

Methyl Esters Production by Heterogeneous Catalyst Mixtures of CaO/Nb₂O₅ with Simulation of Analysis of Environmental Impacts

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The conventional biodiesel process, although it reaches high conversion yields and productivity, faces problems related to the use of homogeneous catalysts. This work aims to study mixtures of calcium oxide (CaO) and niobium oxide (Nb₂O₅) as the heterogeneous catalyst. It was used a full 2³ factorial design with four central points to analyze how the mass percentage of the oxides, the molar ratio of reactants, and the reaction temperature affect the conversion yield to methyl esters. The best conversion yield was found near to 89% using 1.8% of catalyst, a 1:36 oil to methanol ratio and at 77 °C as reaction temperature. Finally, it was performed a simplified simulation to compare the heterogeneous catalyst process with the conventional process, and an algorithm to compare the effects of the exit streams of each process would have on the environment. The simulations results display a better performance for the heterogeneous catalyst process studied.

Keywords: biodiesel, heterogeneous catalyst, calcium oxide, niobium, process simulation

Introduction

The production of biofuels such as biogas, bioethanol, biodiesel and others, is a strategic aspect when looking for energy, environmental, social and agronomic autonomy among other aspects. Biodiesel is defined as a fuel consisting of a mixture of fatty acid methyl esters derived from vegetable oils or animal fats. It is a complement or substitute to petroleum fuel, biodegradable, nontoxic, has a high oxygen content (10 to 11%), high heat value, has a favorable energy balance, and does not contain aromatic compounds and sulfurs.^{1,2} Typically, methanol is used for the transesterification producing methyl esters and glycerin as a byproduct. Only homogeneous chemical catalysts are used on a large scale industrially.³ Although the traditional process presents high conversion yields and high productivity, it faces some problems, generating a demand for the study of alternatives, including new raw materials, the development of heterogeneous catalysts, the study of different mixing conditions (molar ratio

oil:alcohol), temperature and pressure during reactions, among others.⁴ Heterogeneous catalysts are studied in this process mainly because they simplify the recovery and reuse of the catalysts and can eliminate difficulties related to the use of conventional basic homogeneous catalysts as saponification, formation of emulsions and highly polluting effluents.^{5,6} In these systems, the possibility of recovery and reuse results in processes with lower environmental impact, although higher temperatures and molar ratios of oil:alcohol are required.³

As a basic catalyst, calcium oxide has been extensively studied for biodiesel production, mainly due to its low cost and effectiveness, reporting conversions higher than 90% using lower reaction temperatures, with reaction times between 1 and 3 h.⁷⁻¹² However, leaching problems limiting its reuse were reported because a significant mass is lost in each cycle affecting the product quality derived from the calcium contents in the final product.^{13,14} To solve this issue, the use of complexing agents,^{14,15} lithium additives,¹⁶⁻¹⁸ and mesoporous silica as carrier¹⁹⁻²¹ has been reported. Calcium oxide mixed with zinc oxide was studied, obtaining a conversion ratio above 94% (palm

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oil, 3 h of reaction, 1:30 molar ratio of oil to methanol, and 6 wt.% of Ca:Zn ratio of 0.25) and could be reused up to three times.^{22,23} A mix of oxides of Ca and Mg was used by Albuquerque *et al.*²⁴ in the transesterification of acetate butyrate with ethanol, obtaining 60% conversion using as molar ratio Ca/Mg of 3 and without detection of any leachate substance. Sudsakorn *et al.*²⁵ used CaO/MgO doped with strontium catalyst (Sr²⁺-CaO/MgO) to produce biodiesel from *Jatropha* oil and methanol, obtaining conversion of 99.6% at 65 °C for 2 h with molar ratio of 9:1 and 5 wt.% of catalyst, while Teo *et al.*²⁶ used mixed CaO–MgO with *Elaeis guineensis* derived triglycerides, with 4 wt.% of catalyst loading, 60 °C and 15:1 molar ratio of methanol to oil, the yield reached was 99.0% at 6 h.

Wong *et al.*²⁷ evaluated the thermic pretreatment effect in catalytic properties of mixtures of calcium oxide and niobium oxide. Wen *et al.*²⁸ prepared KF/CaO using the impregnation and reached a 96% biodiesel conversion rate at 65 °C.

Using potassium acetate (PA) to prepare PA/CaO solid base catalyst, Fadhil *et al.*²⁹ tested two non-edible oils, using 9:1 methanol to oil molar ratio, at 60 °C, 120 min, and obtaining a maximum conversion of 93%.

To test a reaction between sunflower oil with methanol, Reyero *et al.*³⁰ used Ca/Ce oxides as heterogeneous catalysts, reporting conversion values of 70% after 6 h of reaction at 60 °C. Using chicken fat, Seffati *et al.*³¹ tested a CaO/CuFe₂O₄ nanocatalyst, and reported a maximum conversion of 94%, with a reaction time of 4 h, reaction temperature of 70 °C, catalyst content of 3%, and molar ratio methanol to oil 15:1. A biodiesel yield of 95% was obtained by Wong *et al.*³² by a solid base CaO–CeO₂ mixed with oxide catalysts (5 wt.%), methanol to palm oil molar ratio of 12:1, reaction temperature at 65 °C and reaction time of 4 h.³²

Niobium is a transition metal, identified in the periodic table of elements by the symbol Nb, with atomic number 41 and mass 92.1 u. The terrestrial abundance of this element is about 20 ppm, its appearance is bluish gray and is not found free in nature, only in minerals such as columbita.³³ Brazil has the world's largest reserves of niobium and is the largest producer of the substance, with more than 90% of the total.³⁴ Some niobium compounds (niobium ammonium oxalate, niobium oxide and niobium pentachloride) have been studied in the production of biodiesel, involving its application as a Lewis acid.³⁵⁻³⁷

The niobium oxide, Nb₂O₅.nH₂O, has both Lewis acid sites (which increase with the pretreatment temperature rise to over 500 °C and then decrease at higher temperatures), and Brønsted acid sites (which are more abundant at 100 °C and decrease at elevated temperatures) on its surface.^{37,38}

There is a consensus that it is strategic for Brazil to diversify the sources of raw materials for biodiesel production. An example of this would be the potentialities arising from the cultivation of macauba (*Acrocomia aculeata*) in the North, Northeast and Central West of Brazil.³⁹ This palm is a source of oil for food purposes, soap production and energy production. A fine oil is extracted from the almond, which represents about 15% of the total oil of the plant, rich in lauric and oleic acids. Pulp oil is dominated by oleic and palmitic acids which have good characteristics for industrial processing.⁴⁰⁻⁴⁴ For this potential, macauba oil was chosen as raw material to develop the experimental procedures in this work.

Looking to improve the separation process, reutilize the catalyst and diminish the reaction temperature in biodiesel production, mixes of Nb₂O₅ and CaO as heterogeneous catalysts were investigated. Using statistical methods to plan, analyze and optimize reactions, the biodiesel conversion was evaluated as a function of mass percentage of the oxides (1, 2 and 3% with respect to oil), oil:methanol molar ratio (1:18, 1:27 and 1:36) and temperature (60, 70 and 80 °C). Finally, a simplified process simulation was performed using the software 'DWSIM Open Source Process Simulation, Modeling and Optimization® v.5.1',⁴⁵ with the waste reduction algorithm,^{46,47} and the WAR_GUI software,⁴⁸ to compare heterogeneous catalyst process with the conventional process and to analyze the environmental impacts.

Experimental

Experimental planning

The experimental biodiesel design helps in investigating the effects of the reaction condition variables on the production. The experiments were carried out randomly according to a complete experimental design with four central points. In this context, the levels of independent variables studied were defined based on preliminary results, considering working conditions for each chemical species and limits for the experiment set up. Table 1 lists the range and levels of the independent variables studied.

Table 1. Levels of the transesterification condition variables

Variable	Coded levels/actual values		
	-1	0	+1
Catalyst / %	1	2	3
Molar ratio oil:methanol	1:18	1:27	1:36
Reaction temperature / °C	60	70	80

Catalyst preparation

The Nb₂O₅.nH₂O (HY-340), donated by the Brazilian Metallurgy and Mining Company, and CaO (90%) bought from Sigma-Aldrich, were preheated at 300 °C for 2 h. Then, equal masses of both oxides were mixed in an agate mortar, using acetone as a milling medium to ensure good mixing. Finally, the calcination was carried out in a Microprocessed Mufla-Q318M oven for 5 h at 600 °C, those values being defined by previous results.²⁷ After cooling in a desiccator to room temperature, the catalyst was used in the synthesis of biodiesel.

Synthesis of biodiesel

The transesterification reactions were performed in a reflux system. The macauba oil (bought in a local market) was heated to 65 °C in a water bath before it was poured into a flask. Measured amounts of methanol and catalyst, defined by the experimental design, were mixed by a magnetic stirrer for 10 min. Thereafter, they were gently poured into the reactor. The reaction system was maintained at a controlled temperature with magnetic stirring for the required reaction time. At the end of each reaction, the reaction product was decanted from the reactor and centrifuged at 6000 rpm for 10 min, where the catalyst was separated from the reaction product. Then, the mixture was poured into a separating funnel and allowed to settle overnight to evaporate the methanol part and separate the glycerin from the biodiesel. The lower glycerin layer was drawn off and the upper biodiesel layer was then removed, distilled to separate methanol, washed, dried and weighed.

Determination of physicochemical properties

The kinematic viscosity at 40 °C of approximately 10 mL of sample was obtained in duplicate. The experiments were performed on a SCHOTT automatic viscometer, model AVS350, equipped with a digital thermostatic bath for temperature control and a Cannon-Fenske type 200 capillary tube for the oil and 150 for biodiesel.

The specific mass analysis at 20 °C of the fluids was performed in duplicate using an Anton Paar DMA-5000 digital densimeter. The acid index was determined using 5 g of the sample dissolved in a 1:1 (v/v) toluene and isopropyl alcohol, which was then titrated with a 0.1 mol L⁻¹ KOH solution in isopropyl alcohol using phenolphthalein as the indicator. The equation 1 was used to calculate the acid number.

$$\text{Acid number} = \frac{(A - B) \times C \times 56.1}{m} \quad (1)$$

where A is the titrant solution volume, in milliliters, used in the titration of the sample, B is the titrant solution volume, in milliliters, used in titration of a blank. C is the concentration of the titrant solution in mol L⁻¹, and m is the mass of the sample in grams.

Determination of methyl esters yield

The ¹H nuclear magnetic resonance (NMR) spectra of biodiesel were performed on a Varian VNMRS 400 spectrometer, operating at 9.4 T, using a 5 mm BroadBand ¹H/X/D NMR probe. The ¹H NMR experiments were performed at 25 °C, using 10 mg of biodiesel diluted in deuterated chloroform. Tetramethylsilane (TMS) was used to reference the chemical shifts. A spectral width of 6410.3 Hz with a relaxation delay of 5.2 s and 32 scans were accumulated, with a pulse flip angle of 90 (12.7 ms). From the spectra, quantification was performed relating the signal integration area related to the hydrogen of the ester methoxy (3A_b) and the sum of the areas of the methoxy signal and one of the doublets attributed to the methylene hydrogens of the glyceride part of the triglyceride (3A_b + 2A_o) (A_o and A_b represent the area value of the integration signal absorbed by the triglyceride hydrogens and by the methoxy hydrogens, respectively, see Supplementary Information). From the number of hydrogens generating the signals in the spectrum, the respective areas of integration were multiplied, and the yield conversion was calculated as shown in equation 2.

$$\text{Conversion}(\%) = \frac{3A_b}{3A_b + 2A_o} \times 100 \quad (2)$$

Statistical analysis of experimental results

The statistical analysis was performed using the trial version of the software Design Expert 9.0.⁴⁹ The experimental data obtained were analyzed by response surface methodology, regression analysis and analysis of variance. Response surfaces and contour plots were developed holding two of the independent variables at a constant value corresponding to the stationary point and changing the other two variables using the fitted quadratic polynomial equation obtained from the regression analysis. To validate the equation, a confirmatory experiment using combinations of independent variables that were not part of the original experimental design but within the experimental region was carried out.

Process simulation

A computer simulation was developed to describe the biodiesel production using a transesterification reactor for triglycerides and methanol. For this, it was used the flow sheet free software DWSIM.⁴⁵ The thermodynamic models nonrandom two-liquid and Peng-Robinson were employed to simulate vapor-liquid equilibrium because the transesterification reactions occur in a highly nonideal chemical system. The reaction steps and the general form of equations of the reactions can be found elsewhere.⁵⁰

The model substrate chosen is based on triolein, which is routinely used as a model compound of vegetable oils because it composes around 40-80% of fatty acids in a variety of vegetable oils.¹ Considering that the oil does not contain water and free fatty acids, the saponification reaction was assumed negligible. When sodium hydroxide was used as a catalyst, it was assumed that the reactions follow a first-order model with respect to the catalyst concentration, therefore, the effective reaction constants depend on the catalyst concentration and the rate constants of the catalyzed reaction follow those reported by Marjanović *et al.*⁵¹ In the process simulation using the mixtures of oxides as a catalyst, the kinetics used were those reported by Veljković *et al.*⁵²

The simplified flow sheets for both processes are shown in Figure 1. The catalyst determines the process routes for the biodiesel production; thus, the differences between

homogeneous and heterogeneous catalyst processes are mainly in the downstream processing. The two flow sheets were constructed using a plant capacity of 360 kg h⁻¹ of oil feed. When using sodium hydroxide, alcohol and catalyst are mixed with the oil before entering the two reactors in series. The product mixture from reactor 1 is sent to the first separator, after a specified extent is reached, to obtain a stream rich in methanol that goes to a distiller for purification and later recirculation. The other stream is mixed with fresh reactants and enters reactor 2 where a total conversion near 90% is attained. The outlet stream from reactor 2 enters a second decanter that allows the separation of the methanol excess, joins with the previous stream recovery from reactor 1, and goes to the distiller for recirculation.

The polar substances such as glycerol, salts and residual substances from the stream rich in methyl esters and glycerol are neutralized with acid in the water phase and separated to obtain a glycerol stream (waste 1). The biodiesel product phase is dried to meet specifications.

When the heterogeneous catalyst is used, the excess methanol is again removed by distillation from the polar phase and recycled. The glycerol has a very high purity because it is not mixed with water. The nonpolar phase is distilled to meet specifications. The use of a heterogeneous catalyst gives some favorable changes as to the required number of unit operations, waste production and glycerol product quality.

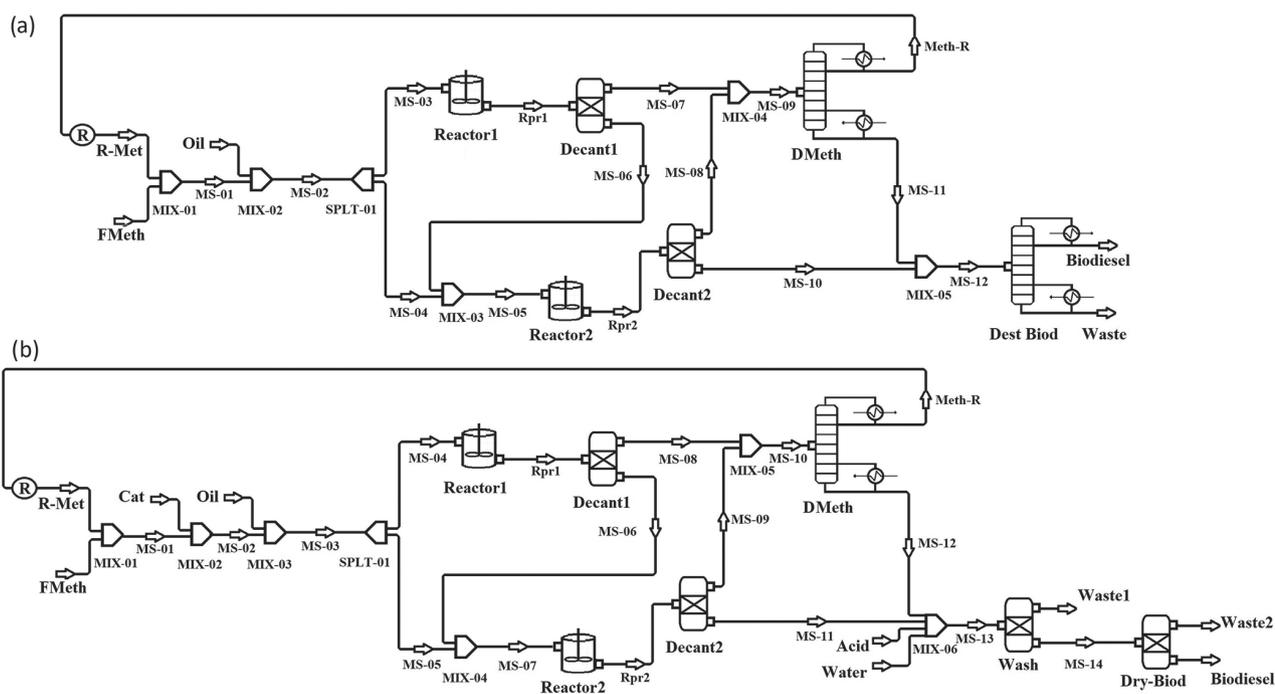


Figure 1. Simplified flow sheets of biodiesel production catalyzed with (a) homogeneous catalyst, and (b) heterogeneous catalyst. Summary of unit operating conditions for each process is presented in the Supplementary Information.³⁶

The waste reduction algorithm

This algorithm was developed by the United States Environmental Protection Agency scientists to evaluate and reduce environmental and related human health impacts at the design stage.^{46,47} To estimate the potential environmental impacts (PEI) for both simulated process, the free WAR_GUI software⁴⁸ was used. The input information was the rate and composition of each stream entering and leaving the chemical process and the energy consumption rate. The PEI is defined as the effect that a chemical would have on the environment if it were simply emitted into the environment. The algorithm includes PEI from eight categories: human toxicity potential by ingestion, human toxicity potential by exposure, aquatic toxicity potential, terrestrial toxicity potential, global warming potential, ozone depletion potential, smog formation potential and acidification potential.^{46,47}

Results and Discussion

The complete design matrix and biodiesel yields at condition variables are listed in Table 2. The experimental biodiesel conversions yields obtained were in the range from 26.1 to 88.7%.

To determine the experimental error, runs 9 to 12 were used at the center point of the design. Table 3 shows the analysis of variance result. The Prob > *F* less than 0.05 indicated that the particular term was statistically significant, in other words, the particular term significantly affected the measured response of the system. The analysis confirmed that the conversion's significant terms were the

Table 2. Values for transesterification yield on macauba according to the 2³ full factorial design

Catalyst / %	Experimental variable		Yield / %
	Molar ratio oil:methanol	Reaction temperature / °C	
1	1:36	60	45.0
3	1:36	60	58.5
1	1:18	60	26.1
3	1:18	60	88.7
1	1:36	80	85.7
3	1:36	80	52.9
1	1:18	80	77.0
3	1:18	80	80.7
2	1:27	70	59.0
2	1:27	70	60.0
2	1:27	70	64.2
2	1:27	70	67.4

catalyst, molar ratio oil:methanol, reaction temperature and the interactions between the catalyst and the molar ratio and between catalyst and reaction temperature. The coefficient of determination (R^2) for the model was 95.9%. This indicates that only 4.1% of the total variability was not explained by the regressors in the model.

The high R^2 value specifies that the model obtained will be able to give a good estimate of the response of the system in the range studied. The lack of fit test, which is not significant for the model developed, shows that the model satisfactorily fits the data.

Figure 2a shows the Pareto chart in the statistical analysis for the response variable reaction yield (in

Table 3. Analysis of variance for the model that represents the transesterification yield, on macauba oil using the 2³ full factorial design

Source	Sum of squares	Degrees of freedom	Mean square	<i>F</i>	<i>p</i> -Value Prob > <i>F</i>
Model	3473.69	7	496.24	37.60	0.0017 ^a
(A) Catalyst	274.72	1	274.72	20.81	0.0103
(B) Molar ratio	115.06	1	115.06	8.72	0.0419
(C) Temperature	760.89	1	760.89	57.65	0.0016
AB	913.35	1	913.35	69.20	0.0011
AC	1382.33	1	1382.33	104.73	0.0005
BC	7.49	1	7.49	0.57	0.4932
ABC	19.84	1	19.84	1.50	0.2874
Residual	52.79	4	13.20		
Lack of fit	7.73	1	7.73	0.51	0.5250 ^b
Pure error	45.06	3	15.02		
Corrected total	3526.48	11			

^aSignificant; ^bnonsignificant; 95% confidence level. *F*: statistical test of variance comparison in the tests, allowing the evaluation of the quality of fit of the model.

percentage). In this figure, bars represent the standardized effects (calculated t) related to response variables. In this way, variables represented by bars that exceed the tabulated t are statistically significant at the 95% confidence level. In this way, the interaction between the amount of catalyst and the molar ratio has a significant positive effect in conversion yield, as well as temperature, while catalyst interaction with temperature has a negative effect.

As can be seen from Figure 2b, the three-dimensional response surface show the effects of the transesterification condition variables on biodiesel yield. Stoichiometrically, the transesterification reaction requires three moles of methanol for each mole of triglyceride. It is expected that an excess of alcohol will increase the conversion rate due to the dynamic equilibrium, and inhibit the chemisorption of triglyceride molecules on the active site of catalyst, where the carbonyl group forms a carbonium ion.¹² In addition, products (such as glycerin and methyl esters) can be extracted from the system to renew the surface of the catalyst and dilute the oil. Nevertheless, an excessive amount of alcohol should be avoided because it can affect the processes of separation and purification, and promote the hydrolysis of methyl esters during the reaction, resulting in reversible reaction and decreased yield.^{12,53}

Temperature is one of the factors that positively influence the reaction and yield of the biodiesel product. Being an equilibrium reaction, the equilibrium constant is influenced by temperature and pressure. A higher reaction temperature can decrease the viscosities of oils and results in an increased reaction rate and a shortened

reaction time.⁵³ Nevertheless, a high reaction temperature can decrease biodiesel yield due to alcohol evaporation, and because it accelerates the saponification reaction of triglycerides. In addition, the presence of a solid catalyst forms a three-phase system, and consequently the diffusion resistance between different phases would slow down the reaction and more quantity will increase the complexity of the catalyst removal and involve additional costs.¹¹

The optimization of biodiesel conversion was carried out based on all variables in the studied range of experimental runs. The region that favors the yield optimization (in percentage) of the macauba oil was 1.8% of catalyst, 77 °C and molar ratio oil to methanol 1:36. The validity of the predicted model was examined by experiments at the suggested optimum synthesis conditions.

The oil and biodiesel characterization (Table S1, in Supplementary Information) shows similar values to those observed in the literature,⁴⁰⁻⁴⁴ and in agreement with values accepted by the National Petroleum, Natural Gas and Biofuels Agency ANP in Resolution No. 45, in 2014.⁵⁴

It can also be found that the used CaO/Nb₂O₅ catalyst can be easily recovered by centrifugation and rinsed with methanol. Further recycling experiments illustrate that there was a negligible loss of the catalyst amount and after 3 cycles, the yield was decreased to 82.1%.

As was mentioned in the Introduction section, other mixtures of CaO and metals have been reported with conversions superior to 90%, but to compare our experimental results, the only published work²⁵ that uses

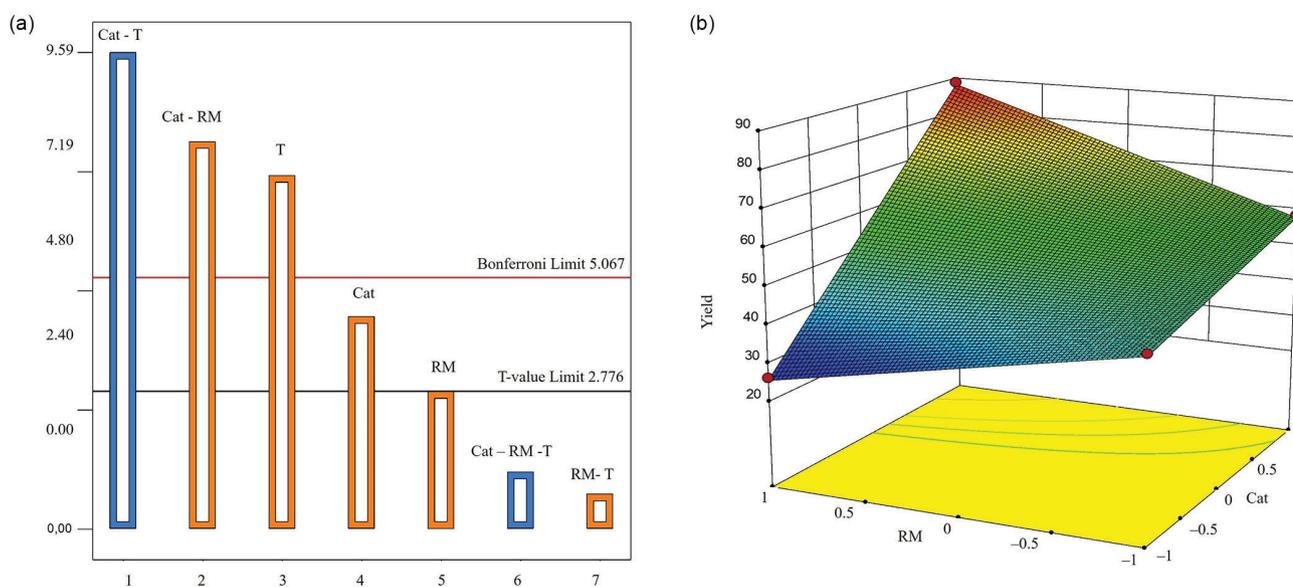


Figure 2. Statistical analysis results of the biodiesel production at 95% confidence level ($p < 0.05$) (Design Expert Software).⁴⁹ (a) Pareto chart showing the contribution of main factors and their interactions; (b) response surface contour plot for the interaction between the amount of catalyst and molar ratio oil to methanol, reaction temperature 60 °C.

the same mixture with Nb_2O_5 studied just a single variable value (molar ratio of palm oil to methanol 1:11, 3% of catalyst, 65 °C for 2 h) and their focus was to analyze the effect of heat pretreatment on the catalytic performance. By comparing with other CaO modified catalyst reports, the niobium/calcium oxides mix display higher conversion respect to Ca/Mg,²⁴ Ca/Ce³⁰ catalysts, similar values when compared with PA/CaO²⁹ and CaO/CuFe₂O₄³¹ catalysts, and lower conversion when relates with the yield performane of catalyst as Ca:Zn,^{22,23} Sr²⁺-CaO/MgO,²⁵ CaO-MgO,²⁶ KF/CaO,²⁸ and CaO-CeO₂.³² Considering that the optimal temperature is higher than the boiling point of methanol, which cause the loss of reactant by vaporization, this can influence the results on the optimization of the molar ratio, which is higher compared with other reports²²⁻³² for CaO catalysts (1:9 to 1:30). About other aspects like reaction time (2 to 6 h) and mass amount of catalyst (2 to 5 wt.%) our results are in the range.

Regarding the simulations carried out, the results and specification of the units used are presented in the Supplementary Information. The composition and flow rate data of all the streams involved in the two simulated processes (inlet and outlet material streams) allowed evaluating the environmental assessment. The total PEI generated within the system is shown in Figure 3a and the output rate of environmental impact for the processes examined is shown in Figure 3b. It is obvious that the heterogeneous process has lower generated PEI, which can be interpreted as the PEI of the substances entering the system is increased by their transformation. For the homogeneous process, the value of generated PEI indicates that the conversion of entering substances occurs to a higher degree. On the other hand, the homogeneous catalyst process has a lower impact on the environment compared with the heterogeneous process: the latter process exhibits a lower PEI *per* mass of products. This environmental

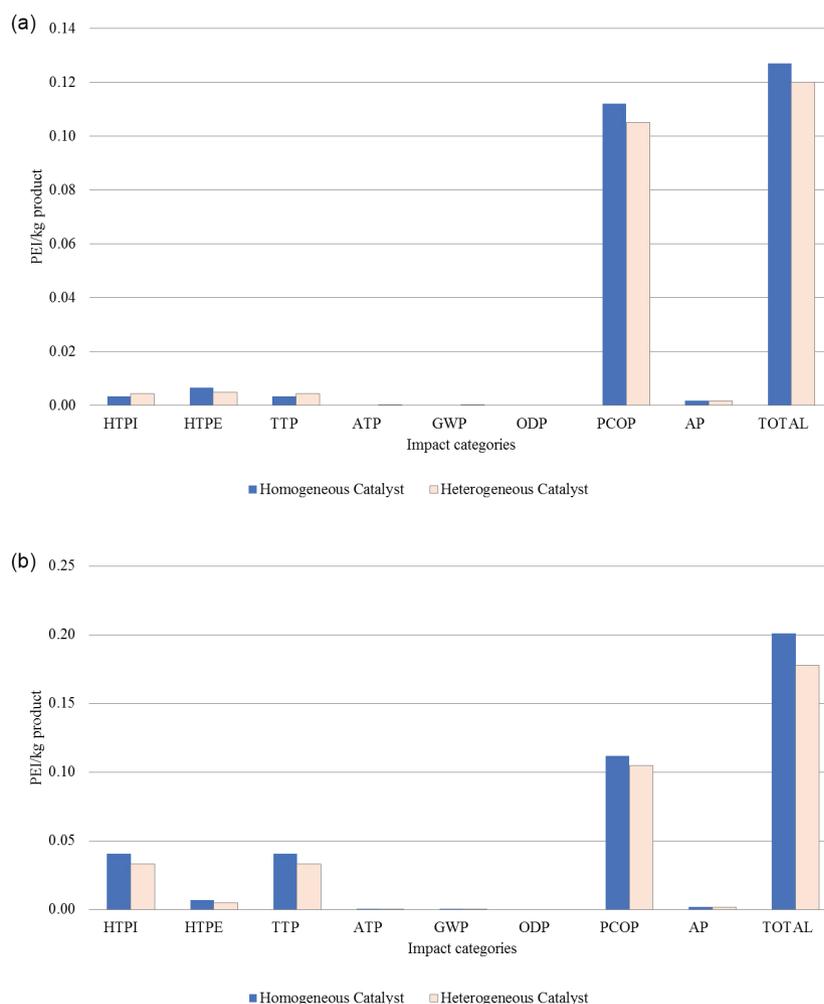


Figure 3. (a) Potential environmental impact generated within the studied processes; (b) total output rate of environmental impact for the studied processes. The impacts are expressed as the PEI generated within the process *per* mass of product streams. HTPI: human toxicity potential by ingestion; HTPE: human toxicity potential by inhalation or dermal exposure; TTP: terrestrial toxicity potential; ATP: aquatic toxicity potential; ODP: ozone depletion potential; PCOP: photochemical oxidation potential; AP: acidification potential. WAR_GUI Software.⁴⁸

indicator is the index to be considered for the overall evaluation of both processes. This feature can be related to the fact that the streams that leave the process in the homogeneous case have remaining catalyst, whereas that does not occur in the heterogeneous case.

Conclusions

The main goal of this study was to analyze the variables that affect the methyl esters (biodiesel) production using a mixture of calcium oxide and niobium oxide as a heterogeneous catalyst. A maximum experimental conversion yield near 90% was found, the experimental design methodology permitted a careful evaluation of the process variables and allowed to conclude that the interaction between the percentage of mass of catalyst and the molar ratio has a positive effect, and the amount of catalyst and reaction temperature has a negative effect on biodiesel yield conversion. The reaction temperature by itself indicated a significant positive effect. The biodiesel kinematic viscosity, specific mass and acid value are within accepted values of Brazilian legislation. Those experimental results were used in a simulation to compare with a conventional homogeneous catalytic process. It was concluded that there was a lower potential environmental impact and this way there is potential for further advanced studies, such as a techno-economic analysis to evaluate the economic feasibility of this technology.

Supplementary Information

¹H NMR details and simulation specification are available free of charge at <http://jbcs.sbq.org.br> as PDF file.

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