THE CONVERSION RESPONSE.

Factor Code	Factor	Level	Real value (%)
A	incorporation of oleic acid	-1	20 %
B	molar ratio oil/methanol	+1	1:40 (mol/mol)
C	reaction time	+1	8 h

In Table VIII it is presented the ANOVA results corresponding to the FAME content response, again developed using the software Experimental Design 11.

ANOVA FOR THE FAME CONTENT RESPONSE WITH $\alpha = 0.05$.

Variation	Square Sum	DF	Average Squares	F_{calc}	F_{tab}	p-value
Model	1109.94	6	184.99	257.21	3.37	1.52352×10^{-9}
A	1028.09	1	1028.09	1429.46	5.12	3.14374×10^{-11}
B	7.24	1	7.24	10.07	5.12	0.0113
C	61.67	1	61.67	85.75	5.12	6.7582×10^{-6}
AB	0.6869	1	0.6869	0.9551	5.12	0.3540
AC	10.89	1	10.89	15.14	5.12	0.0037
BC	1.37	1	1.37	1.90	5.12	0.2014
Residual	6.47	9	0.7192			
Lack of fit	1.74	1	1.74	2.95	5.32	0.1241
Pure error	4.73	8	0.5910			
Total	1116.42	15				

DF – degrees of freedom

From the ANOVA study, it is evident the significance of the model obtained for the FAME content response, through the comparison of F_{calc} (257.21) and F_{tab} (3.37). Since $F_{calc} > F_{tab}$ the significance of the model is established. The comparison of the p-value for the model (1.52×10^{-9}) with α (0.05), reaffirms the significance of the model. So, the regression is statistically significant and, therefore, the model fits well with the experimental data, with a confidence level of 95%. Furthermore, regarding the lack of fit, the comparison between the F_{tab} (5.32) and the F_{calc} (2.95) indicates its non-significance. Therefore, for the FAME content response, the model is significant, while the lack of fit is not.

The significant factors are A, B, C and the AC interaction. On the other hand, the AB and BC interactions are non-significant. In this way, the descending order of significance of the factors is A, C, AC interaction and B.

The mathematical model (see equation 6) constructed to relate the FAME content response (R_2) of the biodiesel produced and the studied factors obtained a coefficient of determination (R^2) of 0.9942, which also represents a good fit to the statistical model.

$$R_2 = 24.51 + 8.02A - 0.6727B + 1.96C - 0.2072\,AB + 0.8250\,AC - 0.2922BC \quad (6)$$

From the equation one can realize that factors A and C have a positive effect on the response, while the B factor has a negative effect. The descending order of influence of factors is described as A > C > B, and the model confirmed this feature by the values of the coefficients associated with each factor. AB and BC interactions have no significant influence in the response, represented by low coefficient assigned in the model. The interaction AC shows greater influence than the other interactions.

For the conditions studied, the factors and their respective levels, it was possible to determine the best settings which provided the highest FAME content in the biodiesel produced from the simulated oil. These optimal conditions with coded and real values are presented in Table IX.

OPTIMAL CONDITIONS FOR THE FAME CONTENT RESPONSE.

Factor Code	Factor	Level	Real value (%)
A	incorporation of oleic acid	+1	40 %
B	molar ratio oil/methanol	-1	1:20 (mol/mol)
C	reaction time	+1	8 h

XIII. CONCLUSIONS

The use of waste cooking oils makes it possible to decrease the cost of production of biodiesel, as this is a key feature for the final product to be competitive with petrochemical market. The oil used shows an acid value of 1.56 mg KOH/g and the determination of the FAME profile leads to the conclusion that it is similar to a used sunflower oil (9 % C16:0, 3 % C18:0, 27.4 % C18:1 and 37.7 % C18:2).

For both responses, conversion and FAME content, the three factors: (A) percentage of incorporation of oleic acid, (B) molar ration oil/methanol and (C) reaction time, showed statistical significance. For the conversion, the influence of the factors was C>B>A and thus, it was possible to determine the best experimental conditions in order to get the highest conversion: 20%wt. incorporation of oleic acid, oil/methanol molar ratio 1:40, 8 h of reaction time, reaction temperature of 90 °C, and 10%wt. of catalyst load, leading to a conversion of 96.6%. In relation to the content in FAMEs, the influence of the factors was A>C> B and the best conditions for the highest FAME yield (with 36.5%wt.) were: 40%wt. incorporation of oleic acid, oil/methanol molar ratio 1:20, 8 h of reaction time, reaction temperature of 90 °C, and 10% wt. of catalyst load. With a high conversion rate and a yield of FAME next to the amount of oleic acid added, it was concluded that the IL used, promoted essentially the esterification reaction, having demonstrated almost null influence on the catalysis of the transesterification reaction.

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