ReGeo ISSN: 2177-3246

PYRIDINIUM P-TOLUENESULFONATE IONIC LIQUID: SYNTHESIS, CHARACTERIZATION, AND APPLICATION AS CATALYST IN ETHANOL-BASED TRANSESTERIFICATION OF BABASSU OIL

LÍQUIDO IÔNICO DE PIRIDÍNIO P-TOLUENOSULFONATO: SÍNTESE, CARACTERIZAÇÃO E APLICAÇÃO COMO CATALISADOR NA TRANSESTERIFICAÇÃO DO ÓLEO DE BABASSU À BASE DE ETANOL

LÍQUIDO IÓNICO DE P-TOLUENOSULFONATO DE PIRIDINIO: SÍNTESIS, CARACTERIZACIÓN Y APLICACIÓN COMO CATALIZADOR EN LA TRANSESTERIFICACIÓN BASADA EN ETANOL DEL ACEITE DE BABASÚ

https://doi.org/10.56238/revgeov17n8-174

Data de submissão: 04/07/2026 **Data de publicação:** 18/08/2026

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ABSTRACT

This paper describes the synthesis of the ionic liquid (IL) pyridinium p-toluenesulfonate [HPy][p-TSA], and its characterization as a catalyst in biodiesel production via ethanol-based transesterification of babassu oil. The IL was characterized by FT-IR, ^{1}H NMR, TG-DSC, and Single-crystal XRD. [HPy][p-TSA] showed an orthorhombic molecular structure and presented 76% w/w yield, and thermal stability up to 300 °C. Factorial design and response surface method (RSM) were applied to optimize and verify the efficiency of [HPy][p-TSA] in

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ethyl biodiesel production from babassu oil. The Analysis of variance (ANOVA) results showed that at a 95% confidence level, molar ratio EtOH: oil and temperature were the only factors significantly affecting ethyl esters' formation. The best reaction conditions for the process were found at molar ratio alcohol: oil 30:1, IL 1.0% w/w, temperature 200 °C, and reaction time of 8 hours. The maximum conversion rate of biodiesel with pyridinium p-toluenesulfonate was around 79%.

Keywords: Biodiesel. Babassu Oil. Ionic Liquid. Biofuel.

RESUMO
Este artigo descreve a síntese do líquido iônico (LI) p-toluenossulfonato de piridínio [HPy][p-TSA], e sua caracterização como catalisador na produção de biodiesel via transesterificação de óleo de babaçu baseada em etanol. O LI foi caracterizado por FT-IR, ^{1}H NMR, TG-DSC e DRX de monocristal. [HPy][p-TSA] apresentou estrutura molecular ortorrômbica e obteve rendimento de 76% p/p, com estabilidade térmica até 300 °C. Desenho fatorial e método de superfície de resposta (RSM) foram aplicados para otimizar e verificar a eficiência do [HPy][p-TSA] na produção de biodiesel etílico a partir de óleo de babaçu. Os resultados da Análise de Variância (ANOVA) mostraram que em um nível de confiança de 95%, a razão molar EtOH:óleo e a temperatura foram os únicos fatores que afetaram significativamente a formação de ésteres etílicos. As melhores condições de reação para o processo foram encontradas em razão molar álcool:óleo de 30:1, LI 1,0% p/p, temperatura de 200 °C e tempo de reação de 8 horas. A taxa máxima de conversão de biodiesel com p-toluenossulfonato de piridínio foi de aproximadamente 79%.

Palavras-chave: Biodiesel. Óleo de Babaçu. Líquido Iônico. Biocombustível.

RESUMEN
Este artículo describe la síntesis del líquido iónico (LI) p-toluenosulfonato de piridinio [HPy][p-TSA], y su caracterización como catalizador en la producción de biodiésel mediante transesterificación de aceite de babasú basada en etanol. El LI fue caracterizado por FT-IR, ^{1}H NMR, TG-DSC y DRX de monocristal. [HPy][p-TSA] presentó estructura molecular ortorrómbica y logró un rendimiento del 76% p/p, con estabilidad térmica hasta 300 °C. Se aplicaron diseño factorial y método de superficie de respuesta (RSM) para optimizar y verificar la eficiencia del [HPy][p-TSA] en la producción de biodiésel etílico a partir de aceite de babasú. Los resultados del Análisis de Varianza (ANOVA) mostraron que en un nivel de confianza del 95%, la relación molar EtOH:aceite y la temperatura fueron los únicos factores que afectaron significativamente la formación de ésteres etílicos. Las mejores condiciones de reacción para el proceso se encontraron en relación molar alcohol:aceite de 30:1, LI 1,0% p/p, temperatura de 200 °C y tiempo de reacción de 8 horas. La tasa máxima de conversión de biodiésel con p-toluenosulfonato de piridinio fue de aproximadamente 79%.

Palabras clave: Biodiésel. Aceite de Babasú. Líquido Iónico. Biocombustible.

1 INTRODUCTION

The energy matrix is shifting worldwide to address the alarming consequences of global warming and increasing greenhouse gas emissions in the last century. As a result, there has been a surging demand for new low-carbon, renewable energy sources.

In Brazil, adding biodiesel to the diesel produced in oil refineries has been an efficient strategy to reduce greenhouse gas emissions, and also contributes to the economic and social development of a region or country. Several studies have addressed biodiesel production in the last decades and many approaches have been presented to improve quality and use of alternative fuels. Chemical methods, such as pyrolysis and transesterification have been proposed to chemically alter vegetable oils and animal fats in order to better meet fuel industry expectations and requirements.

Transesterification is still the method of choice of most industries to produce biodiesel (Chimezie *et al.*,2022), rendering fatty acid methyl/ethyl esters (FAMEs/FAEEs) as its major components. Industries employ chemical catalysts to activate and accelerate the transesterification process. These catalysts can be classified as: homogeneous catalysts (acid or base), heterogeneous catalysts (solid acid or solid base), and enzymes (Zhao *et al.*, 2021).

Developing more efficient and cost-effective catalysts still poses a strategy challenge for the chemical industry as it includes energy, environment, and life sciences studies. Considering that most of the biodiesel production employs transesterification with homogenous catalysts, many scientists have focused on seeking solutions to some of their current issues, as they are difficult to recover and reuse – resulting in greater economic costs –, generate high amounts of waste and effluents that may be toxic to the environment, and present high saponification potential, which may cause severe corrosion and environmental problems (Orege *et al.*, 2022).

Ionic liquids (ILs) – non-molecular compounds composed exclusively of ions with melting point below 100 °C – appear in several chemical Fields due to their high catalyst activity, low inflammability and easy recycling. They may act as solvents or catalysts in biodiesel production (Andreo-Martínez *et al.*, 2020). Using ILs may contribute to overcome some limitations of the traditional methods.

ILs are commonly classified in four groups according to their cations, as follows: quaternary ammonium ILs, N-alkyl-pyridinium-based ILs, N-alkyl-N-isoquinolinium ILs, and 1-alkyl-3-methylimidazolium Ils (Liu *et al.*, 2012). Li *et al.* (2015) produced biodiesel using

Jatropha curcas L. oil and pyridinium ILs as catalysts. Results showed ester yield and triglycerides conversion rate of 88.5 e 95.1%, respectively. Ionic liquid [BSPy]CF_3SO_3 presented the best catalyst activity. Santos *et al.* (2021). Synthesized a series of pyridinium ILs based on p-toluenesulfonate and applied to babassu oil transesterification, obtaining FAME yield up to 88.6 % in the presence of [HPy][p-TSA]. Han *et al.* (2009) used residual oils, pyridinium IL containing SO_3H and FAME catalysts and got a 93.5% yield under ideal conditions. Qiu *et al.* (2016) prepared 4 Brønsted acidic ionic liquids (BAILs) and studied their catalyst properties in biodiesel production via FAME and coconut oil transesterification. Of all ionic liquids, [CyN1,1PrSO3H][Tos] presented the most efficacy, with a 98.7% yield. Tankov *et al.* (2022) studied reaction kinetics, thermodynamics and ideal reaction conditions to produce FAME biodiesel employing ionic liquids pyridinium hydrogen sulfate (PHS), pyridinium nitrate (PN), and 4-amino-1H-1,2,4-triazol-1-ium nitrate (ATN) as catalysts. They noted the superior performance of PHS in biodiesel production compared to nitrate-based ionic liquids since biodiesel synthesis rate depends on the acidity of the ionic liquids.

Pyridinium ionic liquids are nonvolatile, noncorrosive compounds immiscible with a lot of organic solvents that offer great catalyst activity and stability in water. As such, these compounds can facilitate the reaction and are more easily recovered (Chimezie *et al.*, 2022). The literature, however, still lacks a thorough discussion on pyridinium ionic liquids as catalysts for transesterification via FAEE.

In this research, the synthesis of the ionic liquid pyridinium p-toluenesulfonate [HPy][p-TSA] was studied, and the efficiency of this IL in the production of ethyl biodiesel from babassu coconut oil was assessed.

2 EXPERIMENTAL

2.1 REAGENTS AND EQUIPMENTS

The p-toluenesulfonic acid (Sigma; 98.5 %), pyridine (J.T.Baker; 99.98 %), petroleum ether (Quimex; 99.5%), ethanol alcohol (Synth 99.8%), Talco USP (Cromoline; 96.0%), were all used without further purification. Babassu oil commercial was purchased from Maita Factory (Brazil).

The FT-IR spectrum of pyridinium p-toluenesulfonate was measured on a Shimadzu IR Prestige-21 spectrophotometer in the region between 4000 and 400 cm-1 using potassium bromide (KBr) pellets as support. The 1H NMR spectrum of the IL was obtained by an Agilent 400/54 Premium Shielded 9.4 T spectrometer, operating at 399.8 MHz using a 30 mg/mL

solution in D2O. Chemical shifts are measured in ppm relative to TMS (internal reference). TG/DTA measurements were performed on a Thermal Analyzer Simultaneous DTG 60 brand Shimadzu. The conditions of the thermal measurements were: alumina crucible, weight of sample around 17 mg, nitrogen atmosphere with flow of 50 mL/min, heating rate 10 °C/min, at the temperature ranges 25-800 °C.

2.2. Synthesis of IL p-toluenesulfonic pyridinium [HPy][p-TSA] and, FT-IR,1H NMR, X-ray data

The methodology for synthesizing the ionic liquid p-toluenesulfonic pyridinium followed Santos *et al.* (2021). Single-crystal XRD analysis was carried out on a BRUKER APEX II Duo diffractometer using Mo-Kα radiation (λ = 0,71073 Å). Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with SHELXS97 and SHELXL2014. All non-hydrogen atoms were refined with anisotropic displacement parameters with SHELXL2014. Hydrogen atom positions were calculated for idealized positions and treated with the “riding model” option of SHELXL 2014. More details on data collection and structure calculations are contained in Table 1.

Table 1

X-ray structure data collection and refinement parameters

Formula	$C_{12}H_{13}NO_3S$
Fw	251.29
Temperature	133(2) K
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
***a* (Å)**	5.8633(2)
***b* (Å)**	8.8814(3)
***c* (Å)**	22.6510(6)
***α* (°)**	90
***β* (°)**	90
***γ* (°)**	90
V (Å^3)	1179.54(6)
Z	4
ρ_{calcd} (Mgm^{-3}) / μ(mm^{-1})	1.415
θ Range for data collection (°)	1.798 to 26.439
Reflections collected	-7<=h<=7, -11<=k<=10, -28<=l<=28
Reflections unique/ R_{int}	2430 / 0.0178
Data/restraints/param.	2430 / 0 / 155
Absorption correction	SADABS
Max/min. transmission	0.7454 and 0.7124
R_1 [$I > 2\sigma(I)$] / wR_2 [$I > 2\sigma(I)$]	R_1 = 0.0244, wR_2 = 0.0622
GOF on F^2, S	1.066
Largest diff. peak and hole (e.Å^{-3})	0.270 and -0.274
CCDC code	1511745

Source: Prepared by the authors.

2.3 ANALYSIS PHYSICO–CHEMICAL OF THE BABASSU COCONUT OIL (ATALLEA SSP.)

The physicochemical analysis of babassu oil was carried out in accordance with international standards AOCS (2009) and ASTM 6751 (2017), such as acidity, saponification index, percentage of fatty acids, humidity, kinematic viscosity, and specific mass. The babassu oil was purchased in the local market.

2.4 SYNTHESIS BABASSU ETHYLIC BIODIESEL (BEB) USING THE [HPY][P-TSA]

Initially, moisture was removed from the babassu oil by heating at 110 °C for 4 hours. After that, the reactions were carried out in a high-pressure reactor (Parr model 4843) with the addition of 50.0 g of babassu oil, ethanol in a molar ratio of 10:1-30:1, and IL (1.0-2.0%), with temperature in the range of 130-200 °C and stirring of 500 rpm for 8 hours. The ester-glycerin mixture was distilled, transferred to a separation funnel, and kept at rest for 24 hours. After this time the crude biodiesel was separated, weighed, purified, and dried (Santos et. al., 2021).

2.5 CHARACTERIZATION OF THE BIODIESEL FROM BABASSU COCONUT OIL

The physicochemical characterization and quality assessment of the biodiesel produced were carried out by ANP nº 04/2012 (ANP, 2023): acidity (AOCS Cd3d -63), kinematic viscosity (ASTM D 445), specific mass (ASTM D 4052) and ester content (CEN EN 14103).

2.6 FACTORIAL DESIGN 2³

A factorial design 2³ was applied to evaluate the statistically significant variables in obtaining ethyl biodiesel from babassu oil. The response surface methodology (MSR) was used to assess the data obtained. (Nascimento *et al.*, 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 shown in Table 2. The variables were: the molar ratio of alcohol: oil (x1), reaction temperature (x2), and content of ionic liquid (x3). 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.

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

Table 2

Factorial design for studying the effect of molar ratio of alcohol: oil, reaction temperature, and percentage of ionic liquid

Factors	**Levels**		
	-1	**0**	**+1**
Molar ratio (alcohol:oil)	10:1	20:1	30:1
Temperature (°C)	130	165	200
Ionic Liquid (%)	1.0	1.5	2.0

Source: Prepared by the authors.

3 RESULTS AND DISCUSSION

3.1. SYNTHESIS IONIC LIQUID P-PYRIDINIUM TOLUENESULFONATE [HPY][P-TSA]

The IL pyridinium p-toluenesulfonate synthesis reaction generated 76% yield of a white crystalline solid. As shown in Table 3, the IL melting temperature (72 °C) is related to the cations and anions size which results in a less efficient packing and consequently there is a decrease of the melting point and, in order for them to be liquid at room temperature, the IL

melting temperature should be close to the glass transition temperature (Tg) (Ohno, 2011) which does not occur with the IL pyridinium p-toluenesulfonate. Another feature of IL is the solubility in reaction medium, in which the p-toluenesulfonate anion $(p\text{-TSA})^-$ is solvated by polar protic solvents (water, alcohols) that can form hydrogen bonds, becoming a homogeneous catalyst in the reaction. On the other hand, the pyridinium cation is commonly solvated by dipolar aprotic solvents (acetone, acetonitrile, dimethyl sulfoxide -DMSO), which contain pairs of electrons that can act as "donors" in the IL solubilization (Hayes *et al.*, 2010). The conductivity of the IL depends principally of the mobility of the cation because the diffusion coefficient of the IL cation being larger than the anions. The [HPy][p-TSA] showed high ionic conductivity (10^{-1} S cm^{-1}) due to movement by diffusion, due to the cation's volume about their vibrational energies.

Table 3

Physical-chemical analysis of the pyridiniump-toluenesulfonate

Properties	Values
Melting point (°C)	72.00
Density (kg/cm^3)	111.92
Conductivity (Scm^{-1})	4.97
Acidity	3.75
Yield (w /w) g	17.17
Yield (%)	76.00
Solubility	H_2O, MeOH[a], EtOH[b], Acetone, ACN[c], DMSO[d]

Subtitle: aMeOH (methanol), bEtOH (ethanol), cACN (acetonitrile), dDMSO (dimethyl sulfoxide)
Source: Prepared by the authors.

3.2 CHARACTERIZATION OF PYRIDINIUM P-TOLUENESULFONATE [HPY][P-TSA] BY FOURIER TRANSFORMED INFRARED SPECTROSCOPY AND 1H NMR ANALYSIS

The FT-IR spectrum of [HPy][p-TSA] can be used to check the presence of the pyridine and of the p-toluene moieties. The strong bands at 1624 and 1541 cm^{-1} can be assigned, respectively, to the C=N and C=C stretching modes of the pyridinium ring. The broad band at 3415 cm^{-1} is attributed to the N-H bond stretching, while another broadband found at 3483 cm^{-1} indicates the presence of water due to the hygroscopic nature of the ionic liquid. Two bands of high intensity are observed at 1190 cm^{-1} and 1120 cm^{-1}, which can be assigned to asymmetrical and symmetrical stretching modes, respectively, of the sulfonate group ($-SO_3^-$), showing the incorporation of p-toluenesulfonate anion. The high-intensity band at 1350-1340 cm^{-1} expected for sulfonic acids was not observed, indicating the formation of a sulfonic salt with a high delocalization of π-electron density. Below 1120 cm^{-1} it is possible to observe

other types of vibrational modes with medium-high intensity related to the sulfonate group such as the scissoring vibration of the O-S-O and the out-of-plane bending movements of the para-substituted aromatic ring (Silverstein *et al.*, 2021). Therefore, the IR analysis shows interesting features which indicates the formation of the proposed ionic liquid.

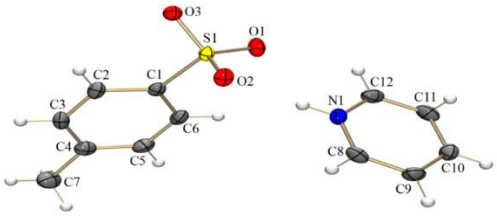
The ^{1}H NMR data of [HPy][p-TSA] (experimental section) shows the cation and the anion features of the IL in study. A signal characteristic of the methyl group related to the ion [p-TSA$^-$] is observed as a singlet peak at δ 2.27 ppm. The hydrogen atoms from the benzene ring are found in the characteristic region, appearing as doublets with chemical shifts in the range at 7.23 and 7.57 ppm. The signals related to the aromatic hydrogen atoms from the pyridinium ring appear at δ 7.96, 8.51 and 8.66 ppm. These data added to FT-IR results strongly indicate that the IL pyridinium p-toluenesulfonate was obtained. However, the NH hydrogen atom signal could not be found ambiguously.

3.3 STRUCTURAL STUDIES OF THE [HPY][P-TSA]

The crystal structure of the compound [HPy][p-TSA] was also studied by single-crystal X-ray diffraction. The Figure 1 illustrates the molecular structure of the compound [HPy][p-TSA], which crystallizes in orthorrombic crystal system and space group P212121. Selected bond lengths and angles are given in Table 4.

Figure 1

ORTEP Representation of the [HPy][p-TSA] with ellipsoids at the 50 % probability level



Source: Prepared by the authors.

The C(1)-S(1) has a single bond character, while the S(1)-O(1), S(1)-O(2) and S(1)-O(1) with values of 1.4537 (15), 1.4672 (15) and 1.4529 (14) Å, respectively, present a pronounced double bond characters. This occurs because of the resonance effect, making all the sulfonate group to present similar bond lengths. This fact was also indicated by the IR spectrum of the compound. The same happens inside the pyridine ring whose N1-C8 and N1-C12 bond distances are in the same order (1.331 (2) and 1.339 (2) Å, respectively).

Table 4

Selected bond lengths(Å) and angles (°) for [HPy][p-TSA]

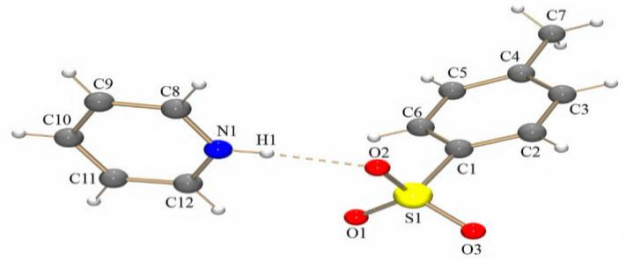
N1–C8	**1.331(3)**	**N1–C12**	**1.339(3)**
S1–O1	1.4537(15)	S1–O2	1.4672(15)
S1–O3	1.4529(14)	S1-C1	1.780(2)
C1–C2	1.388(3)	C8–C9	1.372(3)
O1–S1–O2	112.40(9)	O1–S1–O3	113.57(9)
O3–S1–O2	112.14(9)	O1–S1–C1	106.86(9)
O3–S1–C1	106.87(9)	O2–S1–C1	104.26(9)
N1–C8–C9	119.8(2)	C8–N1–C12	122.3(2)

Source: Prepared by the authors.

The pyridine nitrogen atom N1 is protonated, therefore the HPy^+ group is positively charged while the p-toluenesulfonate is negatively charged. The proton transfer from p-toluenesulfonic acid to the pyridine is confirmed by location of the acidic H atom on the Fourrier map, besides the fact that the hydrogen atom bonded to the nitrogen N1 is involved in an intermolecular hydrogen bond with the oxygen atom O2 of the sulfonate group forming a N-H···O interaction (see Figure 2). This hydrogen bond as well as the electrostatic attraction keeps the two units together in the solid state. The presence of the hydrogen bond between N1 and O2 slightly elongates the S(1)–O(2) in comparison to the S(1)–O(1) and S(1)–O(3) bonds. Overall the structure of the ionic liquid proposed by the data FT-IR and 1H NMR and confirmed by the X-ray analysis.

Figure 2

Hydrogen bonds observed in the crystal structure of the compound. [N(1)-H(1)···O(2) = 2.718(2) Å, N(1)-H(1)···O(2') = 158.6 º]



[N(1)-H(1)···O(2) = 2.718(2) Å, N(1)-H(1)···O(2') = 158.6 º].
Source: Prepared by the authors.

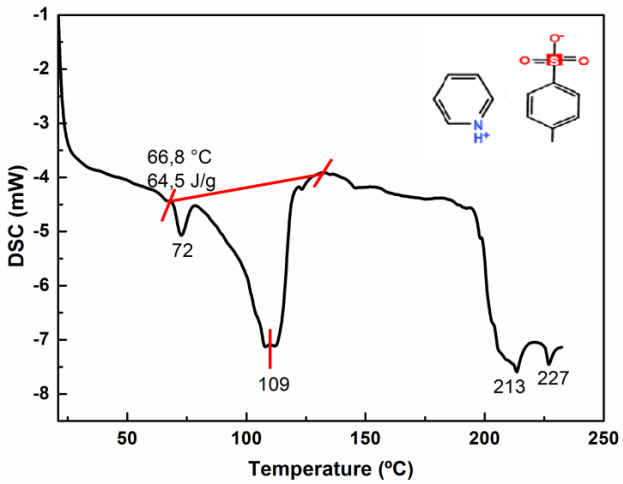
3.4 THERMAL ANALYSIS

The thermogravimetric curves of [HPy][p-TSA] are shown in Figures 3 and 4. The Figure illustrates the thermal properties varying as a function of temperature, therefore, the DTA curve (Figure 3) shows a broad signal with endothermic peak at 66 °C, which can be associated with fusion of the IL, elimination of adsorbed water and loss of 1.35% mass. At temperatures close to 250 °C, a considerable weight loss of about 70% was observed. Afterward the material loses weight until complete decomposition at the temperature of 331 °C showing an endothermic process (Figure 4). At the temperature of 109 °C the elimination

of the absorbed water molecules and volatile materials occur, causing a mass loss of 5.03%. In the temperature range 66.8-109 °C, endothermic melting peaks related to the compound are shown. The ionic liquid is thermally stable until 210 °C. This thermal stability is due to anion structure that has a significant effect on the composition of ionic liquid (Akçay *et al.*, 2014; Clough *et al.*, 2013).

Figure 3

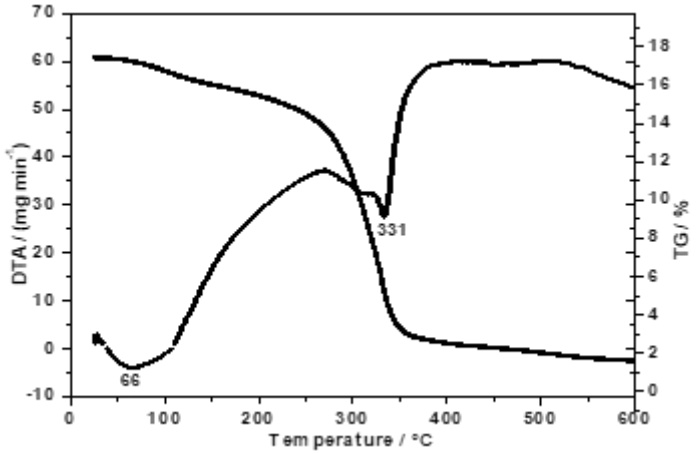
TG/DTA [HPy][p-TSA] thermogravimetric curve



Source: Prepared by the authors.

Figure 4

DSC IL [HPy][p-TSA] thermogravimetric curve



Source: Prepared by the authors.

3.5 CHEMICAL PHYSICAL ANALYSIS OF BABASSU OIL

According to the established quality standards for acceptability of vegetable oils (AOCS, 2009) it is important that acidity and humidity values are low, since high values are indicative changes that can limit their use in the biofuels production (Zheng *et al.*, 2013; Oliveira *et al.*, 2013). As shown in Table 5 the acidity value (0.27 mg KOH g^{-1} oil) and humidity (0.001%) are in accordance with the acceptable values for biodiesel production. When the acidity value is high, the fatty acids form, in alkaline medium, fatty acid salts (soap) which are responsible for emulsion formation during the biodiesel wash, therefore, the mass efficiency will be lower (Lee & Lee, 2014; Bi *et al.*, 2015). The presence of water in vegetable oil can promote oxidation (hydrolytic oxidation), however in a lower extent (Oliveira *et al.*, 2010). The peroxide index (7.18 meq kg^{-1}) was less than 10 meq O_2 1000 g^{-1} of oil, while the iodine index value was 12.31 g / 100 g^{-1} of oil. Those two measurements are related to oxidative degradation of oil. The highest number of unsaturation the more susceptible to both thermal and oxidative degradation the molecule will be, forming insoluble products and decreasing the ester content. The natural antioxidants of vegetable oils promote greater oxidation stability (tocopherols), however, they may be lost during by the refining process or by thermal degradation (Vaskova & Buckova, 2015).

Table 5

Babassu oil chemical physical characterization

Parameters	Babassu oil	Limits (AOCS/ASTM)
Acid value (mg KOH g^{-1})	0.27	0.3%
Peroxide index (meq.kg^{-1})	7.18	max. 10
Iodine index (g 100 g^{-1})	12.31	10-18
Humidity (%)	0.001	-
Density 20 ° C (kg.m^{-3})	921	903-924
Kinematic viscosity 40 ° C (mm^2 s^{-1})	35.96	-
Free Fatty Acid (%)	0.01	<2% oleic acid

Source: Prepared by the authors.

Another interesting parameter to be analyzed is the oil viscosity, which showed the value equal to 35.96 mm^2 s^{-1}. The viscosity is related to the length of the carbon chain and the grade of unsaturation (Giakoumis, 2013). The size of the carbon chain, the number of unsaturations present in the oil, the amount of catalyzer used in the reaction medium are features which can result in the increase of the viscosity (Amin *et al.*, 2016). The residual soaps as well as the unreacted glycerides (mono-, di- and triglycerides) and oxidative

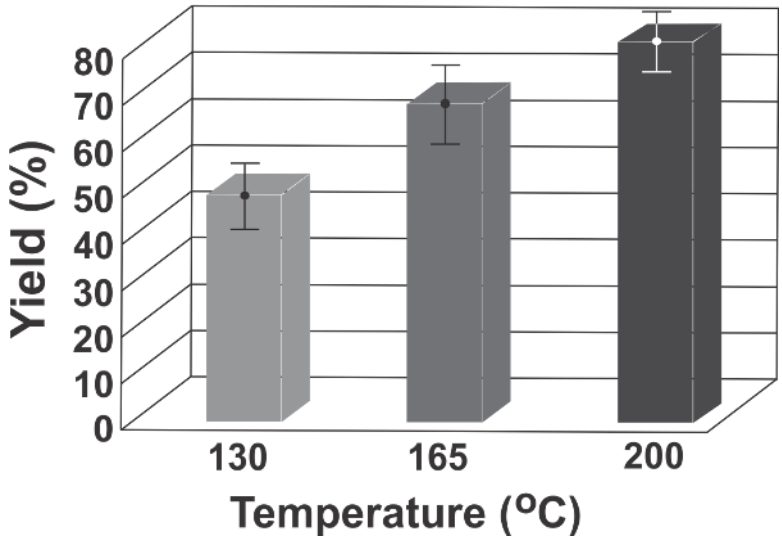
degradation products such as the presence of water, peroxides and low molecular weight carboxylic acids increase the oil viscosity affecting the reaction yield (Ayetor *et al.*, 2015).

3.6 CATALYTIC ESSAYS FOR BABASSU ETHYLIC BIODIESEL (BEB)

The results of the conversion to esters obtained with IL as a function of the temperature can be observed in Figure 5. The increase of the temperature is an important parameter to obtain a higher ester concentration (Ab Rashida *et al.*, 2014). At 130 °C a low yield was found (49.8 2.5)%, whilst at 165 °C a increase in esters content was verified (67.4 3.5)% and at 200 °C the best yield (76.5 4.0)%. Catalytic results are correlated with different variables like amount of catalyst and molar ratio that influence the reaction yield, thereby, [HPy][p-TSA] showed relevant catalytic performance in the transesterification reaction of babassu oil by ethylic route.

Figure 6

Babassu oil conversion in the transesterification reaction with ethanol using different temperatures (130, 165, 170 and 200 °C), nEtOH: noil = 11:1, amount of catalyst 2% (w / v), reaction time 16 hours



Source: Prepared by the authors.

Regarding to BEB results shown in Table 6, it was observed that the acidity index, specific mass (ASTM D 4052) and kinematic viscosity (ASTM D 445) are according to the established standards by ANP (2023).

Table 6

Babassu Ethylic Biodiesel Characterization

Parameters	BEB	ASTM D EN/ISO
Acid value (mg $KOHg^{-1}$)	0.27	< 0.50
Density 20 ° C (kg m^{-3})	879	850-900
Kinematic viscosity 40 °C (mm^2 s^{-1})	3.49	3-5

Source: Prepared by the authors.

3.7 BABASSU ETHYLIC BIODIESEL (BEB) 23 FACTORIAL DESIGN

The experimental design matrix (Table 7) presents the experimental conditions with three replicates at the central point and the results of the study of the optimization of the biodiesel production process catalyzed by ionic liquid.

Table 7

Matrix of the factorial design 2^3

Runs	Variables			Yield %)
	x1(MR)	x2 (T/°C)	x3 (C/%)	
1	-1(10)	-1(130)	-1 (1.0)	75.30
2	-1 (10)	-1 (130)	+1 (2.0)	76.70
3	-1 (10)	+1 (200)	-1 (1.0)	76.50
4	-1 (10)	+1 (200)	+1 (2.0)	73.30
5	+1 (30)	-1 (130)	-1 (1.0)	68.10
6	+1 (30)	-1 (130)	+1(2.0)	78.20
7	+1 (30)	+1 (200)	-1 (1.0)	78.70
8	+1 (30)	+1 (200)	+1 (2.0)	77.20
9	0 (20)	0 (165)	0 (1.5)	77.20
10	0 (20)	0 (165)	0 (1.5)	74.20
11	0 (20)	0 (165)	0 (1.5)	74.60

Source: Prepared by the authors.

The experimental conditions that presented the best yield of ester content were the reactions with the highest molar ratio alcohol: oil, around 79%, a moderate yield when compared to other methods tested (Guo *et al.*, 2013). Its 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 (Elsheikh *et al.*, 2011; Man *et al.*, 2012). However, this result demonstrates the potential for the application of non-alkylated IL in obtaining ethyl biodiesel.

3.8 RESPONSE SURFACE METHODOLOGY (RSM)

Using the response surface methodology, a non-linear estimation was carried out, generating a polynomial that represents the production process of ethyl biodiesel from babassu coconut oil (Hajra et. al.., 2015), as shown in Equation 2.

$$y = 75{,}46 - 113{,}03RM + 0{,}93T + 0{,}05C - 2{,}03RMT + 1{,}30RMC + 1{,}48TC + 113{,}87RM^3 + 5{,}31 \quad (2)$$

Evaluating the transesterification of babassu oil catalyzed by IL [HPy[p-TSA was observed that the ester content obtained was strongly influenced by the molar ratio EtOH: oil and the amount of catalyst less influenced in the process. The increase in the molar ratio 10:1 to 30:1 led to an increase from 73.3 to 78.7% conversion. It is possible to conclude that this enlargement range corresponds to the experiment conducted at temperature of 200 °C, the molar ratio EtOH:oil equal to 30:1 and IL 1.0%. This behavior is different from other types of vegetable oils and methodologies applied (Caldas *et al.*, 2016; Zanin *et al.*, 2013). There was an isolated assay with a greater quantity of catalyst and observed that the yield increased transesterification reaction in ethanolic babassu oil. We used the following reaction conditions: molar ratio ethanol:oil 30:1, the amount of ionic liquid 4%, temperature 200 °C, time of 8 hours and the result of the yield ethyl esters was very significant 89.7%.

Previous works have reported that in the ethanolysis the chemical properties of vegetable oil can be significantly influenced by the temperature (Velic˘kovic´ *et al.*, 2013), as well the amount of catalyst and the molar ratio has a positive effect in this process (Musa, 2013). When the molar ratio is increased from 10 to 30, there is a slightly increase of about 5% in the yield, and there is no evidence that this increase depends on the levels of other variables in the experimental range investigated.

3.9 ANALYSIS OF VARIANCE (ANOVA)

From the analysis of variance (ANOVA) the statistic F value was determined; the results were valid in relation to the normal distribution of data, as shown in Table 8. An ideal model should have insignificant residues, in other words, the observed results would be the same as those expected (Nascimento, *et al.*, 2009). The coded values of the regression coefficients are given in Equation (2). The molar ratio variable EtOH:oil was statistically significant at the confidence level used α = 0.05 (5%), confirming the significance of the results with 95% confidence limit. So, a robust model without a large variation for the content

of ethyl esters was obtained from babassu oil, in which 93.9% of the points acquired experimentally are explained and adjusted to the model.

Table 8

ANOVA of the model for Production of Babassu Ethylic Biodiesel with IL

Source of variation	Quadratic Sum	Degree of freedom	Mean Quadratic	$F_{calc.}$	$F_{tab.}$
Regression	76.375	7	10.910	2.848	8.887
Residual	11.492	3	3.831		
Lack of fit	11.448	1	11.448	4.315	18.513
Pure Error	5.3067	2	2.653		
Total	87.867	10	8.787		
% explained variance:			0.869		
% maximum explainable variance:			0.939		

Source: Prepared by the authors.

The regression analysis was statistically significant, since the value calculated $F_{7,3}$ (2.848) is lower than the FR,r value tabulated (8.887), but the $F_{1,2}$ value (4.315) is smaller than FLa,p tabulated (18.513), evidencing that the lack of adjustment concerning the pure error in the nonlinear model presented a good adjust. The value found in the F test of the MQfaj /MQep ratio (Fcal = 4.31) can be used as a variance estimative to assess the model adjustment in relation to those observations. Another way to evaluate the fit of the model is the coefficient of determination (R^2), in which a value equal to 0.869, showing that this model explains 86.9% of the variance, and it was possible to explain 93.9% of these variables, it can be said that modeling was significant. The 86.9% value, however, should not be compared to 100%, because of the contribution due to pure error.

4 CONCLUSIONS

The IL pyridinium p-toluenesulfonate was synthesized and its structure was confirmed using a set of analytical methodologies (FT-IR, ^{1}H NMR, TG-DSC, Single-crystal XRD etc.). The IL 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 EtOH:oil, temperature and concentration of IL on the ester content response to optimize the ethanolysis process of babassu oil were evaluated. This methodology provided a more adequatestudy 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 EtOH:oil and temperature significantly affected the formation of ethyl esters. The model shows good agreement between predicted and observed values in biodiesel production (R^2 = 0.869; a percentage of average deviation ± 2.65%), 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 EtOH:Oil 30:1, reaction temperature of 200 °C and amount of pyridinium p-toluenesulfonate 1.0%. The ionic liquid showed good catalytic activity for the transesterification reaction of babassu oil content of approximately 79.0% esters. After the biodiesel synthesis of the viscosity measurement value was 3.49 $mm^2s^{-1}$and the acidity of 0.27 mg KOH g^{-1} which is in the range established by ANP.

ACKNOWLEDGEMENTS

We thank CNPq, CAPES, FAPESP (Grant 2009/54011-8) and FAPEMA Universal (Grant 2015/00366) for supporting this work.

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