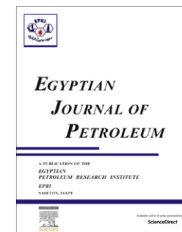HOSTED BY

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REVIEW

The study of biodiesel production using CaO as a heterogeneous catalytic reaction

Kamila Colombo [a,*], Laercio Ender [a], António André Chivanga Barros [b]

[a] *Universidade Regional de Blumenau (FURB), Centro de Ciências Tecnológicas, Departamento de Engenharia Química, Rua Antonio da Veiga, 140, Blumenau-SC, Brazil*
[b] *Instituto Superior Politécnico de Tecnologias e Ciências, Departamento de Engenharias e Tecnologias, Av. Luanda Sul, Rua Lateral, Via S10, Talatona, Luanda Sul, Angola*

Abstract With the aim of developing a process of biodiesel production that is environmentally benign much interest has been focused on the use of solid base catalysts, such as calcium oxide, for the transesterification of vegetable oils with methanol. In the study reported herein a recycling reactor was used in bench scale, with the capacity to produce 3 L of biodiesel. The reactor was designed especially for this research study. A full 2^3 factorial plan was used to evaluate the process parameters related to this study, in particular, the catalyst concentration, the alcohol to oil molar ratio and the reaction time. Using this equipment for the transesterification reaction resulted in the recovery of the excess alcohol. The reaction products were characterized using gas chromatography and liquid analysis to determine the ester and calcium concentrations, respectively. The main conclusions drawn were that the best conversion percentage (100% of biodiesel) was reached when the methanol:oil molar ratio was 6:1, the reaction time was 75 min and the catalyst mass was 3% in relation to the oil mass used in this process. The CaO concentration determined exceeded the limit of concentration defined by legislation and thus a secondary operation was carried out to purify the reaction products obtained. The results of this study showed a high performance, and the proposed experiment could be used as a new and innovative way to produce biodiesel in the future.

Contents

* Corresponding author. Tel.: +55 41 88423267, +55 49 84093731.
E-mail address: kamicolombo@gmail.com (K. Colombo).

1. Introduction

Interest in fuels obtained from renewable sources, such as bio-fuels, has increased significantly in recent years due to the political and economic instability of the oil market, and also because of the environmental benefits associated with decreasing levels of gaseous emissions from the combustion of fuels from non-renewable sources [1–4].

Biodiesel is defined as a non-petroleum fuel produced through a chemical reaction to break down the triglyceride present in fatty acids [5,6]. This reaction is called transesterification or esterification when using as catalyst hydroxides or acids, respectively [7,8]. Biodiesel is a promising alternative to conventional diesel fuel due to its renewable nature and the associated reduction in the emission of particles and greenhouse gases [9–12].

The transesterification reaction is used to break down the chemical structure of the triglycerides in oil via the exchange of the alkyl groups between an ester and an alcohol with the alcohol being used as a reactant. Vegetable oil is subjected to transesterification to decrease the viscosity and increase the volatility of biodiesel [13]. The transesterification process has difficulty converting into esters in the presence of free fatty acids (FFA) and water and, therefore, requires high quality raw materials to avoid undesirable side reactions and hydrolysis (saponification) or additional pre-treatment to remove the initial FFAs [14–16].

The reactions involved in biodiesel production can be homogeneously catalyzed to obtain high yields in a relatively short time; however, biodiesel does not compete favorably with fossil fuels because the catalyst cannot be reused and must be neutralized after the reaction [17]. Environmental concerns have led to the search for solid catalysts which are eco-friendly and effective [18]. The chemical process used to obtain biodiesel is based on the solid in the system catalyzing the reaction to reduce the time and the cost of the process through the reuse of the catalyst, decreasing the level of impurities in the reaction products and carrying out the operation in a continuous fixed bed [19–22].

Studies indicate that the combustion of biodiesel (100%) decreases emissions of greenhouse gases, making it ideal for use in sensitive environments [6,23–25].

The transesterification process efficiency with the use of a heterogeneous catalyst is related to the fact that the catalyst is a solid. Generally, a heterogeneous catalyst provides higher conversion efficiency than a homogeneous catalyst, and further studies are required to determine the most appropriate time and temperature for each reaction [26].

Recently, research studies have been carried out using calcium oxide (CaO) as a heterogeneous catalyst because of its low production cost [26–30] and its high basicity [28,31].

Liu et al. [32] studied the transesterification of oil using CaO as a heterogeneous catalyst and achieved 95% conversion of the oil to the ester using a methanol to oil molar ratio of 12:01, 8% of CaO in relation to the oil mass and a reaction time of 3 h. Viola et al. [33] performed the same reaction and reached 93% of conversion with 80 min of reaction time using CaO as the catalyst at a reaction temperature of 65 °C using 5% of catalyst in relation to oil (m/m). The authors used a methanol to oil molar ratio of the 6:1. Zhu et al. [34] achieved 93% of conversion using oil from *Jatropha curcas* and a solution of CaO with ammonia carbonate. Watkins et al. [35] carried out a similar study using CaO mixed with lithium as a catalyst. For the biodiesel production in continuum processes, all of the tests by the above-cited authors were conducted in a fixed-bed reactor on laboratory scale, due to the higher production ratio in relation to traditional processes based on bench reactors [36–38].

The results of these studies indicate that the conversion of vegetable oil to biodiesel through transesterification using CaO as a heterogeneous catalyst provides a maximum conversion of 95% in the production of biodiesel when all of the parameters are optimized, manly the reaction time and molar ratio. These studies were carried out with a bench reactor inside which a mechanical agitator was installed. This equipment can also be used with a solid catalyst. In the literature other similar studies have been reported, where the flow rate of the heterogeneous mixture in the system was determined during the reaction.

In the study reported herein, a commercial oil was used for the transesterification with a heterogeneous catalyst. This paper proposes the innovative use, compared to conventional methods, of a recycling reactor to evaluate a new design for the equipment used in the biodiesel production process. A full 2^3 factorial plan was applied, with a bench reactor and a heterogeneous mixture, to optimize the operating conditions. With respect to the production of biodiesel in this continuous process the conversion was improved, with the possibility of increasing the scale of the process. The ester concentrations were determined by gas chromatography and the CaO concen-

trations were determined by absorption atomic spectroscopy to verify the quality of the biodiesel produced.

2. Experimental

2.1. Materials

Soya® soybean oil (edible grade, purchased from a local market) with an acid value of 0.2 mgKOH/g and average molecular weight of 884.65 g/mole was used in all experiments. The other chemical products used in the experiments were methanol (AR grade 99%; Dinâmica) and calcium oxide (CaO; AR grade 92%; Dinâmica). Commercial CaO was used as a catalyst in the studies on the transesterification reaction.

2.2. The recycling reactor

As can be seen in Fig. 1, a reactor was used in this study to carry out the conversion of soybean oil to biodiesel by transesterification using a heterogeneous catalyst. The heterogeneous reactor was designed, constructed and installed in the Development Processes Laboratory (LDP) of the Chemical Engineering Department (DEQ) at Blumenau Regional University (FURB). The reactor was designed to be bench scale with internal recirculation in all steps. The reactor tanks are connected via 2″ pipes. The feed tank capacity is 3.5 L and the reactor 2 L.

The feed tank was jacketed and used initially with the reactants, soybean oil and methanol. The mixture in this tank was increase the temperature using water from the thermostatic recirculation system. The mixture was moved along the reactor system, using a positive displacement diaphragm pump (Netzsch, model IR ARO II2GDX), with the flow rate controlled in each step by the pipe connections. The electrical resistance installed in the bottom of the heating tank was used to heat the reactants. When the reaction was completed the temperature was increased in order to recover the excess methanol used in the process, to ensure the irreversibility of the reaction. The reactor is operated at atmospheric pressure since the condenser is situated on the top of the feed tank and is open to the atmosphere.

The design of the equipment shown in Fig. 1 differs from the reactors described in the literature because in our experiments the reagent and catalyst are recirculated throughout the entire system. The turbulent interaction between the reac-

tant and the solid catalyst in the mixture increases the process efficiency by improving the conversion of oil to biodiesel.

2.3. Transesterification reaction

The biodiesel produced through the transesterification of soybean oil using the bench reactor is described in Fig. 2.

In the recirculation reactor, for each step, the mass concentration of biodiesel was increased until the total conversion of oil in biodiesel and can be calculated based on the mass balance equation as show in Eq. (1).

$$\frac{dNA}{dt} = F_{A0} - F_A + r_A V \tag{1}$$

$$r_A = KC_A^3 \tag{2}$$

In this operation the oil was heated to 60 °C using the one heating tank, as show in Fig. 4. The methanol and the catalyst were placed in the system to start the process, using the flash tank, used too to recovery the excess of reactant, as show in Fig. 3.
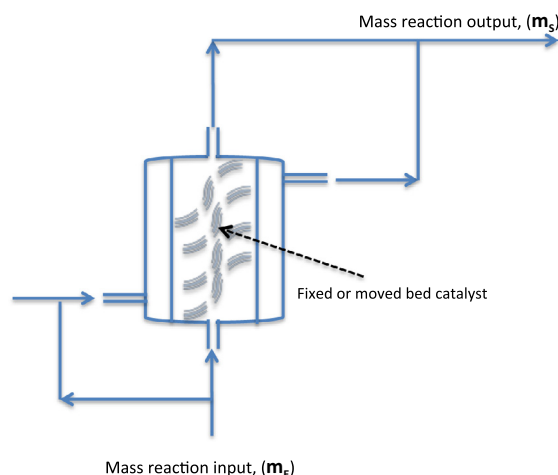
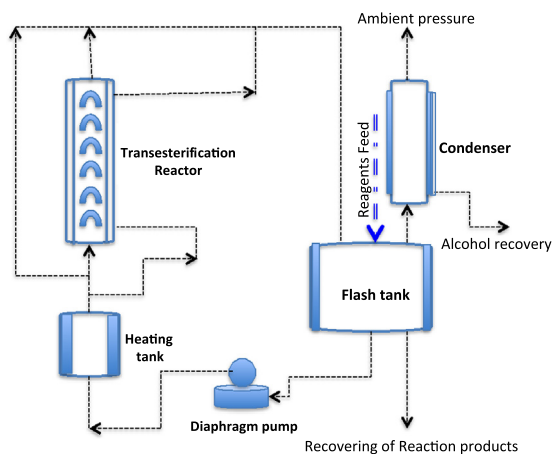**Figure 2** Reactor used in this study.

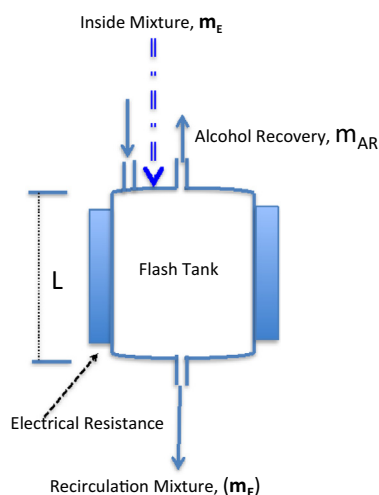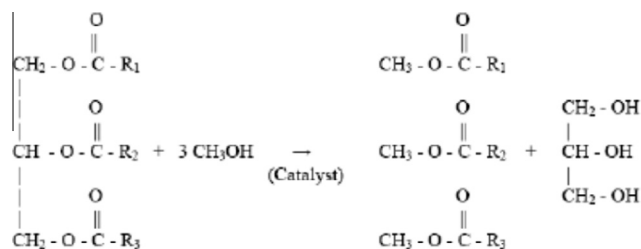**Figure 3** Flash tank used to inside the reactant mixture and to recover the excess of alcohol.

Figure 1 Recycling reactor used in this study.

Figure 4 Transesterification reaction. R_1, R_2 and R_3 represent the fatty acid chains.

The catalyst and methanol masses were calculated based on the stoichiometric relation defined at the beginning of the study based on the factorial plan.

In this step the temperature was controlled using a PID (proportional–integral–derivative) controller developed by Softlution. The mixture was heated using electrical resistances installed inside the cylinder (Fig. 5). When the reaction was completed, the temperature was increased to recover the excess methanol.

The heat associated with heating of oil in Fig. 5 was calculated using Eq. (3), which is related between the flow rates involved in the tank.

$$Q = (mCpT)_{out} - (mCpT)_{input} \qquad (3)$$

After the alcohol had been removed the mixture was placed into a funnel for the separation of the product of the initial reaction with a single phase and then decanted to form three phases designated as: the heavy concentration phase with the catalyst; the intermediate concentration phase, essentially consisting of glycerol; and the light concentration phase, which is present on the top of the concentrated biodiesel mixture.

Fig. 6 shows the sequential stages of the decantation process with the separation occurring in the decantation funnel. The photo on the right shows the three phases after the biodiesel, glycerol and catalyst have been completely separated.

The biodiesel produced was submitted to a secondary purification process using centrifugation under controlled temperatures. In this process the particles of calcium present in the biodiesel were removed. After drying the biodiesel, the methanol was removed in a stove with controlled heat to maintain the temperature required for the process.

2.4. Experimental plan

The study was carried out based on a factorial plan using a full factorial design with 3 variables and 2 levels, which resulted in
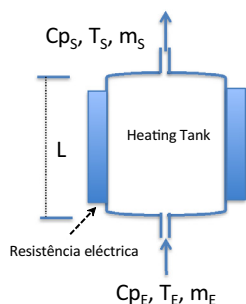
Figure 5 Heating tank used in this study.
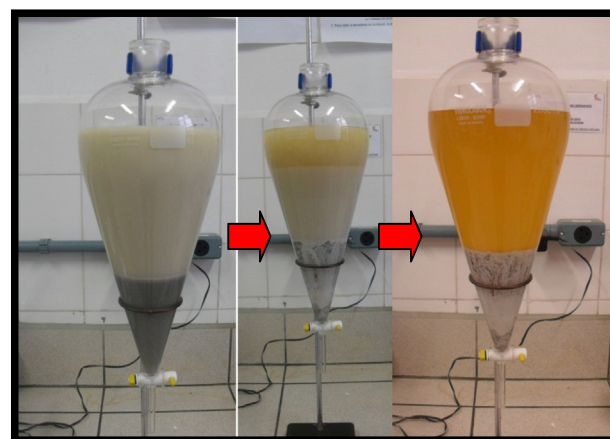
Figure 6 The reaction products of transesterification processes.

Table 1 The factor levels for 2^3 full factorial design with median.

Level	−1	0	+1
Catalyst concentration (g)	M_1	M_2	M_3
Reaction time (min)	t_1	t_2	t_3
Molar ratio	RM_1	RM_2	RM_3

8 experiments with 5 as the median. Table 1 shows the variables analyzed in the experiment and their levels.

The variable factors and their values used for the optimization of the transesterification processes were as follows: (a) ethanol:oil molar ratios of 3:1, 4.5:1 and 6:1; (b) catalyst concentrations of 3%, 4% and 5% in relation of the initial oil mass; and (c) reaction times of 45, 60 and 75 min.

The masses of the reactants used in this process were determined via stoichiometric balances, and the mass of methanol was extrapolated by reversing the esterification or transesterification reaction. For this, the mass of methanol was 4 times greater than the mass of the stoichiometric balance.

The operating conditions applied in the experiments were: (a) reaction temperature 65 °C; (b) flow rate 169.73 cm³/s, related to the 4 bar pressure equivalent to the pump operation pressure; and (c) oil mass 2205 g.

The procedure used to evaluate the results was based on the use of STATISTICA software 7.0® with Six Sigma and was used to gain a better understanding of the methodology and the process parameters evaluated in this study. The experimental plan was based on a full factorial design and was carried out twice to improve the results.

2.5. Characterization techniques

The analysis method used for the characterization of the biodiesel was based on the quantification of esters by gas chromatography, according to the European standard of EN14103. The calcium was determined by atomic absorption spectrophotometry.

3. Results and discussion

3.1. Experimental apparatus

The equipment proposed for this experiment has many differences when compared to that which is commonly used in other studies on transesterification. Traditionally, a single cylinder jacketed with a mechanical device for agitation is generally used. The reaction, the methanol recovery, the decanting of other products and the separation are all carried out in this cylinder. The secondary process also takes place in this cylinder. However, the traditional procedure is associated with several limitations.

As innovation and contribution in the development processes from this work, the apparatus of the proposed experiment has a compact structure composed of three cylinders connected by pipes where the mixture is circulated by a pump. Initially, the homogeneous mixture flows into the system and when it reaches the reaction temperature the solid catalyst is added to the cylinder to give a heterogeneous mixture and the chemical reaction starts. In this process the heterogeneous mixture is agitated by the action of a pump during the circulation process.

One innovation of this process relates to the possibility of use the equipment for transesterification with heterogeneous or homogeneous mixtures and it can be operated with a movable or fixed catalyst bed. The operational flexibility of the equipment represents an important contribution to the technology for the production of biodiesel with the aim of developing a continuous process with an optimized reaction time.

In the approach applied in this study, all of the steps of the process take place in the same reactor system. The mixture heating, the agitation controlled by the pump, the reaction and the recovery of excess methanol all occur in the same reactor system. A limitation associated with this system is the deposition of the solid catalyst in the curves, valves or other accessories installed in the system. This can be minimized by increasing the turbulence level applied during the process. At the end of the reaction the catalyst mass was the same as the initial mass. The catalyst remained in the system and less than 5% of the initially mass in the system was recovered.

The operational evolution was investigated through an analysis of the process parameters of the biodiesel production by transesterification using a heterogeneous catalyst to constant of the temperature of the chemical reaction. In the design of the equipment installed two PT-100s sensors (Samrello; model KJRS) were used to control the reaction temperature in the previous step.

The behavior of the transesterification process was evaluated considering the temperature profile shown in Fig. 7, where the three steps of the process can be observed.

The experimental tests were carried out with control of the reaction temperature. The results in Fig. 7 show the three steps of the process: (a) the dynamic process characterized by the heating of the mixture which is represented by an increase in this parameter over time; (b) the stabilization of the temperature during the transesterification reaction; and (c) the recovery of the excess methanol through increasing the temperature (this being the most volatile component in the mixture).
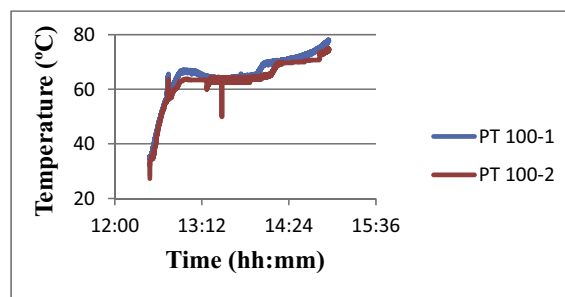
Figure 7 Temperature profile showing the behavior of the process during 75 min of the experiment.

3.2. Factorial plan with full 2^3 factorial design

The factorial plan was used to identify the most significant operating parameters in the study on the conversion of soybean oil to biodiesel through the transesterification reaction in a recycling reactor using the heterogeneous catalyst.
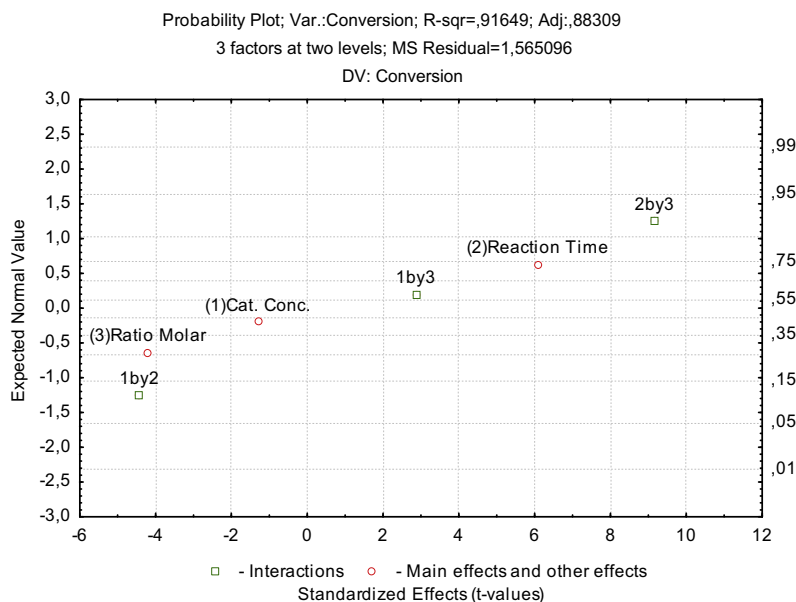
The factorial plan and the fatty acid methyl esters (FAME) data showed was obtained through chromatography which illustrated good.

With the use of Statistica®7.0 software, the relation between all operational parameters in this study can be evaluated, where possible to define betters operations.
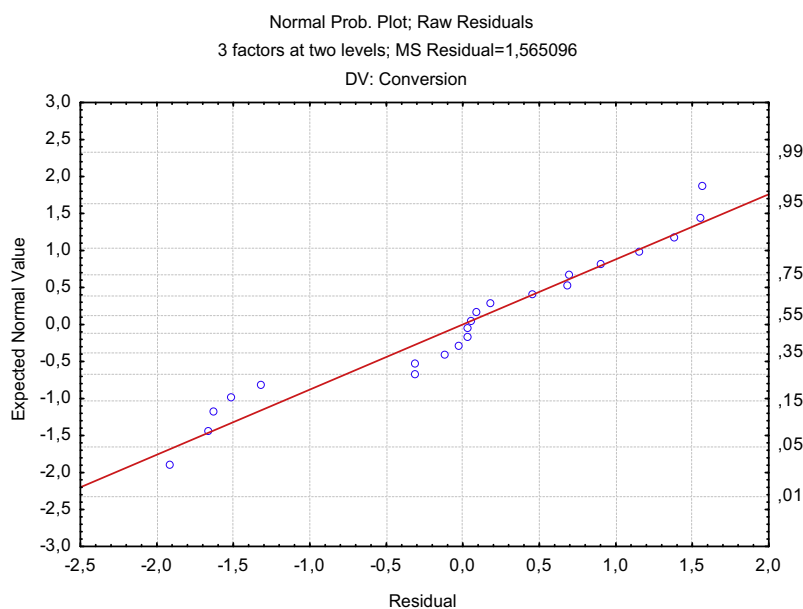
The experimental data show the effects of the main operational parameters on the interactions between two factors to give the standard error and time values within a range of 95%. All relations between the process parameters were statistically significant within the intervals specified with the exception of the catalyst concentration. The parameters were the relation between the molar ratio and the reaction time and between the catalyst concentration and the reaction time, respectively. The values for all parameters were far from zero, which has been shown in the qualitative analysis of Gaussian distribution to have a positive effect on the conversion. The relations between reaction time and molar ratio and between catalyst concentration and molar ratio have, in this order, negative effects on the conversion. However, the values for the concentration of catalyst are close to zero and thus this parameter does not have a significant influence on the conversion results.

The relation between the parameters studied and their combinations are shown in Fig. 8 according to their influence on the conversion to methyl esters.

The regression of the data obtained from the linear fractional plan gives and R^2 value of 0.9165, which verifies the quality of the results and the satisfactory nature of this analysis. Therefore, further analysis was carried out using Statistica®7.0 software to relate the parameters evaluated by the surface response method. These combinations provided a higher conversion rate of the raw materials used into fatty acid esters. This analysis revealed the relationship between the predicted regression values and those obtained experimentally, as shown in Fig. 9, verifying the high degree of reliability of the results, observed earlier via the R^2 value.

Probability Plot; Var.:Conversion; R-sqr=,91649; Adj:,88309
3 factors at two levels; MS Residual=1,565096
DV: Conversion

Figure 8   The relation between parameters in the 2^3 factorial plan.

Normal Prob. Plot; Raw Residuals
3 factors at two levels; MS Residual=1,565096
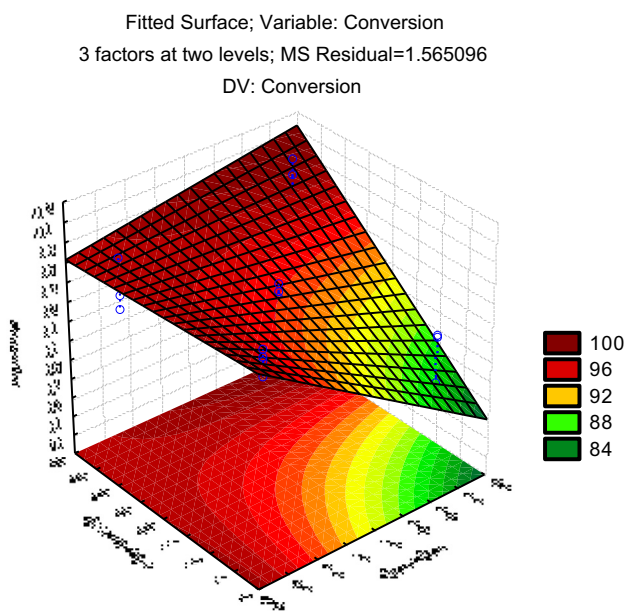DV: Conversion

Figure 9   Values predicted by the linear model versus experimental data.

3.3. Analysis of data through response surface technique

In this study the combination of two factors in the process was analyzed to determine which had a greater influence in the conversion of oil to biodiesel. To obtain the maximum conversion the best conditions were combined and observed on the graphs with a catalyst concentration of 3%. For this, the catalyst mass was fixed to obtain a new response surface, as shown in Figs. 10 and 11.

This operation showed that the use of a catalyst mass of 3% relative to the oil mass, with a 75 min reaction time and a 6:1 methanol:oil molar ratio, ensured high levels of conversion of the oil to biodiesel.

The reaction yield increases with an increase in the molar ratio above 3 to the point at which the alcohol:oil ratio is considered to be adequate. Increasing the molar ratio beyond this point does not improve the yield, it only increases the cost because of the alcohol recovery. The optimum molar ratio is associated with the type of catalyst used but, in general, a molar ratio of 6:1 is applied in studies on alkaline catalysts. For oils with a high content of free fatty acids, for example, waste frying oils, where the biodiesel is produced with the use of an acidic catalyst, molar ratios of 15:1 are common [2]. The use of high molar ratios, for instance, 42:1, has been reported by Saka and Kusdiana [39] in the transesterification

Fitted Surface; Variable: Conversion

3 factors at two levels; MS Residual=1.565096

DV: Conversion

Figure 10 Response surface which correlates the methanol:oil molar ratio and the reaction time (min) with the conversion (%) using a catalyst concentration of 3%.

reaction of supercritical methanol using a ratio of 53:1 to reach a conversion of 98% [40].

The behavior shown in Fig. 11 can be compared to that reported in [2], where the ester conversion rate increased with the reaction time. In the beginning, the reaction is slow due to the dispersion of the reactants in the mixture and after a certain period of time the reaction proceeds rapidly. In general, within 3 min from the start of the reaction the yield has reached its maximum and it remains relatively unchanged with increasing reaction time. Increased reaction time results in

reduced yields due to the reversibility of the transesterification reaction.

On varying the catalyst mass in the range of 1.0–9.0% of the oil mass the results show that the transesterification reaction is strongly dependent on the catalyst used. When the catalyst mass is in the range of 1.0–6.0%, the biodiesel yield increases. However, with an increase in the catalyst mass the biodiesel yield is lower, probably due to the mixing of the reagents, the products and the solid catalyst. The highest catalyst mass used in this experiment was 6.0% with a methanol to oil molar ratio of 14:1 at 60 °C and a reaction time of 2 h. The conversion obtained in this case was 92.40% [41].

In studies reported in the literature methodologies are proposed with different reaction times, for instance, using mixed oxides of Ca and Zr a conversion level of 87.3% was reached in 45 min of reaction [42]. On the other hand, Liu et al. [32] used CaO as a catalyst and after 3 h of reaction 95% conversion was obtained. The authors noted that within 80 min of reaction 93% of the conversion [33] was completed. In another study, 10% KOH (KOH/NaX) supported on NaX zeolite resulted in a conversion of 85.6% after 8 h of reaction [43].

3.4. Calcium concentration in biodiesel

Samples of the biodiesel obtained from the experiment were collected and used to determine the calcium concentrations, due to the calcium leaching phenomenon based on the mass transfer from a solid phase to a liquid phase. The presence of calcium in the biodiesel would limit the results of the proposed methodology and require the development of a new procedure for biodiesel purification.

The calcium concentration affects the biodiesel quality and the Brazilian National Petroleum Agency (ANP) has defined a maximum limit of calcium plus magnesium of 5 mg/kg. The experimental data derived from this study exceeded this limit and thus an assessment of the use of other catalysts in the
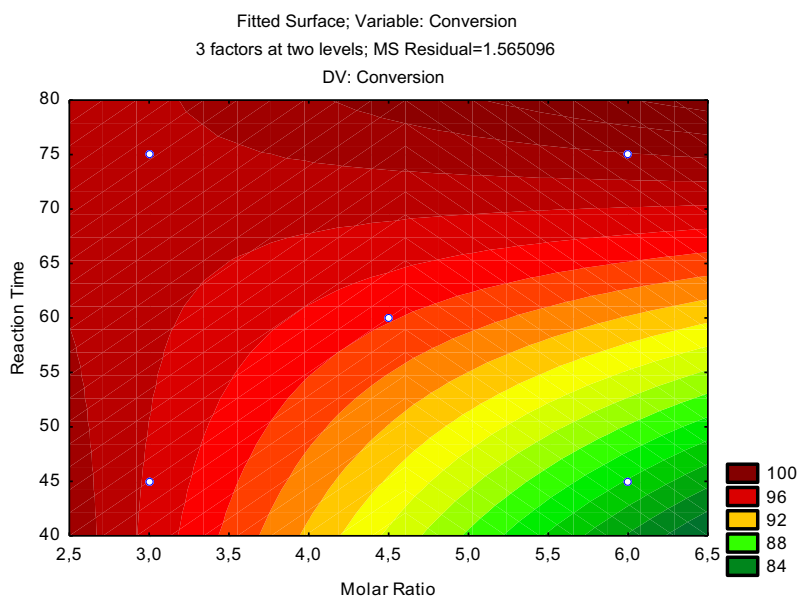
Figure 11 The curve that correlates the methanol:oil molar ratio and the reaction time (min) with the conversion (%) using a catalyst concentration of 3%.

methodology is required to test their ability to minimize the concentration of calcium or other precipitates in the biodiesel or, alternatively, a secondary purification process could be applied.

Based on the results of the analysis it appears that calcium was present in the biodiesel in high concentrations due to the calcium leaching phenomenon. For this reason, a centrifugation process to transfer the calcium present in the biodiesel liquid phase to solid phase by precipitation was applied, based on the principles of centrifugation. This procedure was carried out for 30 min at 5 °C and at 5000 rpm in a high velocity rotary centrifugation apparatus with refrigeration (Sorvall Evolution RC).

Centrifugation can decrease the calcium mass concentration in the biodiesel phase by eliminating the precipitates formed in the new phase in the mixture. This procedure is essential in order to obtain biodiesel samples with the quality necessary for the determination of the methyl esters concentration by gas chromatography.

Experiment 2 was carried out to determine the calcium concentration in the initial biodiesel (127.94 mg/kg) and after the centrifugation process, when the concentration had reduced by 60% to 51.48 mg/kg, which is still above of the limits established by ANP. This procedure can be performed as the secondary process necessary for the purification of biodiesel, essentially eliminating the remaining mass of calcium.

The degree of leaching affects the lifetime of the catalyst and the biodiesel can become contaminated with Ca, according to Kouzo and Hidaka [44]. The purification test to remove the leached CaO catalyst was carried out by passing the prepared biodiesel through a column packed with cation-exchange resin. Four resins were employed, differing in terms of the polymer matrix, the acidic functional group and the counter-cation. The protonated resins consisting of a macro-reticular polymer matrix resulted in the highest removal efficiency. The influence of the internal mass transfer on the removal efficiency was then investigated on the basis of data collected by purifying the biodiesel–methanol mixture with the addition of methanol which promoted internal mass transfer and 100% removal of the leached CaO catalyst was achieved successively. Furthermore, a reduction in the free glycerol was examined for the resin purification [44].

An increase in the leached species was observed in the presence of glycerol, which is the final stage of the transesterification reaction after the formation of the products. Ca is formed due to the reaction between CaO and glycerol. This compound is more soluble than CaO. The solid can be reused for a relatively large number of reactions. The catalyst was often used correspond to 1% by weight, based of mass of the oil. It was observed that the contribution of the species resulting in a homogeneous leached species can be considered insignificant since the catalyst loading is small [45].

4. Conclusions

The proposed methodology and design of the equipment for the production of biodiesel, based on the flow rate, phase mixture, heating and chemical reaction, is a new innovation in biodiesel technology, based on the studies which have been reported in the scientific literature to date.

The procedure for the conversion of oil to esters described herein has advantages over those commonly reported in the literature, since the transesterification process can be carried out with a homogeneous or a heterogeneous catalyst, yielding a high conversion of the oil to biodiesel. The proposed equipment used in this research offers operational flexibility given the possibility of using a fixed or a mobile bed.

The use of commercial CaO as the heterogeneous catalyst in biodiesel production implemented in a bench scale reactor with recycling represents a further contribution and innovation in this study. The optimum reaction conditions were determined to obtain the highest conversion according to the analysis carried out in this study. The biodiesel produced was evaluated and characterized to determine the conversion level in relation to the concentration of methyl esters.

The difficulties associated with this procedure are related to the presence of CaO in the biodiesel produced. Thus, a separation step needs to be added to this procedure to purify the biodiesel produced.

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