DOI: 10.5327/Z2176-947820200600

BIODIESEL PRODUCTION BY ETHYLIC AND METHYLIC ROUTE BASED ON FACTORIAL DESIGN

PRODUÇÃO DE *BIODIESEL* POR ROTA ETÍLICA E METÍLICA A PARTIR DE PLANEJAMENTO FATORIAL

Laurênio Ferreira Lopes

Master's student of the Graduate Program in Biosystems Engineering (PGEB), Universidade Federal Fluminense (UFF) – Niterói (RJ), Brazil.

Flávio Castro da Silva

Doctor Professor in Agricultural Engineering, UFF – Niterói (RJ), Brazil.

Rita Colman Simões

Doctor Professor in Chemical Engineering, UFF – Niterói (RJ), Brazil.

Leandro Vahia Pontual

PhD student of the Graduate Program in Civil Engineering, UFF – Niterói (RJ), Brazil.

Luan Alves de Souza

Master's student of the PGEB, UFF – Niterói (RJ), Brazil.

Leomário Guedes do Nascimento

Undergraduate student in Chemical Engineering, Centro Universitário Anhanguera de Niterói – Niterói (RJ), Brazil.

Carlos Michel dos Anjos dos Santos

Undergraduate student in Mechanical Engineering, Centro Universitário Anhanguera de Niterói – Niterói (RJ), Brazil.

Correspondence address: Laurênio Ferreira Lopes – Avenida Jornalista Roberto Marinho, 255 – Colubandê – CEP: 24451-045 – São Gonçalo (RJ), Brazil – E-mail: laurenio_lopes@id.uff.br

Received on: 11/11/2019
Accepted on: 05/01/2020

RESUMO

A análise realizada nesta pesquisa teve como objetivo o desenvolvimento de um processo para a produção de *biodiesel* em escala de bancada. A reação foi realizada pelo método de transesterificação alcalina, em que os reagentes foram submetidos à temperatura de 60 ± 2ºC mantendo constante agitação mecânica. Por meio de um planejamento experimental fatorial, avaliaram-se os níveis máximos e mínimos de três variáveis: catalisador, razão molar e tempo de reação, combinando seus efeitos sem alterar a qualidade da resposta, verificando os rendimentos e interpretando com base nos tratamentos estatísticos as possíveis variações para justificar o melhor desempenho. Como ponto principal, foram utilizados dois álcoois, um obtido mediante importação, com alta qualidade no processo; e outro, com grande capacidade de produção nacional, metanol e etanol, respectivamente. A pesquisa surgiu como forma de aumentar o quantitativo quanto à afirmação de que o *biodiesel* é uma das soluções para amenizar os impactos ambientais e contribuir socioeconomicamente para o país, entretanto o custo de produção é superior ao processamento de diesel pelo petróleo. Assim, a verificação das melhores condições do processo diminuirá os custos operacionais e para o consumidor final. A variável que mais influenciou foi a quantidade de catalisador na síntese dos biodieseis etílicos e metílicos, porém os rendimentos para os ensaios B2 e B8 não apresentaram diferença significativa no nível de 5% pelo teste Tukey, e o maior rendimento foi realizado pelo ensaio B7 (97,44%), utilizando metanol em razão molar 1:9, 0,5% de catalisador em 90 minutos de reação. Depois de pesquisas para determinar melhores condições de processo para promover a produção e o uso de biocombustíveis, concluiu-se que, na produção de *biodiesel* via rota metílica, os resultados são mais satisfatórios e os rendimentos são maiores.

Palavras-chave: *biodiesel*; transesterificação; planejamento experimental.

ABSTRACT

The analysis carried out in this research had as objective the development of a process for the bench-scale production of biodiesel. The reaction was produced by the alkaline transesterification method, in which the reagents were subjected to a temperature of 60 ± 2°C, maintaining constant mechanical agitation. From a factorial experimental design, we evaluated the maximum and minimum levels of three variables: catalyst, molar ratio, and reaction time, combining their effects without altering the response quality, verifying the yields, and interpreting the possible variations based on statistical treatments to justify which one has the best performance. As the main point, two alcohols were used, one imported (methanol) that underwent a high-quality process, and another with a large national production capacity (ethanol). The research emerges as a way to reinforce the statement that biodiesel is one of the solutions to mitigate environmental impacts and socioeconomically contribute to the country. However, the production cost is higher than that of diesel derived from petroleum; thus, ensuring the best process conditions will decrease the operational costs and the costs for the end consumer. The variable with the most influence was the amount of catalyst for the synthesis of ethyl and methyl biodiesel. However, the yields for the B2 and B8 tests did not show a significant difference at the 5% level according to the Tukey test, and the highest yield was achieved by the B7 test (97.44%), using methanol at a 1:9 molar ratio and 0.5% catalyst in 90 minutes of reaction. After the research to determine the best process conditions to promote the production and use of biofuel, we concluded that the methyl route led to more satisfactory results and higher yields.

Keywords: biodiesel; transesterification; experimental design.

INTRODUCTION

Fossil fuels significantly contribute to the emission of pollutant gases, sulfur compounds, and particulate matter, whether from stationary sources — industries — or mobile sources — combustion in Otto and Diesel cycle engines. Mineral diesel, derived from the distillation of petroleum, is one of the fuels that harm the atmosphere and the health of the population, becoming an obstacle in political-economic and environmental issues, since it has been part of the energy matrix in Brazil and the world. A potential substitute is biodiesel, a renewable and less polluting fuel, whose participation in the energy matrix has been growing since the oil crises of the 1970s, which made commercial relations unfeasible given the high prices of oil barrels. The percentage of biodiesel added to mineral fuel is increasing annually due to significant public policy participation and popular support.

Incentives such as the National Program of Biodiesel Production and Use (Programa Nacional de Produção e Uso do Biodiesel — PNPB) boosted production on a significantly large scale, making biomass one of the main energy sources in the country, which has contributed to the growth of the national industry. As a result, Brazil became the second-largest producer of biodiesel, with the possibility of reaching the leading position in a short time according to the growth rate established by the National Agency of Petroleum (*Agência Nacional do Petróleo* — ANP) criteria. Biodiesel production grows about 0.83% per year and had a processing capacity of 7.7 billion liters in 2018. In the matter processing, it is important to pay attention to the production quality as well as include new ways to improve the process and the product.

In this study, we used a three-factor two-level (2^3) factorial design (catalyst, molar ratio, and time) for each alcohol (methanol and ethanol) to optimize the reaction parameters and obtain the best yield in the biodiesel production by transesterification.

THEORETICAL FRAMEWORK

Biodiesel

Biodiesel has been increasingly studied since the 1973 oil crisis, which contributed to the rise in barrel prices, but it was not until 1920 that Brazil took a significant role in the search for new biomass knowledge. From the mid-2000s onwards, the country started to develop new biodiesel production technologies due to its higher significance in the composition of the Brazilian energy matrix (FERNANDES *et al*., 2015). However, biodiesel production has barriers caused by the cost of the raw material, which may be impractical when the intent is increasing production and consumption turnover (SUOTA *et al*., 2018).

According to ANP (2016), biodiesel is a renewable fuel obtained from a chemical process called transesterification. Through this process, triglycerides present in animal oils or fat react with primary alcohol, methanol, or ethanol, generating two products: ester and glycerin. According to Gonçalves *et al*. (2019), gas chromatography made it possible to identify the predominance of acids in biodiesel and their relation to the oils used. Using this fuel is important because of its lower contribution to adverse effects on the well-being of humans and the environment, such as the lower emission of pollutant gases, mitigating environmental impacts and ensuring higher income for the smallholder rural category through public policies (ALMEIDA; DUARTE; NETO, 2018).

In this case, cleaner production (CP) can be adopted, as the tool is able to reduce the negative impacts to the environment and thereby increase the competitive advantage (RODRIGUES; PADILHA; MATTOS, 2011). The use of this biofuel is essential when comparing gaseous emissions, since petroleum-derived diesel has the potential to release harmful gases into the atmosphere while biodiesel has low sulfur and aromatic content, in addition to being biodegradable and renewable (MORAIS *et al.*, 2013).

Transesterification reaction

According to Taketa *et al.* (2013), transesterification, shown in Figure 1, consists of a reaction between triglyceride and alcohol, resulting in a new ester and glycerol (MENEGHETTI; MENEGHETTI; BRITO, 2013). Transesterification is the most common method for biodiesel production in industries when using an alkaline catalyst due to some advantages, such as higher yield, being more selective and less corrosive, its low cost, and the lower amount of catalyst required (VIEIRA *et al.*, 2018; GERIS *et al.*, 2007). The main reagents with better conversion results are methyl alcohol, soybean oil, and alkaline catalyst (TEBAS *et al.*, 2017).

According to Paula *et al.* (2017), the characteristic reaction molar ratio is 1:3, that is, every mol of triacylglycerol requires 3 moles of alcohol for the stoichiometric balance of the reaction molar ratio, leading to a complete transesterification reaction and ensuring that all oil is consumed in the process.

Alcohol

The choice of alcohol is as relevant as temperature conditions, molar ratio, reaction time, and catalyst percentage. Short-chain alcohols should be chosen, such as methanol, ethanol, propanol, butanol, and amyl alcohol (DANTAS *et al.*, 2016). Nogueira *et al.* (2018) compared the advantages and disadvantages of using ethanol in biodiesel production. Ethanol requires a higher stoichiometric ratio, higher temperature, longer reaction time, makes production more expensive, and produces higher amounts of soap emulsions. In contrast, it is derived from renewable sources, is biodegradable, has low toxicity, provides greater lubricity, results in higher cetane numbers, and has consolidated production in Brazil. For Uribe, Alberconi and Tavares (2014), methanol has high toxicity; however, its advantages include the greater use in biofuel plants for biodiesel production, since it is more reactive than ethanol and relatively cheaper, the shorter reaction time, and the lower molar ratios.

Catalyst

In the development of their research, Rossi *et al.* (2018) explain that catalysts increase the rate of reagent consumption and product formation. The choice of catalysis should be based on the raw material used. Heterogeneous basic

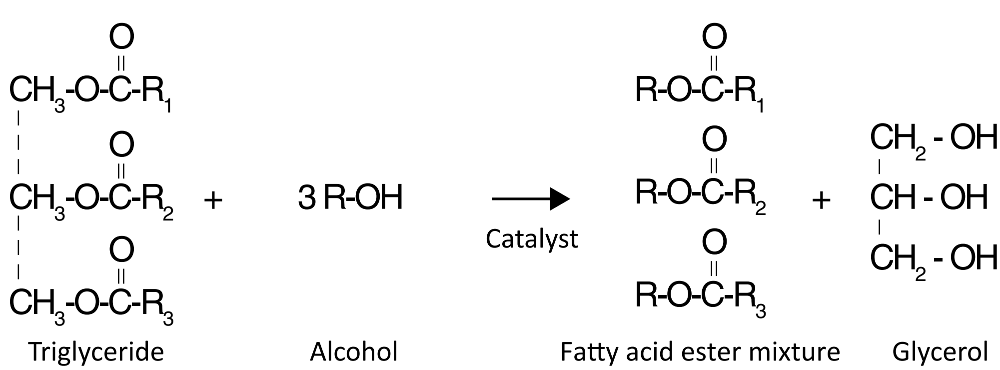

Figure 1 – Global transesterification reaction of soybean oil with primary alcohol, producing biodiesel and glycerol.

catalysts require the use of excess alcohol to obtain a good yield. In contrast, heterogeneous acid catalysis has lower corrosivity and toxicity than alkaline catalysis but presents diffusivity and high-cost problems. There are also enzymatic catalysts that facilitate washing and reuse but gradually lose their efficiency. Homogeneous catalysis is mainly used in transesterification reactions with oils high in fatty acids. However, the homogeneous alkaline transesterification process requires high-purity raw materials, with practically no free fatty acids, phosphatides, and water. These impurities react with traditional basic catalysts, leading to the formation of soaps and the consumption of part of the catalyst. Consequently, the process requires excess catalyst to guarantee catalytic efficiency. Also, separating glycerin and biodiesel at the end of the process is more difficult (OLIVEIRA; CARNEIRO JUNIOR; ALVES, 2015).

Factorial Design

The factorial design method is an analytical strategy to select the most relevant variables in a given process, generally used in studies that cover many variables, and an essential tool for optimization. It is used in several research fields, especially in chemistry, chemical engineering, food engineering, and biotechnology. The most used experimental designs in Brazil are the factorial and central composite designs (SILVA *et al*., 2008; CAMARGO; MOREIRA; VACCARO, 2009; VICENTINI *et al*., 2011).

For Cunico *et al*. (2008), factorial design is the most suitable to study the effects of two or more influencing variables, as in each trial, all possible combinations between the levels of each variable are investigated. The assessment of the effects and interactions of the variables is extremely important to understand the processes monitored in a given system. As the number of factors (variables) grows, making observations in all possible level combinations large enough to allow statistical inference becomes more difficult (PEREIRA-FILHO; POPPI; ARRUDA, 2002; SILVA; SANT'ANNA, 2007).

According to Pereira and Pereira-Filho (2018), factorial design systems have many advantages and applications, for example:

- simultaneously evaluating the effect of many variables, based on a small number of experiments;
- saving financial resources;
- obtaining results with greater chemical and statistical reliability;
- possibility of building a mathematical model that will allow making predictions under conditions that have not been tested (CUNICO *et al*., 2008).

Ruschel *et al*. (2016) declare that the literature presents, among countless applications, the use of experimental design as an efficient way of evaluating and improving biodiesel synthesis methods, aiming at maximizing yields through the optimization of multivariate models of experimental conditions, allowing the study of several variables simultaneously with the aid of statistical, mathematical, and computational methods to extract as much information as possible (LIMA *et al*., 2017).

METHODOLOGY

Bench-scale production was carried out in the General Chemistry Laboratory of the Centro Universitário Anhanguera in Niterói. The inputs required for biodiesel production were methanol (CH_3OH) and ethanol (C_2H_5OH) with 99.8% purity from the Exodus brand, refined non-residual soybean oil from the Soya TYPE 1 brand, purchased from a local supermarket, and sodium hydroxide (NaOH) in Micro Pearl P.A. with 99.2% content from the Neon brand, as an alkaline catalyst. The study of the variables involved a 2^3 factorial design in random order of experiments, performed in triplicate, to evaluate the influence of the independent variables, such as molar ratio (oil/alcohol) (grams), NaOH concentration (grams), and reaction time (minutes), on reaction yield.

According to Arruda *et al*. (2017), these levels are coded as +1 and -1, for the highest and lowest levels, respectively, to determine the effect and influence of the levels of each factor on the proposed system. For data treatment, we used the Excel® software to create electronic calculation spreadsheets that were converted into a graph to compare the biodiesel yields via ethyl and methyl. The Statistica software (version 10) was used to calculate the variance (ANOVA) through the multiple comparison technique between the means of experimental treatments and obtain results of the effects and interactions of the variables that influence the biodiesel yield in the construction of both the Pareto chart, at a 5% significance level for the effect of the variables on the biodiesel synthesis process, and a linear graph for yield showing predicted and observed values, determining the quality of the adjustment.

Sisvar 5.6 is a free Brazilian statistical analysis software copyrighted by the Universidade Federal de Lavras (UFLA) and the most used in the country, either directly in the statistical analysis of scientific data from the most different areas of knowledge or in the teaching of basic and experimental statistics. In the present study, it was used for statistical analysis, comparing the means by the Tukey test (5% significance) and the average yields of the ethyl and methyl biodiesel tests to identify the best production (FERREIRA, 2008; NASCIMENTO; NEIDE; GONZATTI, 2016; DENARI; SACILOTO; CAVALHEIRO, 2016; REIS; PINTO; SOARES, 2016; ZORZO *et al.*, 2018). Table 1 presents the variables evaluated for both types of alcohol.

The production started by preparing the catalyst. The chosen catalysis method was homogeneous alkaline, that is, the alcohol (methanol and ethanol) was subjected to solubilization with sodium hydroxide forming sodium methoxide. Next, both the catalyst solution and oil were heated in a hotplate until they reached the temperature range of 55 ± 2ºC, since, at lower temperatures, the transesterification reaction speed decreases, according to the Arrhenius law. However, when the temperature exceeds 55ºC, the reaction speed may decrease due to the ethanol loss caused by evaporation (MENDOW *et al*., 2012).

After reaching the intended temperature, the oil was added to the Erlenmeyer flask and mixed with methoxide at a constant temperature until the desired reaction time. Following completion of the reaction, the formed products — biodiesel and glycerin — were placed in separatory funnels to partition the phases, after 24 h of absolute rest. Once all glycerin had been removed, the purification process started with neutralization with a 37% hydrochloric acid solution and finished with deionized water at a temperature range of 60 ± 2ºC until the wash water became transparent, and the pH was close to 7.0 — verified with a pH tape for qualitative analyses.

According to Victorino, Pereira, and Fiaux (2016), this crude glycerin proved to be a suitable raw material for the *Aspergillus niger* biotechnological process. The technological use of these two environmental liabilities — glycerin and residual cooking oil — contributes to reducing the environmental and economic impacts of their generation and disposal.

The biodiesel was then oven-dried at 110ºC for 3 hours to remove traces of water. Concluding the process, the biodiesel mass was assessed, and its percentage yield (m/m) was calculated according to Equation 1, described by Galina (2018). Figures 2A and 2B show the processes of bench-scale biodiesel production from methanol and ethanol, respectively, with the main difference being the decantation stage. Methyl biodiesel presents a heterogeneous mixture facilitating glycerin extraction, while in ethyl biodiesel, the excess carbon in the molecules makes the esters miscible with glycerin, hindering the purification process and reducing mass yield due to loss of biodiesel during the washing process.

$$Yield = \frac{biodiesel\ mass}{biomass\ mass} \quad (1)$$

In which:
Biodiesel mass = experimental biodiesel mass obtained after the purification process (g);
Biomass mass = vegetable oil mass (g).

All 8 experiments were performed in triplicate, totaling 24 experiments, to evaluate the combination of the

Table 1 – 2^3 Experimental Design.

Variables	Methanol		Ethanol	
	-1	+1	-1	+1
Catalyst	0.5	1.5	0.5	1.5
Molar ratio	1:3	1:9	1:12	1:18
Time	30	90	30	90

best conditions based on the average yield of the three samples produced by each biodiesel. The factorial design investigated the influences of all experimental variables of interest and the interaction effects on the response or responses. The effects of each variable, their main impacts, and their interactions (presented in Equation 2) were calculated (TEÓFILO; FERREIRA, 2006). According to Teófilo and Ferreira (2006), the coefficient b0 is the average population value of all responses obtained, b1, b2, and b3 are the coefficients related to the variables x1, x2, and x3, respectively, and ε is the random error associated with the model. The values for x1x2, x1x3, and x2x3 correspond to the effects of second-order interactions, and x1x2x3 represents the third-order effect.

$$y = b0 + b1\ x1 + b2\ x2 + b3\ x3 + b12\ x1x2 + b13\ x1x3 + b23\ x2x3 + b123\ x1x2x3 + \varepsilon \quad (2)$$

RESULTS AND DISCUSSION

After producing the biodiesel in triplicate, we calculated the yields (η) of each reaction, the average (μ), the standard deviation (σ), and the coefficient of variation (CV), which evaluated the dispersion of the results in relation to the average. According to Tables 2 and 3, all CV values are lower than 10%, indicating that the yield data of each biodiesel are homogeneous and less dispersed around the average.

Table 4 shows the analysis of average results obtained from the studied variables in the factorial design: cat-

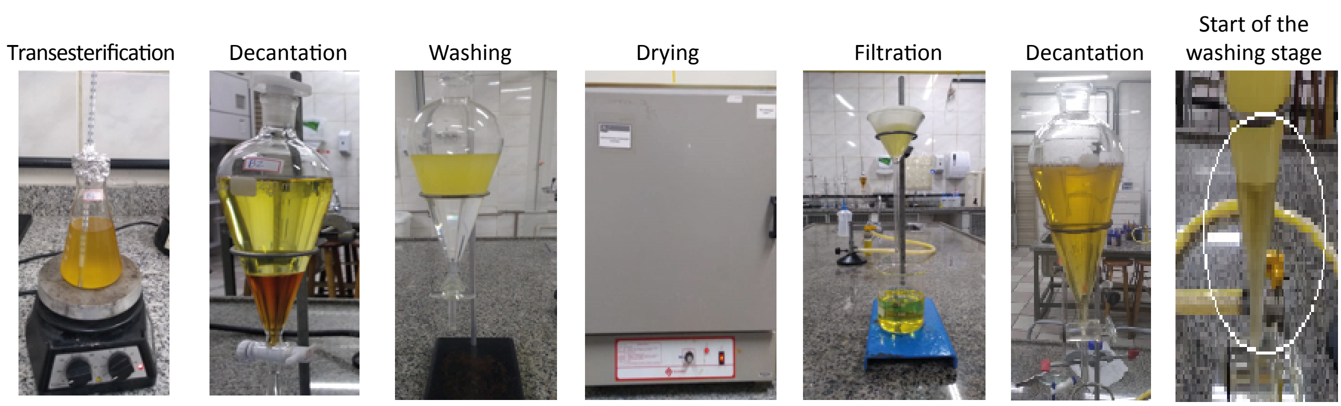

Figure 2 – Synthesis steps of (A) methyl and (B) ethyl biodiesel.

Table 2 – Analysis of methanol biodiesel experimental results.

Biodiesel	η 1	η 2	η 3	μ	σ	CV (%)
B1	92.88	93.44	94.51	93.61	0.8282	0.8847
B8	21.02	20.40	21.22	20.88	0.4275	2.0470
B3	87.32	87.54	87.87	87.58	0.2768	0.3161
B7	58.30	57.90	59.00	58.40	0.5568	0.9533
B2	95.20	95.54	94.38	95.04	0.5963	0.6274
B6	40.25	40.10	39.92	40.09	0.1652	0.4121
B4	97.25	97.32	97.75	97.44	0.2707	0.2778
B5	80.20	80.15	80.49	80.28	0.1836	0.2287

CV: coefficient of variation.

alyst percentage (% Cat.), alcohol/oil molar ratio (MR), and time (t). The difference in methanol use revealed that higher amounts of catalyst influenced the reaction yield — B8 (20.88%), B7 (58.40%), and B6 (40.09%). However, B5 had an increase in yield with the catalyst at 1.5% because the other variables, such as molar ratio and time, were at higher levels. Regarding ethanol, the catalyst remains the most important variable, as it has the strongest influence on the reaction yield; the B1 and B2 biodiesel had yields above 90%. The performance of the *t*-test and construction of the Pareto chart are necessary to reach the best experimental conditions (ARRUDA *et al.*, 2017).

The interaction effect of each variable was calculated, with x1 corresponding to the main catalyst effect, x2 to alcohol-related molar ratio, and x3 to time. Table 5 presents the test at a 5% significance level; within this limit, p-value = 0.0141 was related to the catalyst mass percentage, considerably affecting the yield of the transesterification reaction.

Table 3 –Analysis of ethanol biodiesel experimental results.

Biodiesel	η 1	η 2	η 3	μ	σ	CV (%)
B1	92.55	92.88	92.01	92.48	0.4392	0.475
B8	20.75	21.42	21.06	21.08	0.3353	1.591
B3	76.45	76.35	76.40	76.40	0.0500	0.065
B7	30.50	30.22	30.63	30.45	0.2095	0.688
B2	95.09	95.12	95.03	95.08	0.0458	0.048
B6	27.50	27.70	28.47	27.89	0.5121	1.836
B4	87.43	87.60	87.86	87.63	0.2166	0.247
B5	50.65	50.44	51.31	50.80	0.4540	0.894

CV: coefficient of variation.

Table 4 – Factorial experimental design with mass yields for each alcohol.

		Independent variables			Average mass yields (%) Methanol	Average mass yields (%) Ethanol
Experiments	Random Order	% Cat.	MR	T (min)		
1	B1	-	-	-	93.61	92.48
2	B8	+	-	-	20.88	21.08
3	B3	-	+	-	87.58	76.40
4	B7	+	+	-	58.40	30.45
5	B2	-	-	+	95.04	95.08
6	B6	+	-	+	40.09	27.89
7	B4	-	+	+	97.44	87.63
8	B5	+	+	+	80.28	50.80

% Cat.: catalyst percentage; MR: alcohol/oil molar ratio; t: time.

Table 6 presents the coefficient values that represent the experimental model of ethyl biodiesel synthesis via homogeneous NaOH catalysis. Based on these values, a polynomial function describing the response variables was obtained.

Considering the main coefficients and interactions until the second order, the coefficient of determination had a value of $R^2 = 0.999956$. Teófilo and Ferreira (2006) argue that the R^2 value represents the fraction of the variation explained by the lack of model fit. The closer the coefficient value is to 1, the better the model fits the observed responses.

Figure 3 shows the Pareto chart representing the effects of each first- and second-order variables and their influence at a 5% significance level, with p-value < 0.05 on the reaction yield. The Pareto chart presents the effects of the

Table 5 – Statistical analysis of effects at a 95% significance level for ethanol.

Effect Estimates: Yield (%); R^2 = 0.99956; Ethanol MS Residual = 3.013513										
	Effect	Standard Error	t (1)	p-value	-95% Cnf. Limit	+95% Cnf. Limit	Coef.	Standard Error Coef.	-95% Cnf. Limit	+95% Cnf. Limit
Average	60.23	0.61	98.13	0.0065	52.43	68.02	60.23	0.62	52.43	68.02
(1) Catalyst	-55.34	1.23	-45.08	0.0141	-70.94	-39.74	-27.67	0.62	-35.47	-19.87

Cnf.: confidence; Coef.: coefficient.

Table 6 – Results of main and interaction effects of ethyl biodiesel.

Average	Coefficient	Coefficient
	60.23	β0
x1	-27.70	β1
x2	1.094	β2
x3	5.124	β3
x1x2	6.976	β12
x1x3	1.666	β13
x2x3	2.771	β23

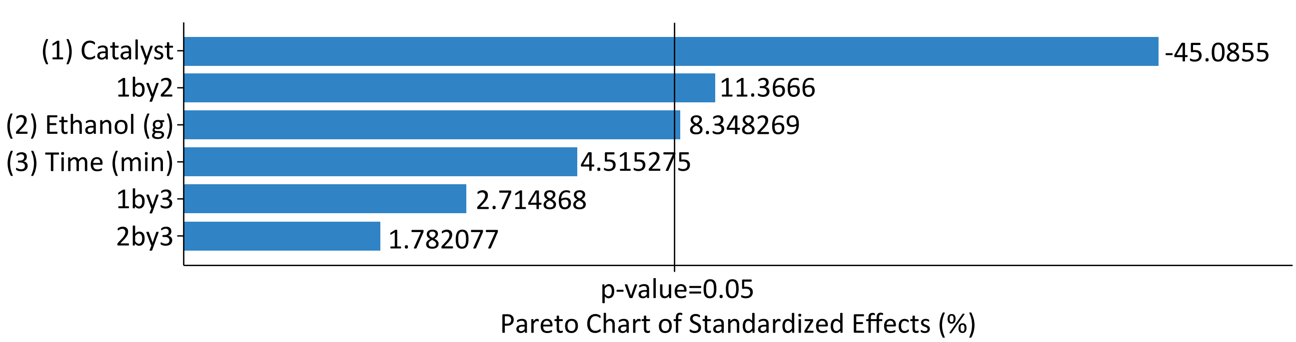

Figure 3 – Pareto chart of standardized effects for ethyl biodiesel variables.

studied variables, and the variables with the most effective influence are in longer bars (PAGAN; LUZ; FERREIRA, 2016).

Regarding the first-order effects presented in the diagram, the variable that most influenced the increase in yield was the catalyst. The negative sign indicates that moving from level +1 (1.5%) to -1 (0.5%) increases the yield. Pagan, Luz, and Ferreira (2016) confirmed this finding when they used residual oil in their tests and found that ethyl transesterification has good conversions (93.87%) in a low percentage of catalyst (0.5% NaOH).

Alkaline homogeneous catalysts, at concentrations of 0.5 mass% and 1.5 mass% relative to oil mass, competitively activate saponification reactions reasonably faster due to the availability of free fatty acid in the medium and transesterification, which decreases the reaction yield (LIMA *et al.*, 2010). The positive sign of the variables time and ethanol, corresponding to the molar ratio, shows that larger values promote higher reaction yields, which do not present significant contributions when below 5%. Nevertheless, in the tests conducted by Silva Neto *et al.* (2018), the variables molar ratio of coconut oil/ethanol and percentage of catalyst at high levels showed the greatest influence for results above 95% conversion. As for the second-order effects, positive values indicated that the reaction yield increases when the level rises from -1 to +1, but all of them were below the significance level.

The experimental design was developed by other authors analyzing variables not investigated in this work. Lima *et al.* (2010), in the transesterification reaction of corn oil triglycerides with ethanol, found that the order of significance for the effects of process factors is: catalyst concentration > molar ratio > type of catalyst > rotation speed > time > temperature. Biodiesel with the lowest percentage of catalyst has the best results.

Disregarding the influence of variables below the 95% significance level, Equation 3 defines the work of ethyl biodiesel synthesis. After performing the experiments and obtaining the answers related to each experimental point, we adjusted a mathematical function to describe the behavior of the responses according to the variation of the levels of the studied variables. (NOVAES *et al.*, 2017).

$$y(x1, x2, x3) = 60.23 - 27.70x \quad (3)$$

Figure 4 represents the relationship between the experimentally observed values and the predicted theoretical values of the reaction process to determine the yield. Thus, the proximity of the values demonstrates a distancing from the experimental error, increasing the confidence in the results.

For methyl biodiesel, the main coefficients and interactions until the second order presented a very significant determination coefficient, $R^2 = 0.999928$, for mass yield. As the R^2 is close to the theoretical value, we can infer that the values obtained for the modeling proved to be adequate. Table 7 presents the effects and, among them, the catalyst (x1), methanol (x2), and the interaction (x12) had a 5% significance level (p-value < 0.05).

Second-order interactions are also described to study the factor effect on the response, which we must make vary and observe the result of the variation. This situation im-

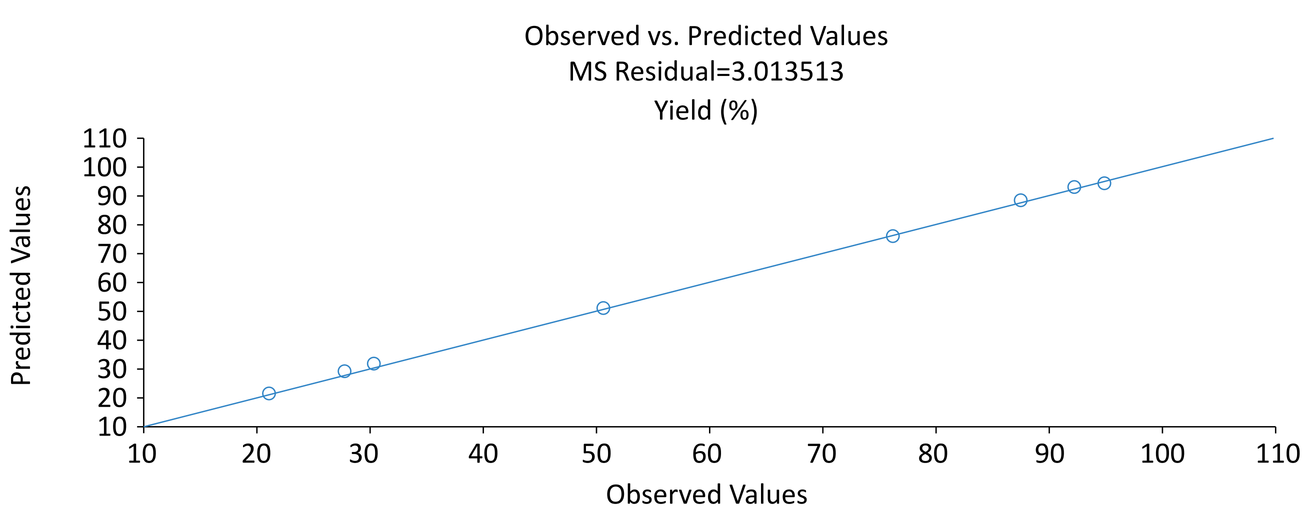

Figure 4 – Linear graph for ethyl biodiesel yield.

plies testing on at least two-factor levels. The design in which all variables are studied at only two levels is, therefore, the simplest of them all (MARINHO; CASTRO, 2005).

Table 8 presents the coefficient values to describe a polynomial model related to the use of methanol, showing the intensity of the effect of the variables on the mass yield of the reaction.

According to Castro (2013), the use of factorial design and statistical analysis allowed expressing the process yield as a linear model, and the answer could be written as a function of the significant variables (Equation 4) with factors that had influence at a 95% level of significance; the remaining effects were neglected for presenting values above p-value > 0.05. Thus, concerning catalyst use, the molar ratio (alcohol) and interaction between these two factors had a significant effect on the reaction yield.

$$y(x1, x2, x3) = 71.67 - 21.80x1 + 9.26x2 + 10.14x1x2 \tag{4}$$

The order of significance found for the effects of process factors on the soybean oil transesterification reaction, regardless of the algebraic sign, is as follows: catalyst concentration > catalyst/molar ratio (alcohol) > alcohol > time > catalyst/time > molar ratio (alcohol)/time.

Starting with the first-order variables, the higher the percentage of catalyst, the lower the conversion, as stated by Bernardo, Oliveira Junior, and Fagundes (2015) in the research that carried out tests to optimize the production process of biodiesel from soy via methyl route. According to the results obtained, they identified a greater influence of the amount of catalyst, which showed a reduction in yield in concentrations above 1.2%. Consequently, in Figure 5, the catalyst pres-

Table 7 – Statistical analysis of effects at a 95% significance level for methanol.

Effect estimates: Yield (%); R^2 = 0.999928; Methanol MS Residual = 4.1472										
	Effect	Standard Error	t (1)	p	-95% Cnf. Limit	+95% Cnf. Limit	Coef.	Standard Error Coef.	-95% Cnf. Limit	+95% Cnf. Limit
Average	71.66	0.72	99.53	0.0064	62.52	80.81	71.66	0.72	62.52	80.81
(1) Catalyst	-43.50	1.44	-30.21	0.0211	-61.80	-25.21	-21.75	0.72	-30.90	-12.60
(2) Methanol	18.52	1.44	12.86	0.0494	0.22	36.82	9.26	0.72	0.11	18.41
Catalyst/ Methanol	20.33	1.44	14.12	0.0450	2.04	38.63	10.17	0.72	1.02	19.32

Cnf.: confidence; Coef.: coefficient.

Table 8 – Results of main and interaction effects of methyl biodiesel.

Average	Coefficient	Coefficient
	71.67	$\beta 0$
x1	-21.80	$\beta 1$
x2	9.26	$\beta 2$
x3	6.54	$\beta 3$
x1x2	10.17	$\beta 12$
x1x3	3.72	$\beta 13$
x2x3	1.38	$\beta 23$

ents a negative sign, indicating that the yield increases at lower levels. However, the influence of methanol is considerable with the increase in positive levels (1:9), since time is below 5%; therefore, methanol does not cause a significant effect on the reaction yield, contrary to part of the research by Schneider *et al*. (2009), who observed proportions of 1:8 oil-methanol leading to the maximum conversion of the frying oil used in methyl esters, with a low percentage of catalyst and temperature, but with 3 hours of reaction.

Martins *et al*. (2015) declare that the temperature and concentration of the catalyst used in the reaction must be at moderate levels to optimize the transesterification process of soybean oil through a 2^3 factorial design, resulting in excellent yields. As to the second-order catalyst/time and catalyst/molar ratio effects, they are below 5% and have no significant level of reaction yield. The opposite happened with the catalyst/molar ratio, which showed a positive value Y ++, growing with increasing levels and within the significance level.

Figure 6 presents a graph proposed by Statistics as a way to analyze the quality of the model and have a linear correlation close to ideal. Noticeably, the predicted and observed values are similar to the observed versus predicted value of the model, representing another way to analyze the quality of the studied model.

The column graph in Figure 7 shows that, when comparing the average yields of different types of biodiesel, in general, the production via methyl is more viable, being superior in most of the experiments, except B8 and B2, which become equal due to the proximity of the values, with a mass percentage difference of 0.95 and 0.04%, respectively. The greatest conversion of soybean oil into methyl esters was in the B4 test — 97.44% when using a 0.5% catalyst, 1:9 molar ratio in 90 minutes of reaction. Carvalho *et al*. (2009) achieved

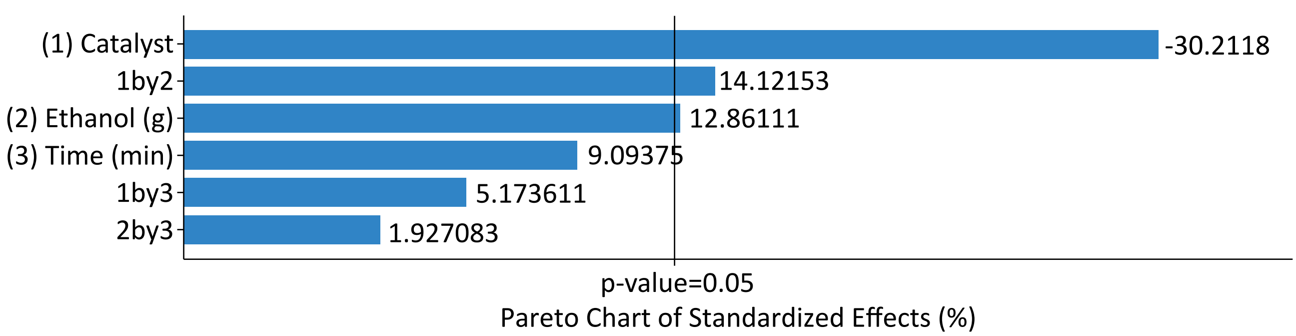

Figure 5 – Pareto chart of standardized effects for methyl biodiesel variables.

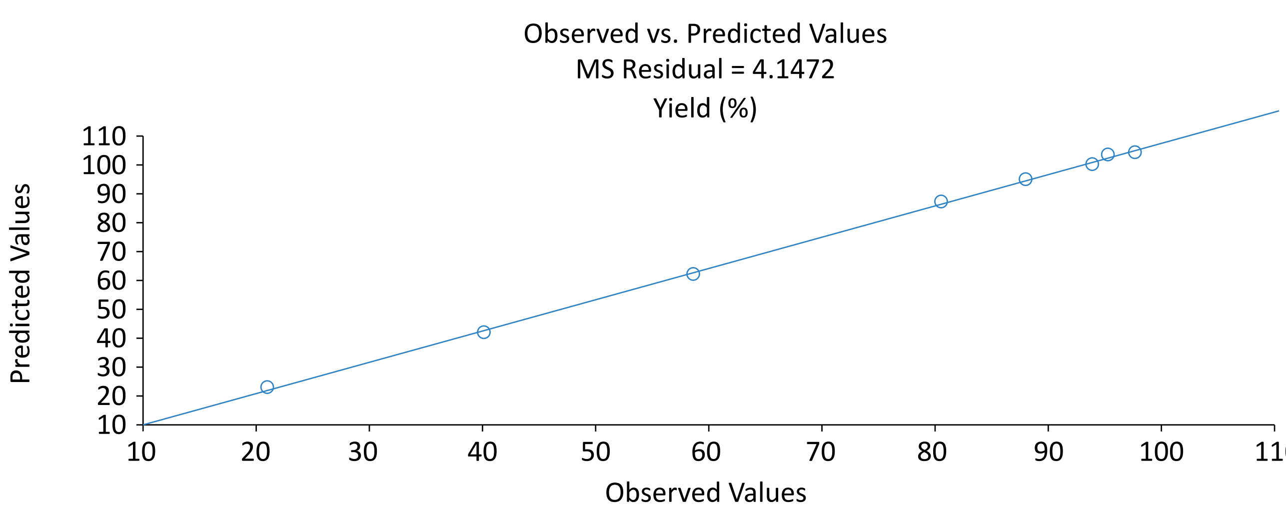

Figure 6 – Linear graph for methyl biodiesel yield.

RBCIAMB | v.55 | n.2 | jun 2020 | 226-241 - ISSN 2176-9478

similar results when using experimental design for the synthesis of biodiesel from cotton and revealed that the best conversion result occurred under the following conditions: 1:8 molar ratio, temperature of 40ºC, and 1% catalyst, reaching a conversion of 96.79%; changing the percentage of catalyst to 0.5% led a yield of 96.656%, a reduction of approximately 0.14%.

The best ethanol conversion happened in test B2 (0.5% catalyst, 1:12 molar ratio in 90 minutes of reaction) — 95.08%. Several authors obtained excellent results, but under different conditions than the one presented in this work.

For Arruda *et al*. (2017), the influence of variables on the transesterification of pequi oil by ethyl route showed best results with the use of KOH as a catalyst in a molar ratio inversely proportional to the reaction temperature. Thus, in a 12:1 molar ratio and a temperature of 60ºC, the maximum yield was 73%, while at a molar ratio of 6:1 and a temperature of 80ºC, the conversion was 70%. When using NaOH, the yields were below 50%. By modifying the biomass and using corn oil in smaller percentages of catalyst, either KOH or NaOH, as well as variations in rotation during the process, the reaction was inversely proportional to the molar ratio when using KOH and directly proportional when using NaOH, presenting conversions of 96.18 and 92.88%, respectively (LIMA *et al*., 2013). According to Borges *et al*. (2015), the evaluation of the fractional factorial experimental design of operational variables in ethyl transesterification in soybean oil showed growth in yield when the rotation, molar ratio, and temperature (55ºC) increased in a short time reaction with KOH catalyst compared to NaOH.

To make the yield analysis safer, we performed a comparison test — Tukey test — to demonstrate the statistical difference (5% significance). According to Oliveira (2008), the Tukey test, based on the total studied amplitude (Studentized range), can be used to compare any contrast between two treatment averages. The test is accurate and very simple to use when the number of repetitions is the same for all treatments. Table 9 presents the results obtained for each biodiesel yield processed by methanol and ethanol. The results showed no statistical difference (5%) between the methanol and ethanol biodiesel samples (B2 and B8), but the average yields of the other samples differed significantly and presented better results when using methanol.

CONCLUSIONS

The result of the production based on experimental design to combine the studied variables, reducing the number of samples together with statistical graphs, was satisfactory. The average yields of the transesterification reaction by both ethyl and methyl route presented values above 90%, which are considered excellent results. However, when comparing the two types of alcohol, methanol proved to be more viable because, as the production costs are high, maximizing yields may be a solution to make the process feasible.

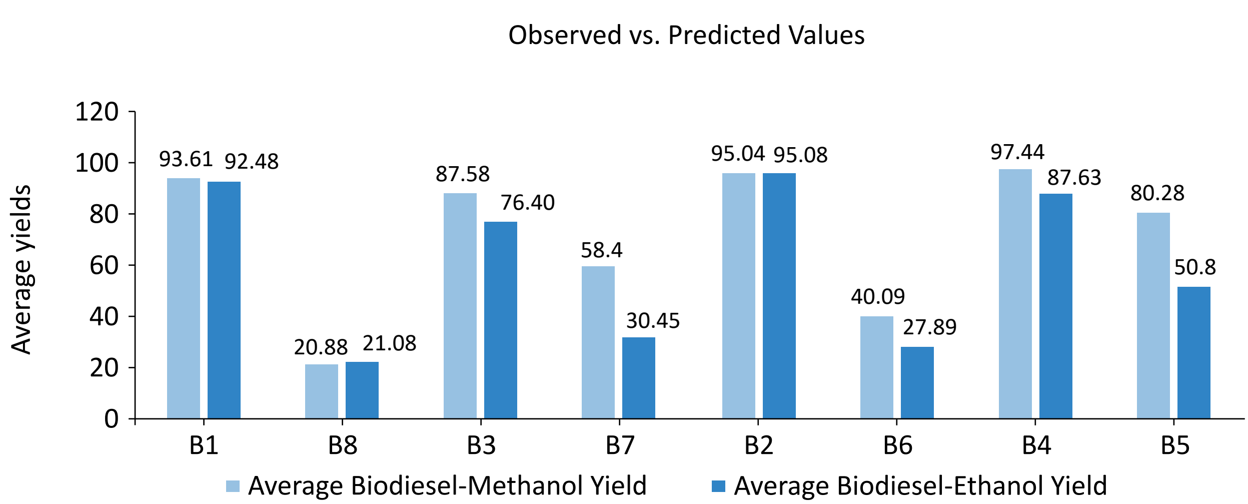

Figure 7 – Column chart comparing yields of ethyl and methyl biodiesel.

Table 9 – Tukey test (5% significance level) between yields of each biodiesel (methanol and ethanol).

Biodiesel	Alcohol	
	Methanol Yields	Ethanol Yields
B1	93.61 Bf	92.48 Ag
B2	95.04 Ag	95.08 Ah
B3	87.58 Be	76.40 Ae
B4	97.44 Bh	87.63 Af
B5	80.28 Bd	50.80 Ad
B6	40.09 Bb	27.89 Ab
B7	58.40 Bc	30.45 Ac
B8	20.88 Aa	21.08 Aa

ACKNOWLEDGMENTS

We thank the Fundação Nacional de Desenvolvimento do Ensino Superior Particular (FUNADESP) for funding the scientific initiation scholarship.

REFERENCES

AGÊNCIA NACIONAL DO PETRÓLEO, GÁS E BIOCOMBUSTÍVEIS (ANP). *Dados estatísticos em relação a produção de biodiesel em metros cúbicos em escala comercial no Brasil*. Brasília: Ministério de Minas e Energia, 2016. Available at: <http://www.anp.gov.br/dados-estatisticos>. Accessed on: July 22, 2019.

ALMEIDA, H. M. L.; DUARTE, E. S. A.; NETO, J. G. V. Síntese de Biodiesel pela Reação de Transesterificação Básica com Óleo de Soja. *Processos Químicos*, v. 12, n. 23, p. 95-98, 2018. https://doi.org/10.19142/rpq.v12i23.434

ARRUDA, A. P.; FRAGA, I. M.; SOUSA, D. de A.; ITOKAGI, D. M.; PEREIRA, C. S.; PEREIRA, N. G. Planejamento fatorial para otimização das condições da reação de transesterificação alcalina do óleo de pequi (Caryocar brasiliense Cambess). *Engevista*, v. 19, n. 1, p. 132-145, 2017. https://doi.org/10.22409/engevista.v19i1.809

BERNARDO, J. da S.; OLIVEIRA JUNIOR, W. P. de O.; FAGUNDES, F. P. Otimização das variáveis reacionais no processo de obtenção do biodiesel de soja. *Tecnologia & Informação*, ano 2, n. 1, p. 7-17, 2015.

BORGES, K. A.; PORTELA, F. M.; SANTOS, D. Q.; NETO, W. B.; FABRIS, J. D.; HERNÁNDEZ-TORRONES, M. G. Performance das variáveis operacionais na transesterificação etílica do óleo de soja. *Eclética Química*, v. 40, n. 1, p. 126-132, 2015. https://doi.org/10.26850/1678-4618eqj.v40.1.2015.p126-132

CAMARGO, L. F. R.; MOREIRA, V.; VACCARO, G. L. Aplicação das técnicas de planejamento e análise de experimentos no desenvolvimento de novos produtos em uma empresa de saneantes. *Estudos Tecnológicos*, v. 5, n. 3, p. 404-420, 2009. https://doi.org/10.4013/ete.2009.53.11

CARVALHO, R. H.; CONCEIÇÃO, M. M.; DANTAS, M. B.; SOUSA, E. M. B. D. Aplicação do Planejamento Fatorial e Metodologia de Superfície de Resposta na Produção de Biodiesel de Óleo de Algodão (*Gossipium hisutum* L.) Utilizando Catalisador Comercial. *In*: CONGRESSO BRASILEIRO DE P&D EM PETRÓLEO E GÁS, 5., 2009. *Annals*... Fortaleza, 2009.

CASTRO, W. B. de. Uso de planejamento fatorial para avaliar a influência das variáveis da técnica de fluxo no nível de super-resfriamento da liga eutética Sn-57%Bi. *Revista Eletrônica de Materiais e Processos*, v. 8, n. 2, p. 74-79, 2013.

CUNICO, M. W. M.; CUNICO, M. M.; MIGUEL, O. G.; ZAWADZKI, S. F.; PERALTA-ZAMORA, P.; VOLPATO, N. Planejamento fatorial: uma ferramenta estatística valiosa para a determinação de parâmetros experimentais empregados na pesquisa científica. *Visão Acadêmica*, v. 9, n. 1, 2008. http://dx.doi.org/10.5380/acd.v9i1.14635

DANTAS, J.; LEAL, E.; MAPOSSA, A. B.; SILVA, A. S.; COSTA, A. C. F. M. Síntese, caracterização e performance catalítica de nanoferritas mistas submetidas a reação de transesterificação e esterificação via rota metílica e etílica para biodiesel. *Matéria*, v. 21, n. 4, p. 1080-1093, 2016. https://doi.org/10.1590/s1517-707620160004.0099

DENARI, G. B.; SACILOTO, T. R.; CAVALHEIRO, E. T. G. Avaliação do uso de planilhas computacionais como uma ferramenta didática em química analítica qualitativa. *Química Nova*, v. 39, n. 3, p. 371-375, 2016. https://doi.org/10.5935/0100-4042.20160029

FERNANDES, F. M.; SILVA, M. S.; LIMA, A. M. F.; ROCHA, A. M.; SOARES, P. M.; KONISH, F. Biodiesel no mundo e no Brasil: situação atual e cenários futuros. *In*: CONGRESSO SOBRE GERAÇÃO DISTRIBUÍDA E ENERGIA NO MEIO RURAL, 2015. *Annals*..., p. 1-10. 2015.

FERREIRA, D. F. SISVAR: um programa para análises e ensino de estatística. SISVAR: a program for statistical analysis and teaching. *Revista Científica Symposium*, Lavras, v. 6, n. 2, p. 36-41, 2008.

GALINA, D. *Análise da influência da temperatura e do tempo na transesterificação direta da Nannochloro psisoculata para produção de biodiesel*. 71f. Tese (Mestrado em Energia) – Centro Universitário Norte do Espírito Santo, Universidade Federal do Espírito Santo, São Mateus, 2018.

GERIS, R.; SANTOS, N. A. C.; AMARAL, B. A.; MAIA, I. S.; CASTRO, V. D.; CARVALHO, J. R. M. Biodiesel de soja – reação de transesterificação para aulas práticas de química orgânica. *Química Nova*, v. 30, n. 5, p. 1369-1373, 2007. https://doi.org/10.1590/S0100-40422007000500053

GONÇALVES, M.; SILVA, F. C.; LOPES MARIA, A. C.; SOUZA, L. A.; OLIVEIRA, P. O. Produção e caracterização de biodiesel produzido com óleos unitários e misturas binárias. *Revista Brasileira de Ciências Ambientais (Online)*, n. 53, p. 33-50, 2019. https://doi.org/10.5327/Z2176-947820190426

LIMA, A. L.; LIMA, A. P.; PORTELA, F. M.; SANTOS, D. Q.; NETO, W. B.; HERNÁNDEZ-TERRONES, M. G.; FABRIS, J. D. Parâmetros da reação de transesterificação etílica com óleo de milho para produção de biodiesel. Eclética Química, São Paulo, v. 35, n. 4, p. 101-106, 2010. https://doi.org/10.1590/S0100-46702010000400013

LIMA, de A. P.; LIMA, de A. L.; SANTOS, D. Q.; NETO, W. B. Application of factorial design and response surface methods to optimize ethyl biodiesel production from corn oil. *Revista Virtual de Química*, v. 5, n. 5, p. 817-827, 2013. http://dx.doi.org/10.5935/1984-6835.20130059

LIMA, Y. M. M.; VIEGAS, I. M. A.; BARRADAS FILHO, A. O.; SILVA, L. M. S.; MARQUES, A. L. B.; MARQUES, E. P. Otimização multivariada do rendimento da síntese de biodiesel de dendê. *In*: CONGRESSO BRASILEIRO DE QUÍMICA, 57., 2017. *Annals*... Rio Grande do Sul, 2017.

MARINHO, M. R. M.; CASTRO, W. B. Planejamento fatorial: uma ferramenta poderosa para os pesquisadores. *In*: CONGRESSO BRASILEIRO DE ENSINO DE ENGENHARIA, 33., 2005. *Annals*... Campina Grande, 2005.

MARTINS, G. A. de S.; PELUZIO, J. M.; ALMEIDA, L. de J.; ADORNO, W. T.; MOURA, B. A. de. Otimização da transesterificação de óleo de soja produzido no estado do Tocantins. *Enciclopédia Biosfera*, Centro Científico Conhecer, v. 11, n. 21, p. 1452-1459, 2015.

MENDOW, G.; QUERINI, C.; BENÍTEZ, B.; CARVALHO, M. Produção de biodiesel através de transesterificação etílica em duas etapas: influência da temperatura e do catalisador. *In*: CONGRESSO DA REDE BRASILEIRA DE TECNOLOGIA DE BIODIESEL, 5., 2012; CONGRESSO BRASILEIRO DE PLANTAS OLEAGINOSAS, ÓLEOS, GORDURAS E BIODIESEL, 8., 2012. *Annals*... Salvador, 2012.

MENEGHETTI, S. P.; MENEGHETTI, M. R.; BRITO, Y. C. A reação de transesterificação, algumas aplicações e obtenção de biodiesel. *Revista Virtual de Química*, v. 5, n. 1, p. 63-73, 2013. http://dx.doi.org/10.5935/1984-6835.20130007

MORAIS, F. R.; LOPES, C. S.; LIMA NETO, E. G.; RAMOS, A. L. D.; SILVA, G. Influência da Temperatura e Razão Molar na Produção Contínua de Biodiesel. *Scientia Plena*, v. 9, n. 10, 2013.

NASCIMENTO, J. O.; NEIDE, I. G.; GONZATTI, S. E. M. Objetos de aprendizagem e o Microsoft Excel como ferramentas auxiliares no ensino de física. *Caderno Pedagógico*, Lajeado, v. 13, n. 1, 2016.

NOGUEIRA, A. S. L.; PINHEIRO, F. D. P.; REIS, N. P.; LUCENA, K. O. C. *Etanol e metanol: vantagens e desvantagens quanto ao uso na produção de biodiesel no Brasil*. Ceará: Pró-Reitoria de Pesquisa e Inovação do Instituto Federal do Ceará, 2018.

NOVAES, C. G.; YAMAKI, R. T.; PAULA, V. F.; NASCIMENTO JÚNIOR, B. B.; BARRETO, J. A.; VALASQUES, G. S.; BEZERRA, M. A. Otimização de Métodos Analíticos Usando Metodologia de Superfícies De Resposta - Parte I: Variáveis de Processo. *Revista Virtual de Química*, v. 9, n. 3, p. 1184-1215, 2017. http://dx.doi.org/10.21577/1984-6835.20170070

OLIVEIRA, A. F. G. Testes estatísticos para comparação de médias. *Revista Eletrônica Nutritime*, v. 5, n. 6, p. 777-788, 2008.

OLIVEIRA, C. J.; CARNEIRO JUNIOR, J. A. M. C.; ALVES, C. T. Influência da variação da razão molar álcool/óleo e percentual de catalisador na síntese do biodiesel a partir de óleo residual. *e-xacta*, v. 8, n. 1, p. 43-56, 2015. http://dx.doi.org/10.18674/exacta.v8i1.1445

PAGAN, F. de S.; LUZ, M. S.; FERREIRA, D. C. Otimização estatística da produção de biodiesel a partir de óleos residuais de frituras em rota etílica. *Enciclopédia Biosfera*, Centro Científico Conhecer, Goiânia, v. 13, n. 24, p. 1692-1702, 2016. http://dx.doi.org/10.18677/EnciBio_2016B_155

PAULA, C. D.; BARROS, F. J. S.; CORREIA, L. M.; VIEIRA, R. S. Avaliação de catalisador a base de conchas de ostras para a produção de biodiesel utilizando planejamento fatorial. *Holos*, v. 1, p. 316-324, 2017. https://doi.org/10.15628/holos.2017.5204

PEREIRA, F. M. V.; PEREIRA-FILHO, E. R. Aplicação de programa computacional livre em planejamento de experimentos: um tutorial. *Química Nova*, v. 41, v. 9, p. 1061-1071, 2018. http://dx.doi.org/10.21577/0100-4042.20170254

PEREIRA-FILHO, E. R.; POPPI, R. J.; ARRUDA, M. A. Z. Emprego de planejamento fatorial para a otimização das temperaturas de pirólise e atomização de Al, Cd, Mo e Pb por Etaas. *Química Nova*, v. 25, n. 2, p. 246-253, 2002. https://doi.org/10.1590/S0100-40422002000200013

REIS, B. C. M.; PINTO, R. L. M.; SOARES, C. L. Aplicação da análise estatística via teste de Tukey e análise de variância para a avaliação dos parâmetros de qualidade de corte em um processo de fabricação. *In*: XXXVI Encontro Nacional de Engenharia de Produção, 36., 2016. *Contribuições da Engenharia de Produção para Melhores Práticas de Gestão e Modernização do Brasil*. João Pessoa, 2016.

RODRIGUES, R.; PADILHA, A. C.; MATTOS, P. Princípios da produção mais limpa na cadeia produtiva do biodiesel: análise da indústria de óleo vegetal e usina de biodiesel. *Revista Brasileira de Ciências Ambientais (Online)*, n. 20, p. 1-11, 30 jun. 2011.

ROSSI, G. Z.; BORGES, I. R.; PEREGO, T. F.; TOLEDO, V. D. M.; FERREIRA, L. F. P. Análise técnica da produção do biodiesel a partir do óleo de fritura residual. *Journal of Engineering and Exact Sciences*, v. 4, n. 1, p. 1-8, 2018. https://doi.org/10.18540/jcecvl4iss1pp0101-0108

RUSCHEL, C. F. C.; FERRÃO, M. F.; SANTOS, F. P.; SAMIOS, D. Otimização do processo de transesterificação em duas etapas para produção de biodiesel através do planejamento experimental doehlert. *Química Nova*, v. 39, n. 3, p. 267-272, 2016. https://doi.org/10.5935/0100-4042.20160018

SCHNEIDER, R. de C. de S.; MOCELLIN, R.; TRINDADE, M. M. da; LARA, L. R. S.; FERRÃO, M. F. Used frying oil biodiesel production: experimental factorial design and multivariate analysis. *Tecno-Lógica*, v. 13, n. 1, p. 19-24, 2009. http://dx.doi.org/10.17058/tecnolog.v13i1.924

SILVA, C. R. da; SANT'ANNA, A. P. Uma aplicação do planejamento de experimentos na indústria farmacêutica. *Sistemas & Gestão*, v. 2, n. 3, p. 274-284, 2007.

SILVA, J. A.; DAMASCENO, B. P. G. L.; SILVA, F. L. H.; MADRUGA, M. S.; SANTANA, D. P. Aplicação da metodologia de planejamento fatorial e análise de superfícies de resposta para otimização da fermentação alcoólica. *Química Nova*, v. 31, n. 5, p. 1073-1077, 2008. https://doi.org/10.1590/S0100-40422008000500024

SILVA NETO, L. D.; LOURENÇO, J. E. S.; SILVA, C. S.; SOLETTI, J. I.; COÊLHO, D. G. Planejamento experimental no estudo das variáveis de processo do biodiesel de óleo de coco. *In*: CONGRESSO BRASILEIRO DE ENGENHARIA QUÍMICA, 22., ENCONTRO BRASILEIRO SOBRE O ENSINO DE ENGENHARIA QUÍMICA, 16., 2018. *Annals*... São Paulo, 2018.

SUOTA, M. J.; SIMIONATTO, E. L.; SCHARF, D. R.; MOTTA, V.; MOSER, D.; OLIVEIRA, L. B.; PEDROSO, L. R. M.; WISNIEWSKI JÚNIOR, A.; WIGGERS, V. R.; BOTTON, V.; MEIER, H. F. Avaliação de características de biodieseis de fontes alternativas submetidos a condições de armazenagem diferenciada. *Química Nova*, São Paulo, v. 41, n. 6, p. 648-655, 2018. Available at: <http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0100-40422018000600648&lng=en&nrm=iso>. Accessed on: July 22, 2019. http://dx.doi.org/10.21577/0100-4042.20170222

TAKETA, T. B.; FERREIRA, M. Z.; GOMES, M. C. S.; PEREIRA, N. C. Influência da temperatura, razão molar (óleo de soja/etanol) e tipo de óleo de soja na reação de transesterificação. *Revista Tecnológica Maringá*, Maringá, v. 22, n. 1, p. 75-82, 2013. https://doi.org/10.4025/revtecnol.v22i1.10719

TEBAS, S. O. G.; PEREIRA, A. F.; SILVA, P. H. A.; PINHEIRO, P. F.; PINHEIRO, C. A.; BARAÑANO, A. G. Obtenção de biodiesel. *In*: SEMANA DA ENGENHARIA QUÍMICA DA UNIVERSIDADE FEDERAL DO ESPÍRITO SANTO, 5., 2017. *Annals*..., v. 4, n. 1, p. 100-104, 2017. Available at: <https://www.proceedings.blucher.com.br/article-details/obteno-de-biodiesel-25549>. Accessed on: July 22, 2019. https://doi.org/10.5151/SEQUFES2016-023

TEÓFILO, R. F.; FERREIRA, M. M. Quimiometria II: Planilhas eletrônicas para cálculos de planejamentos experimentais, um tutorial. *Química Nova*, v. 29, n. 2, p. 338-350, 2006.

URIBE, R. A. M.; ALBERCONI, C. H.; TAVARES, B. A. Produção de biodiesel a partir do sebo bovino; viabilidade econômica e métodos de produção. *In*: CONGRESSO NACIONAL DE EXCELÊNCIA E GESTÃO, 2014. *Annals*... Bauru, 2014.

VICENTINI, F. C.; FIGUEIREDO-FILHO, L. C. S.; JANEGITZ, B. C.; SANTIAGO, A.; PEREIRA-FILHO, E. R.; FATIBELLO-FILHO, O. Planejamento fatorial e superfície de resposta: otimização de um método voltamétrico para a determinação de Ag(I) empregando um eletrodo de pasta de nanotubo de carbono. *Química Nova*, v. 34, n. 5, p. 825-830, 2011. https://doi.org/10.1590/S0100-40422011000500018

VICTORINO, T.; PEREIRA, R.; FIAUX, S. Aproveitamento da glicerina de biodiesel obtida a partir de óleo de fritura para o cultivo do fungo Aspergillus niger. *Revista Brasileira de Ciências Ambientais (Online)*, n. 42, p. 56-66, 30 dez. 2016. https://doi.org/10.5327/Z2176-947820160107

VIEIRA, J. S. C.; SOUSA, T. L.; ROSAS, L. S.; LIMA, A. L.; RONCONI, C. M.; MOTA, C. J. A. Esterificação e transesterificação homogênea de óleos vegetais contendo alto teor de ácidos graxos livres. *Química Nova*, v. 41, n. 1, p. 10-16, 2018. https://doi.org/10.21577/0100-4042.20170148

ZORZO, L. S.; BOTH, C. L.; BOLZAN, E.; ZORZO, L. V.; AJALA, R. S. A utilização do excel no controle gerencial e na tomada de decisão nas organizações. *Gestão e Desenvolvimento em Revista*, v. 4, n. 1, p. 73-86, 2018.