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COBALT CATALYST FOR BIODIESEL PRODUCTION FROM ACIDIC RAW MATERIALS

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ABSTRACT

The use of raw materials with high acidity is one of the options to reduce the production cost of biofuels, such as biodiesel. The reaction commonly used to produce biodiesel is basic transesterification, in which the triglyceride feedstock reacts with an alcohol, in the presence of a catalyst, producing biodiesel and glycerol. This reaction requires raw materials with low fatty acid content, such as soybean, canola, corn and sunflower vegetable oils, to avoid soap formation, emulsions and reduced process efficiency. Currently, the cost of these vegetable oils is high, especially after the pandemic period, leading companies to look for lower cost solutions, and therefore higher acidity, such as residual oils, which seriously impairs the reaction yield. In this sense, a solution that would make it possible to obtain good yields in the production of biodiesel from raw materials with high acidity could be the use of suitable catalysts, which together with the transesterification of triglycerides, allow the esterification of the fatty acids present. The present study proposes the use of cobalt spinel metal oxides, which are considered bifunctional catalysts for having a structure with acidic and basic active sites, being able to simultaneously catalyze the transformation of triglycerides and fatty acids. Model samples of vegetable oil of different acidity were tested and the catalysts were synthesized using the combustion method. The full factorial design methodology in blocks was applied to evaluate the relationship between the reaction yield and the operational parameters catalyst concentration and alcohol/oil molar ratio and temperature. In the reactions catalyzed by $CoAl_2O_4$, the variable of greatest statistical significance was the catalyst concentration, followed by the interaction of catalyst concentration with temperature. It was statistically proven that fatty acid contents up to 20% in the raw material do not affect the transesterification yield.

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INTRODUCTION

Catalysis is the phenomenon in which a relatively small amount of a material, called a catalyst, increases the rate of a chemical reaction without being consumed in the process (SCHMAL, 2011). Catalysts are widely found in nature, in industry and in laboratories, it is estimated that they contributed 1/6 of the value of all industrialized products. Catalysts can be divided into homogeneous or heterogeneous, depending on the way they act, restricted to a single phase or distributed at the interface present between the phases of the reaction system. In heterogeneous catalysis, object of this study, several combinations of phases are possible, however, in general, the catalyst is a solid, and the reactants and products are distributed in one or more gaseous or liquid phases. These materials have large surface areas mainly associated with high microporosity where active sites that can be acidic or basic are located.

Therefore, it can be said that the catalytic activity is associated with the geometric area that presents the material and not with its mass. The synthesis of biodiesel through heterogeneous catalysis offers technical and environmental advantages as it facilitates the purification of the biodiesel produced, reducing the cost and time used in the washing and drying stages of the products, it also enables the recovery and reuse of the solid catalyst throughout its useful life, minimizing the generation of effluents and residues. Together, it facilitates the recovery and purification of glycerin. Another problem in the biodiesel industry is the need to use raw materials with low acidity, which makes the process more expensive and the type of raw material to be used. In Brazil, several studies are being carried out with the objective of expanding the use of raw materials with high acidity, mainly industrial waste (Tavares, 2020; Moura, 2021). Several heterogeneous catalysts have been proposed as catalysts for the synthesis of biodiesel, but what stands out in the use of spinel-type catalysts is related to the nature of the acidic and basic sites

found in these materials (DI SERIO, 2008; Semwal, 2011). Spinel oxides have a regular structure with a face-centered cubic compact packing of oxygen at the vertices and faces. They have 8 cubes that form a unit cell, totaling 56 atoms (32 anions and 24 cations). Although they contain 96 interstices between the anions of the cubic unit cell (64 tetrahedral and 32 octahedral), only 8 of the tetrahedral and 16 of the octahedral cations are occupied by them. Greater occupancy of these sites is not possible, due to the short distances and the coulombic interactions between the guest ions in interstitial sites and the ions in the A and B sites (Sickafus, 1999). The oxides with typical AB_2O_4 spinel structure, when used as heterogeneous catalysts in the production of biodiesel, in addition to having high selectivity, have the advantage of being able to esterify free fatty acids and at the same time transesterify triglycerides (Nuñez, 2022). Thus, aimed to evaluate Cobalt metal oxides (cobalt aluminate) as catalysts in the production of biodiesel from the transesterification of model mixtures based on vegetable oil with different fatty acid contents.

MATERIALS AND METHODS

Preparation of the heterogeneous catalyst: The catalyst used in this study was Cobalt Aluminate ($CoAl_2O_4$) synthesized by the combustion method at the Laboratory of Industrial Processes and Nanotechnology LPIN at the Universidade do Estado do Rio de Janeiro UERJ. The methodology started with the solubilization of nitrates in distilled and deionized water, in a porcelain crucible, on a plate at 150ºC. To the homogenized mixture, urea was added in stoichiometric amounts. The solution remained on the plate for partial evaporation of water, forming a solution of higher viscosity in the form of a gel. It was immediately placed in a muffle furnace at 600°C to start the combustion reaction. After combustion, the product obtained is the catalyst that will be used in the reactions. The steps that finalize the catalyst and that are decisive to reach the activity of the active sites are the maceration until obtaining a powder and the calcination in a muffle (Perez, 2017). The calcination of the catalyst, which eliminates small amounts of carbon residues remaining from the combustion, was carried out at 700ºC for 3 hours with a heating rate of 10ºCmin-1, under an air flow of 60 mL.min-1.

Design of Experiments: In order to determine the suitable experimental conditions for obtaining biodiesel from highly acidic vegetable oil, the effect of some variables of the reaction system was investigated using a factorial experimental design in blocks 23. The independent variables selected in the study, called factors were catalyst concentration (C) and temperature (T). The alcohol/oil molar ratio (R) was set at 6 and the reaction time at 60 minutes, the stirring speed at 700 rpm and the alcohol used was anhydrous methanol from TediaBrasil. The definition of these parameters, both fixed and variable, was carried out considering studies carried out previously (Perez, 2017; Silva, 2014). The blocking variable was the fatty acid content added to the vegetable oil (GA) mixture. The selected vegetable oil was soybean oil, and to prepare the model mixtures, 0, 10 and 20% oleic acid were added to the vegetable oil, representing 3 model mixtures each with 4 experiments with duplicates, totaling 24 experiments. The response variable will be the Reaction Yield, which indicates how much of the raw material was transformed into biodiesel. Table 1 displays the maximum and minimum levels for each factor and the blocking variable.

Transesterification Reaction: All reactions were performed in a Parr® Instruments Inc. batch autoclave reactor, model 4836, in stainless steel, 450 mL capacity and 2,000 psi maximum working pressure. The model mixture of vegetable oil was transesterified with methanol in the presence of cobalt aluminate following the experimental conditions defined in the design of experiments. The temperature control was for 60 minutes, counting the reaction time when the reaction temperature was reached. The progress of the transesterification reaction was monitored by converting the fatty acids to methyl esters in % w/w to determine the reaction yield.

RESULTS AND DISCUSSION

Response measured for the Reaction Yield of the experiments were represented in Table 2. From the results obtained, showed in table 2, a statistical analysis was performed to obtain 1st and 2nd order regression models. Analysis of variance (ANOVA) was used to define the process parameters that significantly influence the reaction yield. The ANOVA results for the response variable and its corresponding F and P statistics are shown in Tables 3 and 4.

Table 1. Variables employed in the experimental design

Factor		Factor levels	Values
C, %m/m	*Catalyst concentration**	2	1; 10
T, °C	*Temperature*	2	50; 150
AG, % m/m	*Added of oleic acid**	3	0; 10; 20

**in fuel mixtures*

Table 2. Experimental matrix used with response vectors

Experiment	AG	C	T	Yield
1	0	1	50	40.16± 0,05
2	0	1	150	45.15± 0,02
3	0	10	50	80.23± 0,13
4	0	10	150	90.85± 0,03
5	10	1	50	35.76± 0,24
6	10	1	150	41.37± 0,3
7	10	10	50	81.83± 0,48
8	10	10	150	91.33± 0,37
9	20	1	50	43.8± 0,38
10	20	1	150	43.87± 0,43
11	20	10	50	74.91± 0,61
12	20	10	150	89.41± 0,17

The mathematical model was developed to understand the effect of the variables studied and their interactions on the transesterification yield. ANOVA, illustrated in Tables3 and 4, is used to decide which model parameters significantly affect the response variable. These tablesprovide the percentage of variance explained by the mathematical model compared to the variance contained in the experimental results. The estimated regression coefficients for the first order model, Table 3, show that the only variable that is not significant is the added fatty acid content. This result is important because it demonstrates the potential of application of the spinel-type cobalt catalyst to transform acidic raw materials into biodiesel. The significance of F (probability for ANOVA) was $3.32X10^{-7}$, expressively smaller than 0.05, confirming the validity of the suggested model. Similar results of these parameters were obtained in the second order model (Montgomery, 2019). The confidence level was specified at 95%, representing the degree of statistical reliability of the regression model, which infers a degree of uncertainty or risk of up to 5% (Calado, 2003). If the P value of the factor is less than or equal to the degree of risk (0.05), it can be inferred that there is a significant correlation with the response variable, while P values greater than 0.05 show that there is no adequate correlation. A marginal effect (p value = 0.09) was observed in the CT interaction (Catalyst concentration- and temperature). Both 1st and 2nd order regression models have high values of R-Sq and adjusted R-Sq (adj), 97.36 and 97.93 % respectively, which shows that the model has good predictability. In the 2nd order model, the p values of C and the C-T Interaction are below the accepted value of 0.05, demonstrating their statistical significance on the response variable, Table 4.

The model equation for the transesterification yield is shown in Equation 1.

$$Yield = 33.13 + 4.15*C + 0.0089 * C*T \pm 3.32 \quad \text{..... Eq.1}$$

Residual analysis was performed to prove compliance with the ANOVA assumptions and validate the regression model.

Table 3. ANOVA of factorial design for the Reaction yield (1th order model)

Sourceofvariation	Degree of freedom (D.F)	Sum ofsquares (SQ)	Meanssquares (MQ)	F	Significanceof F
Regression	3	5709.3675	1903.1225	136.1884	3.32×10^{-7}
Residue	8	111.7935	13.9742		
Total	11	5821.1610			
Term	Coeficients	Standart Error	Stat t	Value-P	
intercept	29.9531	3.0511	9.8173	9.74×10^{-6}	
AG	-0.0545	0.1322	-0.4124	0.6909	
C	4.7735	0.2398	19.9057	4.23×10^{-8}	
T	0.0753	0.0216	3.4866	0.0082	
S = 3,7382					
R-sq= 98.08%					
R-sq (adj) = 97.36%					

Table 4. ANOVA of factorial design for the Reaction yield (2th order model)

Sourceofvariation	Degree of freedom (D.F)	Sum ofsquares (SQ)	Meanssquares (MQ)	F	Significanceof F
Regression	6	5798.0511	966.3418	87.6839	6.68×10^{-5}
Residue	5	55.1037	11.0207		
Total	11	5853.1548			
Term	Coeficients	Standart Error	Stat t	Value-P	
intercept	33.1259	4.5164	7.3347	0.0007	
AG	0.1103	0.2991	0.3689	0.7273	
C	4.1524	0.5429	7.6479	0.0006	
T	0.0293	0.0383	0.7648	0.4789	
AG*C	-0.0253	0.0261	-0.9713	0.3760	
AG*T	-0.0003	0.0023	-0.1108	0.9161	
C*T	0.0089	0.0043	2.0826	0.0918	
S = 3.3197					
R-sq= 99.06%					
R-sq (adj) = 97.93%					

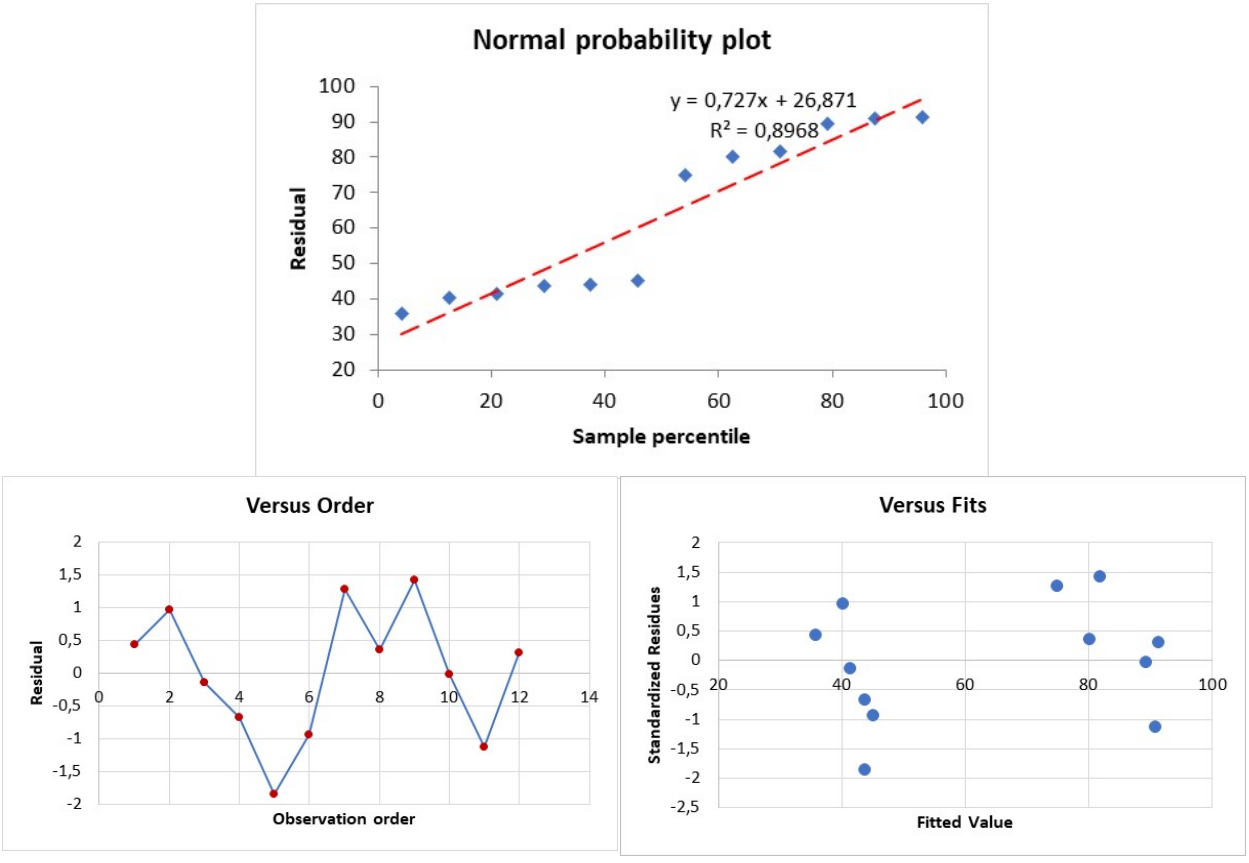

Figure 1. Residual plots for transesterification yield

For validation, the error terms must be normally and independently distributed with zero mean and constant variance. Residual analysis results are shown in Figure 1. Figure 1 presents the residual plots for transesterification yield showing the accuracy of the model used.

In the Normal probability plot, the residual is seen to be well distributed along the midline and there is no possible outlier that reveals any non-normality in the distribution (Montgomery, 2019). The Residues versus order plot is satisfactory, as there is no positive

correlation indicating violation of the independence assumption. The residues versus Fitted value, Figure 1, configures an unstructured pattern demonstrating that the assumption of constant variance is answered. Figure 2 shows the Pareto diagram of the effects of factors and interactions on the transesterification yield, in which the effects were plotted in descending order of their absolute values.

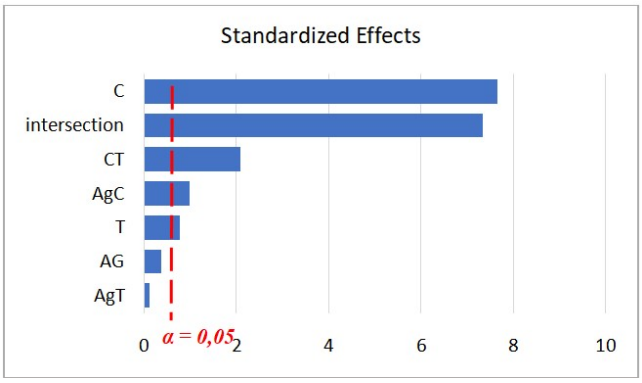

Figure 2. Pareto diagram

The reference line in the graph (in red) indicates which effects are significant, in this study the Lenth method was used to draw this line. In Figure 2 it is possible to corroborate the results shown in Table 4, the effects of the C factor and the CT interaction are located to the right of the reference line and therefore it can be said that they are statistically significant. Furthermore, it is seen that the greatest effect is the concentration of the catalyst (C) because it extends the farthest.

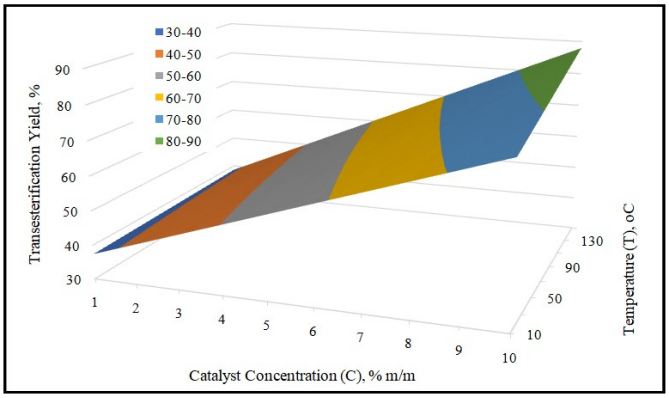

Figure 3. Response surface of variation of transesterification yield with catalyst concentration and temperature

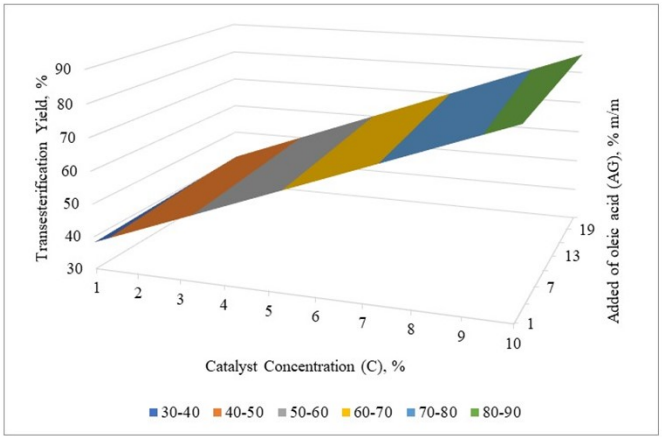

Figure 4. Response surface of variation of transesterification yield with catalyst concentration and added of oleic acid

Figure 3 shows response surface of the *CxT* on transesterification yield, it is observed that the increase cobalt catalyst concentration positively influences on the reaction yield, a logical result considering that the catalyst function is to increase the formation of products. Factorial design made it possible to analyze the influence of factors on response variable. Considering the values presented in the response surface analysis, it is possible to observe that to reach 70% of reaction yield it is necessary to use between 7 and 9% of catalyst in the reaction mixture.Figure 4 confirms the non-influence of the oleic acid content added in the reaction mixture on the transesterification yield, up to additions of 20% m/m.

CONCLUSION

Currently, the use of metal oxides for heterogeneous catalysis has been increasing due to the objective of finding catalysts with high activity and selectivity, and which can, mainly, be easily separated from the reaction mixture, allowing the reactor to operate continuously.In the present study, the catalytic action of spinel-type cobalt oxide, synthesized by combustion, was tested during the transesterification of vegetable oil mixtures of different acidity levels.The statistical study proved to be effective for evaluating the parameters that exert the greatest influence on the biodiesel production process; conducting experimental designs allowed the determination of the effect of the main process parameters on the reaction yield. The variable that had the greatest influence was the catalyst concentration (C) followed by the interaction of catalyst concentration with temperature (C-T).The analysis also showed that the variable Added of oleic acid (AG) has no significant influence on the reaction yield, when the maximum AG limit is 20% oleic acid. This result is important because it demonstrates the potential application of this cobalt compound as a catalyst in the production of biodiesel.

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