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SYNTHESIS AND APPLICATION OF PIRIDINIUM P-TOLUENESULFONATE AS CATALYST IN THE METHANOLIC TRANSESTERIFICATION REACTION OF BABASSU OIL

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ABSTRACT

The optimization process of biodiesel production using the ionic liquid (IL) piridinium p-toluenesulfonate [HPy][p-TSA] as catalyst in methanolic reaction with babassu oil is described. The ionic liquid efficiency in babassumethanolic biodiesel was verified by complete factorial design, response surface methodology (RSM) and the analysis of variance (ANOVA) was used to evaluate the statistical model. The ANOVA results show the 95 % confidence level, only the molar ratio MeOH:oil and temperature significantly affected the formation of methyl esters. The best reaction conditions in the process were in the molar ratio alcohol:oil 15:1, IL 2.0 % w/w, temperature 130 °C and 8 hours of reaction. The maximum conversion of the biodiesel with the piridinium p-toluenesulfonate was around 88.6 %.

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INTRODUCTION

The increasing use of fossil fuels such as petroleum and its derivatives has increased concern about environmental pollution and has aroused interest in other types of energy sources from less polluting renewable sources (Ugurlu, 2015). An alternative for that is the use of biodiesel clean-burning fuel currently being produced from different sources vegetable oils or animal fats. It is used as an alternative fuel to conventional petroleum diesel, mainly because biodiesel has advantageous properties such as renewable resources and biodegradable. The chemical structure of biodiesel molecule is almost entirely of fatty acid alkyl esters of long chain (Teo *et al.,* 2014) produced by the transesterification or esterification from methanolic (Shimamoto and Tubino, 2016) or ethanolic (Silva *et al.,* 2016)routes in the presence of basic and acid catalysts. However, the conventional preparation of a biodiesel uses acids as catalysts which lead to many problems such as: the use of higher molecular chain alcohols which are slightly active in the reaction medium, high pressure and temperatures, long time of reaction and possibility of corrosion of the reactor (Assadi *et al.,* 2016; El-Galad *et al.,* 2016).Ionic liquid catalysts are an alternative for the production of biofuels, which have been identified as excellent catalysts in organic synthesis such as transesterification of fatty acids since these new catalysts can be easily recovered and reused, besides minimizing the amount of organic solvents and also generating less amount of by-products in such (Das et al., 2014). Ionic liquids are salts with low melting point (<100 °C), which show many advantages including low vapor pressure, low flammability (Chennuri andGardas, 2016), low toxicity and are recyclable (Wu *et al.,* 2014). The properties of ionic liquids can be easily modified by changing the nature of the cation or anion, providing the application in various types of reactions, in addition, the careful selection of the cation and anion may lead to a high solvation capacity making them sometimes *green* catalysts (Wei *et al.,* 2012). Ionic liquids have been widely used for many research groups in transesterification reactions of vegetable oils for biodiesel conversion. The 1-butanesultonepyridinium trifluoromethanesulfonate [BSPy] [CF_3SO_3] was used in the transesterification of Jatropha oil and obtained high catalytic activity in the conversion to esters with an yield equal to 92 %, molar ratio methanol:ratio:catalysts 1:10:0.12, temperature 100 °C, time 5 hours and the catalyst was reused for seven reaction cycles without losing its effectiveness in the reaction(Li et al., 2010).Subrata Das et al. (2014)employed the IL 1-n-butanesultone-3-methylimidazolium chloride ([BSMIM]Cl) in two stages using Jatropha oil, in which esterification followed by 1.3 % KOH catalyzed transesterification, obtaining 93.9 % of esters under the following conditions: molar ratio 12:1, 10.0 % amount of catalyst, temperature 70 °C during 6 hours and the catalyst was reused by four reaction cycles. In another work, the choline chloride·$2ZnCl_2$ was applied in transesterification of soybean oil and obtained conversion rate of 54.52 %, molar ratio of methanol to oil of 16:1 with addition of 10 % catalyst at temperature 70 °C for 72 hours.[16] The ionic liquid 1-butyl-3-methylimidazolium hydroxide ([Bmim]OH) in glycerol trioleate transesterification and obtained 87.2 % yield of methyl ester. [Bmim]OH can be easily recovered and reused six times without intense decrease in ester yield (Zou et al., 2012). Yanfei *et al.* (2013) used the ionic liquid [$(CH_3CH_2)_3N(CH_2)_3SO_3H$]$HSO_4$ in soybean oil transesterification. The Central Composite Rotational Design (CCRD) and response surface methodology (RSM) was used to evaluate the influence of variables molar ratio methanol: oil, amount of catalyst and reaction time in the optimization process of biodiesel production. The optimum conditions for the transesterification of soybean oil were methanol:oil 14:1, amount of catalyst 4 %, reaction time 8.7 h, and reaction temperature 120 °C and yield of biodiesel 94.8 %. In the present work, we describe the preparation of the ionic liquid (IL) piridinium*p*-toluenesulfonate, [HPy] [*p*-TSA], and its use as acid catalyst in the methanolic reaction with babassu oil, a vegetable oil extracted from the seeds of the babassu palm (*Attaleaspeciosa*), found in the Amazon region of South America. Furthermore, the experimental design was applied in order to optimize three factors, molar ratio alcohol:oil,amount of catalyst and temperature in the biodiesel production.

MATERIALS AND METHODS

Synthesis of IL p-toluenesulfonic pyridinium [HPy][p-TSA]: The *p*-toluenesulfonic acid (0.12 mol) (Sigma; 98.5 %), was mixed in pyridine (0.12 mol)(J.T.Baker; 99.98 %). The mixture was refluxed with constant stirring for a period of 10 hours at 80 °C. The compound is recrystallized at room temperature. The solid which precipitated it filtered, washed five times with petroleum ether (Quimex; 99.5%)to remove unconverted reagents and dried under vacuum at 120 °C, the desired product was obtained. Yield: g (76 %). Selected IR bands (ν_{max}/cm^{-1}): 3483 m, br (OH), 3415 m, br (NH), 1624 m (C=N), 1541, 1489 (C=C), 1190 vs (SO_{asy}), 1120 vs (SO_{sy}), 684 s (Aromatic, oop bend). ^{1}H NMR (D_2O, ppm): 2.27 (s, 3H, CH_3), 7.24 (d, J = 8 Hz, 2H, *p*-tsa), 7.56 (d, J = 8 Hz, 2H, *p*-tsa), 7.96 (t, J = 8 Hz, 2H, py), 8.51 (t, J = 8 Hz, 1H, py), 8.66 (d, J = 8 Hz, 2H, py).

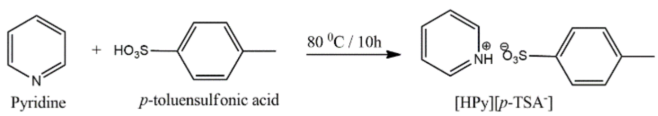
Synthesis Babassu Methylic Biodiesel (BMB) using the [HPy][p-TSA]: The babassu oil (Maita Factory, Brazil) was dried initially in an oven at 110 °C for four hours to remove moisture. After that it was placed in desiccator until reaching room temperature (25 °C). 50.0 g of babassu oil, methanol (Synth 99.8%)in a molar ratio of 10:1-30:1, the ionic liquid concentration 1.0-2.0% were added to the high-pressure reactor (Parr model 4843), with temperature in the range of 130-200 °C and stirring of 500 rpm for 8 hours. The ester-glycerin mixture was distilled to remove the excess alcohol and after transferred to a separatory funnel and kept at rest for 24 hours. After this time the organic phases were separated and weighed. The crude biodiesel was purified and dried with addition of 2.0% w/w Talco USP(Cromoline; 96.0%) stirred for one hour and filtered. Methyl biodiesel of babassu was produced in optimized conditions and subjected to some physico-chemical tests for quality control according to the standards established by ANP nº 04/2012 (2016): acidity (AOCS Cd3d -63), kinematic viscosity (ASTM D 445), especific mass (ASTM D 4052) and ester content (CEN EN 14103).

Factorial Design 2^3: To assess the influence of variables on the yield of the transesterification reaction of the babassu coconut oil, a factorial design 2^3 with three variables was used. Then the results were evaluated by applying Response Surface Methodology (RSM) (Nascimento, 2009). The statistical treatment of the data and the graphics were analyzed by the computer program Statistica 10.0 and EXCEL (Microsoft Office Professional Plus 2010 – 14.0.4760.1000 (32 bits) version), using the non-linear estimation module to obtain an empirical equation (1) to interpret the experimental data. The variables were: molar ratio of alcohol:oil (x1), reaction temperature (x2) and percentage of ionic liquid (x3)shown in Table 2. The mass of the babassu coconut oil, reaction time and agitation used in all experiments were kept constant at 50.0 g, 8 hours and 500 rpm, respectively.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 + \beta_{111} x_1^3 \quad (1)$$

RESULTS AND DISCUSSION

Synthesis Ionic liquid p-pyridiniumtoluenesulfonate [HPy][p-TSA]: The ionic liquid pyridinium*p*-toluenesulfonate[HPy][*p*-TSA] was obtained through an ionic reaction resulting in a crystalline white solid, with percentage yield (76.0 %) as described in Scheme 1.



Scheme 1. Synthesis of the ionic liquid pyridinium p-toluenesulfonate

Catalytic tests for BabassuMethylic Biodiesel (BMB): Preliminary catalytic tests were carried out in order to make an initial assessment of the transesterification reaction of babassu oil through methylic route. The reactions were performed under fixed conditions for the following variables: 2 % IL, 16 hours of reaction, temperature 130-200 °C and molar ratio MeOH:oil 11:1. However, these tests allowed verifying the reaction profile depending on the used variables in the production of biodiesel process, regardless the complex interactions among the variables that affect the transesterification reaction mediated by ionic liquid. The increase of the temperature is an important parameter to obtain a higher ester concentration (Ab Rashida et al., 2014). At 170 °C low yield (71.4 %) was found, at 130 °C a decrease in esters content was verified (74.8 %) and at 165 °C the best yield (82.4 %) there is another increase, but not so significant in relation to the temperature of 200 °C (81.6 %). These levels are correlated with different variables, amount of catalyst and molar ratio that influenced the reaction yield. Based on the catalytic tests was performed an isolated reaction of 8 hours (83.6 %) and it was observed that the yield significantly influence esters. [HPy][*p*-TSA] showed relevant catalytic performance in the transesterification reaction of babassu oil throughmethylic route.

Characterization BabassuMethylic Biodiesel (BMB): The use of vegetable oils to produce biofuels is important, one of the parameters to be determined is the acid value, because the excess of free fatty acids can cause hydrolysis in the reaction, that is, saponification. A value less than 0.50 mg KOH g^{-1} of oil results in the elimination of the neutralization step, thereby reducing the purification steps. Regarding to BMB results shown in Table 1, it was observed that the acidity index, specific mass (ASTM D 4052) and kinematic viscosity (ASTM D 445) are within the established standards by ANP (2016) and there was a moderate conversion (88.6 %) to esters in process optimization.

Table 1. BabassuMethylic Biodiesel Characterization

Parameters	BMB	ASTM D EN/ISO
Acid value (mg KOH g^{-1})	0.42	0.50
Density 20 ° C (kg m^{-3})	880	850-900
Kinematic viscosity 40 °C (mm^2 s^{-1})	3.31	3-6
Ester Content (%)	88.60	96.5

Table 2. Matrix of the factorial design 2^3

Runs	Variables			Yield (%)
	x1 (MR)	x2 (T/°C)	x3 (C/%)	
1	-1(5)	-1(130)	-1 (1.0)	54.30
2	-1 (5)	-1 (130)	+1 (2.0)	85.40
3	-1 (5)	+1 (200)	-1 (1.0)	71.50
4	-1 (5)	+1 (200)	+1 (2.0)	85.40
5	+1 (15)	-1 (130)	-1 (1.0)	81.40
6	+1 (15)	-1 (130)	+1(2.0)	88.60
7	+1 (15)	+1 (200)	-1 (1.0)	73.00
8	+1 (15)	+1 (200)	+1 (2.0)	81.60
9	0 (10)	0 (165)	0 (1.5)	82.4
10	0 (10)	0 (165)	0 (1.5)	85.00
11	0 (10)	0 (165)	0 (1.5)	83.60

Table 3. ANOVA of the model for Production of BabassuMethylic Biodiesel with IL

Source of variation	Quadratic Sum	Degree of freedom	Mean Quadratic	F_{calc}.	F_{tab}.
Regression	841.377	6	140.230	4.609	0.220
Residual	121.688	4	30.420		
Lack of fit	118.301	2	59.151	34.931	0.053
Pure Error	3.387	2	1.693		
Total	963.065	14	231.496		
% explained variance:				0.874	
% maximum explainable variance:				0.996	

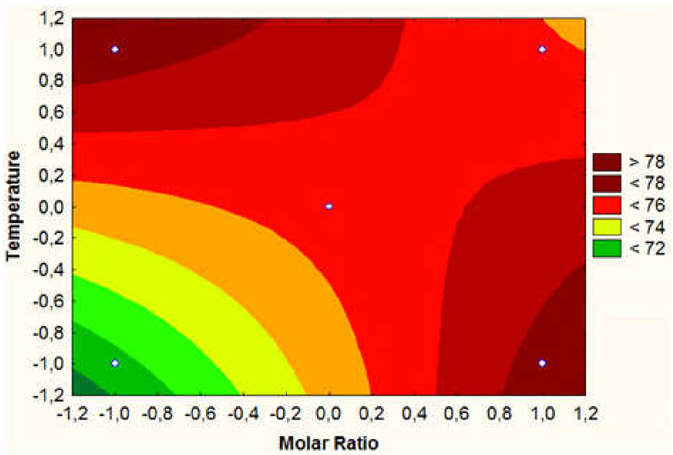


Figure 1:Surface shapeinteractiongraphiccatalyst versus molar ratioMeOH: oil for 8 hours (codedvariables)

Babassu Methylic Biodiesel (BMB) 2^3 Factorial Design: The optimization performed was based on the factorial design 2^3 with three replicates in central point for BMB and the independent variables, methanol molar ratio: oil (x1) (MR), temperature (x2) (T) and the IL content (x3) (C), as shown in Table 2. In the experiments was observed that when have been used larger amounts of catalyst in the transesterification reaction allows to obtain ester content in high yield (89 %) compared to other methods tested (Guo et al., 2013). It is possible that the yield of ester content was not very high because the new synthetic route of the catalyst [HPy^+*p*-TSA^-] is different from most IL already used in the transesterification process. In general, these IL are alkylated in order to increase the side chain and promote the entry of a Lewis or Bronsted acid, thus providing higher acidity and yield in the reaction (Man et al., 2012). However, it was verified that, in the absence of alkylation, the IL presented satisfactory catalytic activity in the biodiesel production. Another factor to consider is the adequacy of the working range in process optimization to obtain higher yields.

Response Surface Methodology (RSM): The Surface Response Method (SRM) is a statistical technique appropriate to maximize or minimize the response in the model adjustment and find the great goal. Many variables can influence the optimization process (Hajra et al., 2015). From the non-linear estimation module, a polynomial with the highest determination coefficient that represents the experimental points was obtained, as shown in Equation 2.

$$Y = 79.43 + 3.44MR + 0.29T + 7.66C - 4.14RT - 3.71MRC - 1.91TC + 3.39 \quad (2)$$

In the evaluation of the biodiesel production process conditions, it was observed that the ester content obtained was strongly influenced by the molar ratio MeOH: oil and the amount of IL and the temperature less influenced in the process. The interaction of the variables catalysts and the molar ratio MeOH:oil shown in surface contour (Figure 1), where it is observed that for a time of 8 hours, to obtain a better yield of 100 % it's necessary to extend the range of work, in other words, to move the region to larger values x1 (molar ratio) and x3 larger values (catalyst) for the model to adjust to the biodiesel production process. Increasing the 5:1 molar ratio to 15: 1 favored an increase in conversion from 54.3 to 88.6 %. The conclude that this enlargement range corresponds to the experiment conducted at temperature of 130 °C, the molar ratio MeOH:oil equal to 15:1 and IL 2.0 %. This behavior is different from other types of vegetable oils and methodologies applied (Caldas *et al.,* 2016). It's possible to observe in the surface contour graphic that the ester content get higher by increasing the amount of catalyst and the molar ratio methanol:oil. Previous works have reported that in the methanolysis the chemical properties of vegetable oil can be significantly influenced by the temperature and catalyst loading,[43] as well the amount of catalyst and the molar ratio has a positive effect in this process.[44] When the molar ratio and the amount of IL are increased from 5 to 15 and from 1 % to 2 % respectively, there is a relevant increase of about 34.3 % in the yield, and there is no evidence that this increase depends on the levels of other variables in the experimental range investigated.

Analysis of Residues: The analysis of residue is required to evaluate whether the model is adjusted. A suitable model should not leave a lot of residues; otherwise it would be considered as a bad model. An ideal model should have insignificant residues, in other words, the observed results would be the same as those expected (Nascimento, 2009). The coded values of the regression coefficients are given in Equation (2). The molar ratio variable MeOH:oil was statistically significant at the confidence level used α = 0.05 (5 %), confirming the significance of the results with 95 % confidence limit. The interaction effect of the molar ratio and catalyst showed a statistically significant positive effect, this means that the values should trend for high levels. There is no evidence of interaction of the temperature with the variable molar ratio. So, a robust model without a large variation for the content of methyl esters was obtained from babassu oil, in which 99.6 % of the points acquired experimentally are explained and adjusted to the model.

Analysis of variance (ANOVA): From the variance analysis (ANOVA) the statistic F value was determined; the results were valid in relation to the normal distribution of data, as shown in Table 3. The regression analysis was statistically significant, since the value calculated $F_{6.4}$ (4.609) is greater than the $F_{R,r}$ value tabulated (0.220), but the $F_{2.2}$ value (34.931) is high than $F_{faj,p}$ tabulated (0.053), evidencing that the lack of adjustment in relation to the pure error in the nonlinear model was statistically and presented a good linearity. The 34.931 value found in the F test of the MQ_{faj}/ MQ_{ep} ratio can be used as a variance estimative to assess the model adjustment in relation to those observations. The model was also expressed by the coefficient of determination (R^2), in which a value equal to 0.874 to the BMB yield in ester content was found, showing that this model explains 87.4 % of the variance, and it was possible to explain 99.6 % of these variables, it can be said that modeling was significant. The 87.4 % value, however, should not be compared to 100 %, because of the contribution due to pure error.

CONCLUSION

In this study, the IL pyridinium*p*-toluenesulfonate was synthesized and characterized by spectroscopic methods (FT-IR and ^{1}H NMR) and its structure was confirmed the formation its structure. By TG / DTA analysis it was verified that the ionic liquid is stable below 330 °C. The ionic liquid acid showed significant good catalytic performance for babassu oil transesterification, which is assigned to its Bronsted acidity. In the factorial design the effects of variables molar ratio MeOH:oil, temperature and concentration of IL on the ester content response to optimize the methanolysis process of babassu oil were evaluated. This methodology provided a more adequate study to maximize the most significant effect on yield of biodiesel production. The method helps to understand how factors can influence the process and statistically assess their combined effects. The ANOVA results show the 95 % confidence level, only the molar ratio MeOH:oil and temperature significantly affected the formation of methyl esters. The model shows good agreement between predicted and observed values in biodiesel production (R^2 = 0.874; a percentage of average deviation ± 1.69 %), demonstrating the validity of the regression analysis on process optimization and prediction a differentiated model. The best conditions in the optimization process were: molar ratio MeOH:Oil 15:1, reaction temperature of 130 °C and amount of pyridinium *p*-toluenesulfonate 2.0 %. The ionic liquid showed good catalytic activity for the transesterification reaction of babassu oil content of approximately 89.0 % esters. After the biodiesel synthesis of the viscosity measurement value was 3.31 $mm^2 s^{-1}$ and the acidity of 0.42 mg KOH g^{-1} which is in the range established by ANP.

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