Article:

Lourenço, VA, Nadaleti, WC, Vieira, BM et al. (1 more author) (2021) Investigation of ethyl biodiesel via transesterification of rice bran oil: bioenergy from residual biomass in Pelotas, Rio Grande do Sul - Brazil. Renewable and Sustainable Energy Reviews, 144. 111016. ISSN 1364-0321

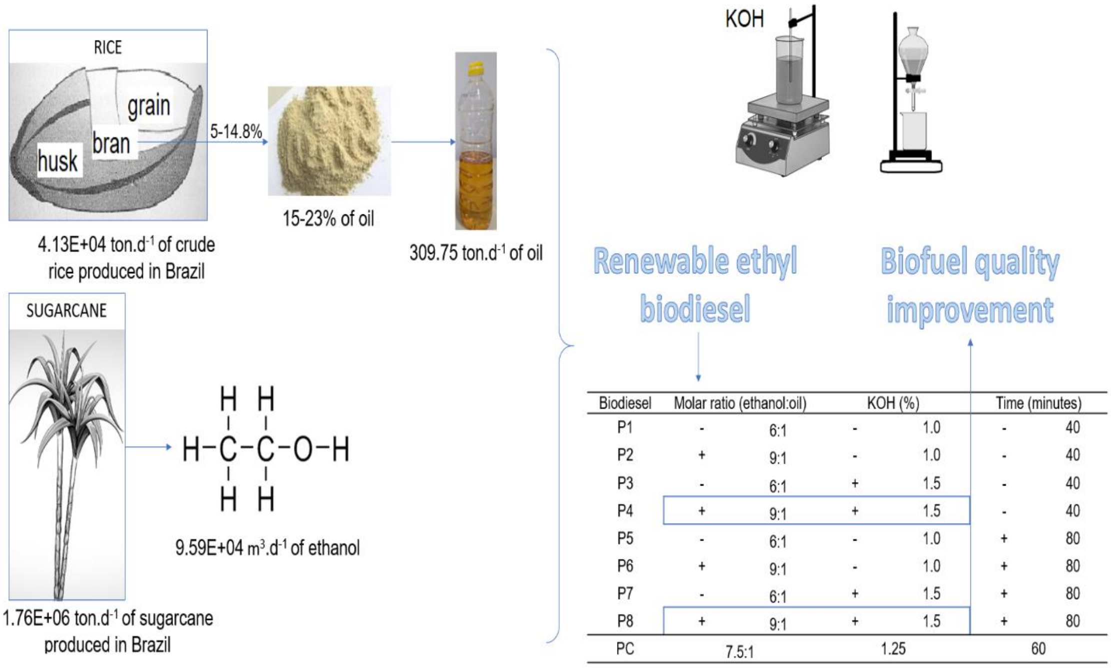
https://doi.org/10.1016/j.rser.2021.111016

Investigation of ethyl biodiesel production via transesterification of rice bran oil

Vitor Alves Lourenço[a]; Willian Cézar Nadaleti[a]; Bruno Müller Vieira[a],Hu Li[b]

[a]Engineering Center, Post-Graduation Program in Environmental Sciences, Federal University of Pelotas, Brazil
[b]School of Chemical and Process Engineering, University of Leeds, UK

GRAPHICAL ABSTRACT



Biodiesel	Molar ratio (ethanol:oil)		KOH (%)		Time (minutes)	
P1	-	6:1	-	1.0	-	40
P2	+	9:1	-	1.0	-	40
P3	-	6:1	+	1.5	-	40
P4	+	9:1	+	1.5	-	40
P5	-	6:1	-	1.0	+	80
P6	+	9:1	-	1.0	+	80
P7	-	6:1	+	1.5	+	80
P8	+	9:1	+	1.5	+	80
PC	7.5:1		1.25		60	

ABSTRACT

The energy sector in Brazil produces liquid biofuels as bioethanol and biodiesel. The most common technique to produce biodiesel is the transesterification of oils extracted from biomass. Rice processing generates grain bran, an agricultural residue. Brazil is one of the main countries that produce this grain. Therefore, the objective of this study was to produce a renewable biofuel using vegetable oil from grain bran via homogeneous basic transesterification. There are only three experimental studies reported in the literature on the production of biodiesel from rice bran oil via alkaline transesterification. Furthermore, the studies do not include results regarding biodiesel acidity, iodine, saponification and moisture content. Although potassium hydroxide (KOH) is the most commonly deployed alkaline catalyst in industrial biodiesel production, there are no reports regarding ethyl biodiesel production using rice bran oil with this catalyst. Therefore, this study applied a factorial arrangement in the experimental phase to produce ethyl biodiesel from rice bran oil using KOH as a catalyst on transesterification. The factors including reaction time, alcohol/oil molar ratio and amount of catalyst allowed to determine the best conditions for biodiesel production. To determine the viability of the biodiesel production, it was necessary to analyze the main parameters required by the national standards, which were kinematic viscosity, iodine index, acidity index, saponification index and moisture. All the yielded biodiesel were complied with the standards of ANP, ASTM and EN, except kinematic viscosity, which ranged from 8.061 to 22.791 mm²s^{-1}. According to the conditions of the factorial arrangement, the calculated kinematic viscosity indicated the need to raise the proportion of catalyst and/or the molar ratio between ethanol and alcohol. The lower kinematic viscosity, around 8-9 mm²s^{-1}, occurred with 1.5% catalyst and, in general, with molar ratio 9:1. These results suggest that future studies could explore the production of high-quality ethyl biodiesel using rice bran vegetable oil. According to the results, it represents a viable possibility to produce fully renewable and sustainable biodiesel within the socio-economic, environmental and agricultural context in Brazil.

Keywords: Transesterification; ethyl biodiesel; rice bran; biofuel.

1. Introduction

Hydroelectric power plants represent about 70% of the renewable energy production in Brazil. However, despite high energy efficiency, such power plants cause several environmental concerns [1]. Moreover, an increase in the diversification of the Brazilian energy grid would be both environmentally and socioeconomically advantageous [2]. The development and use of biofuels can supply bioenergy in solid, liquid or gaseous forms for different uses [3,4].

Currently, the production of bioethanol and biodiesel uses different agricultural raw materials of oilseed and leguminous crops [4,5]. The most common technique to produce biodiesel is the transesterification of oils extracted from biomass. This approach ensures that biofuels acquire similar characteristics to diesel oil [6]. During the transesterification, a reaction between triglycerides in the raw material and short-chain alcohols produce methyl esters or ethyl esters of Fatty Acids (FA) and glycerol [7,8]. In this reaction, the use of catalyst is important to increase the reaction efficiency [9].

The industrial production of biodiesel gmostly uses fossil methanol, as production or availability of ethanol is low in most countries. Thus, the production using methyl transesterification becomes cheaper. In Brazil, the industrial production of biodiesel is also carried out using methanol of fossil origin. However, this scenario does not match the national reality, as the country has an internal supply of renewable ethanol for the production of ethyl biodiesel. The country has about 377 ethanol plants [10] and produced more than 35 million cubic meters of fuel in 2019 [11]. However, according to the literature, research on the optimization of ethyl biodiesel production from different raw materials is scarce [12]. Taking it into consideration, the use of methanol is even more financially advantageous, due to its low cost combined with its high production efficiency. Boz and Kara [13] observed a 96% conversion rate of methanol to methyl esters, while the conversion rate of ethanol to ethyl esters did not exceed 65% under similar transesterification reaction conditions. However, besides the lower toxicity , bioethanol is greatly available in Brazil and safeguards the production of a fully renewable fuel [14].

As a result of the mandatory requirement on the gradual increase in the concentration of biodiesel mixed with fossil diesel, biofuel production grows in the country. In the 2018, the production of biodiesel in the country grew by 24.7% in relation to the previous year, reaching the amount of 5,350,036 m^3 [15,16]. The socio-economic benefits of producing biodiesel in Brazil are due to the high production of raw materials for biofuel in the country [17], with the mostly used in the country being soybean oil and animal fat. The vegetable oils and the bovine tallow represent 77.7% and 18.8% of the national biodiesel production, respectively [18]. Therefore, the growing production of biodiesel in Brazil will result in an increase in the demand for soybeans. However, the uptake of planting areas for the cultivation of soybeans on national soil has caused several negative environmental impacts related to deforestation. Between 2001 and 2018, 21.5 Mha were deforested in the Legal Amazon and 202 Mha were burned, while the total soybean area increased from 14 Mha to 35 Mha [19].

The state of Rio Grande do Sul is the national leader in biodiesel production from soybean oil and bovine tallow. However, other crops could become potential sources of biofuel production, not only in this state, but throughout Brazil [20,21]. The great diversity of vegetable oils in Brazil combined with its high agricultural productivity highlights the potential of Brazilian biofuel production and the possibility of mitigating the growing use of land for the cultivation of soybeansRice processing provides the grain bran, a low-cost source of triglycerides for biodiesel production. Grain bran is a byproduct of cereal processing or an agricultural residue from the stages of peeling and polishing of the grain [22-25]. However, there are no reports about the production of biodiesel from this raw material on small or large scales.

The rice grain presents from 5% to 14.8% of bran [26-28] and the bran contains 15% to 23% of oil [25-29]. In the 2018/19 harvest period, the rice production in Brazil reached 12 million tons, of which 70.1% was from Rio Grande do Sul [30]. Thus, the possibility of a large biofuel production from the rice bran oil in the country, especially in Rio Grande do Sul, is evident.

According to Nadaleti and Przybyla [31], the potential for energy production from wastewater and rice husk of rice parboiling industries in Brazil can help achieve energy self-sufficiency of these industries through biogas and syngas. The authors highlighted the high energy potential of the sector — in addition to self-sufficiency, rice industries could generate surplus energy that can be made available for sale. However, the authors did not address the possibility of producing biodiesel from rice bran oil. Although a few studies [32-37] have already investigated the production of methyl biodiesel from this raw material, there are no reports in the literature for biodiesel production using ethanol and KOH as a catalyst.

Therefore, the aim of this study was to assess the possibility of production of a renewable biofuel using the vegetable oil from rice grain bran produced in the state of Rio Grande do Sul. This study applied a 2^3 factorial arrangement considering the lack of studies on the production of ethyl biodiesel from rice bran oil using KOH as a catalyst. The analysis was comprised of the variation in the reaction time (40 and 60 minutes), the molar ratio of alcohol to oil (6:1 and 9:1) and the amount of KOH (1.0 and 1.5%). The biodiesel purification and the moisture removing, as well as the analysis of kinematic viscosity, iodine index, acidity index, saponification index and moisture enabled production of a high-quality biofuel compliant to ANP, ASTM and EN standards.

2. Literature Review

Biodiesel is a liquid biofuel widely used in Brazil. The use of this biofuel shows social and environmental benefits derived from good utilization of biodiesel feedstocks in Brazil [4-6], making the country one of the pioneers in biodiesel production and ensuring an important role in the development and use of this energy source [17]. The transesterification reaction, the most common technique used to produce biodiesel, is a chemical reaction between raw material triglycerides and short-chain alcohols in the presence of a catalyst that results in FA (Fatty Acids) and glycerol esters [8,9,12,32,38]. Despite great scientific advancement in biodiesel production over the last three decades, industrial production has not undergone significant changes in its mechanism [33]. On an industrial scale, biofuel production continues to be carried out through the transesterification of vegetable oils using homogeneous catalysts [33,39].

In general, the catalysts deployed are alkali metal hydroxides and alkoxides [40] such as sodium hydroxide (NaOH) and potassium hydroxide (KOH). The use of excess catalyst in the reaction leads to emulsion formation resulting in higher viscosity, while insufficient amounts hinder the catalyst capability to increase the conversion efficiency of the reaction [41,42-47]. According to Nadaleti [48], the yield of biodiesel depends on the type of catalyst, the source of triglycerides and the other parameters involved in the reaction.

In the transesterification reaction, triglycerides or triacylglycerols present mainly in the composition of oils, react with short-chain alcohols generating esters and glycerin [23,22,49-51]. The reaction involves three consecutive and reversible steps; one mole of ester is released at each step of the reaction [23,49-52]. According to Verma [53], the type of alcohol, the molar ratio between alcohol and vegetable oil, the type of catalyst and its concentration, temperature and reaction time are parameters which affect the transesterification reaction.

Studies indicate that increasing the temperature accelerated the transesterification reaction, resulting in higher yields [41,54-60]. Higher temperatures reduced oil viscosity and resulted in better oil-alcohol mixing and subsequent rapid separation of glycerol from biodiesel. However, an excessive increase in temperature may decrease yield as it may cause faster side reactions than the transesterification. Another important factor in the transesterification is the reaction time due to the reversible nature of the reactions involved in the transesterification [48]. The reaction equilibrium can occur at varying times according to the type of catalyst, alcohol and raw vegetable oils.

Due to the reversible nature of the reactions, the use of a surplus of alcohol is necessary to shift the equilibrium balance towards the formation of products and to favor the complete conversion of FA [14,41]. Thus, instead of the 3:1 alcohol-to-oil molar ratio, it is common to use a ratio ranging from 6:1 to 12:1 depending on the type of alcohol and oil used [62-64]. A low molar ratio of alcohol to oil may negatively affect the conversion of triglyceride to ester, while a higher molar ratio may decrease the yield [53].

Jain and Sharma [65] observed that an increase in methanol from 10% to 30% (v/v) led to an increase in the yield of biodiesel. However, a further increase in methanol resulted in a 90.6% drop in efficiency after its peak. The most popularly used short-chain alcohols for the transesterification reaction are methanol and ethanol, followed by propanol, butanol and amyl alcohol [22,66]. Methanol promotes higher reaction yield [22], lower alcohol consumption and greater separation of esters and glycerin when used under similar conditions to the others [32]. However, methanol is highly toxic, especially when compared to ethanol, an alcohol produced on a large-scale and from renewable sources in Brazil. Table 1 summarizes the advantages and disadvantages regarding the use of the two most common transesterification alcohols.

Table 1 - Advantages and disadvantages when comparing the use of fossil methanol and renewable ethanol in biodiesel production through transesterification

Alcohol	Advantages	Disadvantages
Fossil methanol	- Process consumption is about 45% lower; - Cost reduced by almost 50%; - Greater Reactivity; - Reaction time reduced by more than 50%; - Lower energy expenditure to promote reaction.	- Fossil product; - High toxicity; - Higher volatility; - It has invisible flame.
Renewable ethanol	- Consolidated production in Brazil; - Biodiesel with higher cetane content and higher lubricity; - Produces 100% renewable fuel; - Generates higher occupation and income in rural areas; - Lower toxicity; - Lower volatility.	- Produces esters with higher affinity to glycerin; - Production costs can be 100% higher.

Source: Adapted ~~of~~ from Silva [32].

Despite the high toxicity of fossil methanol, all commercial biodiesel produced in Brazil is based on methyl source. This is due to the greater efficiency of methanol in the transesterification reaction and its low cost. However, the supply of fossil resources and oil-derived products is uncertain. In this regard, Li et al. [40] stated that the availability of ethanol for biodiesel production is promising. Ethanol can be easily produced from biomass due to the maturity of commercial production of bioethanol as a substitute for gasoline. Moreover, from an environmental point of view, the use of ethanol becomes attractive because it enables a fully sustainable and renewable Brazilian biodiesel production since ethanol from different biomasses is produced on a large scale in Brazil. Given this scenario, the use of ethanol to produce biodiesel, i.e. fatty acid ethyl esters, has high significance in societal and environmental benefits.

Results of studies using different approaches and raw materials for the production of ethyl biodiesel [67-71] suggest that as the molecular structure of ethanol and methanol differs only by a methyl group so that there is no big difference in the chemical and physical properties between methyl and ethyl biodiesels. However, studies reported advantages from the use of ethanol for biofuel production, such as reduced emissions of particulate matter and greenhouse gases, higher biodegradability and yield in terms of the mass ratio of FA and triglycerides [71]. Moreover, the literature indicates that ethyl FA has better fuel properties compared to methyl esters, although they hinder the separation and purification processes [72,73]. Thus, considering a more sustainable approach from an environmental and social point of view, this review suggests the adoption of ethanol for the transesterification reaction. Despite the high production of renewable ethanol in Brazil, its adoption on an industrial level to produce biodiesel is poorly explored. There are some studies on the use of alcohol in the reaction in the scientific literature, but with few types of vegetable oils.

2.1 Rice bran vegetable oil

Despite the possibility of biodiesel production from different sources (e.g. oilseeds, animal tallow, waste oil, microalgae and sewage treatment residues) [84,85], biofuel production is mainly from soybean in Brazil which accounts for more than 65% of the national production, followed by beef tallow [74]. This situation becomes alarming because deforestation and burning of the Amazon Rainforest and the Cerrado region has become recurrent due to the expansion of soy cultivation in the country. Other oilseeds with potential for biodiesel production are currently studied [21] and in this context, Brazil has a high exploratory potential due to its high agricultural productivity.

A case study in the rice parboiling industry in Brazil evaluated the energy potential from waste and effluents in the systems operating with a Combined Heat and Power (CHP) generator set, using hydrogen-rich syngas from rice husks and biogas from anaerobic effluent treatment [75]. The author determined a power generation potential to promote the self-sufficiency of the industry, with the possibility of selling the surplus. However, the study does not mention rice bran, which is produced largely from grain processing and can be a source of low-cost triglycerides for biodiesel production [22-25].

During the grain processing, an agricultural residue from the husking and polishing stages that are generally intended to produce animal feed is generated and termed rice bran [24,33]. Bran contains 15 to 23% of oil [25,29], consisting of about 68 to 71% triacylglycerols, 2 to 3% diglycerols, 5 to 6% monoglycerols and 2 to 3% Free Fatty Acids (FFA) [76]. The oil derived from rice bran is one of the most nutritious vegetable oils [22,32,34] and widely consumed in Asian countries, especially in the eastern region of Asia particularly for its benefits to human health [28,77,78], although the oil has no relevant human consumption in Brazil. Rice bran oil has approximately 80% unsaturated FA, which would make the oil prone to oxidation if natural antioxidants were not part of its composition [79-82]. The main difference between rice bran raw oil and most vegetable oils is the higher FFA content of rice oil due to active lipase [83]. Table 2 shows the composition of the oil for the FA present .

Table 2 - Composition of rice bran oil by FA

FA	(%)
C14:0 Myristic	0.1 - 2.4
C16:0 Palmitic	12.3 - 20.5
C16:1 Palmitoleic	0.1 - 0.2
C18:0 Stearic	1.1 - 3.0
C18:1 Oleic	37.1 - 52.8
C18:2 Linoleic	27.0 - 40.7
C18:3 Linolenic	0.5 - 2.3
C20:0 Archaic	0.3 - 0.7
C22:0 Behenic	0.5 - 1.0
C24:0 Lignoceric	0.4 - 0.9

Source: [84]

The enzymatic systems present in the bran allow triglycerides to be rapidly hydrolyzed in FFA leading to increased acidity [33]. Thus, extracting oil for human consumption must take place only when the acidity is low. The National Health Surveillance Agency of Brazil (ANVISA) [85] determines that the percentage of FFA in vegetable oils used for human consumption must be at most $0.3g.100g^{-1}$. In the study of Zullaikah et al. [29], rice bran showed a higher FFA percentage than ANVISA endorses even in the initial storage time, [85]. The restrictions associated with the human consumption of bran oil make biodiesel production through oil extracted from rice bran more appealing.

Sinha, Agarwal and Garg [25] found that rice bran vegetable oil produced biodiesel has excellent physicochemical properties because of its natural antioxidants. According to Evangelista [43], a high quality biodiesel also supports its use in blends with biodiesel from other oilseeds or mineral diesel. However, the literature review carried out about this topic revealed the absence of studies on the production of ethyl biodiesel from vegetable oil from rice bran. In addition, only a few studies were found on the production of methyl biodiesel from such raw material [32-37]. Although a large-scale production is present through the use of methanol, environmental and social demands make it necessary to investigate the production of ethyl biodiesel. Such research is fundamental for the transition from the use of methanol to ethanol in the biodiesel production chain.

Zaidel et al. [86] discussed in their review study the production of biodiesel from rice bran oil. The authors reported the use of methanol as the reaction alcohol. Hoang et al. [87] reviewed the rice bran oil biodiesel as a promising renewable alternative fuel to diesel, reporting only one study in the literature that uses ethanol as chain alcohol [88]. The authors used CaO as catalyst. Table 3 presents the literature data on the production of biodiesel from rice bran oil according to the alcohol and alkaline catalyst applied.

Table 3 – Literature data regarding rice bran biodiesel production alkaline catalysis

Alcohol	Molar ratio (alcohol:oil	Catalyst	Catalys (%)	Reaction (minutes	Temperatur (°C)	Referenc
Methanol	15:1	CaO	2.00	360	60	[89]
	35: 1	CaO	0.50	120	65	[35]
	6:1	$Fe_2(SO_4)_3$	3.00	180	60	[90]
	15:1	KI/Al_2O_3	5.00	480	reflux	[33]
	10:1	K_2CO_3/zeolit	4.00	180	65	[91]
	5:1	KOH	0.50	40	55	[92,93]
	6:1	KOH	0.50	48	55	[94]
	6:1	KOH	0.75	60	65	[95]
	6:1	KOH	0.90	60	60	[96]
	6:1	KOH	-	60	70	[97]
	30:1	Mg(Al)La	7.50	540	100	[98]
	9:1	$NaOCH_3$	0.75	45	60	[99]
	9:1	NaOH	0.75	60	55	[25]
	-	NaOH	1.00	60	55-60	[100]
	15:1	Na_2SIO_3	2.00	90	50	[101]
Ethanol	9:1	CaO	3.00	90	70	[88]
	9:1	NaOH	0.18	20	80	[102]

Based on the review carried out, two other studies show the use of-ethanol to produce ethyl biodiesel from air bran oil [102,103]. However, none of them have used KOH as catalyst. Kanitkar et al. [102] investigated the production of ethyl biodiesel from rice bran oil using NaOH as catalyst and the batch microwave system for the reaction. The authors evaluated the best conditions of biodiesel production by varying the temperature (60, 70, and 80 °C) and the reaction time (5, 10, 15 and 20 minutes). The kinematic viscosity varied from 5.09±0.120 at 6.73±0.226 mm^2.m^{-1}, values above 6 mm^2.m^{-1}, the maximum limit stipulated by the ASTM. The study used a two-stage process for ethyl biodiesel production. Firstly the authors used acid catalysis esterification and then proceeded a transesterification reaction using alkaline catalysis. The authors simultaneously dmployed Ca and NaOH as catalysts for transesterification. The study did not evaluate the biodiesel quality such as iodine index, saponification, acidity, and humidity as its focus was the evaluation of the yield and the rate of reactions..

3. Material and methods

A 2^3 factorial arrangement was designed to find the most suitable conditions for the biodiesel production from rice bran refined vegetable oil using

KOH as catalyst. The Central Point (PC) conditions were adapted from the Nadaleti's biodiesel production method [48]. The experiment had 8 combinations of molar ratios between the vegetable oil and ethanol, amounts of catalyst and time of heating and stirring, resulting in eight different biodiesels being produced (Table 4).

Table 4 – Experimental Delineation

Biodiesel	Molar ratio (alcohol:oil)	Catalyst (%)	Time (minutes)
P1	6.0:1	1.00	40
P2	9.0:1	1.00	40
P3	6.0:1	1.50	40
P4	9.0:1	1.50	40
P5	6.0:1	1.00	120
P6	9.0:1	1.00	120
P7	6.0:1	1.50	120
P8	9.0:1	1.50	120
PC	7.5:1	1.25	60

Nadaleti’s Methodology [48] was used to produce biodiesel from rice vegetable oil. The first stage of biodiesel production was to heat the vegetable oil in a magnetic stirrer at 80 °C. The next step was to add alcohol and catalyst previously homogenized to start transesterification reaction.. Next, it was necessary to activate the magnetic stirrer to agitate the medium (600 rpm). The last phase of production was to transfer the reaction product to a separating flask to remove glycerol after 3 hours of settling (Fig.1).

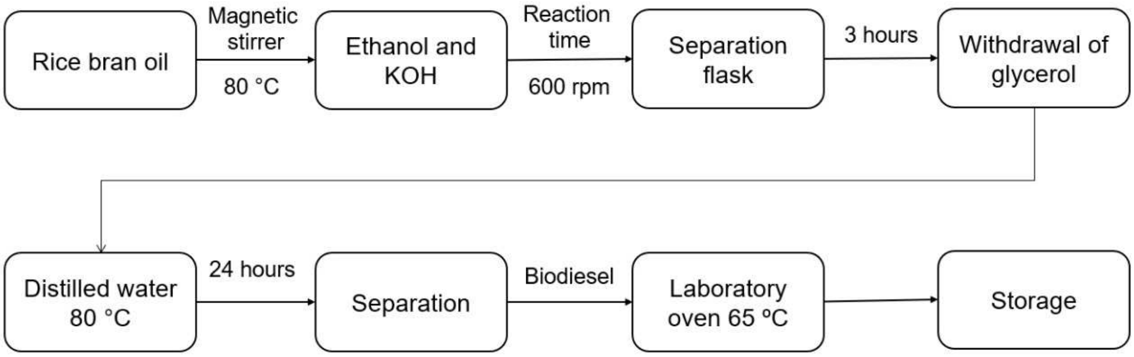


Fig. 1 – Stages of biodiesel production and purification.

After removing the glycerol, the next process was to add distilled water heated at 80 °C in the flask, in a proportion equal to one-third of the volume of oil used in the transesterification, to purify the biodiesel. After 24 hours, the last step was to remove the water and transfer the biodiesel to an oven at 65 °C for 12 hours to remove moisture for further analysis.

After the biodiesel production it was necessary to analyze the biofuel for kinematic viscosity (Eq. 1), iodine index (Eq. 2), and acidity index (Eq. 3) according to the ASTM standard methods [104-106]; saponification index (Eq. 4) according to the AOAC International method [107]; and moisture using desiccation loss at 105 °C, according to the Adolfo Lutz Institute's methodology [108] (Eq. 5). The equipment used to determine the Kinematic Viscosity at 40 ° C was a Saybolt Viscometer model Q288SR:

$$v = C * t \tag{1}$$

where:

v: kinematic viscosity values ($mm^2.s^{-1}$);
C: calibration constant of the viscometer ($mm^2.s^{-2}$);
t: measured flow time (s).

$$II = [(B - V)N \ * \ 12.69]/S \tag{2}$$

where:

II: iodine index ($gI_2.g^{-1}$);
B: $Na_2S_2O_3$ solution required for titration of the blank (mL);
V: $Na_2S_2O_3$ solution required for titration of the sample (mL);
N: normality of the $Na_2S_2O_3$ solution;
S: sample used (g).

$$AI = [(A - B) * M * 56.1]/S \tag{3}$$

where:

AI: acidity index ($mgKOH.g^{-1}$);
A: alcoholic KOH solution required for titration of the sample (mL);
B: volume corresponding to A for blank titration (mL);
M: concentration of alcoholic KOH solution ($mol.L^{-1}$);
S: sample used (g).

$$SI = [56.1 * (B - A) * N]/S \tag{4}$$

where:

SI: saponification index (mgKOH.g^{-1});

B: hydrochloric acid solution required for titration of the blank (mL);

A: hydrochloric acid solution required for titration of the sample (mL);

N: normality of the standard hydrochloric acid;

S: sample used (g).

$$M = (100 * N)/P \tag{5}$$

where:

M: Moisture (%);

N: loss of sample mass after drying at 105 °C (g);

P: mass of sample (g).

The last methodological approach was statistical analysis of the results using the IBM SPSS Statistics software with 5% significance level. To interpret the F Test in the Analysis of Variance, the null hypothesis was: none of the means of the triplicates of each point of the factorial arrangement differ statistically. If rejected, Tukey's test detected which means differed from each other.

4. Results and Discussion

The National Agency of Petroleum, Natural Gas and Biofuels (ANP) of Brazil published in 2014 the Resolution nº 45. This resolution enforced the quality control obligations to be fulfilled by agents responsible for biofuel commercialization in Brazil. Furthermore, this resolution stipulated that the characterization of biodiesel must be done following the Brazilian Association of Technical Standards (ABNT), the international standards of *American Society for Testing and Materials* (ASTM), the International Organization for Standardization (ISO) and the "*European Committee for Standardization*" (EN) [109]. Each standard has different maximum and/or minimum limits for the biofuel parameters. Table 5 shows the results obtained from the analyses performed in this study. The acidity index of the biodiesel produced varied from 0.165 to 0.348

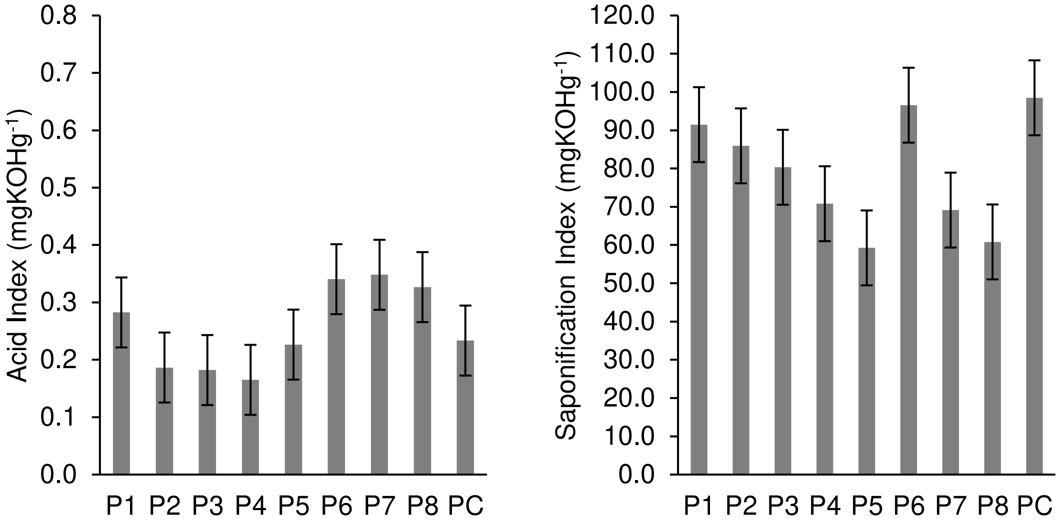
mgKOH.g^{-1}, while the saponification index and iodine index were around 60.813-96.553 mgKOH.g^{-1} and 84.925-104.691 gI$_2$.g^{-1}, respectively. The humidity ranged from 0.016 to 0.031%, with most biofuels having little moisture variation. While statistically, the lowest moisture occurred in points P1, P3, P4, P6, P7 and P8, the highest moisture occurred in P2, P3, P4, P5, P7 and P8. That is, the points that belong statistically to the group with the lowest results of moisture also belong to the group with the highest moisture. This occurs because the conditions that varied, according to the factorial arrangement, do not influence the moisture content of biodiesel. The entire process of purification and drying of biodiesel remained constant for all productions.

Table 5 – Results of the analyses. Equal letters in the same column do not differ statistically by Tukey test at 5% significance.

	AI (mgKOH.g^{-1})	SI (mgKOH.g^{-1})	II (gI$_2$.g^{-1})	Moisture (%)	v (mm^2.s^{-1})
P1	0.283^{ab}	91.473^{bc}	104.691^{d}	0.016^{a}	22.311^{d}
P2	0.187^{ab}	85.927^{abc}	084.925^{a}	0.031^{c}	11.175^{c}
P3	0.182^{ab}	80.322^{abc}	088.830^{ab}	0.021^{abc}	08.061^{a}
P4	0.165^{a}	70.797^{abc}	086.292^{a}	0.025^{abc}	08.120^{a}
P5	0.226^{ab}	59.247^{a}	101.560^{cd}	0.029^{bc}	22.791^{d}
P6	0.340^{b}	96.553^{bc}	095.290^{bc}	0.017^{a}	10.425^{bc}
P7	0.348^{b}	69.129^{ab}	103.662^{d}	0.020^{abc}	09.614^{abc}
P8	0.327^{ab}	60.813^{a}	102.515^{cd}	0.025^{abc}	08.789^{ab}

AI: Acidity Index; SI: Saponification Index; II: Iodine Index; v: Kinematic viscosity.

The ANP requires that the acidity index of biodiesel should be less than 0.8 mgKOHg^{-1}, while the ASTM and the EN have a maximum limit of 0.5 mgKOHg^{-1}. The lowest indexes were associated with the shortest reaction time used in the study. Although the highest result obtained in the analysis was 0.348 mgKOHg^{-1} in P7, the only point that differed statistically from this result was P4. All the biodiesels produced were within the limits of ANP, ASTM and EN (Fig. 2a); as shown in the graph. In fact, the results were significantly lower than the maximum allowed limit. High levels of acidity can lead to corrosion in storage tanks and engines. Moreover, this index provides data on oil status and product quality [110] and can be used to evaluate the level of biodiesel degradation [111]. An acidity Index of 0.13-0.50 mgKOHg^{-1} is reported in the literature for methyl biodiesel produced from rice bran oil [35,36], 0.14-0.18 mg mgKOHg^{-1} for soybean oil [40,67] and 0.45-0.60 mgKOHg^{-1} for bovine tallow [48,112].

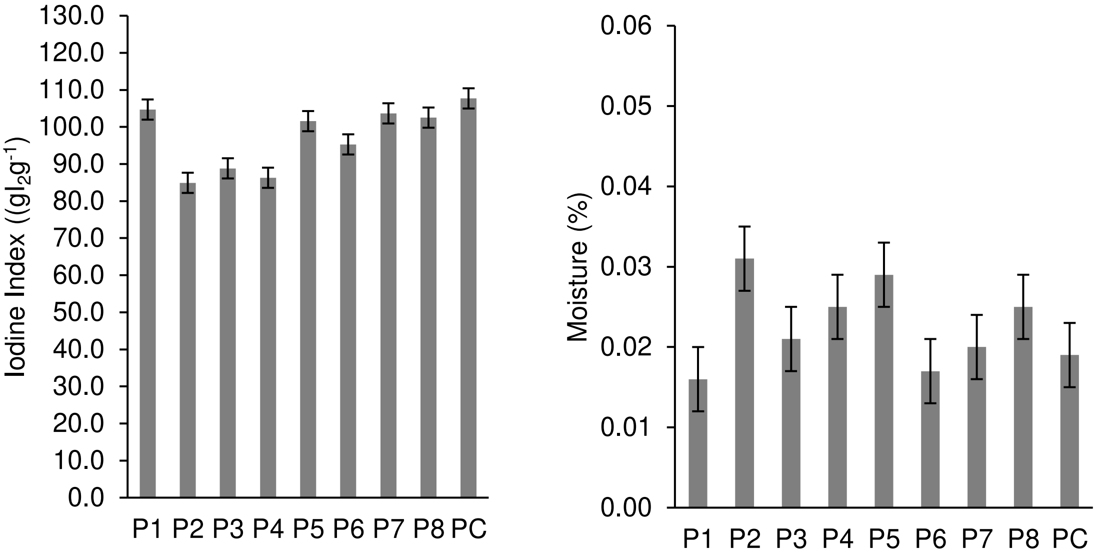


a) b)

Fig. 2 – a) Graph of the results of acidity index; b) Graph of the results of saponification index.

Regarding the saponification index, there is no regulatory limit , although such index influences the costs of biofuel production and use. Thus, lower indexes are preferable by reducing operating and maintenance costs [113]. In this study, the highest index was 96.553 mgKOHg^{-1} (Fig. 2b). The lowest saponification index was found in P5 (Fig. 2b), differing statistically only from P1 and P6 (Table 5). The literature reported an acidity index of 186.64 mgKOHg^{-1} for rice bran vegetable oil methyl biodiesel [33]. For biodiesel from bovine tallow, the values found in the literature are between 34.9 and 67.6 mgKOHg^{-1} [112] and 195.03 mgKOHg^{-1} from soybean oil [114]. The lowest saponification indexes obtained in this study occurred with a longer reaction time.

Only the EN requires a maximum limit for the iodine indexwith a maximum of 120 gI$_2$.g^{-1} [36] (Fig. 3a). This index is related to the degree of chain unsaturation and depends on the source of triglycerides used to produce biofuel [115]. Statistically, the lowest Iodine Index was obtained in P2, P3 and P4 (Table 5). All biodiesels produced in this study had iodine index within the EN recommendation (Fig. 3a) and indexes reported in the literature (118-128 gI$_2$.g^{-1}) in relation to biodiesel of soybean oil [116, 117]. Bovine tallow is a raw material which can produce biodiesel with a lower iodine index than the others mentioned, reported to be between 50 and 93 mg gI$_2$.g^{-1} [112]. The maximum moisture allowed by ASTM is 0.05%, thus all biodiesels produced in this study were within the specified limit (Fig. 3b).



a) b)

Fig. 3 – a) Graphs of the results of the iodine index; b) Graphs of the results of the moisture.

Kinematic Viscosity is one of the most important factors for the use of biodiesels in compression ignition engines. The high viscosity of vegetable oils is associated with low volatility, poor atomization of fuel, clots, deposits, fuel coking and dilution of the lubricating oil.[20]The kinematic viscosity of the fuel oil increases proportionally to the increase in the length of the chain of FA and decreases with the increase in the number of unsaturation [110,115]. For biodiesel of soybean oil, the literature indicates a range of 4.10-4.20 mm^2s^{-1} of kinematic viscosity [36,116,117]. As can be seen in Table 5 and Fig. 4, the results of Kinematic Viscosity analysis ranged from 8.061 to 22.791 mm^2s^{-1}, and the biodiesels that showed lowest viscosity according to the Tukey test occurred in P3, P4, P7 and P8 (Table 4).

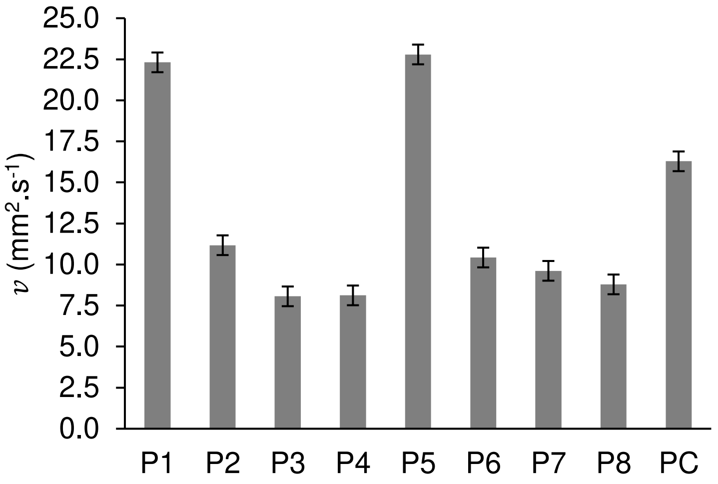


Fig. 4 – Graph of the results of the Kinematic Viscosity analysis.

Therefore, all biodiesels produced in this study had Kinematic Viscosity above the recommended limits according to the ANP, ASTM and EM, indicating that the conditions used in the study did not effectively promote transesterification reactions. Studies on the production of methyl diesel from rice bran vegetable oil reported kinematic viscosity of 4.30-4.76 mm^{2}s^{-1} [7,33] at 26 °C and 4.12-8.45 mm^{2}s^{-1} at 40 °C [35,115,32,118].

The results obtained in this study indicate reduced kinematic viscosity with the use of a larger amount of catalyst. Those reactions at 1.5% of KOH and 9:1 molar ratio of alcohol to oil resulted in an overall lower viscosity. Therefore, raising the amount of catalyst to promote biodiesel production and/or the molar ratio of ethanol to rice bran vegetable oil is recommended. Regarding reaction time, both presented similar results while fixing the other factors of the factorial arrangement.

The results obtained are of paramount importance since the ideal conditions for the production of biodiesel vary according to the raw material, the alcohol and the catalyst used. Cardoso et al. [119], for example, investigated the production of ethyl biodiesel from the transesterification of another waste largely generated in Brazil, fish oil. The authors reported that the optimum condition, was obtained with 0.7% alkaline catalyst (NaOH), temperature of 54 °C and molar ethanol:oil ratio of 11.7:1. Such conditions resulted in a biodiesel with 0.32±0.08 mgKOHg^{-1} of acidity index, 90 ± 0.40 gI$_2$.g^{-1} of iodine index, and 4.62±0.08 mm^2.s^{-1} of cinematic viscosity at 40 °C. Sinha et al. [25] evaluated the biodiesel production of rice bran oil using methanol as a short-chain alcohol and NaOH as a catalyst. In their study, the optimal conditions for transesterification were obtained at 55 °C, one hour of reaction time, molar ratio of 9:1 of oil to alcohol, and 0.75% of catalyst.

Biodiesel production in Brazil is mainly from soy, about 68.3%. Despite that biodiesel is a renewable fuel, it becomes less sustainable because the soy cultivation in the country is directly associated with deforestation and burning in the Legal Amazon area (Fig. 5).

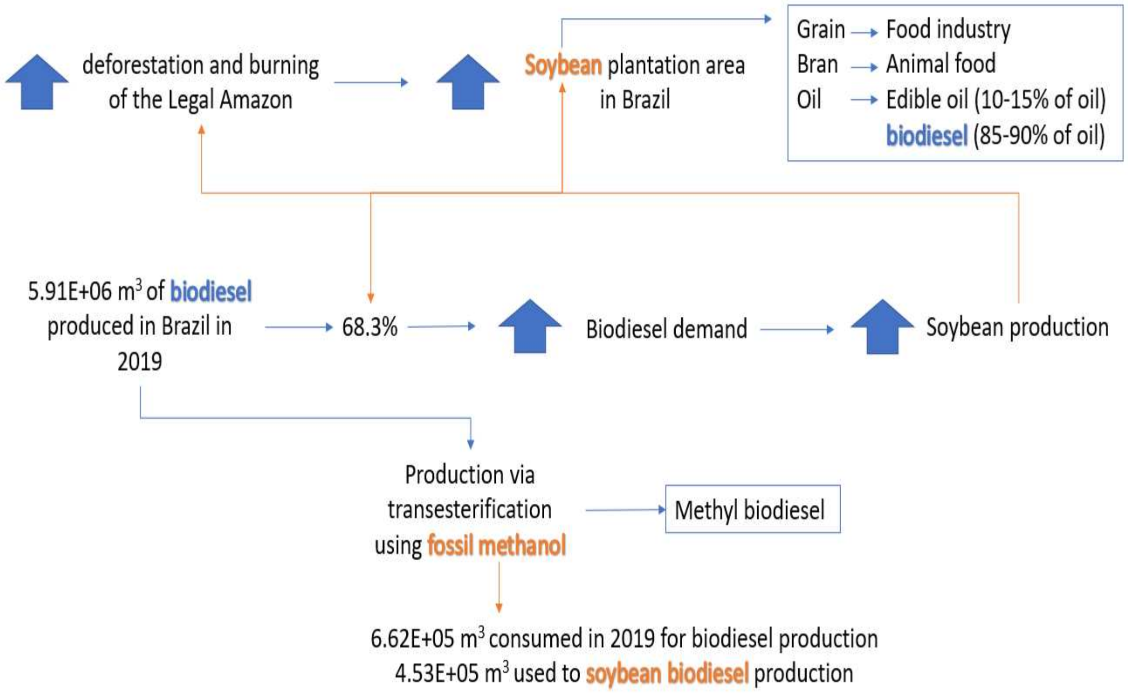


Fig. 5 – Current scenario of biodiesel production in Brazil.

According to the first survey of the Brazilian harvest of 2020/2021 carried out by the National Supply Company (CONAB) [120], the estimated production is equal to 1.34E+08 tons for the 2020/2021 harvest, corresponding to an increase of 2.5% cultivation area. In other words, 3.79E+07 hectares to be planted. Among the reasons for this increase, the CONAB cites the use of soy for biodiesel production since it is expected to increase the biofuel concentration in blends with diesel, i.e. reaching 13%. Another reason for reducing the biodiesel sustainability character is the use of fossil methanol for the transesterification reaction. (Fig. 5). According to the ANP's 2020 Brazilian Statistical Yearbook, in 2019 the country consumed of 6.62E+05 m^3 of methanol during the biodiesel production [120].

The prospects projected by this study for greater sustainability in the biodiesel production include the raw materials diversification in main agro-industrial residues, such as rice bran (Fig. 6).

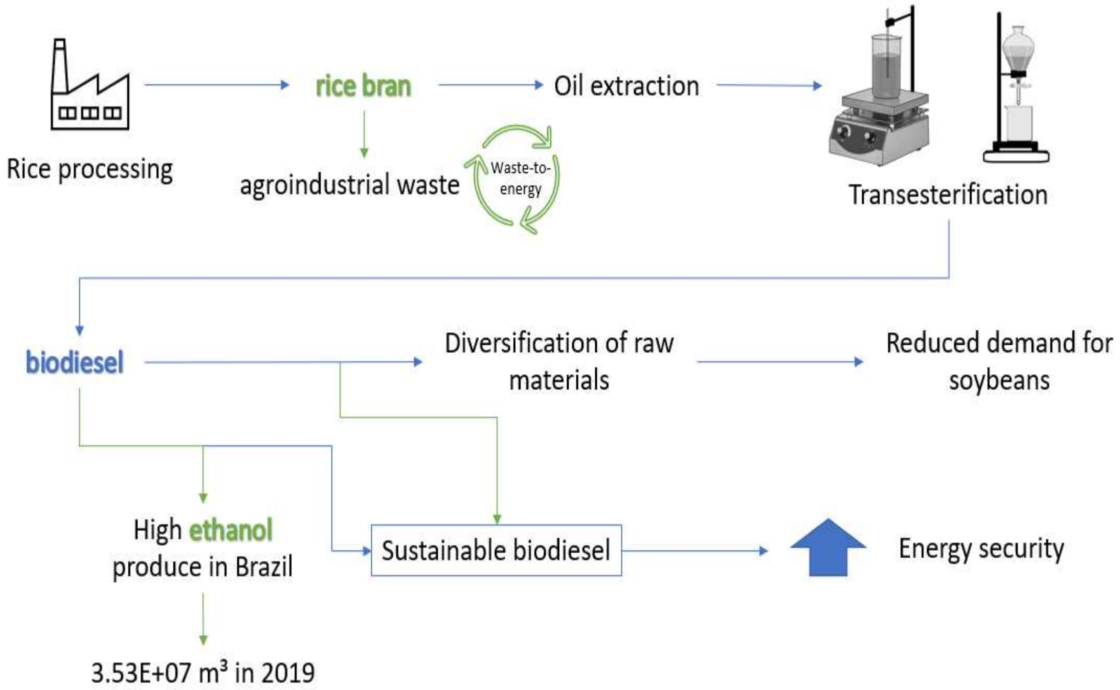


Fig. 6 - Perspectives of the study for the production of biodiesel in Brazil.

The use of residues for the biofuels generation allows for waste-to-energy application and contributes to the circular economy in the energy and industrial sector. Furthermore, the study promotes the use of ethanol as a substitute for fossil methanol to increasing energy security and the sector sustainability by using renewable alcohol widely produced in the country (Fig. 6). However, it is important to note that Brazil has barriers that hinder the implementation of such a perspective, emphasizing the need for studies in the area. The standards used in the chromatographic analysis to define the esters present in biodiesel in Brazil are standards for methyl esters, there are no standards for ethyl in the Brazilian national market. A similar situation occurs with the methodologies disseminated in the literature and in the area of biodiesel as a whole. What is found in the literature for the estimated determination of the biodiesel composition regarding ethyl esters are recent adaptations and still without scientific validation [121-123]. Although it are not recent studies from a chronological point of view, they are current in terms of methodologies in the area.

5. Conclusion

The main conclusions obtained from this study is detailed as follows:

1) According to the parameters analyzed in this study, the biodiesels obtained via ethyl transesterification of the rice bran oil were compliant with the requirements of ASTM, EN and ABNT except kinematic viscosity. Both reaction times had similar results while fixing the other factors of the factorial arrangement;

2) It is recommended to adopt 40 minutes for the reaction time to reduce the energy expenditure for the production of biodiesel from the rice bran oil;

3) The results on viscosity variation from the factorial arrangement demonstrated the need to raise the ratio of catalyst and/or the molar ratio between ethanol and alcohol, as the lower kinematic viscosities were around 8-9 $mm^2.s^{-1}$ with 1.5% catalyst and, generally, with a 9:1 molar ratio;

4) The possibility of producing biodiesel with the raw materials of this study could guide future studies and contribute to a scenario with the use of rice oil and ethanol in the industrial production of biodiesel. The scientific validation of the viability of producing rice oil based ethyl biodiesel in this study sets the basis for the futureresearch to optimize its production and assess its viability on a large scale. Ultimagely, the technology reported in this studywill makeit possible to reduce the emission of greenhouse gases, the diversity of the national energy matrix, and greater energy security in the Brazilian agro-industrial sector.

References

[1] Ziembowicz MM, Marchesan J, Baratto J, Alba E, Silva RR, Pereira RS. Geotecnologias aplicadas na análise dos impactos no uso e cobertura da terra causados pela construção de uma usina hidrelétrica. Ciência e Natura 2018;40. http://dx.doi.org/10.5902/2179460X29847.

[2] Ruffato-Ferreira V, Barreto RC, Júnior AO, Silva VL, Viana DBV, Nascimento JAS et al. A foundation for the strategic long-term planning of the renewable energy sector in Brazil: Hydroelectricity and wind energy in the face of climate change scenarios. Renewable and Sustainable Energy Reviews 2017;72:1124–37. https://doi.org/10.1016/j.rser.2016.10.020.

[3] Creutzig F, Ravindranath NH, Berndes G, Bolwig S, Bright R, Cherubini F et al. Bioenergy and climate change mitigation: an assessment. GCB Bioenergy 2015;7:916–44. https://doi.org/10.1111/gcbb.12205.

[4] González-González LM, Correa DF, Ryan S, Jensen, Pratt S, Schenk PM. Integrated biodiesel and biogas production from microalgae: Towards a sustainable closed loop through nutrient recycling. Renewable and

Sustainable Energy Reviews 2018;82:1137–48. https://doi.org/10.1016/j.rser.2017.09.091.

[5] [5]Ramos LP, Kothe V, César-Oliveira MAF, Muniz-Wypych AS, Nakagaki S, Krieger N, et al. Biodiesel: Matérias-Primas, Tecnologias de Produção e Propriedades Combustíveis. Rev. Virtual Quim. 2017;9. https://doi.org/10.21577/1984-6835.20170020.

[6] Lima Filho LR, Gouveia LGT, Ruzene DS, Silva DP. Revisão: biodiesel – gases emitidos, produção e sua influência na matriz energética brasileira. In: IX Simpósio de Engenharia de Produção de Sergipe 2017:559–67.

[7] Singh SP, Singh D. Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. Renewable and Sustainable Energy Reviews 2010;14:200–16. https://doi.org/10.1016/j.rser.2009.07.017.

[8] Visentainer JV. Aspectos Reacionais e da Química Analítica na Produção e Controle de Qualidade do Biodiesel de Óleos e Gorduras, first ed., Editora da Universidade Federal de Maringá, Maringá, 2013.

[9] Sajid Z, Khan F, Zhang Y. Process simulation and life cycle analysis of biodiesel production. Renewable Energy 2016;85:945–52. https://doi.org/10.1016/j.renene.2015.07.046.

[10] Nadaleti WC, Lourenço VA, Belli Filho P, dos Santos GB, Przybyla G. National potential production of methane and electrical energy from sugarcane vinasse in Brazil: a thermo-economic analysis, Journal of Environmental Chemical Engineering, 2020; 8(2):103422. https://doi.org/10.1016/j.jece.2019.103422.

[11] ANP - National Agency of Petroleum, Natural Gas and Biofuels. Statistic data; http://www.anp.gov.br/dados-estatisticos [accessed 28 October 2020].

[12] Magalhães TO. Síntese e Caracterização de Biocombustíveis obtidos a partir do arroz e seus derivados. Dissertation (Master in Chemistry) - Faculty of Chemistry, Pontifical Catholic University of Rio Grande do Sul, Porto Alegre, Brazil 2008.

[13] Boz N, Kara M. Solid base catalyzed transesterification of canola oil. Chemical Engineering Communications 2009;196:80–92, https://doi.org/10.1080/00986440802301438.

[14] D'agosto MA, Silva MAV, Oliveira CM, Franca LS, Marques LGC, Murta ALS et al. Evaluating the potential of the use of biodiesel for power generation in Brazil. Renewable and Sustainable Energy Reviews 2015;43:807–17. https://doi.org/10.1016/j.rser.2014.11.055.

[15] BRAZIL. Law No. 11,097, of January 13, 2005. 2005; http://www.planalto.gov.br/ccivil_03/_Ato2004-2006/2005/Lei/L11097.html/ [accessed 28 October 2020].

[16] BRAZIL. Law No. 13,263, of March 23, 2016. 2016; http://www.planalto.gov.br/ccivil_03/_Ato2015-2018/2016/Lei/L13263.html/ [accessed 29 October 2020].

[17] Ribeiro MD, Calera GC, Flu Mignan DL. Determinação e quantificação do teor de ésteres em biodiesel provenientes de matérias-primas de baixa qualidade por cromatografia gasosa. Revista Brasileira de Energias Renováveis 2017;6:29–38. http://dx.doi.org/10.5380/rber.v6i1.49403.

[18] ANP - Agência Nacional do Petróleo, Gás Natural e Biocombustíveis. Anuário Estatístico 2018, http://www.anp.gov.br/publicacoes/anuario-estatistico/anuario-estatistico-2018/; 2018 [accessed 05 February 2019].

[19] Govoni C. Dynamics and potential environmental implications of soybean expansion and beef production in Brazil: fires, deforestation and water scarcity. Thesis (PhD in Civil, Environmental and Territorial Engineering) - School of Civil, Environmental and Territorial Engineering, Milan Polytechnic, Milan, Italy, https://www.politesi.polimi.it/handle/10589/164733; 2020 [accessed 28 October 2020].

[20] EMBRAPA - Empresa Brasileira de Pesquisa Agropecuária - Ministério da Agricultura, Pecuária e Abastecimento. Agroenergia ganha importância no Rio Grande do Sul, https://www.embrapa.br/busca-de-noticias/-/noticia/1485718/agroenergia-ganha-importancia-no-rio-grande-do-sul/; 2012 [accessed 28 April 2018].

[21] Micuanski VC. A cultura energética: Canola (Brassica napus L.). Acta Iguazu 2014;3:141–49.

[22] Lai C, Zullaikah S, Vali SR, Ju Y. Lipase-catalyzed production of biodiesel from rice bran oil. Journal of Chemical Technology and Biotechnology 2005;80:331–37. https://doi.org/10.1002/jctb.1208.

[23] Oliveira PM. Produção de biodiesel de blendas dos óleos de mamona e arroz em escala piloto. Dissertation (Master in Technological and Environmental Chemistry) - Federal University of Rio Grande, Rio Grande, Brazil , http://repositorio.furg.br/handle/1/6225; 2012 [accessed 24 August 2020].

[24] Pereira AIC. Co-digestão anaeróbia de resíduos verdes e lamas de ETAR para produção de biogás. Dissertation (Master in Energy and Bioenergy) - Faculty of Sciences and Technology, New University of Lisbon, Lisbon, Portugal, http://hdl.handle.net/10362/10659, 2013 [accessed 24 August 2020].

[25] Sinha S, Agarwal AK, Garg S. Biodiesel development from rice bran oil: Transesterification process optimization and fuel characterization. Energy Conversion and Management 2008;49:1248–57. ttps://doi.org/10.1016/j.enconman.2007.08.010.

[26] Chaud LCS, Arruda PV, Felipe MGA. Potencial do farelo de arroz para utilização em bioprocessos. Nucleus 2009;6. http://dx.doi.org/10.3738/nucleus.v6i2.268.

[27] Lacerda DCL, Soares Júnior MS, Bassinello PZ, Castro MLV, Lobo VLS, Campos MRH et al. Qualidade de farelos de arroz cru, extrusado e parboilizado. Pesq. Agropec. Trop. 2010;40:521–530. https://doi.org/10.5216/pat.v40i4.7266.

[28] Walter M. Composição química e propriedades antioxidantes de grãos de arroz com pericarpo marrom-claro, vermelho e preto. Thesis (PhD in Agronomy) - Center for Rural Sciences, Federal University of Santa Maria, Santa Maria, Brazil , http://repositorio.ufsm.br/handle/1/3185; 2009 [accessed 24 August 2020].

[29] Zullaikah S, Lai CC, Vali SR, Ju Y. A two-step acid-catalyzed process for the production of biodiesel from rice bran oil. Bioresource Technology 2005;96(17):1889–96. https://doi.org/10.1016/j.biortech.2005.01.028.

[30] CONAB. Companhia Nacional de Abastecimento. Séries Históricas das Safras, Arroz Total (Irrigado e Sequeiro). Brasília: Conab, https://www.conab.gov.br/info-agro/safras/serie-historica-das-safras/; 2019 [accessed 29 January 2019)].

[31] Nadaleti WC, Przybyla G. Emissions and performance of a spark-ignition gas engine generator operating with hydrogen-rich syngas, methane and biogas blends for application in southern Brazilian rice industries. Energy 2018;154:38–51. https://doi.org/10.1016/j.energy.2018.04.046.

[32] Silva, TOM. Síntese e caracterização de biocombustíveis obtidos a partir do arroz e seus derivados. Dissertation (Master in Engineering and Materials Technology) - Catholic University of Rio Grande do Sul, Porto Alegre, Brazil, http://hdl.handle.net/10923/3276; 2008 [accessed 24 August 2020].

[33] Evangelista JPC. Obtenção de biodiesel através da transesterificação do óleo de farelo de arroz utilizando ki/Al2O3. Dissertation (Master in Chemistry) - Federal University of Rio Grande do Norte, Natal, Brazil, https://repositorio.ufrn.br/jspui/bitstream/123456789/17642/1/JoaoPCE_DISSERT.pdf; 2011 [accessed 24 August 2020].

[34] Lin L, Ying D, Chaitep S, Vittayapadung S. Biodiesel production from crude rice bran oil and properties as fuel. Applied Energy 2009;86: 681–8, 2009. https://doi.org/10.1016/j.apenergy.2008.06.002.

[35] Mazaheri H, Ong HC, Masjuki HH, Amini Z, Harrison MD, Wang CT et al. A. Rice bran oil based biodiesel production using calcium oxide catalyst derived from Chicoreus brunneus shell. Energy 2018;144:10–19. https://doi.org/10.1016/j.energy.2017.11.073.

[36] Pacheco BS, Silva CC, Freitas SC, Berneira LM, Silva VL, Winkel K et al. Employment of Alternative Raw Materials for Biodiesel Synthesis. In: Trindade M editors. Increased Biodiesel Efficiency: Alternatives for Production, Stabilization, Characterization and Use of Coproduct, Springer, Cham; 2018, p. 33–55. https://doi.org/10.1007/978-3-319-73552-8_2.

[37] Giakoumis EG, Sarakatsanis CK. Estimation of biodiesel cetane number, density, kinematic viscosity and heating values from its fatty acid weight composition. Fuel 2018;222:574–85. https://doi.org/10.1016/j.fuel.2018.02.187.

[38] Ghesti GF, Macedo JL, Dias JÁ, Dias SCL. Produção de biodiesel via transesterificação etílica com zeólitas básicas. Quím. Nova 2012;35(1):119–23. http://dx.doi.org/10.1590/S0100-40422012000100022

[39] Martínez A, Mijangos GE, Romero-Ibarra IC, Hernández-Altamirano R, Mena-Cervantes VY. In-situ transesterification of Jatropha curcas L. seeds using homogeneous and heterogeneous basic catalysts. Fuel 2019;235:277–87. https://doi.org/10.1016/j.fuel.2018.07.082.

[40] Li Q, Xu J, Du W, Li Y, Liu D. Ethanol as the acyl acceptor for biodiesel production. Renewable and Sustainable Energy Reviews 2013;25:742–8. https://doi.org/10.1016/j.rser.2013.05.043.

[41] Nautiyal P, Subramanian KA, Dastidar MG. Kinetic and thermodynamic studies on biodiesel production from Spirulina platensis algae biomass using single stage extraction–transesterification process. Fuel 2014;135:228–34. https://doi.org/10.1016/j.fuel.2014.06.063.

[42] Dorado MP, Ballesteros E, Mittelbach M, Lo´pez FJ. Kinetic parameters affecting the alkali-catalyzed transesterification process of used olive oil. Energy Fuels 2004;18:1457–62. https://doi.org/10.1021/ef034088o.

[43] Rathore V, Tyagi S, Newalkar B, Badoni RP. Jatropha and karanja oil derived DMC–biodiesel synthesis: a kinetics study. Fuel 2015;140:597–608. https://doi.org/10.1016/j.fuel.2014.10.003

[44] Darnoko D, Cheryan M. Kinetics of palm oil transesterification in a batch reactor. J Am Oil Chem Soc 2000;77(12):1263–7. https://doi.org/10.1007/s11746-000-0198-y.

[45] Rashid U, Anwar F. Production of biodiesel through optimized alkalinecatalyzed transesterification of rapeseed oil. Fuel 2008;87:265–73. https://doi.org/10.1016/j.fuel.2007.05.003

[46] [69] Pullen J, Saeed K. Investigation of the factors affecting the progress of basecatalyzed transesterification of rapeseed oil to biodiesel FAME. Fuel Process Technol 2015;130:127–35. https://doi.org/10.1016/j.fuproc.2014.09.013.

[47] Akhihiero ET, Oghenejoboh KM, Umukoro PO. Effects of process variables on transesterification reaction of jatropha curcas seed oil for the production of biodiesel. Int J Emerg Technol Adv Eng 2013;3(6):388–93.

[48] Nadaleti WC. Blendas de biodiesel: síntese, otimização e estabilidade termo-oxidativa, 1st ed. São Paulo: All Print; 2015.

[49] Hansen CF, Hernandez A, Mullan BP, Moore K, Trezona-Murray M, King RH et al. A chemical analysis of samples of crude glycerol from the production of biodiesel in Australia, and the effects of feeding crude glycerol to growing-finishing pigs on performance, plasma metabolites and meat quality at slaughter. Animal Production Science 2009;49:154–61. https://doi.org/1010.1071/EA08210.

[50] Fontinele GSP, Leite SCB, Cordeiro CN, Goulart CC, Costa AC, Neves JO et al. Glycerin from biodiesel in the feeding of red-egg layers. Semina: Ciências Agrárias, Londrina, 2017;38(2):1009–16. http://dx.doi.org/10.5433/1679-0359.2017v38n2p1009.

[51] Silva DB, Souza BR, Antero RVP. Produção biotecnológica de produtos de valor agregado utilizando glicerol residual proveniente da síntese de biodiesel. Evidência 2017;17(2):63-86. https://doi.org/10.18593/eba.v17i2.15411.

[52] Ijaz M, Bahtti KH, Anwar Z, Dogar UF, Irshad M. Production, optimization and quality assessment of biodiesel from Ricinus communis L oil. Journal of Radioation Research and Applied Sciences 2016;9(2):180–184. https://doi.org/10.1016/j.jrras.2015.12.005.

[53] Verma P, Sharma MP. Review of process parameters for biodiesel production from different feedstocks. Renewable and Sustainable Energy Reviews 2016;62:1063–71. doi:10.1016/j.rser.2016.04.054.

[54] Noureddini H, Zhu D. Kinetics of transesterification of soybean oil. J Am Oil Chem. Soc. 1997;74(11):1457–63. https://doi.org/10.1007/s11746-997-0254-2.

[55] Kumar R, Tiwari P, Garg S. Alkali transesterification of linseed oil for biodiesel production. Fuel 2013;104:553–60. https://doi.org/10.1016/j.fuel.2012.05.002.

[56] Vujicic, D Comic D, Zarubica A, Micic R, Boskovic G. Kinetics of biodiesel synthesis from sunflower oil over CaO heterogeneous catalyst. Fuel 2010;89:2054–61. https://doi.org/10.1016/j.fuel.2009.11.043.

[57] Yunus R, Fakhru'l-Razi A, Ooi TL, Biak DRA, Iyuke SE. Kinetics of transesterification of palm-based methyl esters with trimethylolpropane. J Am Oil Chem Soc 2004;81(5):497–503. https://doi.org/10.1007/s11746-004-0930-7

[58] Karmee SK, Mahesh P, Ravi R, Chadha A. Kinetic study of the base-catalyzed transesterification of monoglycerides from pongamia oil. J Am Oil Chem Soc 2004;81(5):425–30. https://doi.org/10.1007/s11746-004-0917-4.

[59] Darnoko D, Cheryan M. Kinetics of palm oil transesterification in a batch reactor. J Am Oil Chem Soc 2000;77(12):1263–7. https://doi.org/10.1007/s11746-000-0198-y.

[60] Clark WM, Medeiros NJ, Boyd DJ, Snell JR. Biodiesel transesterification kinetics monitored by pH measurement. Bioresour Technol 2013;136:771–4. https://doi.org/10.1016/j.biortech.2013.03.089.

[61] Encinar JM, González JF, Rodríguez JJ, Tejedor A. Biodiesel Fuels from Vegetable Oils: Transesterification of Cynara cardunculus L. Oils with Ethanol. Energy Fuels 2002;16(2):443–50. https://doi.org/10.1021/ef010174h.

[62] Ramadhas AS, Jayaraj S, Muraleedharan C. Biodiesel production from high FFA rubber seed oil. Fuel 2005;82(4):335–50. https://doi.org/10.1016/j.fuel.2004.09.016

[63] Balasubramanian R, Sircar A, Sivakumar P. Synthesis and Characterization of Surface Functionalized Maghemite Nano Particle for Biofuel Applications. In: Anand G, Pandey J, Rana S. Nanotechnology for Energy and Water. ICNEW 2017. Springer Proceedings in Energy. Springer Cham 2018. https://doi.org/10.1007/978-3-319-63085-4_23.

[64] Khiari K, Tarabet L, Awad S, Loubar K, Mahmoud R, Tazerout M. Optimization of Pistacia lentiscus Oil Transesterification Process Using Central Composite Design. Waste and Biomass Valorization 2019;10:2575–81. https://doi.org/10.1007/s12649-018-0257-2.

[65] Jain S, Sharma MP. Kinetics of acid base catalyzed transesterification of Jatropha curcas oil. Bioresour Technol 2010;101:7701–6. https://doi.org/10.1016/j.biortech.2010.05.034.

[66] Navas MB, Bolla PA, Lick ID, Casella ML, Ruggera JF. Transesterification of Soybean and Castor Oil with methanol and butanol Using Heterogeneous Basic Catalysts to obtain Biodiesel. Chemical Engineering Science 2018;187:444–54. https://doi.org/10.1016/j.ces.2018.04.068.

[67] Hailegiorgis SM, Mahadzir S, Subbarao D. Enhanced in situ ethanolysis of Jatropha curcas L. in the presence of cetyltrimethylammonium bromide as a phase transfer catalyst. Renewable Energy 2011;36:2502–7. https://doi.org/10.1016/j.renene.2011.03.001.

[68] Domingos AK, Saad EB, Wilhelm HM, Ramos LP. Optimization of the ethanolysis of Raphanus sativus (L. Var.) crude oil applying the response surface methodology. Bioresource Technology 2008;99:1837–45. https://doi.org/10.1016/j.biortech.2007.03.063.

[69] Encinar JM, Gonzalez JF, Rodriguez-Reinares A. Ethanolysis of used frying oil. Biodiesel preparation and characterization. Fuel Process Technology 2007;88:513–22. https://doi.org/10.1016/j.fuproc.2007.01.002.

[70] Cavalcante KSB, Penha MNC, Mendonca KKM, Louzeiro HC, Vasconcelos ACS, Maciel AP, et al. Optimization of transesterification of castor oil with ethanol using a central composite rotatable design (CCRD). Fuel 2010;89:1172–6. https://doi.org/10.1016/j.fuel.2009.10.029.

[71] Bouaid A, Martinez M, Aracil J. Production of biodiesel from bioethanol and Brassica carinata oil: Oxidation stability study. Bioresource Technology 2009;100:2234–9. https://doi.org/10.1016/j.biortech.2008.10.045.

[72] Mendow G, Veizaga NS, Querini CA. Ethyl ester production by homogeneous alkaline transesterification: influence of the catalyst. Bioresource Technology 2011;102:6385–91. https://doi.org/10.1016/j.biortech.2011.01.072.

[73] Meher LC, Sagar DV, Naik SN. Technical aspects of biodiesel production by transesterification – a review. Renew Sustain Energy Rev 2006;10:248–68. https://doi.org/10.1016/j.rser.2004.09.002

[74] EPE – Empresa de Pesquisa Energética. Balanço Energético Nacional ano base 2017, https://www.epe.gov.br/sites-pt/publicacoes-dados-abertos/publicacoes/PublicacoesArquivos/publicacao-46/topico-82/Relatorio_Final_BEN_2017.pdf; 2018 [accessed 24 August 2020].

[75] Nadaleti WC. Utilization of residues from rice parboiling industries in southern Brazil for biogas and hydrogen-syngas generation: Heat, electricity and energy planning. Renewable Energy 2019;137:55–72. https://doi.org/10.1016/j.renene.2018.07.014.

[76] Pestana VR, Mendonça CRB, Zambiazi RC. Farelo de arroz: características, benefícios à saúde e aplicações. B.CEPPA 2008;26(1):29–40.

[77] Goffman FD, Pinson S, Bergman C. Genetic diversity for lipid content and fatty acid profile in rice bran. Journal American of the Oil Chemists Society 2003;80:485–90. https://doi.org/10.1007/s11746-003-0725-x.

[78] Pestana VR. Avaliação da qualidade do óleo de arroz e do conteúdo de tocoferóis e orizanóis durante o processo de refino. Dissertation (MSc in Agroindustrial Science and Technology) - Post-Graduate Program in Agroindustrial Science and Technology, Federal University of Pelotas, Pelotas, Brazil, http://repositorio.furg.br/handle/1/8075; 2007 [accessed: 24 August 2020].

[79] Xu Z, Godber JS. Purification and identification of components of γ-oryzanol in rice bran oil. Journal Agricultural and Food chemistry 199;47:2724–8. https://doi.org/10.1021/jf981175j.

[80] Krishna AGG. Nutritional components of rice bran oil in relation to processing. Lipid Technology 2002;14:80–84. https://doi.org/10.1007/s11746-003-0725-x.

[81] Choi Y, Jeong HS, Lee J. Antioxidant activity of methanolic extracts from some grains consumed in Korea. Food Chemistry 2007;103:130–8. https://doi.org/10.1016/j.foodchem.2006.08.004.

[82] Chotimarkorn C, Silalai N. Addition of rice bran oil to soybean oil during frying increases the oxidative stability of the fried dough from rice flour during storage. Food Research International 2008;41:308–17. https://doi.org/10.1016/j.foodres.2007.12.007.

[83] Pereira E, Santos LM, Einloft S, Seferin M, Dullius J. Biodiesel Production from High FFA degummed rice bran oil by a two-step process using ethanol/methanol and a green catalyst. Waste Biomass Valor 2015;6:343–51. https://doi.org/10.1007/s12649-015-9349-4

[84] Tortosa E, Barber CB. El salvado de arroz y su potencial en alimentación animal. Avances en alimentación e mejora animal 1979;20(5):13–21.

[85] ANVISA – Agência Nacional de Vigilância Sanitária. Resolução nº 482, de 1999. Regulamento Técnico, nº196-E, Brasília: Diário Oficial da União, http://portal.anvisa.gov.br/documents/10181/2718376/RES_482_1999_CO

MP.pdf/0b31ce35-6d43-42d6-8184-549de494987a?version=1.0; 1999 [accessed: 24 August 2020].

[86] Zaidel DNA, Muhamad II, Daud NSM, Muttalib NAA, Khairuddin N, Lazim NAM. Production of biodiesel from rice bran oil. Biomass, Biopolymer-Based Materials, and Bioenergy, 2019;409–47. https://doi.org/10.1016/b978-0-08-102426-3.00018-7

[87] Hoang AT, Tabatabaei M, Aghbashlo M, Carlucci AP, Ölçer AI, Le AT, Ghassemi A. Rice bran oil-based biodiesel as a promising renewable fuel alternative to petrodiesel: A review. Renewable and Sustainable *Energy Reviews*, 2020;*135:*110204. https://doi.org/10.1016/j.rser.2020.110204.

[88] Sreedhar I, Kishan, YK. Process standardization and kinetics of ethanol driven biodiesel production by transesterification of ricebran oil. Int J Ind Chem, 2016;7:121-9. https://doi.org/10.1007/s40090-016-0074-z

[89] Rizkianto F, Jindal VK, Jindal R, Thongdara R, Takaoka M, Oshita K. Biodiesel Production from Refined Rice Bran Oil Using Eggshell Waste As Catalyst Impregnated with Silver Nanoparticles. In 2020 4th International Conference on Green Energy and Applications (ICGEA) 2020;134–8.

[90] Pereira E, dos Santos LM, Einloft S, Seferin M, Dullius J. Biodiesel production from high FFA degummed rice bran oil by a two-step process using ethanol/methanol and a green catalyst. Waste and Biomass Valorization 2015;343–51. https://doi.org/10.1007/s12649-015-9349-4

[91] Bani O, Parinduri S, Ningsih PRW. Biodiesel production from rice bran oil by transesterification using heterogeneous catalyst natural zeolite modified with K2CO3**.** IOP conf. Ser. Mater. Sci. Eng., 2018;9:12107

[92] Ganesh R, Chandran J, Manikandan K, Raja T. Performance assessment of a compression ignition engine propelled with rice bran biodiesel/propanol mixtures. International Journal of Ambient Energy, 2019;1-4. https://doi.org/10.1080/01430750.2019.1670734

[93] Rizkianto F, Jindal VK, Jindal R, Thongdara R, Takaoka M, Oshita K.. Biodiesel Production from Refined Rice Bran Oil Using Eggshell Waste As Catalyst Impregnated with Silver Nanoparticles. In *2020 4th International Conference on Green Energy and Applications* 2020;134202038.

[94] Ibrahim H, Silitonga AS, Rahmawaty, Dharm, S, Sebayang AH, Khairil, Sumartono, Sutrisno J, Razak A. An Ultrasound Assisted Transesterification to Optimize Biodiesel Production from Rice Bran Oil. *International Journal of Technology* 2020;11(2):225–34. https://doi.org/10.14716/ijtech.v11i2.905

[95] Kasim NS, Tsai T-H, Gunawan S, Ju Y-H. Biodiesel production from rice bran oil and supercritical methanol. Bioresour Technol 2009;100:2399–403. https://doi.org/10.1016/j.biortech.2008.11.041

[96] Lourinho G, Brito P. Advanced biodiesel production technologies: novel developments**.** Rev Environ Sci Bio/Technology 2015;14:287–316. https://doi.org/10.1007/s11157-014-9359-x

[97] MohamedMusthafa M, Sivapirakasam SP, Udayakumar, M. Comparative studies on fly ash coated low heat rejection diesel engine on performance and emission characteristics fueled by rice bran and pongamia methyl ester and their blend with diesel. Energy 2011;36:2343–51. https://doi.org/10.1016/j.energy.2010.12.047

[98] Chuayplod P, Trakarnpruk W. Transesterification of rice bran oil with methanol catalyzed by Mg (Al) La hydrotalcites and metal/MgAl oxides. Ind Eng Chem Res 2009;48:4177–83. https://doi.org/10.1021/ie8005947

[99] Mumtaz MW, Adnan A, Anwar F, Mukhtar H, Raza MA, Ahmad F, Rashid U. Response surface methodology: an emphatic tool for optimized biodiesel production using rice bran and sunflower oils. Energies 2012;5(9): 3307–28. https://doi.org/10.3390/en5093307

[100] Kattimani VR, Venkatesha BM, Ananda S. Biodiesel production from unrefined rice bran oil through three-stage transesterification. Adv Chem Eng Sci 2014;4:361. https://doi.org/10.4236/aces.2014.43039

[101] M. Rengasamy, V. Pugalenthi, V. Sivasubramanian, N. Jaya. Synthesis OF biodiesel from palm oil & rice bran oil using NA2SIO3 as heterogeneous base catalyst. Eng Reports 2018;1:11–21

[102] Kanitkar A, Balasubramanian S, Lima M, Boldor D. A critical comparison of methyl and ethyl esters production from soybean and rice bran oil in the presence of microwaves. Bioresource technology, 2011;102(17):7896–02. https://doi.org/10.1016/j.biortech.2011.05.091

[103] Lei H, Ding X, Zhao J, Zhang H, Li Y, Ma Y, Wang Z. In situ production of fatty acid ethyl ester from low quality rice bran. *Fuel* 2011;*90*(2):592–7. https://doi.org/10.1016/j.fuel.2010.09.040ASTM - American Society for Testing and Materials. D445 - Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity) 2006.

[104] ASTM - American Society for Testing and Materials. D664 - Standard test method for acid number of petroleum products by potentiometric titration-ASTM D 664-11A. ASTM International, West Conshohocken, PA 2011.

[105] ASTM - American Society for Testing and Materials. D459 - Standard test method for iodine value of drying oils and fatty acids. Int Annual book of ASTM standards 1997.

[106] AOAC - Association of Official Analytical Chemists. Section C: Commercial Fats and Oils, American Oil Chemists Society (AOCS) official method Cd 3–25 for saponification value. Association of Official Analytical Chemists, Washington 1997.

[107] IInstituto Adolfo Lutz, Normas Analíticas do Instituto Adolfo Lutz. v. 1: Métodos químicos e físicos para análise de alimentos, third ed. IMESP, 1985, p. 21-22.

[108] Resolução ANP nº 45 de 25/08/2014, http://legislacao.anp.gov.br/?path=legislacao-anp/resol-anp/2014/agosto&item=ranp-45-2014; 2014 [accessed 24 August 2020].

[109] Knothe G. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters, Fuel Process Technol 2005;86:1059–70. https://doi.org/10.1016/j.fuproc.2004.11.002.

[110] Vieira BM, Elicker C, Nunes CF, Bairros AV, Becker EM, Oliveira DM et al. The synthesis and characterization of Butia capitata seed oil as a FAME feedstock. Fuel 2016;184:533–535. https://doi.org/10.1016/j.fuel.2016.07.052.

[111] Santos PD, Reis NV, Silveira R, Galuch MB, Visenrainer JV, Santos OO. Authenticity investigation of bovine tallow for biodiesel production via mass spectrometry: a comparison with traditional methodology. Chemical Papers 2018;73:1–6. https://doi.org/10.1007/s11696-018-0639-8.

[112] Paula AJA, Krügel M, Miranda JP, Rossi LFS, Costa Neto PR. Utilização de argilas para purificação de biodiesel. Quim. Nova 2011;34. http://dx.doi.org/10.1590/S0100-40422011000100018.

[113] Wu H, Miao X. Biodiesel quality and biochemical changes of microalgae Chlorella pyrenoidosa and Scenedesmus obliquus in response to nitrate levels, Bioresour. Technol. 2014;170:421–7, https://doi.org/10.1016/j.biortech.2014.08.017

[114] Lôbo IP, Ferreira SLC, Cruz RS. Biodiesel: parâmetros de qualidade e métodos analíticos. Quim Nova 2009;32:1596–608. http://dx.doi.org/10.1590/S0100-40422009000600044.

[115] Ramos MJ, Fernández CM, Rodríguez L, Pérez A. Influence of fatty acid composition of raw materials on biodiesel properties. Bioresour Technol 2009;100:261–268. https://doi.org/10.1016/j.biortech.2008.06.039.

[116] Sajjad B, Raman AAA, Arandiyan H. A comprehensive review on properties of edible and non-edible vegetable oil-based biodiesel: composition, specifications and prediction models, Renew Sustain Energy Rev. 2016;63:62–92. https://doi.org/10.1016/j.rser.2016.05.035.

[117] Lin L, Ying D, Chaitep S, Vittayapadung S. Biodiesel production from crude rice bran oil and properties as fuel. Applied Energy 2009;86:681–8. https://doi.org/10.1016/j.apenergy.2008.06.002.

[118] da Costa Cardoso L, de Almeida FNC, Souza GK, Asanome IY, Pereira NC. Synthesis and optimization of ethyl esters from fish oil waste for biodiesel production, Renewable Energy 2019;133:743-748.

[119] CONAB - National Supply Company. Monitoring of the Brazilian Crop, Grains, Crop 2020/2021, 1st Survey, file:///C:/Users/vitor/Downloads/BoletimZdeZSafras_1ZLevantamento.pdf, 2020 [accessed: 01 November 2020].

[120] ANP - Brazilian Oil, Natural Gas and Biofuels Agency. Brazilian Statistical Yearbook, http://www.anp.gov.br/arquivos/central-conteudos/anuario-estatistico/2020/anuario-2020.pdf, 2020 [accessed: 01 November 2020].

[121] Hobuss, C. B. (2011). Aplicação da sonocatálise na esterificação de ácidos graxos e obtenção de biodiesel derivado da microalga chlorella vulgaris (Master's thesis, Universidade Federal de Pelotas).

[122] Garcia R, Martin E. Métodos analíticos alternativos para a determinação da qualidade de ésteres etílicos de óleo residual de fritura. Blucher Chemical Engineering Proceedings, 2015;1(3):469-474.

[123] Gasparini, F. Avaliação e adaptação das condições da EN 14103 para quantificação de ésteres em biodieseis etílicos puros de soja, babaçu, palma e sebo bovino e em suas misturas, 2010.