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EXPERIMENTAL DESIGN AND RESPONSE SURFACE METHODOLOGY FOR TRANSESTERIFICATION REACTION OF TRIGLYCERIDES IN BIODIESEL PRODUCTION

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Abstract. *The global energetic matrix is still highly dependent on fossil fuels. However, the global overview is changing due to reasons related to the environment, the global economy and energy. Among the processes of transesterification, the heterogeneous present limited conversions when comparing with homogeneous processes, however, it reduces water consumption and the occurrence of undesirable parallel reactions. Accordingly, this work evaluated the influence of the independent variables weight percentage of catalyst and methanol/oil molar ratio on the yield of the transesterification reaction for the production of biodiesel, using soybean oil as a source of triglyceride and a heterogeneous catalyst prepared from the impregnation of potassium iodide and titanium dioxide in silica. Using Central Composite Rotatable Design (CCRD) with 11 experimental repetitions, it was verified that the factors studied presented both linear and quadratic significance. By applying the F test, it was possible to confirm the validity of the statistical model generated. From the response surface, the optimum yield was verified to be around 92%, when 7.55% (m/m) of catalyst is used and the methanol/oil ratio is equivalent to 49.79. Experiments using these values showed a yield of 95%, close to the value predicted by the model.*

Keywords: *Si-KI/TiO_2, Biofuel, Variables, Methanol/Oil, Catalyst*

1. INTRODUCTION

The supply of fossil fuels continues to decrease due to the increase of the energy demand in the world. In order to reduce the dependence on these fuels, many countries are interested in biofuels production (Patel et al, 2016). Nowadays, searching for energy sources that can replace fossil fuels became extremely important, not only considering the economic aspect, but also the environmental perspective (Santos et al., 2014).

It is also worth mentioning that matters related to energy and environment are a big concern, and research presenting alternative and sustainable approaches sparked interest in recent years. The high consumption of fossil fuels, its effects on global warming and concerns related to energy security are the main reasons for the interest in the use of biofuels. Studies related to the life cycle assessment of biodiesel show a significant reduction in greenhouse gases, due to its use as a mixture component in transport fuels (Semwal et al., 2011). Biodiesel, which is a biodegradable and renewable type of energy, shows a great potential as an alternative fuel: the blend of biodiesel with fossil diesel represents a good option to reduce the high fuel prices and environmental impacts (Zabeti et al., 2009).

Biodiesel, also known as fatty acid methyl esters, is usually produced from triglycerides, oils or fats (Chen et al., 2013). The availability of the raw material used to obtain vegetable oils is an important aspect which confirms the viability of obtaining biodiesel on a large scale. According to the Systematic Survey of Agricultural Production, conducted by the Brazilian Institute of Geography and Statistics, in 2017, soybean, from which it can be extracted one of the most important oils to biofuel production, had a total of almost 34 million hectares of cultivated area, yielding about 115 million tons. By June 2018, these data were already being surpassed by at least 1.15%.

In general, the most common reactions to produce biodiesel involve esterification and transesterification in homogeneous catalysis. The classic method to produce biodiesel commonly uses sodium hydroxide, potassium hydroxide and sodium methoxide as basic catalysts, because they present a high catalytic activity. However, using these catalysts still presents some difficulties, such as the separation of the catalyst, the formation of soap and wear of the reactor, therefore representing a challenge for industries. In addition to these inconveniences, there is also the consumption of large amounts of water to promote the washing and recovery of biodiesel.

On the other hand, heterogeneous catalysts used in reactions to produce biodiesel can be easily separated, because they do not require many unit operations and can be reused and recycled several times, without requiring neutralization or washing. Another advantage is obtaining a byproduct, glycerol, with high purity. Therefore, using heterogeneous catalysts appears as a efficient and more economical tool in biodiesel production (Cordeiro et al., 2011; Reis et al., 2015).

Experimental design, which is based on statistical principles, is an important tool to obtain optimized conditions for a process, for the development of product formulations and also to evaluate the impacts of some factors on expected responses (Rodrigues & Iemma, 2015). Factorial design maintain combinations between levels with two or more factors. Therefore, this experimental design method is really interesting when studying the interaction among factors such as temperature, amount of catalyst and molar ratio of alcohol to triglycerides in reactions to obtain biodiesel. Factorial experiment is a very useful tool in situations when it is intended to explore several factors of interest in an experiment, allowing to evaluate the effects of one or more response variables that are part of the process (Camorim, 2008).

This work aims to analyze the factors that have an influence on the biodiesel production process. In order to verify the feasibility of obtaining the biodiesel previously mentioned, the yield of the transesterification reaction, which is considered a dependent variable, can be evaluated in function of several operational and process design variables. Intending to evaluate if the oil/methanol and oil/catalyst ratios have significance on the production, a factorial design was performed with these two levels.

2. THEORETICAL FOUNDATION

2.1 Biodiesel Production

High energy demand in the industrialized world and widespread use of fossil fuels are leading to fast depletion of fossil fuel resources as well as environmental degradation. The world petroleum reserves are so unevenly distributed that many regions have to depend on others for their fuel requirements. Degrading air quality due to emissions is the main adverse effect of petroleum-based fuels. All these factors need continued search and sustainable development of renewable energy sources that are environmentally friendly (Ahmad et al., 2012).

The vegetable oils can be used as fuels but can lead to problems such as injector coking, polymerization in the piston ring belt area causing stuck or broken piston rings, and a tendency to thicken lubricating oil causing sudden and catastrophic failure of the rod and/or crankshaft bearings. A method for reducing the viscosity of the oil must be developed and the most appropriate technique for that was transesterification of vegetable oil. After that, various researchers worked to develop and search various resources for the production of biodiesel (Sarin, 2012).

Biodiesel is defined as the mono-alkyl esters of fatty acids derived from vegetable oils or animal fats. In simple terms, Biodiesel is the product obtained when a vegetable oil or animal fat is chemically reacted with an alcohol to produce a new compound that is known as a fatty acid alkyl ester (Vogel, 1994; Friedrich, 2004). The homogeneous catalysis has presented problems with saponification, expensive separation requirement, waste water generation and high energy consumption. The heterogeneous catalysis has the potential of reducing the high cost of biodiesel production by directly producing biodiesel from readily available and low-cost feedstocks (Al-Widyan & Al-Shyoukh, 2002; Lotero et al., 2005; Sani, Daud & Aziz, 2012).

One of the ways to minimize the mass transfer limitation for heterogeneous catalysts in liquid phase reactions is using catalyst supports. The choice of a particular support depends on the nature of application and reaction conditions. In general, the support materials should have a high surface area and suitable mechanical strength to permit dispersion of the metal, also to increase its thermal stability and hence the catalyst life. There are a number of process variables which could affect the transesterification process. In addition, the catalyst efficiency depends on several factors such as specific surface area, pore size, pore volume, acidity or basicity, and active site concentration of catalyst (Smith & Notheisz, 2006; Aminul & Ravindra, 2017).

2.2 Experimental Design

The problem should be specific enough and the conditions under which the experiment will be performed should be understood so that an appropriate design for the experiment can be selected. The factors that are studied in the initial stages of sequential experimentation are those that are believed to be important. The experimenter must address the question of how many levels to use and how the levels will be selected. If only two or three levels are likely to be used in the immediate future, then those levels should be used in the experiment and the inference that is drawn will apply only to those levels (Ryan, 2007).

DOE (Experimental Design) refers to the process of planning, designing and analysing the experiment so that valid and objective conclusions can be drawn effectively and efficiently. In order to draw statistical conclusions from the experiment, it is necessary to integrate simple and powerful statistical methods. The success of any industrially designed experiment depends on planning, appropriate choice of design, statistical analysis of data and teamwork skills. For quantitative factors, one must decide on the range of settings and how they are to be measured and controlled during the experiment. (Vecchio, 1997; Antony, 2014)

In Central Composite Design (CCD), each numeric factor is varied over five levels: plus and minus alpha (axial points), plus and minus 1 (factorial points), and the center point. The greatest advantage of this type is that it allows experimental design outside where the cube points are located. In addition, the presence of these points gives the rotational workability, which is why it is highly preferred by researchers. CCD is divided into three subdivisions: Central Composite Circumscribed (CCC), Central Composite Inscribed (CCI), and Central Composite Face-Centered (CCF) (Turan, 2017).

3. MATERIALS AND METHODS

3.1 Testing and obtaining experimental data

Observing the main goal of the study, the software Statistica was used to generate the factorial design matrix 2^2 with two tests at the central point from the maximum and minimum values that the two variables in the study (alcohol/oil molar ratio and weight percentage of catalyst) could present. In the biodiesel production reaction, soybean oil, methanol and silica impregnated with potassium iodide and titanium dioxide (Si/KI-TiO_2) were used, the last being the catalyst; the mass of the soybean oil was fixed at 10.0 grams, while the ranges of methanol molar ratio and percentage (% m/m) of catalyst were chosen according to values already used in the literature, as shown in Table 1.

Table 1 – Actual values and levels of the factors studied for the factorial design 2^2

Factors	**Level -1,41421**	**Level -1**	**Level 0**	**Level +1**	**Level 1,41421**
Catalyst (%)	0.343	2.0000	6.000	10.000	11.656
Molar Ratio (Methanol/Oil)	18.934	50.0000	125.000	200.000	231.066

The possible combinations between levels and variables were performed and totaled 11 (eleven) experiments. The variable time, as well as the mass, was also fixed, and therefore, all reactions lasted 2h (two hours) and were conducted in standard experimental conditions with temperature and agitation being controlled (63°C e 400 rpm). The tests were carried out in batches in the reactor (round-bottom flask) of 250 mL and the process was followed by thin-layer chromatography. Due to the volatility of methanol when heating, a reflux system was used to prevent mass losses, as presented in Figure 1.

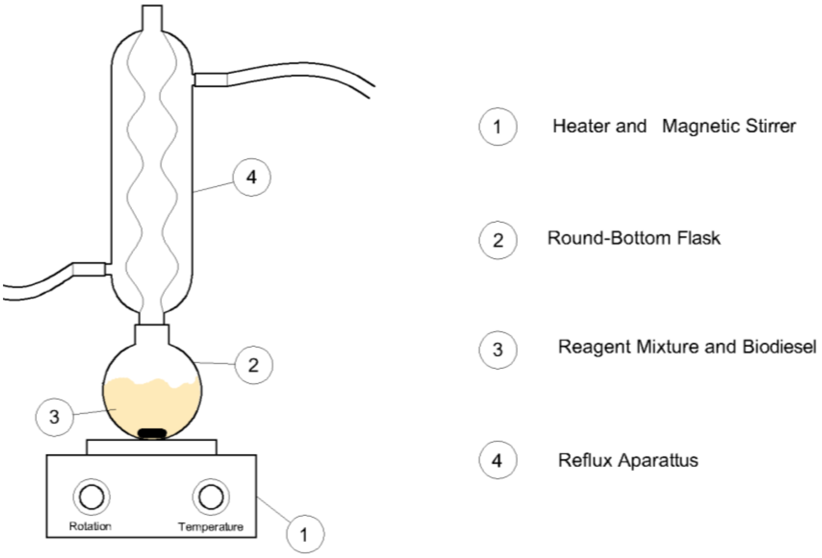
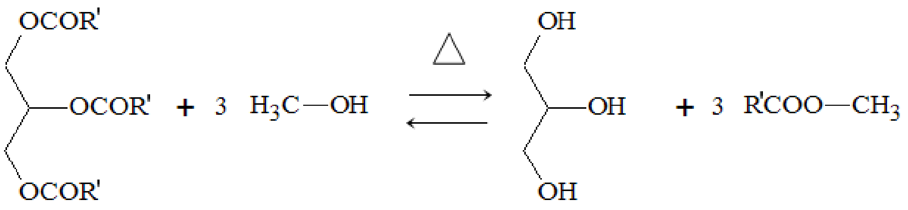


Figure 1 – Experimental assembly for transesterification reactions.

In the end of each experiment, the mixture inside the reactor was centrifuged to remove the catalyst. The liquid part was transferred to a decantation funnel to separate the phases (biodiesel, methanol in excess and glycerol). In order to obtain a higher efficiency, the liquid-liquid separation process was carried out for 24 h (twenty-four hours). After the stipulated time, for each test, the biodiesel was transferred to a pre-weighted beaker, so it was possible to measure the mass of the methyl ester obtained to calculate the yield based on the stoichiometry of the reaction as shown below:



3.2 Data processing and obtaining a model

Using the data obtained from the reactions carried out, it was possible to create the complete planning table including the column showing the yield for each test performed. From the software Statistica and through the Experimental Design (DOE) tool, the behavior and the influence of the variables were verified through the analysis of significance parameters. Hence, the Pareto chart, the ANOVA Table, response surfaces, regression and best fit line were generated.

4. RESULTS AND DISCUSSION

The values found for yield (expressed as a percentage) of the 11 (eleven) transesterification reactions of triglycerides are listed in Table 2. It can be noticed that the response variable of this work had an average value of 83.27%. Based on these data, it can be inferred that there may be a relationship between the factors, because in higher percentages of catalyst and smaller methanol/oil molar ratios, better yields could be observed. In all transformations, the same operational conditions were maintained as much as possible and following the standardized work methodology, in order to guarantee a better comparison of the results.

Table 2 – Matrix for the Central Composite Rotatable Design (CCRD) with 10 (ten) grams of soybean oil

Experiment	**Catalyst**	**Molar Ratio (Methanol / Oil)**	**Yield (%)**
1	-1.00000	-1.00000	85.00
2	-1.00000	1.00000	72.00
3	1.00000	-1.00000	90.00
4	1.00000	1.00000	83.00
5	-1.41421	0.00000	75.00
6	1.41421	0.00000	86.00
7	0.00000	-1.41421	92.00
8	0.00000	1.41421	70.00
9 (C)	0.00000	0.00000	88.00
10 (C)	0.00000	0.00000	87.00
11 (C)	0.00000	0.00000	88.00

In order to estimate the effect of each factor on the variable yield, the Pareto chart was generated to evaluate it. It can be seen in Figure 2 that both Catalyst (%) and Methanol/Oil molar ratio have linear and quadratic significance on the model. Only the two parameters combined did not present any influence at a significance level (p) of 5%.

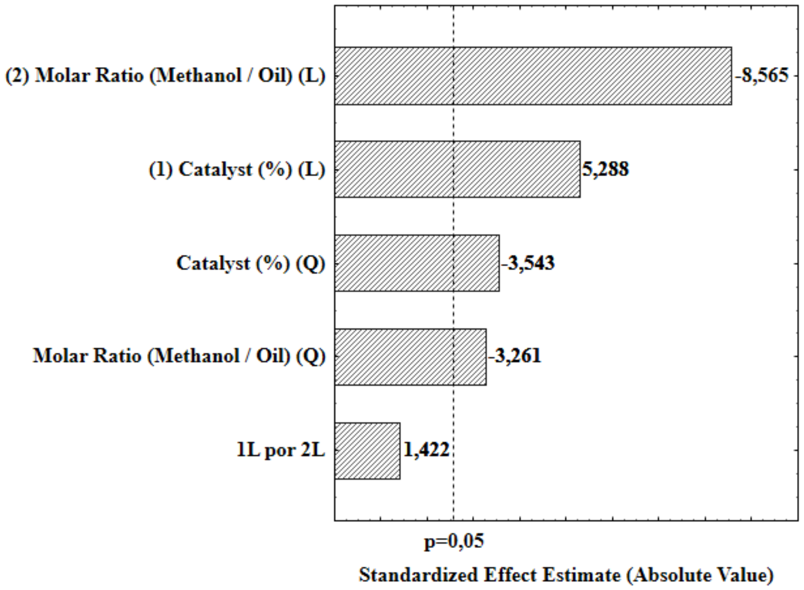


Figure 2 – Pareto chart to verify the influence of parameters on the response variable Yield

From the verification that the two factors factors fitted both quadratic and linear models, the coefficients for them were obtained. The following equation (1) showed a strong correlation (r = 0.96), which means 92.24% of the variation in the yield (%) can be explained by the catalyst (%) and the molar ratio (methanol/oil).

$$Y\,(\%) = \mathbf{(81.02622 \pm 4.0919)} + \mathbf{(2.72051.C \pm 0.8193)} - \mathbf{(0.19661.C^2 \pm 0.0554)} - (0.01352.MO \pm 0.0458) - \mathbf{(0.00051.MO^2 \pm 0.0001)} + (0.00500.C.MO \pm 0{,}0035) \quad (1)$$

C = Catalyst; **MO** = Molar Ratio (Methanol/Oil)

In order to prove the applicability of equation 1, the Analysis of Variance (ANOVA) was performed for yield, and the results are shown in Table 3.

Table 3 – Analysis of Variance (ANOVA) for the variable Yield (%)

	SS	**DF**	**QM**	**Test F**	**p**
(1) Catalyst (L)	124.47	1	124.47	27.96	0.003
Catalyst (Q)	55.88	1	55.88	12.55	0.016
(2) Molar Ratio (Methanol / Oil) (L)	326.56	1	326.56	73.37	0.000
Molar Ratio (Methanol / Oil) (Q)	47.35	1	47.35	10.64	0.022
1L by 2L	9.00	1	9.00	2.022	0.214
Residue	22.25	5	4.45	-	-
Total	562.18	10	-	-	-
% Explained Variance		**Coeff. Correlation**		**F_{calc}**	**F_{tab} (95%)**
92.24		0.96		16.23	4.46
SS = Sums of Squares; **DF** = Degree of Freedom; **QM** = Quadratic Mean					

From the comparison of the values of F, it can be confirmed that the calculated value is almost 4 (four) times greater than the one in the table, which means the model had a good fit and it is significant, and therefore, it can be used in further analysis. Figure 3 corroborates that by exposing good similarities between the experimental data and the data obtained from the equation (1).

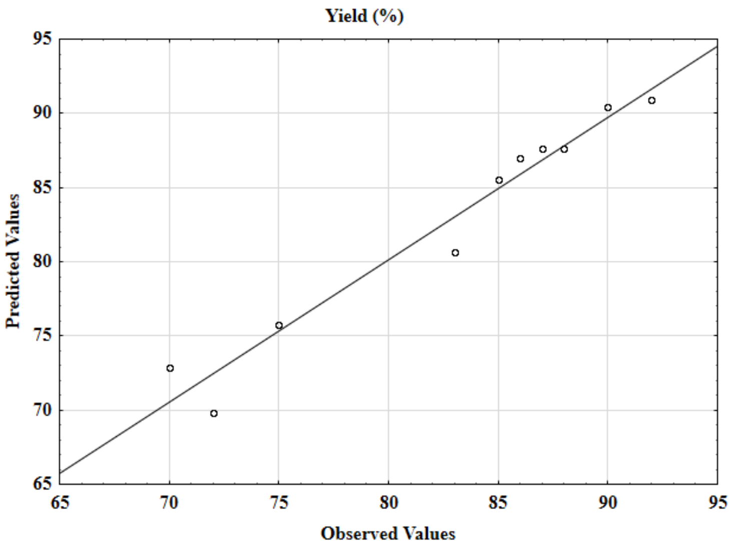
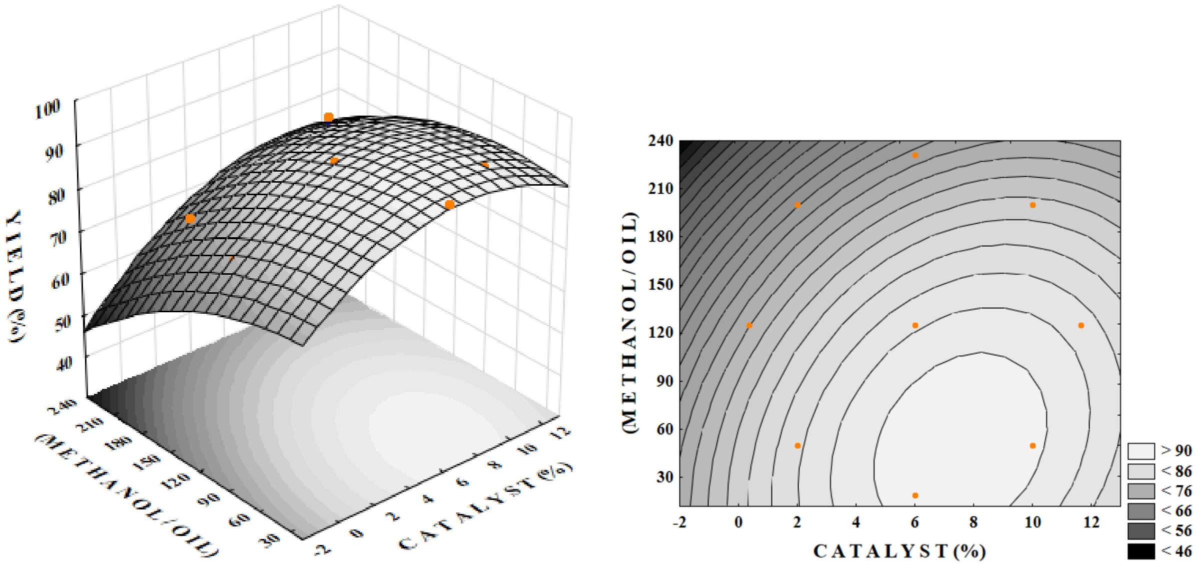


Figure 3 – Values found experimentally compared to the model

Therefore, the response surface and the contour curve of yield versus catalyst (%) and molar ratio (methanol/oil) were plotted and are represented in Figure 4. The orange dots highlighted in the graphs represent the area where the Central Composite Rotatable Design (CCRD) was performed. It can be noticed the reaction conditions in which there are lower methanol contents and central catalyst percentages should result in the best yields. In order to find the optimal condition to produce methyl esters, the maximum critical point on the surface was found.



(a)

(b)

Figure 4 – (a) Response Surface; (b) Contour curve of the studied factors

Table 4 shows the critical point of the curve, that is, the values of catalyst (%) and molar ratio (methanol/oil) that should guarantee the maximum yield for the chemical transformation being studied. When comparing these data to the Experimental Design Matrix (Table 2), it can be verified that points 3 and 7 are close to optimum, which explains the great yield calculated for both.

Table 4 – Critical point found for the response Yield

Factor	Observed Minimum	Critical Values	Observed Maximum
Catalyst (%)	0.34	7.55	11.65
Molar Ratio (Methanol/Oil)	18.93	49.79	231.06

Table 5 shows the comparison at the optimum point between the yield calculated using the model and the yield obtained from the experiment using 7.55% of catalyst and 49.79 molar ratio (methanol/oil). From these data, it can be verified that there is a 3.44% of relative error, which can be explained by the fact the standard deviation for each term of the equation (1) was ignored during the calculations.

Table 5 – Comparison of the optimal yield predicted by the model and yield obtained experimentally

Variable	Model	Experimental	Relative Error (%)
Yield (%)	91.634	95.512	4.06

5. CONCLUSION

From the values found in the experimental design, it was verified that the average yield was 83.27%. In the analysis of the effect using the Pareto chart, it was observed that the two factors studied showed both linear and quadratic influence with a significance level at 5%. As a result, the response surface and the contour curve were found.

Due to the fact that the variables percentage of catalyst and methanol/oil molar ratio have shown to have an effect on the yield, the regression analysis of the data was performed and a model with strong correlation and 92.24% of the variation explained by the factors was obtained. A good fit was observed when plotting the graph containing the experimental values with the ones obtained from the generated equation. Finally, an optimal condition was found, in which the percentage of catalyst should be 7.55% and the methanol/oil molar ratio should be 49.79.

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APPENDIX A

PLANEJAMENTO EXPERIMENTAL E ANÁLISE DE SUPERFÍCIE DE RESPOSTA EM REAÇÕES DE TRANSESTERIFICAÇÃO PARA PRODUÇÃO DE BIODIESEL

Resumo. *A matriz energética mundial ainda se apoia no uso de combustíveis fósseis. No entanto, o panorama mundial está mudando por motivos ambientais, econômicos e energéticos. Entre os processos de transesterificação, a catálise heterogênea apresenta-se com conversões limitadas em comparação com a homogênea, porém, reduz o consumo de água e a ocorrência de reações paralelas indesejáveis. Neste sentido, este trabalho avaliou a influência das variáveis percentual mássico de catalisador e razão molar de metanol/óleo no rendimento da reação de transesterificação para produção de biodiesel, usando óleo de soja como fonte de triacilglicerídeo e catalisador heterogêneo preparado a partir da impregnação de iodeto de potássio e dióxido de titânio em sílica. A partir do Delineamento Composto Central Rotacional (DCCR), com 11 repetições experimentais, verificou-se que os fatores estudados apresentaram significância linear e quadrática. Aplicando-se o teste F foi comprovada a validade do modelo estatístico gerado. A partir da superfície de resposta e equação obtida verificou-se rendimento ótimo, na faixa de 92%, quando se usa 7,55%(m/m) de catalisador e razão molar metanol/óleo equivalente a 49,79. O experimento com esses valores observou rendimento de 95% coerente ao predito.*

Palavras-Chave: *Si-KI/TiO_2, Biocombustível, Variáveis, Metanol/Óleo, Catalisador*