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Optimization of palm oil biodiesel production using response surface methodology

Otimização na produção de biodiesel de óleo de palma utilizando a metodologia de superfície de resposta

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ABSTRACT

The purpose of this paper was to analyze palm oil biodiesel production under different conditions and to verify the relationships between production variables in order to optimize biofuel production using response surface methodology (RSM). Biodiesel was produced through transesterification process by methyl route and alkali catalyst (NaOH) 1% (m/m). The analyzed variables were: four molar ratios (3:1, 4:1, 6:1 and 8:1); three temperature reactions (45°, 52° and 60°C); and three time reactions (40, 60 and 80 minutes). For the palm oil biodiesel production, the highest yield was 93%, obtained via a molar rate of 3:1, 52°C and 60 minutes. This result differs from previous studies that found a higher yield with molar ratio increases, implying greater expenses of methanol. Kinetic viscosity and specific mass were also analyzed, and the values are within the Brazilian, American, and European standards. The results showed that the most influent factor in biodiesel production was the molar rate. In relation to the biodiesel characterization, using the RMN H1 technique, it was possible to obtain the transesterification reaction yield of 79.50% for the 3:1 palm oil biodiesel. Through gas chromatography, it can be verified that the predominant fatty acids in the samples were palmitic and oleic acids. .

Keywords: methyl esters; biofuel viscosity; biofuel specific mass; production efficiency.

RESUMO

O objetivo deste trabalho foi analisar a produção de biodiesel de óleo de palma em diferentes condições e verificar as relações entre variáveis de produção para otimizar a produção de biocombustíveis usando a metodologia da superfície de resposta (*response surface methodology* – RSM). O biodiesel foi produzido através do processo de transesterificação via rota metílica e com catalisador alcalino (NaOH) a 1% (m/m). As variáveis analisadas foram: quatro razões molares (3:1, 4:1, 6:1 e 8:1); três temperaturas de reação (45°, 52° e 60°C) e três tempos de reação (40, 60 e 80 minutos). Para a produção de biodiesel de óleo de palma, o maior rendimento foi de 93%, obtido na razão molar de 3:1, 52°C e 60 minutos. Esse resultado difere de outros estudos que encontraram maior rendimento com o aumento da razão molar, implicando em maiores gastos com metanol. A viscosidade cinética e a massa específica também foram analisadas, e os valores estão dentro dos padrões brasileiro, americano e europeu. Os resultados mostraram que o fator mais influente na produção de biodiesel foi a razão molar. Em relação à caracterização do biodiesel, pela técnica de RMN 1H, foi possível obter o rendimento da reação de transesterificação de 79,50% para o biodiesel 3:1 de óleo de palma. Por meio da cromatografia gasosa, pode-se verificar que os ácidos graxos predominantes nas amostras foram os ácidos palmíticos e oleico.

Palavras-chave: ésteres metílicos; viscosidade de biocombustível; massa específica de biocombustível; eficiência de produção.

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Introduction

Alternative fuel sources have been widely studied due to the non-renewable character of the current and most used energy source, oil. For Razack and Duraiarasan (2016), biodiesel has emerged as the main substitute for petroleum diesel. Biodiesel promotes sustainable development through energy savings, in addition to presenting characteristics, such as low toxicity and low emission of polluting gases (Ambat et al., 2018).

Biodiesel is a renewable energy source, biodegradable and derivates from renewable sources, such as vegetable oils and animal fat. There are several technologies for biodiesel production, such as cracking, esterification and transesterification, which involve the management of variables, such as the molar ratio of alcohol:oil, temperature, time, and catalyst amount, determinants for the efficiency of biodiesel production. The transesterification process of fatty acids present in oils and fats is the most common and can be carried out using ethanol (ethyl route) or methanol (methyl route), which generally present better yields in the presence of an acid or basic catalyst (Rodrigues et al., 2011; Victorino et al., 2016; Abdullah et al., 2017; Gonçalves et al., 2019).

In both processes the production of glycerol is obtained as a by-product, which contributes in the increasing biodiesel competitiveness, since this substance can be used as raw material in the production of paints, pharmaceuticals, and textiles.

Biodiesel or fatty acid methyl ester (FAME), when using methanol, or fatty acid ethyl ester (FAEE), when using ethanol, is a fuel that can be applied pure or mixed with petroleum derived diesel in various proportions in internal combustion engines without the need for mechanical modifications in the engine (Rincón et al., 2014).

Brazilian national law no. 12,490 of September 16, 2011 (in item XXIV of Article 6) defines biofuel as a "substance derived from renewable biomass, such as biodiesel, ethanol and other substances established in Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP) regulations, which can be used directly or through changes in internal combustion engines or for other types of power generation, being able to replace fossil fuels partially or totally" (Brasil, 2011).

Due to its origin, biodiesel provides lower environmental impacts when compared to diesel fuel, emitting less particulate material, carbon dioxide (CO_2) and nitrogen oxides (NO_X), which are gases that contribute to the greenhouse effect. When this biofuel shows similar characteristics to diesel fuel, it is able to replace it as an energy source (Kumar et al., 2016).

However, as stated by Ge et al. (2020), a possible disadvantage is that viscosity and density tend to be slightly higher in biodiesel than in diesel due to the presence of saturated and unsaturated long chain fatty acids.

The USA is the country with the highest biofuel production, followed by Brazil (Sawin et al., 2017). According to Sawin et al. (2017), the total production of biofuels in Brazil was 30.8 billion liters in 2016, 27 billion of which were ethanol and 3.8 billion were biodiesel. In Brazil, biodiesel has soy oil and pork fat as its main feedstocks, with a participation of 72.51 and 14.93%, respectively, while palm oil represents only 0.16%. These facts show the minor participation on a wide variety of potential raw materials for biodiesel production, so it is necessary to increase the participation of raw materials in matrix, especially of products with highly productive yield such as the palm oil crop.

According to Feroldi et al. (2014), palm is considered the raw material with the highest oil productivity among the oilseeds for consumption around the world, with 20 to 22% of oil and a yield of four to six tons per hectare each year. Besides, palm oil is also a significant profitable oil for biodiesel production due to its compositional characteristics, high productivity with low cost, whole year well distributed production and no competition with other crops for feeding purposes. Nowadays in Brazil, most palm oil plantations are concentrated in the states of Pará, Amazonas, Amapá, and Bahia (D'Agosto et al., 2015). Moreover, palm oil biodiesel production is encouraging a new segment for the productive chain that is strengthening, generating, and multiplying employment and increasing income in the agricultural phase, input market and services and transport, storage, blending and biodiesel marketing activities (Lebid and Henkes, 2015).

The cultivation of the African palm (*Elaeis guineenses*), originating from the Gulf of Guinea on the West coast of Africa, is an oleaginous plant species from which oil is extracted out of its fruit mesocarp. This palm has a life cycle of 20 to 30 years and begins to produce clusters at the age of 3.5 years after planting, reaching its peak between 7 and 15 years, after which it begins to decrease slowly until the 25th year. The favourable development conditions are moderate air temperature, solar radiation associated with a good distribution of precipitation with 2,000 mm $year^{-1}$ and deep soils without compaction, with a maximum slope of 5% and an altitude up to 600 meters (Kuss et al., 2015).

Palm oil is the main raw stock for biodiesel production in Malaysia (Mekhilef et al., 2011), which is one of the leading palm oil producers in the world. There are many advantages and disadvantages from the economic, social, and environmental features of the Malaysian biodiesel palm production.

Apart from the economic aspect, the environmental issue is a major fact. According to Kong et al. (2014), the producing biochar from palm oil biomass provides promising co-benefits, including the generation of renewable electricity, liquid and gas biofuels, large amounts of heat or low-pressure steam and the potential of a net withdrawal of carbon dioxide from the atmosphere. In the future, biochar alone is not going to be enough to reduce Greenhouse Gas Protocol (GHG) to manageable safety levels. However, it can be implemented and integrated to the palm oil producing countries using many different approaches to create a substantial positive impact on the challenges of climate change and crop productivity.

Different studies carried out by Ali and Tay (2013), Sukjit and Punsuvon (2013), Feroldi et al. (2014), Wong et al. (2015), Anguebes-Franseschi et al. (2016), among others, analysed the variables associated with the biodiesel production from palm oil, and found that the molar ratio ethanol:oil, temperature and stirring time are the most important factors involved in the reaction. Some authors, such as Ali and

Tay (2013) and Feroldi et al. (2014), found the optimal conditions for palm oil biodiesel production using methanol in the transesterification process: the methanol:oil molar ratio of 6:1, reaction time of 60 minutes and temperature of 60°C with 1% of KOH as a catalyst, resulting in 88% yield. Likewise, Anguebes-Franseschi et al. (2016) obtained a yield of 90% in palm oil biodiesel production with a reaction temperature of 56°C, 135 minutes, and a NaOH catalyst proportion of 0.65%.

It is important to monitor the process from the formation of the main product, the fatty esters, in the transesterification. Thus, high-performance liquid chromatography, gas chromatography, proton nuclear magnetic resonance (1H NMR) and thin layer chromatography methods are used. Among these techniques, gas chromatography is considered the most effective to determine the amount of fatty acid esters present in the biodiesel composition (Marques et al., 2010).

Using response surface methodology (RSM), Sukjit and Punsuvon (2013) determined that the best conditions were a molar ratio of 7:1 methanol:palm oil, temperature of 60°C with 70 minutes of reaction time and a proportion of 1.2% of KOH catalyst, resulting in a 96.24% yield. Using RSM, the highest yield obtained in the reaction with palm oil was 97.67% with a molar ratio of 13.04:1 methanol:oil, time of 2.67 hours and a catalyst proportion of 3.60% (Wong et al., 2015).

Thus, taking into account the different studies about molar ratio, temperature and reaction time for biodiesel production, as well as the importance of determining a more efficient process for the production of renewable energies, this paper aimed to establish the process with the highest yield using RSM in the production of palm oil biodiesel, testing the values of factors, such as molar ratio, temperature and time, as well as analyzing the kinetic viscosity and specific mass.

Materials and Methods

Biodiesel production

The structure of this paper comprised two steps: the first involved the biodiesel produced experimentally and the second consisted in biodiesel characterization and elaboration of the response surface. The palm oil biodiesel production and characterization were performed at the Universidade Federal Fluminense (UFF, Brazil). For biodiesel production, palm oil and methanol were used and NaOH was the catalyst.

The different characteristics of molar ratio, temperature and time were considered for the experimental analyses of biodiesel production. The data were obtained for three temperatures (45, 52 and 60°C), three production times (40, 60 and 80 minutes), and four molar ratios of methanol:oil (3:1, 4:1, 6:1, 8:1), as shown in Table 1.

Table 1 – Analysis of variation sources.

Molar ratio (methanol:oil)	3:1, 4:1, 6:1, 8:1
Temperature (°C)	45, 52, 60
Time (min)	40, 60, 80

Palm oil is red due to the presence of carotenoids and is rich in vitamins, coenzymes, and sterols (Porcayo-Calderon et al., 2017). In addition, it is more saturated than soybean oil and rapeseed due to its higher amount of fatty acids, such as palmitic (C16:0), stearic (C18:0), oleic (C18:1) and linoleic (C18:2) acids (Issariyakul and Dalai, 2014). High-quality palm oil is mainly used in the food industry, and low-quality (non-edible) oil is used to produce soap, waxes, cosmetics, biofuels, and other types of goods (Porcayo-Calderon et al., 2017).

Table 2 shows the fatty acid composition of palm oil. It is possible to observe 50% of saturated fatty acids (SFA), mainly palmitic acid (44%), and lower amounts of stearic acid (5%), 40% of monounsaturated fatty acids (AGMI), mainly oleic acid and 10% of polyunsaturated fatty acids (PUFA), mainly linoleic acid.

Biodiesel was obtained via alkali transesterification reaction. Initially, the quantities of palm oil, methanol and NaOH based on the treatment were weighed. Consequently, the oil was heated in the corresponding treatment temperature (45, 52 and 60°C) and then mixed with the methanol and NaOH mixture in the magnetic stirrer at the temperature and reaction time of the treatment. After the reaction time, the biodiesel was separated from the glycerol phase and washed with distilled water and hydrochloric acid, heated at 105°C and finally filtered. The mass yield production of each treatment was determined from the biodiesel mass divided by oil mass, as shown in Equation 1.

$$\text{Yield (\%)} = (\text{biodiesel mass (g)})/(\text{oil mass (g)}) \quad (1)$$

Biodiesel characterization

The biodiesel characterization was carried out according to the Brazilian (ABNT), American (ASTM) and European (EN ISO) standards (Table 3). A specific mass at 20°C was determined, as well as biodiesel kinetic viscosity, separated according to molar ratio (3:1, 4:1, 6:1 and 8:1). The Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP) defines biodiesel as a fuel composed of alkyl esters of long-chain carboxylic acids, produced through the transesterifica-

Table 2 – Fatty acid composition of palm oil.

Fatty Acid Name		Composition (%)
Lauric	(12:0)	0.2
Myristic	(14:0)	1.1
Palmitic	(16:0)	44
Stearic	(18:0)	4.5
Oleic	(18:1)	39.2
Linoleic	(18:2)	10.1
Linolenic	(18:3)	0.4
Arachidic	(20:0)	0.1

Source: adapted from Mancini et al. (2015).

tion and/or esterification of fatty substances, of fats from vegetable or animal origins (Brasil, 2014).

The specific mass was determined using a pycnometer with biodiesel at 20°C (Lima et al., 2010). The known volume using a pycnometer was 50 mL, and the specific mass was calculated applying Equation 2, considering the mass difference between empty and full pycnometers.

$$\rho = (fpm\text{-}epm)/pv*1000 \quad (2)$$

In which:
ρ = specific mass of biodiesel (kg m^{-3});
fpm = full pycnometer mass (g);
epm = empty pycnometer mass (g);
pv = pycnometer volume (mL).

Kinetic viscosity was calculated from the dynamic viscosity divided by specific mass. Dynamic viscosity was determined using rheometer Haake RS50, and specific mass was calculated. Biodiesel samples at 40°C (ASTM, 2012) were used for these analyses.

Biodiesel characterization by hydrogen nuclear magnetic resonance

1H NMR spectrometry characterization of palm oil and biodiesel samples with higher mass yield was carried out at the Multi-Nuclear Magnetic Resonance Laboratory (LaReMN) at UFF (Brazil). The samples were diluted in deuterated chloroform (CDCl3) and analyzed on a Varian spectrometer — VNMRS 300MHz. Tetramethylsilane (TMS) was used as reference, according to the methodology proposed by Fagundes (2011).

Gas chromatography

Samples with the highest mass yield biodiesel were analyzed qualitatively in the gas chromatograph coupled to mass spectrometry (GC-MS) GCMS-QP2010 (Shimadzu, Tokyo, JP) using the following conditions: injection with flow division in the ratio of 1:20; DB5-MS column (30 m × 0.25 mm D.I. and 1 µm of 5% phenyl-polydimethylsiloxane); the carrier gas used was He (99.999% pure) under a constant flow of 3 mL min^{-1}; oven temperature setting was 50–180°C with heating rate of 8°C min^{-1}, 180–230°C with heating rate of 5°C min^{-1}, 230–310°C with heating rate of 20°C min^{-1}, followed by isotherm for 15 minutes. The chromatographic profiles were made in comparison with the Nist 147 library (US National Institute of Standards and Technology 147), indicating the presence of some methyl esters in the samples. The distribution of the observed substances was determined by standardizing the area of each present peak, that is, in percentage of relative chromatographic area.

Degree of transesterification conversion

The biodiesel sample with the highest mass yield had its transesterification reaction characterized by the spectrum of nuclear magnetic resonance. The conversion of oil into biodiesel was calculated according to Equation 3, following the methodology proposed by Ruschel et al. (2016). Based on this equation, the conversion is determined by the integration of the biodiesel sample 1H NMR signals. The integration of each spectrum was generated using the MestreNova software v. 12.0.

$$C_T = ((I_{CH3}/3)/(I_{CH2}/2))*100 \quad (3)$$

In which:
C_T = the conversion rate of the transesterification process;
I_{CH2} and I_{CH3} = obtained integrating the signals attributed to hydrogen of methylene group adjacent to carbonyl and hydrogen of methyl ester group, respectively.

As mentioned, the signal from methylene group adjacent to carbonyl (2.1–2.4 ppm) is used in the conversion parameter, as it is present in all triglyceride derivatives.

Response surface

In order to elaborate the response surface, the Matlab Software® (academic version) was used. The response surface was obtained for the variables molar ratio (x), reaction time (y), temperature (z), and yield (response), shown in Equation 4, using the linear interpolation method. Maximum yield was then obtained from the maximum value of the surface in Equation 4.

$$Yield = F(xq, yq, zq) \quad (4)$$

Table 3 – Biodiesel specifications established by Brazilian, American, and European regulations.

Characteristic	Limit	Method		
		ABNT	ASTM D	EN ISO
Specific mass at 20°C	850 to 900 kg.m^{-3}	7148 14065	1298 4052	EN ISO 3675 EN ISO 12185
Kinematic viscosity at 40°C	3 to 6 $mm^2.s^{-1}$	10441	445	EN ISO 3104

Source: adapted from Brasil (2014).

Results and Discussion

Specific mass

The specific mass results of biodiesel samples at 20°C are presented in Table 4. The results obtained are according to the Brazilian (ABNT), American (ASTM) and European (EN ISO) standards (Table 3), which demand a specific mass value from 850 to 900 kg m^{-3}. It is also possible to observe that the molar ratio did not significantly alter the specific mass values of the produced biodiesel.

According to Lôbo et al. (2009), biodiesel specific mass is directly linked to its molecular structure. The higher the length of the alkyl ester carbon chain, the greater the density. However, density can decrease with a greater number of unsaturation present in the molecule. Density can also be affected by the presence of impurities, such as alcohol or adulterants. Compared to diesel, biodiesel is less compressible and denser, causing a decrease in the calorific value and increasing consumption.

The specific mass is a determinant parameter of maximum biodiesel percentage in the mixture with diesel, since mixtures with a high proportion of biodiesel or those which diesel density is close to the upper limit allowed could exceed the limits established by the standards (Avellaneda, 2010).

Based on Ali et al. (2014), the raw material used in the production process has a direct influence on the specific biodiesel mass. The results presented for specific mass are according to the ones obtained by Ali et al. (2012), Vargas (2010), Sarkar and Bhattacharyya (2012). These authors indicated values for specific mass from palm oil biodiesel as 867, 871.6 and 874 kg m^{-3}, according to Ali et al. (2012), Vargas (2010), Sarkar and Bhattacharyya (2012)".

Table 4 – Specific mass of biodiesel at 20°C according to molar ratio*.

Molar ratio	Specific mass (kg m^{-3})
3:1	871.90 a
4:1	872.46 a
6:1	872.26 a
8:1	871.58 a

*Average values followed by the same letter do not differ in the 5% probability level by Tukey test.

Table 5 – Biodiesel kinetic viscosity according to molar ratio*.

Molar ratio	Kinetic viscosity (mm^2 s^{-1})
3:1	4.89 a
4:1	5.45 d
6:1	5.39 c
8:1	5.09 b

*Average values followed by different letter differ in the 5% probability level by Tukey test.

Kinetic viscosity

The kinetic viscosity results obtained are presented in Table 5 and are according to the Brazilian (ABNT), American (ASTM) and European (EN ISO) standards (Table 3), which require values of 3 to 6 mm^2 s^{-1}.

Several authors, such as Ali et al. (2012), Yusop et al. (2018), Kim et al. (2019), Tziourtzioumis and Stamatelos (2019), Yoon et al. (2019), and Ong et al. (2020), who produced biodiesel from palm oil, obtained kinematic viscosity values between 4.56 and 4.74 $mm^2.s^{-1}$.

According to Zahan and Kano (2018), biodiesel produced from palm oil has better properties compared to biodiesel produced from other raw materials, including kinematic viscosity. As explained by Yusop et al. (2018), fuel viscosity plays an important role in engine injection systems, as lower viscosities cause injectors and pumps to leak, interfering with the engine's power production. In addition, viscosity also interferes with atomization and spraying within the combustion chamber.

Hydrogen nuclear magnetic resonance

Using the hydrogen nuclear magnetic resonance (1H NMR) technique, it is possible to determine whether the transesterification reaction of triglycerides in monoesters occurred directly. The results from RMN1 H were similar for both palm oil and 3:1 molar ratio biodiesel. Figure 1 shows the 1H NMR spectrum of palm oil, in which the presence of a multiplet signal in the area of 4–4.4 ppm can be observed. This area shows the presence of hydrogen characteristic of triglycerides.

After the transesterification reaction, the 1H NMR spectrum in the produced biodiesel (Figure 1B) has no sign of the characteristic area of triglycerides 4–4.4 ppm. In addition, it is also possible to observe that in this spectrum, unlike the oil sample, a singlet is observed in the 3.4–3.7 ppm area, and this signal is attributed to the hydrogen of the methoxy group -OCH3 present in the produced methyl esters.

Furthermore, it appears that the signal from the 2.1–2.4 ppm area was highlighted, as it can be observed both in the source material (vegetable oil) and in the biodiesel samples. This area is attributed to the hydrogen in the carbonyl (α-CH2) adjacent group. In addition to the chemical information that this signal provides, it is also used to determine the degree of the transesterification conversion process.

The main chemical shifts (ppm) observed in the spectra of the produced biodiesel are shown in Table 6.

Analyzing the 1H NMR spectrum of 3:1 palm biodiesel, a triplet with an integration of approximately 3 H is observed in the displacement range of 0.92–0.84 ppm in relation to TMS. In the displacement range of 1.27–1.21 ppm, a singlet with an integration of approximately 13 H is observed. A singlet is observed in the displacement range of 1.56–1.59 ppm with an integration of approximately 2 H. In the displacement range of 2.32–2.28 ppm, a triplet with an integration of approximately 2 H is observed. In the displacement range of 3.69–3.65 ppm, a singlet with an integration of approximately 3 H is observed

and in the displacement range of 5.42–5.29 ppm a multiplet with an integration of approximately 1 H is observed.

Analysis of the data from the 1H NMR spectrum of the produced biodiesel proved that the transesterification reaction occurred observing the disappearance of the signals from the area of 4–4.4 ppm, indicating the disappearance of the hydrogen attributed to the triglycerides and the appearance of the singlet in the 3.5–3.7 ppm area, which is attributed to the hydrogen of the formed ester. The obtained results for chemical displacement and yield were compared to data already described in previous studies.

Transesterification conversion degree

As shown in Table 7, the 1H NMR analysis suggested that the yield of the transesterification reaction is mainly associated with the presence or absence of signal in the 4–4.4 ppm area attributed to the triglyceride H. As a result, a 79.50% conversion rate was observed.

It is important to note that the greater the conversion of biodiesel, the lower the amount of glycerin produced, suggesting that the cotton-coconut mixture has a lower amount of glycerin compared to other oils.

Gas chromatography analysis coupled to mass spectrometry

In the chromatogram corresponding to the palm oil methyl biodiesel sample (Figure 2), it is evident that the 16–22-minute interval shows signs related to the fatty esters that contribute the most to the composition of palm oil biodiesel. Comparing the experimental data to the data from ANVISA (Brasil, 1999) and Mancini et al. (2015), there is an agreement in relation to the largest compositions, which were oleic and palmitic acids, such as those of a greater area present in the sample (Table 8).

Statistical analysis

The software used for statistical analysis was the SISVAR v. 5.6 (Ferreira, 2014) with the Tukey test at a 5% significance level ($p < 0.05$). 108 samples were also analyzed in order to estimate the effects in biodiesel production yield of the studied variables and their interactions (Table 9). All three studied variables and the interactions between molar ratio versus temperature and temperature versus time had a significant effect on biodiesel production yield. However, the interaction between molar ratio versus time did not present significant effects.

It can be observed in Figure 3 that the highest yield in biodiesel production (93%) was obtained in the 3:1 molar ratio with a temperature of 52°C and stirring time of 60 minutes. The curves are quadratic regressions over average yield and temperature (or time) for all sets of molar ratios experiments. For the other molar ratios, the yield was lower and decreasing as the molar ratio increased. It can also be observed that the yield variation (between temperatures and stirring times) was lower at the 3:1 molar ratio.

Table 6 – Chemical shift (ppm) of biodiesel samples.

Biodiesel	Chemical shift (δ)
Palm 3:1	1H NMR (CDCl3, 300 Hz): 5.42-5.29 (m, 1H); 3.69-3.65 (s, 3H); 2.32-2.28 (t, 2H); 1.59-1.56 (s, 2H); 1.27-1.21 (s, 13H); 0.92-0.84 (t, 3H)

Table 7 – Conversion rate values for higher mass yield biodiesel.

Biodiesel	Conversion (%)
Palm 3:1	79.50

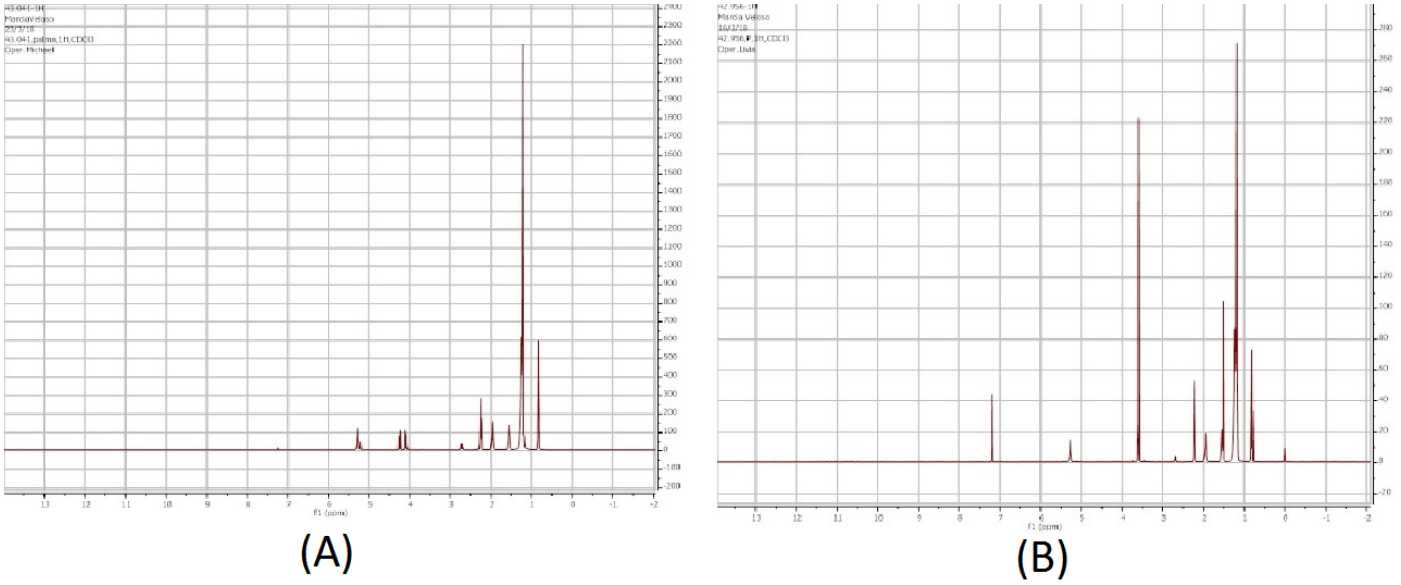

Figure 1 – 1H NMR spectrum of the source of triglycerides in (A) palm oil and (B) biodiesel formed.

Figure 3A shows the temperature performance in the production of biodiesel from palm. It was expected that the yield would be increased at higher temperatures, since, according to Feng et al. (2017), the molecular interaction between the reagents benefits the increase in the reaction temperature. However, the increase in temperature causes loss of reaction yield. According to Ramos et al. (2011), a possible ex-

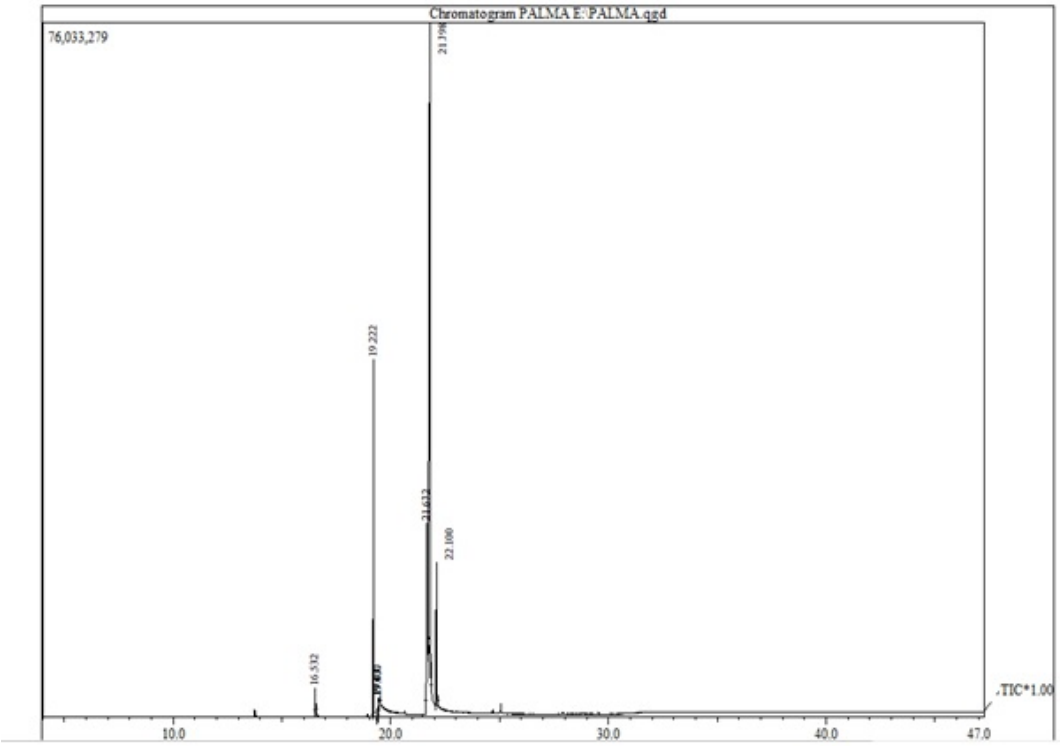

Figure 2 – Palm oil methyl biodiesel chromatogram.

Table 8 – Palm oil biodiesel fatty acid.

Fatty acid	Nomenclature	Retention time (min)	Area (%)	Mancini et al. (2015)	Brasil (1999)
C14:0	Myristic	16.53	0.82	1.1	0.5–2
C16:0	Palmitic	19.22	16.72	44	35–47
C18:0	Stearic	21.10	8.23	4.5	3.5–6.5
C18:1	Oleic	21.79	64.39	39.2	36–47
C18:2	Linoleic	21.67	9.34	10.1	6.5–15

Table 9 – Variance analysis of the effect on biodiesel production yield of the studied variables and their interactions.

Source	Degree of freedom	Sum of squares	Mean of square	F-value	Pr > Fc
Molar ratio	3	0.2213	0.0738	313.528	0.0000
Temperature	2	0.0508	0.0254	107.849	0.0000
Time	2	0.0050	0.0025	10.592	0.0000
Molar ratio*Temperature	6	0.0233	0.0039	16.530	0.0000
Molar ratio*Time	6	0.0023	0.0004	1.653	0.1429
Temperature*Time	4	0.0051	0.0013	5.458	0.0000
Error	84	0.0198	0.0002		
Corrected Total	107	0.3277			
CV (%)	1.78				
Mean	0.8606				

planation is that the increase in temperature not only favors the desired kinetics, but also the competing reactions such as hydrolysis. Ahiekpor and Kuwornoo also (2010) concluded that low temperatures in the reaction decrease the saponification degree.

Figure 3B shows the reaction time effect on the transesterification of palm oil. The yield showed a slight increase when the reaction time went from 40 to 60 minutes in the molar ratio of 3:1. However, the increase in time from 60 to 80 minutes led to a reduction in the reaction yield. For the other molar ratios, the increase in reaction time resulted in decreased yield. These results differ from those of Roschat et al. (2018), which obtained higher yields with increased reaction times.

Figure 4 shows the standardized distribution of production yields, and it is possible to verify that the lower molar ratios (3:1 and 4:1) present a higher density of values in the area of 85 to 90% yield, with emphasis on the molar ratio of 3:1, which showed greater density in the area of 90 to 95% of yield. At the highest molar ratios (6:1 and 8:1), the value density was greater in the area of 85 to 90% yield for the 6:1 molar ratio (with a density lower than the 4:1 ratio), and in the area of 80 to 85% yield for the 8:1 molar ratio. These values are evidenced by the better performance of the 3:1 molar ratio in the different reaction times studied.

Response surface

Figure 5 shows the effects of molar ratio, temperature, and time over a response surface of palm oil biodiesel production yield.

A maximum yield response, indicated by the dark red color, corresponds to a molar ratio of 3:1, temperature of 52°C and 60 minutes time, whose yield is 93%. The response surface indicates that, as molar ratio increases, yield decreases. This is different from the results observed by Feroldi et al. (2014), which suggested that in order to obtain a higher yield it is necessary to increase molar ratio in palm oil biodiesel production. Off the surface maximum, the yield decreases, especially for a molar ratio of 8:1 and 80 minutes, illustrated by the dark blue color on surface, resulting in a yield of 70%. According to Guerrero-Peña et al. (2013), a possible cause of this effect is linked to the reversibility reaction, due to long reaction time, resulting in a decrease of methyl esters production.

Sukjit and Punsuvon (2013), while also using the RSM determined optimum conditions for palm oil biodiesel production at a molar ratio of 7:1, temperature of 60°C and 70 minutes reaction time with a proportion of 1.2% KOH catalyst, resulting in a yield of 96.24%. Wong et al. (2015), using RSM, observed that the highest yield of 97.67% was obtained by molar ratio of 13.04:1, reaction time of 2.67 hours, and a proportion of 3.60% of catalyst.

Using the RSM and the Taguchi method, Tan et al. (2017) found a biodiesel yield around 95% under optimal reaction conditions at a temperature of 65°C, 1.9 at 2 hours' time and a molar ratio of 10 at 11:1, indicating that the integration of both methods is practically effective. However, RSM is more reliable in predicting the nonlinear relationship between the processing variables and response.

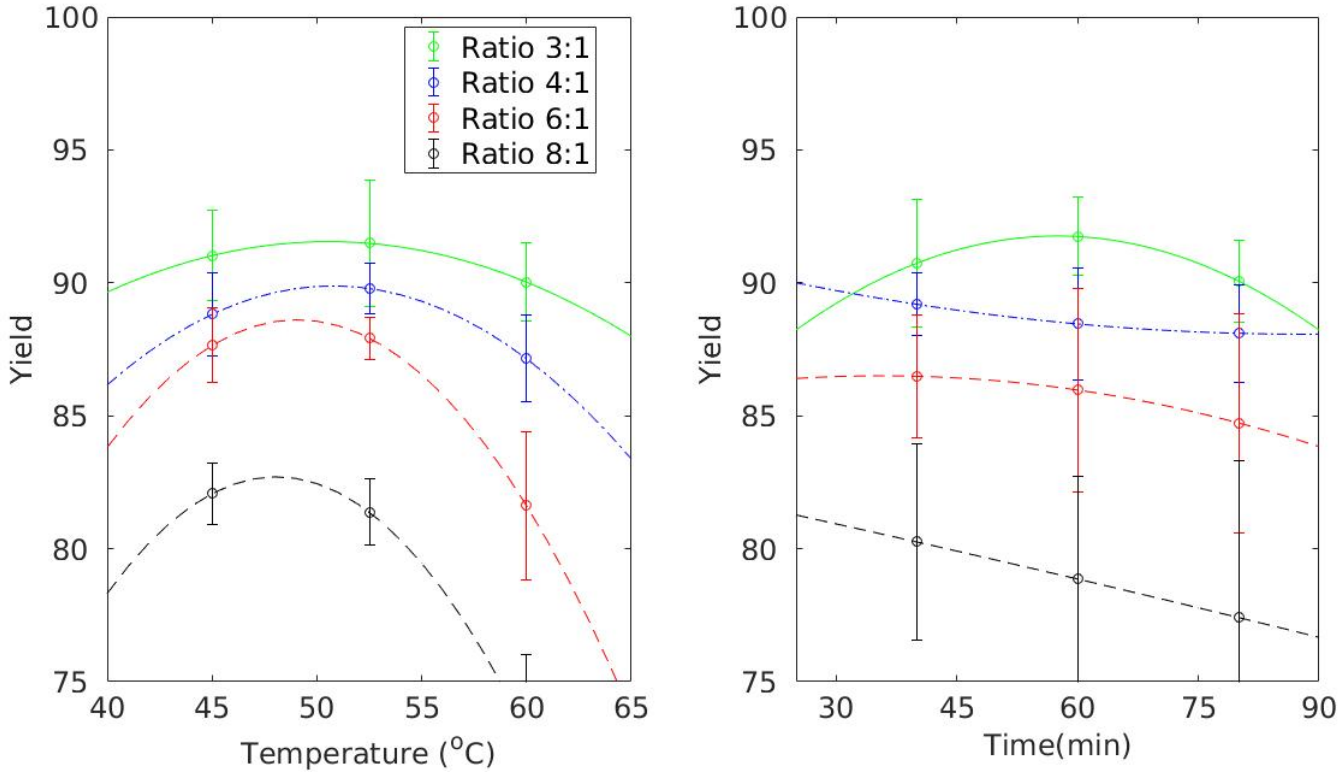

Figure 3 – Average and standard deviation of the experimental set (molar ratio) for (A) temperature (°C) and (B) time (minutes).

According to the results of Alkabbashi et al. (2009), the optimal conditions for biodiesel production with palm oil using methanol in the transesterification process were a reaction time of 60 minutes, a temperature of 60°C, a molar ratio of 10:1 ($m.m^{-1}$), and a proportion catalyst of 1.4% based on the oil mass, thus obtaining a yield of 93.6%.

These results corroborate those obtained by Paula et al. (2017), which state that the characteristic molar ratio of the reaction is 3:1, meaning that for every 3 moles of alcohol, 1 mol of triglycerides is required for the stoichiometric balance of the complete transesterification reaction to ensure that all oil is consumed in the process and transformed into methyl ester and glycerin.

The results found in the current study also corroborate with Uribe et al. (2014), as the authors state that methanol has high toxicity, although its advantages refer to the greater use in biofuel plants for biodiesel production, once it is more reactive and relatively cheaper than ethanol, requiring a shorter reaction time and lower molar ratios.

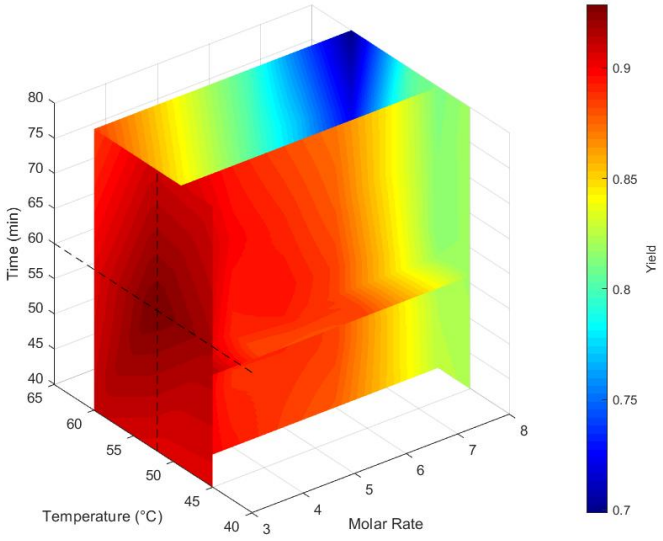

Figure 5 – Response surface of biodiesel production yield based on molar ratio, temperature, and time.

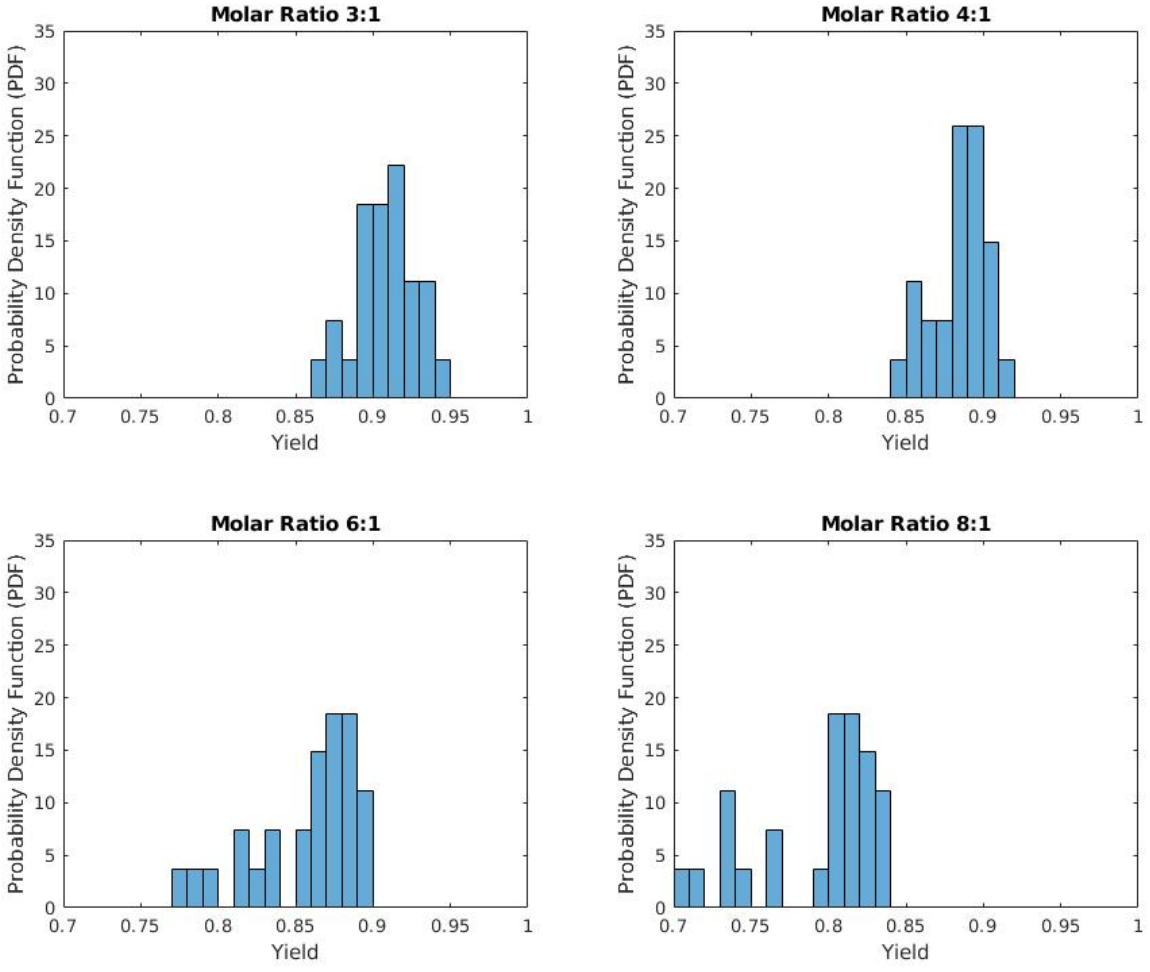

Figure 4 – Normalized probability distribution of production yields for 3:1, 4:1, 6:1 and 8:1 molar ratios.

The optimization method results from the importance of improving the performance of the systems and processes without increasing the costs. The RSM is a set of statistical and mathematical techniques used for the development, improvement and optimization of processes, in which the response is influenced by several variables, with the goal of optimizing the response (Khuri and Mukhopadhyay, 2010).

Conclusions

Based on the methodology and the results, the molar ratio was the most influential variable in the production yield of palm oil biodiesel using alkali catalyst and methyl route. Through response methodology and variation of the production factors (molar ratio, temperature, and time), the highest yield was for the molar ratio of 3:1, 52°C and 60 minutes. This result varies from those previously investigated in other studies, which generally had increased yields for higher molar ratios and indicated that when the molar ratio increases, the yield increases as well, opposing the results in the current study.

The produced biodiesel was characterized according to specific mass and kinetic viscosity properties, and the found values are included in Brazilian, American, and European standards. Therefore, the palm oil biodiesel has may be used as fuel for igniting compression engines.

In relation to the biodiesel characterization, using the H1 NMR technique, the transesterification reaction yield for the 3:1 palm oil biodiesel reached 79.50%. Using gas chromatography, the fatty acids present in the 3:1 palm oil biodiesel showed predominance of palmitic and oleic acids.

Contribution of authors:

Silva, F.C.: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing — original draft, Writing — review & editing, Visualization, Supervision, Project administration. Guardiola, J.F.H.: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing — original draft, Writing — review & editing, Visualization, Project administration. Teixeira, L.P.: Methodology, Validation, Formal analysis, Investigation, Data curation. Maria, A.C.L.: Formal analysis, Data curation, Writing — original draft, Writing — review & editing. Souza, L.: Validation, Formal analysis, Data curation, Writing — original draft. Belém, A.L.: Methodology, Validation, Formal analysis, Investigation, Data curation, Visualization.

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