



Biodiesel production using supercritical alcohols with a non-edible vegetable oil in a batch reactor

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ABSTRACT

In the present work, the transesterification of non-edible oil with methanol and ethanol is studied. The reactor phase transitions are directly observed in a double windowed cylindrical reactor and the conversion to fatty esters is measured. The optimization of the process conditions was carried out based on a statistical design of experiments where the key process variables were studied over different ranges to obtain a reliable model for the efficiency of the reaction as a function of reaction time, temperature, pressure and alcohol to oil molar ratio. From direct observations and the modeling of the phase behavior, a better understanding of the supercritical alcohol transesterification process is obtained as well as the confirmation of the phase equilibrium predictions based on the GCA-EOS model.

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1. Introduction

The production of fatty acid methyl and ethyl esters is of great industrial interest because of their direct use as biodiesel. Most of the biodiesel currently produced uses rapeseed or soybean oil, methanol and an alkaline catalyst. The main products of the reaction are fatty esters and glycerin. The high value of vegetable oils as food products makes production of a cost-effective fuel very challenging [1]. However, crude oils, animal fats and waste cooking oils can also be converted into biodiesel. Some problems with processing these low cost oils are related to the presence of water and free fatty acids [2]. The transesterification of vegetable oils using supercritical alcohols is an alternative for biodiesel industrial production. Recent experimental studies of non-catalytic transesterification by Saka and Kusdiana [3,4] have shown that the process is not sensitive to both free fatty acids and water contents, and high reaction rates are observed at conditions close to the critical properties of methanol.

Non-edible vegetable oils constitute another attractive option for biodiesel production. In the present work, the transesterification of fodder radish—*Raphanus sativus* L. var. *oleiferus* Stokes oil (a non-edible vegetable oil) in supercritical alcohols is studied in order to find optimum operating conditions. Fodder radish oil

has been regarded as an interesting option to produce biodiesel in Brazil, since the seeds have high oil content and the oil can be easily recovered by pressing. The plant has rapid development and has been used for green fertilization [5]. The study of the supercritical transesterification with ethanol, besides like that of methanol, is justified considering the large production of ethanol from renewable resources in South America.

In the present work, a phase equilibrium engineering analysis is applied to the transesterification of fodder radish oil in supercritical ethanol and methanol to study the influence of the pressure and a single phase condition in the transesterification reaction. Phase equilibrium engineering is the design of the phase condition required for a given process. This design is made on the basis of modeling of phase equilibria, knowledge of the phenomenological behavior or experimental information. Examples of phase equilibrium engineering applied to reaction and separation process can be seen elsewhere [6,7]. In this study, direct observations and modeling of the phase behavior is carried out in order to find feasible homogeneous operating conditions at moderated pressures. Then, the different variables affecting the non-catalytic transesterification reaction are evaluated to set the operating conditions and to demonstrate the feasibility of the operating conditions proposed previously. The best values of the variables in the experimental range studied are determined by applying a Doehlert design of experiments [8] and response surface methodology to determine how these variables influence the reaction. The results obtained are also interesting from the point of view of the continuous process

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Table 1
Raphanus sativus L. var. *Oleiferus* stokes oil. Fatty acids composition.

Fatty acid	Carbon number/double bond	Composition (wt.%)
Palmitic	16:0	7
Stearic	18:0	3.6
Oleic	18:1	27.9
Linoleic	18:2	7.6
Linolenic	18:3	4.6
Arachidic	20:0	2.2
Gadoleic	20:1	11.2
Erucic	22:1	33.3
Lignoceric	24:0	0.6
Nervonic	24:1	2.0

considering that when there is a single phase in the system the global density of the reaction mixture controls the residence time for a given flow rate and reactor volume.

2. Experimental

2.1. Materials

R. sativus L. oil extracted by cold press oil was used as vegetable oil. The molar mass of fodder radish oil was calculated as 900.3 g/mol on the basis on its fatty acid composition (Table 1), the oil acid number is (0.713 mg_(KOH)/g_(OIL)). Ethanol (99.5%), methanol (99.7%) and heptane (99.%) were purchased from Anedra. Methyl heptadecanoate (>99%) was purchased from Sigma–Aldrich.

2.2. Equipment

Supercritical biodiesel reactions were carried out in batch mode. A stainless steel tubular reaction cell with an internal volume of 32 cm³ (1.5 cm of internal diameter) was used to carry out the transesterification of crude *R. sativus* L. oil in supercritical ethanol and methanol. The same reaction cell was used to determine the phase behavior of the reaction. Fig. 1 shows a schematic diagram of the experimental equipment, which was similar to the one used by Hegel et al. [9]. Basically, the reaction cell has two 1 cm thick glass windows, which allow the experimental phase behavior observation. A camera (Mitsu cyber-eye) placed in front of one of the windows records the phase behavior. Two electric resistances of 450 W connected to a temperature controller (Novus N480D) were used to heat the reaction cell. The reaction cell also has an external aluminum jacket to act as a solid thermostat. A PT-100 platinum resistance thermometer placed in the external aluminum jacket measures the temperature with an error of ±2 K. The pressure inside the reaction cell is measured by a high temperature pressure gauge (Dynisco PG4 series). The entire system is isolated by a fiberglass mat to allow a better temperature control. The reactor also has a feed line to load a given amount of co-solvent.

2.3. Experimental procedure

The experimental procedure was carried out as follows. The reactor was first loaded with a given amount of oil and alcohol, previously weighed in a balance (Sartorius GE412). Then different molar ratios of the reagents were studied and the residual air was evacuated from the reaction cell by flushing it with nitrogen. After the charge of reagents the entire system was assembled, and the temperature was raised up to the desired value as follows. Initially, the temperature controller was adjusted to give a heating rate of 15 K/min up to 493 K. Then, the system was left at 493 K for 6 min in order to stabilize the pressure inside. Later, the temperature controller was set to a heating rate of 10 K/min up to the

reaction final temperature. The total heating time was approximately 33 min. However, previous studies indicated that there is almost no reaction at temperatures below 540 K [3,4]. The reaction time was arbitrarily assumed as the time the reactor was kept at the selected temperature level. When the reaction finished, the heating was turned off and the reactor was air-cooled to quench the reaction. Considering the heating and cooling periods and the temperature range studied, there is an uncertainty of reported and true reaction times that ranges from 5 to 8 min.

The phase behavior of the system at different temperature and pressure conditions was recorded by a video camera.

Unreacted alcohol present in the products of the reaction was separated in a vacuum oven at 343 K and 25 mmHg. Without the presence of alcohol, the biodiesel and glycerin become practically immiscible. Separation between biodiesel and glycerol was just performed by gravimetric precipitation. Triglycerides, diglycerides, monoglycerides and fatty acid methyl esters remained only in the biodiesel sample after separating methanol and glycerol due to the very low solubilities of the triglycerides and derivatives in the glycerol phase. The biodiesel phase was separated by aspiration and then analyzed by gas chromatography to determine the ester contents by weight fraction.

Triglycerides, diglycerides and monoglycerides in the biodiesel phase were not analyzed. However, according to Eq. (1) and because molecular weight of triglycerides is similar at three times that of fatty esters (e.g. MW_{Triolein} = 885.4 and MW_{M.Oleate} = 296.5) conversion of transesterification reaction is related to the content of fatty esters [10]

$$X = 1 - \frac{Mol_{TG}}{Mol_{TGO}} = 1 - \frac{Mol_{TGO} - Mol_{FE}/3}{Mol_{TGO}} = \frac{Mol_{FE}/3}{Mol_{TGO}} \quad (1)$$

$$X = \frac{M_{FE}/3MW_{FE}}{M_{TGO}/MW_{TG}} \approx \frac{M_{FE}}{M_{TGO}} \approx Ester_content$$

X: conversion; Mol_{TG} : moles of triglycerides, diglycerides and monoglycerides; Mol_{TGO} : moles of triglycerides loaded to the reactor; Mol_{FE} : moles of fatty esters; M_{TGO} : mass of triglycerides; M_{FE} : mass of fatty esters; MW_{TG} : molecular weight of oil; MW_{FE} : mean molecular weight of fatty esters.

It is important to mention that Eq. (1) is valid if decomposition of the vegetable oil or fatty esters is negligible. However, a detailed kinetic study of the transesterification reactions was out of the scope of the present work. The main goal was to analyze the ester content of the biodiesel phase to assure a minimum ester composition 96.5 wt.% to verify one of the specifications of the European norm EN 14214 for biodiesel quality.

2.4. Analytical method

Ester content of biodiesel samples was analyzed by gas chromatograph (GC – Varian Star 3400 CX). The equipment was assembled with a flame ionization detector (FID) and capillary column (J&W Scientific, model DBwax, 30 m length, 0.32 mm inner diameter, and 0.25 μm film thickness). The chromatographic conditions were selected according to BS EN 14103:2003. Hydrogen was used as the gas carrier at a flow rate of 1.5 ml/min and at a split flow rate of 76 ml/min. The injector and detector temperatures were 250 and 270 °C, respectively. The oven temperature program consisted of starting at 120 °C for 6 min, a ramp of 7 °C/min up to 210 °C, a ramp of 15 °C/min up to 250 °C, and finally maintaining 250 °C during 15 minutes. Methyl heptadecanoate was used as internal standard. A stock solution of heptane with a known amount of internal standard was prepared (5 mg/ml). A sample solution was also prepared in heptane (17 mg/ml). The sample injected into the chromatograph consisted of 2 μL of a solution prepared with 0.2 ml of the internal standard stock solution and 0.3 ml of the sample solu-

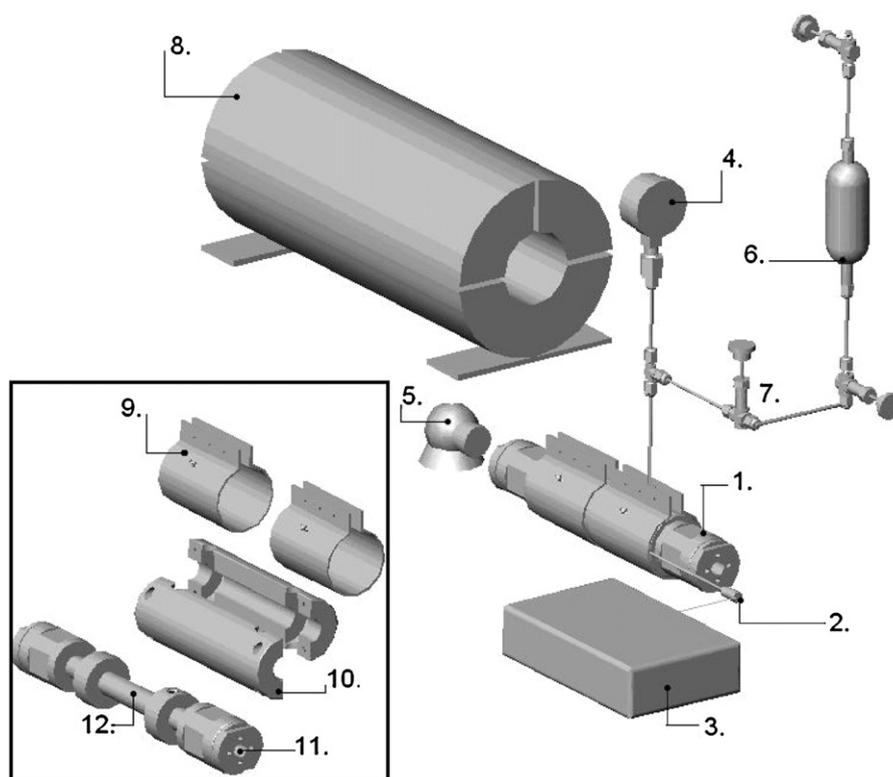


Fig. 1. Equipment used in this work to analyze the phase behavior and the efficiency of a high pressure biodiesel reaction. (1) Reaction cell, (2) temperature sensor, (3) temperature controller, (4) pressure sensor, (5) camera, (6) co-solvent reservoir, (7) valve, (8) fiber mat, (9) electric resistance, (10) aluminum jacket, (11) windows, and (12) stainless steel reactor.

tion (2 mg/ml of methyl heptadecanoate and 10 mg/ml of reaction products).

2.5. Statistical analysis

The analysis of ester production by transesterification of *R. sativus* L. oil using supercritical alcohols was carried out by a Doehlert design of experiments [8]. This experimental design is very useful and offers advantages in relation to other designs. Doehlert designs are easily applied in variable optimization and they require fewer experiments in relation to central composite and Box-Behnken designs [11–13].

Ethanol studies: A three variable Doehlert design was applied in supercritical ethanol studies. The ester contents in the biodiesel samples, $Y_{\text{ester}}\%$, were selected as the response variable. The variables or factors investigated were the reaction temperature, X_T , the reaction time, X_t , and the initial alcohol to oil molar ratio, X_M . The selection of levels for each variable was based on previous works [9,14–16] and on preliminary studies carried out in our laboratory. The lowest temperature value was set at 568 K and the highest was fixed at 598 K. The reaction time varied between 15 and 29 min, and the initial alcohol to oil molar ratio was studied in the 32:1 to 52:1 range for ethanol.

Methanol studies: A two variable Doehlert design was applied to study the transesterification reaction with supercritical methanol. Different authors [3,4,9,10,17,18] generally agree that high alcohol/oil ratios (40:1 methanol: vegetable oil) are required to obtain high conversions and high reaction rates. Based on this and on the previous results obtained with ethanol, the initial methanol/oil molar ratio of 39:1 was selected for these studies. The reaction temperature, X_T and the reaction time, X_t , were chosen for the independent input variables, and the methyl ester contents in the biodiesel samples, $Y_{\text{ester}}\%$, were used as the dependent output vari-

ables. The lowest temperature value was set at 533 K and the highest at 609 K. The reaction time varied between 5 and 27 min.

Once these levels were selected, the Doehlert design of experiments [8] was applied. The Doehlert matrix and the experimental conditions studied in this work are presented in Table 2 for ethanol and Table 3 for methanol. The first columns of data in Tables 2 and 3 show factor levels on a natural scale, and the next show the coded factor levels in the dimensionless co-ordinate. All the runs were performed at random. Three experiments were carried out at the central point level, coded as “0”, for experimental error estimation.

3. Results and discussion

3.1. Experimental phase behavior

The ester contents obtained in the experiments are presented in Tables 2 and 3. A single-phase system at the end of the reaction was observed. As an example, Fig. 2 shows images of a typical evolution of the phase behavior during the non-catalytic transesterification reaction with ethanol, at the reported operating conditions. Fig. 2A and B show that the system exhibits liquid–liquid–vapor (LLV) equilibria at ambient and moderate temperatures, respectively. Fig. 2D shows that at higher temperatures (such as 453 K) the liquid phases become completely miscible and liquid–vapor (LV) equilibria can be observed. However, the system changes to a single-phase supercritical condition (Fig. 2H) at temperatures over 573 K, and the pressure increase with temperature was moderate in all cases. Similar phase behavior results were obtained for methanol studies. However, higher pressures (reported in Table 3) at the final reaction temperatures were reached due to the higher vapor pressure of methanol.

The observed phase behavior is probably due to the reactor global density used in this work. According to Hegel et al. [9],

Table 2
Biodiesel production by transesterification of *R. sativus* L. oil in supercritical ethanol. Experimental conditions studied in this work. Doehlert matrix and experimental results.

Run no.	Real values			Coded values			Pressure (MPa)	Y_{ester} (%)
	T (K)	t (min)	RM	X_T	X_t	X_M		
1	598	22	42	1	0	0	14.0	93.1
2	590.5	29	42	0.5	0.866	0	12.5	95.5
3	590.5	24.3	52	0.5	0.289	0.8166	13.0	76.1
4	568	22	42	-1	0	0	9.0	91.7
5	575.5	15	42	-0.5	-0.866	0	10.5	72.3
6	575.5	19.7	32	-0.5	-0.289	-0.8166	10.0	91.4
7	590.5	15	42	0.5	-0.866	0	12.6	94.8
8	590.5	19.7	32	0.5	-0.289	-0.8166	12.0	92.3
9	575.5	29	42	-0.5	0.866	0	10.5	93.5
10	583	26.7	32	0	0.577	-0.8166	11.0	94.2
11	575.5	24.3	52	-0.5	0.289	0.8166	10.5	74.5
12	583	17.3	52	0	-0.577	0.8166	12.0	66.3
13	583	22	42	0	0	0	11.5	91.6
14	583	22	42	0	0	0	11.5	95.1
15	583	22	42	0	0	0	11.5	92.1

$X_T = (T - T_0)/(T_{\text{max}} - T_0)_B$, T : temperature, T_0 : central temperature, T_{max} : maximum temperature $X_t = (t - t_0)/(t_{\text{max}} - t_0)_B$, t : time, t_0 : central time, t_{max} : maximum time $X_M = (RM - RM_0)/(RM_{\text{max}} - RM_0)_B$, RM: molar ratio, RM_0 : central molar ratio, RM_{max} : maximum molar ratio B : maximum positive coded value.

the global density (ρ_g) defined as the total mass charged into the reactor divided by the reactor volume, is an important factor from a phase equilibrium engineering point of view. In the non-catalytic transesterification of soy oil with supercritical methanol, for example, a high global density ($\rho_g > 0.8 \text{ g/cm}^3$) produced a steep increase in pressure when the liquid phase completely filled the volume of the reactor. At smaller global densities ($\rho_g < 0.5 \text{ g/cm}^3$) the liquid-vapor (LV) equilibrium conditions prevailed up to 560 K. However, it was observed that high efficiencies were achieved at temperatures over 550 K and 10 min of reaction, even in the LV phase regions [9]. This result partially explains why different operating conditions of temperature and pressure have been proposed for non-catalytic supercritical transesterification reactions [3,4,10,17,18].

In this work, different global densities were tested to work at pressures between 10 and 15 MPa in ethanol experiments and in a range of 10–18 MPa in methanol studies. As it is shown in the next section, in this range of pressure at the selected reaction temperatures, a single phase can be obtained according to predictions of the phase behavior of the reaction products effectuated with

the Group Contribution and Association Equation of State, GCA-EOS.

To avoid phase immiscibility in the range of temperature studied, a load reactor global density of 0.55 g/cm^3 was selected in ethanol studies to obtain working pressures no higher than 15 MPa. On the other hand, a global density of 0.52 g/cm^3 was used in methanol experiments to obtain pressures lower than 19 MPa.

3.2. Modeling of the phase behavior and reaction thermal history

The GC-EOS equation was proposed by Skjold-Jørgensen [19]; the model is based on the generalized van der Waals partition function and the group contribution principle. Gros et al. [20] modified the equation by inclusion of a 'group' contribution associating term to the GC-EOS model (GCA-EOS). The application of a group contribution with association equation of state (GCA-EOS) to the supercritical processing of fatty oil derivatives with low molecular weight solvents has been extensively discussed by Ferreira et al. [21,22] and more recently by Andreatta et al. [23]. In previous works [9,24], experimental observations of the multiple phase

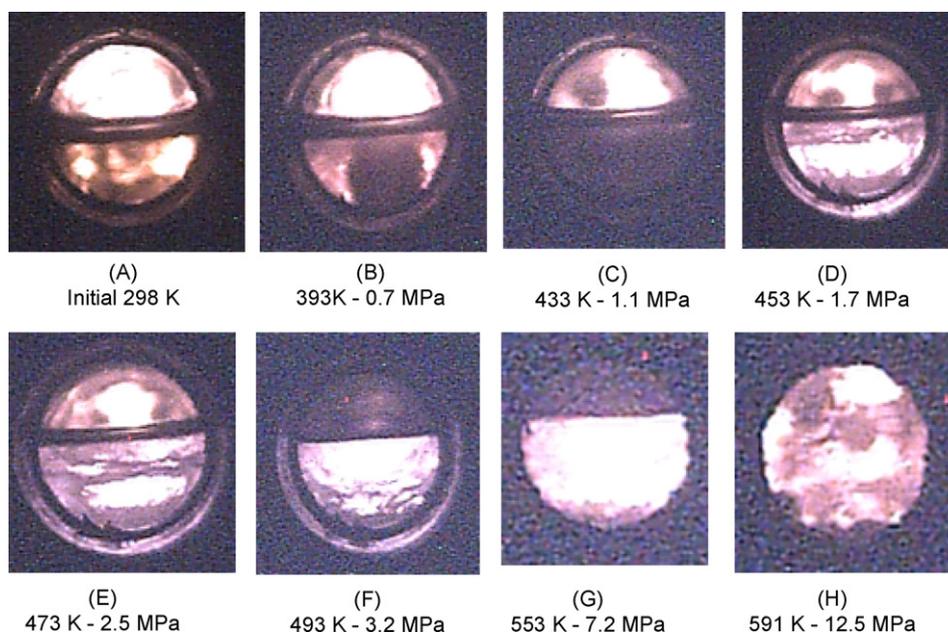


Fig. 2. Phase behavior evolution during the heating process of the reacting mixture in the supercritical ethanol transesterification of fodder radish oil. (A and B) Liquid-liquid-vapor equilibria. (C–G) Liquid-vapor equilibria. (H) Single phase.

Table 3

Biodiesel production by transesterification of *R. sativus* L. oil in supercritical methanol. Experimental conditions studied in this work (39:1 initial molar ratio of methanol/oil). Doehlert matrix and experimental results.

Run no.	Real values		Coded values		Pressure MPa	Y _{ester} (%) (w/w)
	T (K)	t (min)	X _T	X _t		
1	609	16	1	0	18.3	84.2
2	533	16	-1	0	10.0	18.0
3	590	27	0.5	0.866	14.1	99.8
4	552	27	-0.5	0.866	10.7	62.8
5	590	5	0.5	-0.866	15.5	33.7
6	552	5	-0.5	-0.866	11.7	20.7
7	571	16	0	0	13.5	49.1
8	571	16	0	0	14.0	43.0
9	571	16	0	0	13.5	45.0

$X_T = (T - T_0)/(T_{max} - T_0)_B$, T: temperature, T_0 : central temperature, T_{max} : maximum temperature. $X_t = (t - t_0)/(t_{max} - t_0)_B$, t: time, t_0 : central time, t_{max} : maximum time, B: maximum positive coded value.

behavior between the reactants and products of the transesterification of vegetable oils (triacylglycerols, fatty esters, methanol and glycerin) were compared with modeling predictions using GCA-EOS. The observed phase envelope predictions were in agreement with experimental trajectories of the reactive system. Andreatta et al. [25] measured LL and LLV equilibria data for the system methyl oleate–methanol–glycerin, and used GCA-EOS to represent these experimental data.

As an example, Fig. 3 shows the phase behavior of the system methyl laurate and methanol predicted by the GCA-EOS compared with equilibrium data for this system recently reported by Shimoyama et al. [26]. The observed predictions of the GCA-EOS agree well with the experimental results.

In another example, Fig. 4 shows the phase transitions reported by Hegel et al. [9,27] for the biodiesel reaction of soybean oil with supercritical methanol in the presence of propane as cosolvent. In this special case, the presence of propane in the reaction system (in a concentration of 10 wt.%) decreased the critical temperature. Fig. 4 also shows the phase envelope prediction of the GCA-EOS that encloses the liquid–vapor zone for the initial reactive mixture (soy oil + methanol + propane) and the final products (esters + methanol + glycerol + propane). Predictions of the GCA-EOS are in agreement with the experimental observations in the liquid–vapor state at low temperature and pressure (430 K and 5 MPa) up to the supercritical state at a temperature of 520 K and pressures greater than 10 MPa. Hence, the GCA-EOS model can be applied to explore the operating conditions in the reactor.

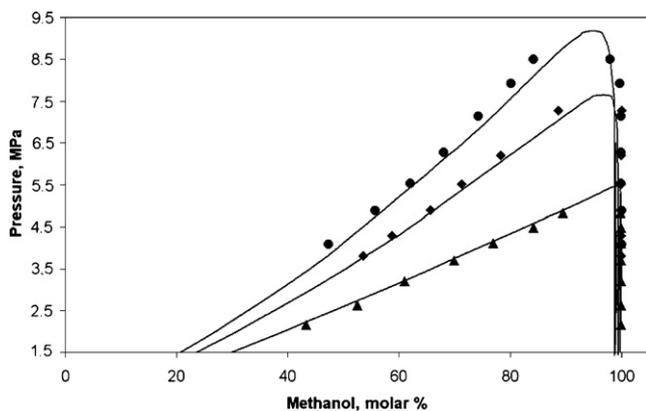


Fig. 3. Phase equilibrium analysis. Prediction capability of the GCA-EOS. Phase equilibria of methyl laurate in methanol. Pressure vs. molar concentration of methanol. The continuous line represents the GCA-EOS predictions, while the symbols denote the experimental data reported by Shimoyama et al. [26]: (▲) 493 K, (◆) 523 K, (●) 543 K.

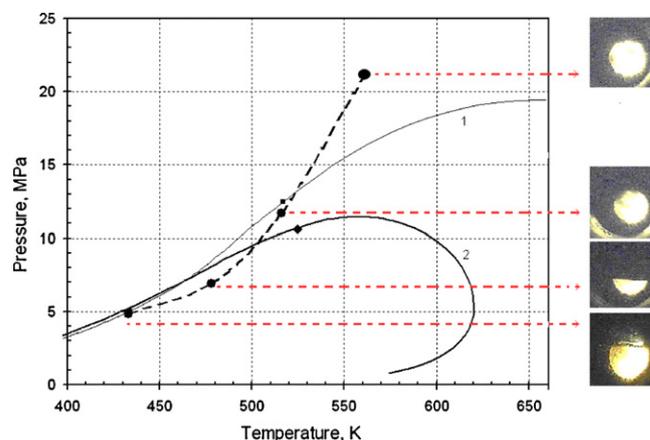


Fig. 4. Biodiesel production by transesterification of soy oil in supercritical methanol. (Lines): 1—phase envelope of the triacylglycerols + methanol + propane (cosolvent). 2—phase envelope of the esters + methanol + glycerol + propane (cosolvent) predicted by GCA-EOS. (Symbols ●): Experimental observations reported by Hegel et al. [8,27].

The critical properties for the esters used in this work were predicted by a group contribution method [28]. The critical properties for the alcohols are those available in the site of NIST [29]. The GCA-EOS group energy and interaction parameters for non-associating groups are those of Espinosa [30,31]. For self-associating groups or groups with cross-association the parameters reported by Ferreira et al. [22] and Gros et al. [20] are used. The alcohol, glycerin and esters interaction specific parameters are those of Andreatta et al. [25].

Ethanol studies: Fig. 5 gives the predicted phase envelopes and critical points of the system composed by ethyl eicosanoate + glycerin + ethanol (3:1:39 molar ratio). Here, the ethyl eicosanoate represents the fatty acid ethyl esters produced by the transesterification according to the fatty acid composition of the vegetable oil (Table 1) and the calculation proposed by

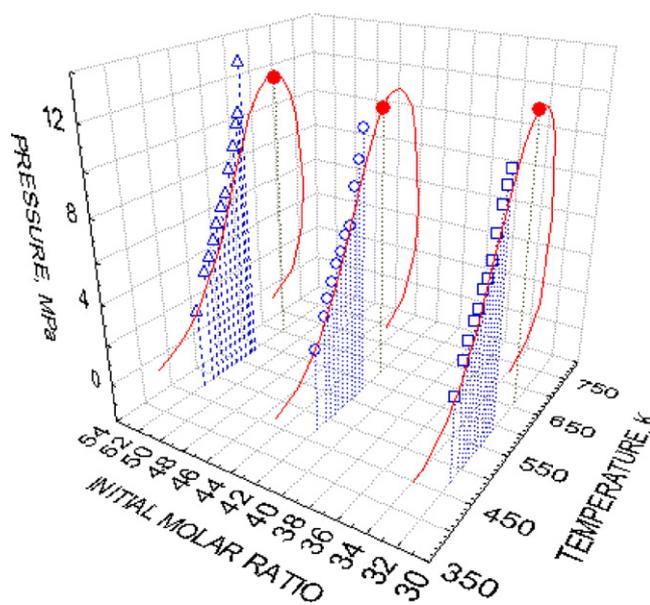


Fig. 5. Biodiesel production from fodder radish oil and supercritical ethanol. Phase equilibrium analysis of the transesterification of *R. sativus* L. oil using supercritical ethanol. Experimental reaction trajectory on a pressure–temperature (PT) diagram for a reactive mixture with 32:1 (□), 42:1 (○) and 52:1 (△) initial EtOH:oil molar ratio, respectively. The solid line (—) represents the GCA-EOS prediction for the liquid–vapor phase envelope for the products of the reaction (ethanol + ethyl esters + glycerin). Critical points predicted by GCA-EOS (○).

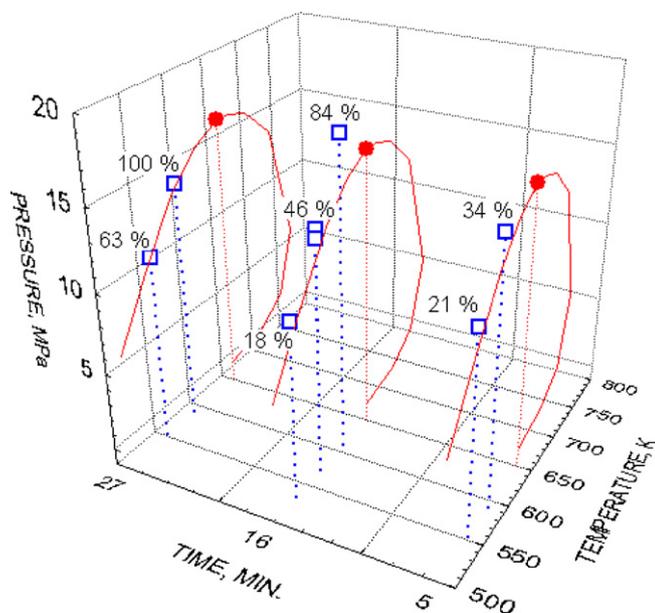


Fig. 6. Biodiesel production from fodder radish oil and supercritical methanol (initial molar ratio of 1:39). Phase equilibria analysis of the experimental reactions. (Lines) Phase envelope of the reaction products assuming a complete conversion of the vegetable oil (esters + glycerol + methanol), GCA-EOS predictions (–). (Symbols) Critical point of the reaction mixture estimated by GCA-EOS (○) Experimental reaction conditions reported in Table 3 and the corresponding ester content analyzed (□).

Espinosa et al. [30]. Phase envelopes and the critical points were predicted based on the GCA-EOS model. Here, it can be seen the two phase liquid-vapor region and the homogeneous regions (liquid, vapor and supercritical) for the reaction products. The GCA-EOS predicts a liquid phase at pressures higher than 11 MPa in a range of temperature of 568–598 K. However, an appropriate global density of the reaction mixture has to be selected to obtain a single phase at the lower pressure.

Fig. 5 also shows the thermal history of three experimental runs for the different initial ethanol to oil molar ratios (32:1, 42:1 and 52:1) studied in supercritical ethanol transesterification for a global density of 0.55 g/cm³. The figure reveals that the predictions agree with the experimental observations of the phase conditions at the final reaction temperature. In fact, a liquid single-phase condition is predicted at the end of the reaction, when almost all the vegetable oil has been converted into fatty ethyl esters, and a near supercritical state can be observed.

Methanol studies: Fig. 6 shows the predicted GCA-EOS phase envelope of the reaction products assuming a complete conversion of the fodder radish oil initially present in a molar ratio of 1:39 with methanol (methyl eicosanoate + glycerol + methanol = 3:1:36). The final operating conditions studied in this work and previously detailed in Table 3, can also be observed. According to the GCA-EOS predictions and the experimental observations, in the range of temperature studied, a global density of 0.52 g/cm³ is adequate to guarantee moderate pressures and a single phase of the reaction products. However, at these conditions the transesterification is carried out in a condensed liquid phase and according to the GCA-EOS prediction, it is necessary to increase the temperature over 650 K to have a supercritical phase.

Fig. 6 also reveals that the operating conditions at temperatures of 533 and 552 K are near the saturated liquid phase from the reaction products point of view. However, the ester content analyzed remains low and an immiscibility region (liquid–supercritical fluid) is observed due to the presence of components of higher molecular weight like diglycerides and triacylglycerols. It has been observed

Table 4

Biodiesel production from fodder radish oil and supercritical ethanol. Three variables Doehlert design. Coefficients of the lineal regression quadratic model and their respective uncertainty and *P*-value associated.

Coefficients	Uncertainty	<i>P</i> -value
b_0	92.943 ± 1.114	0.00014
b_{XT}	3.729 ± 0.965	0.06092
b_{Xt}	6.369 ± 0.965	0.02220
b_{XM}	-12.465 ± 0.964	0.00593
b_{XT^2}	-0.553 ± 1.762	0.78320
b_{Xt^2}	-5.040 ± 1.762	0.10356
b_{XM^2}	-14.333 ± 1.669	0.01330
$b_{XT \cdot Xt}$	-11.801 ± 2.229	0.03386
$b_{XT \cdot XM}$	4.572 ± 2.490	0.20777
$b_{Xt \cdot XM}$	3.115 ± 2.490	0.33745
Significance level α :		0.065

that an increment in the reaction time from 5 to 27 min produces an increase in the ester content from 21% to 63% at a temperature of 552 K. On the other hand, the same increment in the reaction time at 590 K produces a complete conversion of the vegetable oil into esters.

3.3. Model fitting of fodder radish oil transesterification with supercritical alcohols and analysis of response

The multivariable analysis of data is a powerful statistical technique used for studying the effect of several factors and their interactions over one or more response variables in a process [11–13]. Response surface methodology has also been used for biodiesel production optimization [5,18,32].

Ethanol studies: Response surface methodology was performed on experimental data. A lineal regression quadratic model was obtained as shown in Eq. (2) for the ester content in the transesterification with supercritical ethanol as a function of the three coded variables:

$$Y_{\text{ester}\%} = 92.943 + 3.729X_T + 6.369X_t - 12.465X_M - 14.333X_M^2 - 11.801X_TX_t \quad (2)$$

$Y_{\text{ester}\%}$: ester content %; X_T : coded variable for temperature; X_t : coded variable for time; X_M : coded variable for methanol:oil initial molar ratio.

The uncertainty and *P*-value associated with each coefficient of this model can be seen in Table 4. The *P*-value criterion was used to conclude if a given factor is significant in the experimental range studied. Every time the *P*-value is lower than the uncertainty level, α for the test, the statistical hypothesis is considered significant [11,13].

According to its *P*-values, the regression model obtained for the transesterification of fodder radish oil with supercritical ethanol demonstrates a good adjustment with experimental data and is also statistically significant for an uncertainty level, α , for the test lower than 0.065. The coefficient of determination R^2 approaches one (0.92) indicating that the regression model has a good predictive capacity.

Fig. 7 plots experimental versus correlated values for biodiesel production from *R. sativus* L. oil using ethanol. The figure reveals that there are no tendencies in the regression fit; hence the model explains the experimental range studied adequately.

According to the *P*-values in Table 4, from the statistical analysis, and in the experimental range studied, the EtOH:oil molar ratio is the most important factor on the transesterification of the *R. sativus* L. oil with a negative effect (b_{XM} : -12.465). In addition the *P*-value (0.00593) is lower than $\alpha = 0.065$, showing that the effect ethanol to oil molar ratio in the reaction is significantly greater than its uncertainty.

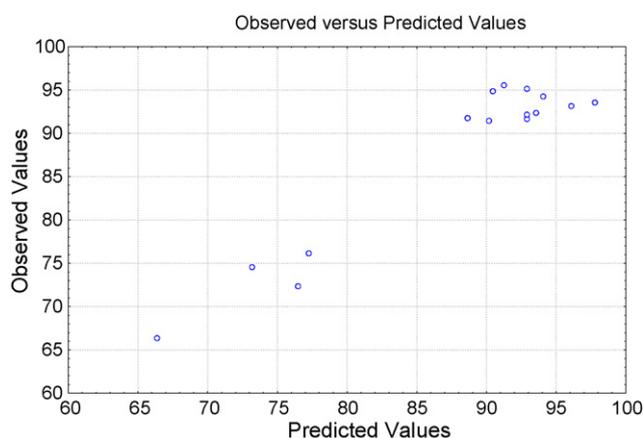


Fig. 7. Straight line of adjust of the quadratic regression model obtained from the three variable Doehlert design for the biodiesel production from fodder radish oil in supercritical ethanol. Observed values (Table 2) vs. predicted values (Eq. (1)).

Silva et al. [15] studied the transesterification of soybean oil at 598 K with supercritical ethanol and different molar ratios of ethanol to oil from 10:1 to 100:1 in continuous mode. The authors observed higher reaction conversions on varying this process variable from 10:1 to 40:1, however, no significant effects were observed for molar ratios of ethanol to oil between 40:1 and 100:1. Similar results were obtained by Varma and Madras [16] for the transesterification of castor oil and linseed oil with supercritical ethanol. In the transesterification of fodder radish oil with supercritical ethanol an increment of the alcohol to oil molar ratio from 32:1 to 42:1 also increased the level of ester content in the reaction products. However, an ethanol to oil molar ratio of 52:1 produced ester contents significantly lower in the range of temperatures and reaction times studied in this work. The negative coefficient for the molar ratio of ethanol to oil (b_{XM} : -12.465) is pointing this effect in the regression model.

Fig. 8 shows the response surface for ester contents (Esters %) in biodiesel samples for an ethanol/oil molar ratio of 42:1, as well as the experimental data obtained for this molar ratio (Table 2).

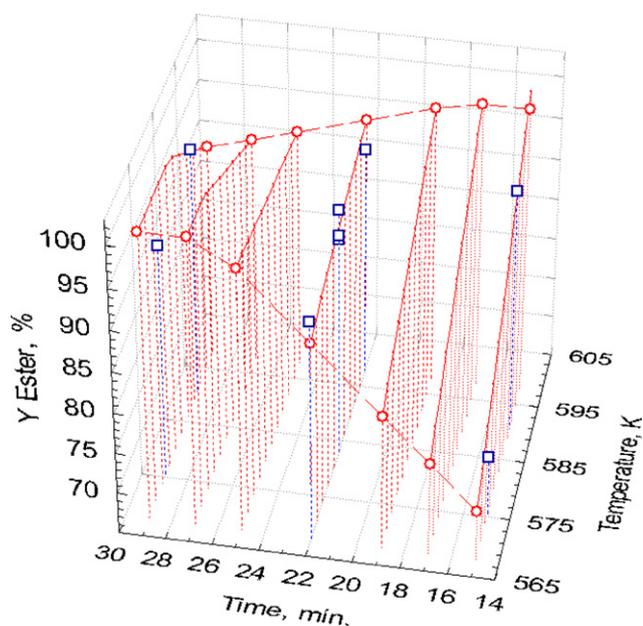


Fig. 8. Biodiesel production from *R. sativus* L. oil in supercritical ethanol. Response surface of ester% vs. time and temperature. EtOH:oil molar ratio 42:1. (□)%, Esters obtained experimentally (Table 2).

Table 5

Values for testing the best conditions of maximum biodiesel production from fodder radish oil in supercritical ethanol.

Parameters	Optimum value
Esters (%)	97.5%
Global density of load (g/cm ³)	0.55
Temperature (K)	592
Ethanol:oil molar ratio	39
Time (min)	22

It shows a good correlation with the model. Fig. 8 helps to identify how the interactions between temperature and reaction time influence the reaction.

Time and temperature of the reaction both had a positive effect in the final content of esters (b_{XT} : 6.369, b_{XT} : 3.729) and they are statistically significantly with P -values lower than $\alpha = 0.065$ of significance level. The maximum ester % is achieved at the maximum temperature level. Also the maximum ester % is obtained at the maximum level for reaction time. This result is in agreement with previous results obtained by other authors for the transesterification of soybean oil [15] and linseed oil [16] with supercritical ethanol.

On the other hand, the interaction between time and temperature according to the model has a negative effect ($b_{XT,XT}$: $-11,801$, P -value: 0,03386). For example for an ethanol to oil molar ratio of 42 (Fig. 8), there is an expected increase in ester % as temperature increases for reaction times between 15 and 25 min. For reaction times over 25 min, the model predicts a decrease in esters % with an increase in temperature. A decomposition of the esters because of high temperatures and reaction time could explain this result [14,33]. Vieitez et al. [14] studied the production of soybean biodiesel with supercritical ethanol in a 42 mL continuous reactor at 623 K observing an ethyl esters decomposition of more than 25% by weight fraction at the lower flow rate (0.8 mL/min) and almost 10% by weight fraction at the highest flow rate (2.5 mL/min). The results obtained in this work are in agreement with these observations and the model is predicting a decreasing amount of fatty ethyl esters at the highest temperature with increasing the exposure time. This result could explain partially the negative influence observed for the molar ratio of ethanol to oil because thermal decomposition of fatty esters could be more important for higher ethanol concentrations.

The quadratic interactions between time/molar ratio ($b_{XL,XM}$) and temperature/molar ratio ($b_{XT,XM}$) both had a positive effect; however, they are not significant according to the P -values (Table 4) and therefore their effects in the model are not statistically greater than the uncertainties associated with its determination. The terms representing the quadratic influence of temperature (b_{XT^2}) and time (b_{XT^2}) are also not significant in the model with P -values much greater than $\alpha = 0.065$ significance level.

The term representing the quadratic influence of the ethanol to oil molar ratio is very negative (b_{XM^2} : $-14,333$) and the P -value is 0.0133. This negative influence in the model suggests that there is a specific value for maximum response. Solving the homogeneous differential equation system (created by partial derivatives of Eq. (1)) it was obtained an optimal ethanol to oil molar ratio equal to 39:1 (Table 5).

To check the model adequacy for predicting the maximum ester %, one additional experiment was carried out under the optimal conditions described in Table 5. Three replicate gas chromatography analyses indicated average contents of ethyl esters of 97.5%. The good agreement between the predicted and experimental results confirmed the validity of the model. The response surface obtained with the model at the optimum molar ratio (ethanol/oil: 39:1) shows a similar behavior to the one reported in Fig. 8.

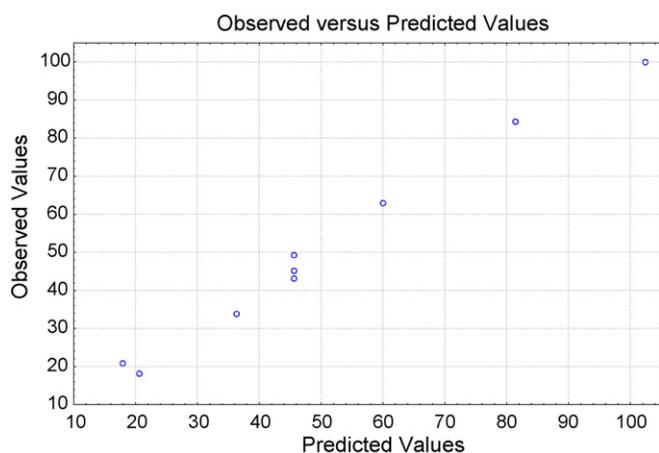


Fig. 9. Straight line of adjusts of the quadratic regression model obtained from the two variable Doehlert design for the biodiesel production from fodder radish oil in supercritical methanol. Observed values (Table 3) vs. predicted values (Eq. (2)).

Methanol studies: Response surface methodology was also performed on experimental data obtained with supercritical methanol. Eq. (3) shows the lineal regression quadratic model, based on the coded values of the variables. As it was explained in the previous section, in these experiments the molar ratio of methanol to oil was fixed in 39:1 and two variables, time and temperature of the reaction were studied.

$$Y_{\text{ester}\%} = 45.7 + 30.4X_T + 31.236X_t + 13.857X_TX_t \quad (3)$$

X_T : coded variable for temperature; X_t : coded variable for time; $Y_{\text{ester}\%}$: concentration of ester obtained by gas chromatograph.

The good fit of the model and the high significance of the statistic test (low P -value of the hypothesis test) lead to a high explicated variance (99.16%) of the experimental data.

Fig. 9 shows that there is not a particular tendency in the distribution of residues between the estimated values and the experimental ones, which is important from a statistical point of view.

The response surface for ester content (Esters %) in biodiesel samples is shown in Fig. 10, as well as the experimental data reported in Table 3. This figure helps to identify the how the interactions between the variables influence the reaction, within the range studied. The model based on the ester content shows in this case a barely quadratic response surface. It is like a plane with a marked slope toward the high values of the variables (temperature and reaction time). Thereafter, there is not a point of maximum inside the experimental domain of study. However, the results are satisfactory because these are showing a region of maximum yield. Table 7 shows the values of temperature and time to reach a complete transesterification of the fodder radish oil to esters in supercritical methanol when the initial molar ratio of alcohol to oil is 39:1.

The studies of transesterification of fodder radish oil with supercritical methanol showed similar results to the ones obtained for supercritical ethanol. Both alcohols showed similar reactivity at a temperature of 590 K and ester contents of 95–100% were obtained after 27–29 min of reaction time.

Table 6 shows that both variables (temperature and time) are important in the model with a positive effect in the final content of esters (b_{XT} : 30.4, b_{Xt} : 31.236) and they are statistically significantly with P -values lower than $\alpha = 0.055$ of significance level, in agreement with results obtained by others authors [3,4,9,10,17,18] for transesterification of vegetable oils with supercritical methanol.

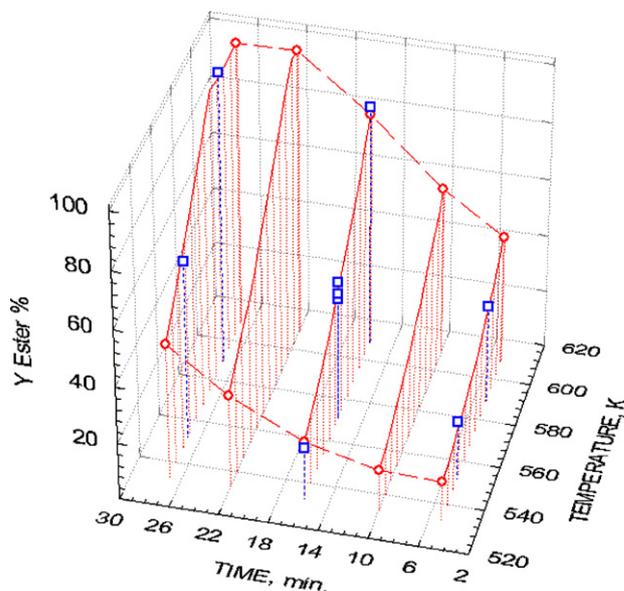


Fig. 10. Biodiesel production from *R. sativus* L. oil in supercritical methanol. Initial MeOH:oil molar ratio 39:1. Doehlert experimental design. Response surface of ester content vs. time and temperature. Experimental points (□) reported in Table 3.

The interaction between the two variables ($b_{XT,Xt}$: 13.857) is also positive and significant in the model, in contrast with the coefficient obtained in the model for the transesterification with supercritical ethanol. This suggests that the best values of ester content are obtained by combining the higher values of both variables (temperature and time) in the experimental range studied.

Imahara et al. [33] studied the thermal stability of biodiesel in supercritical methanol observing that methyl oleate is stable at 543 K, however, it becomes unstable at 573 K and there is a clear decomposition of unsaturated esters with exposure time at temperatures higher than 623 K. Fodder radish oil has a significant composition of C18:1, C20:1 and C22:1 (Table 1), indicating that it could be possible a degradation with temperature and time. This effect was not observed in the interactions between time and temperature studied in this work for the transesterification of fodder radish oil with supercritical methanol. Since the quadratic coefficients of the variables are positive there is no maximum in the range of variability for the experiments with supercritical methanol studied in this work. To find a maximum point it would be necessary to displace the experimental domain of the reaction time and temperature to higher values. In this way higher temperatures could have a negative effect in the methyl esters synthesis result [33].

The results obtained in this work for the transesterification of fodder radish oil with supercritical alcohols are indicating that fatty acid ethyl esters are less stable with temperature than fatty acid methyl esters.

As in the study of transesterification of fodder radish oil with supercritical ethanol, the terms representing the quadratic influ-

Table 6

Biodiesel production from fodder radish oil and supercritical methanol. Two variables Doehlert design. Coefficients of the lineal regression quadratic model and their respective uncertainty and P -value associated.

Coefficients	Uncertainty	P -value
b_0	45.7 ± 1.761	0.0015
b_{XT}	30.733 ± 1.761	0.0033
b_{Xt}	31.813 ± 1.761	0.0031
b_{XT^2}	5.4 ± 2.784	0.2104
b_{Xt^2}	10.267 ± 2.785	0.0704
$b_{XT,Xt}$	15.012 ± 3.522	0.0509
Significance level α :		0.050

Table 7

Values for testing the best conditions of maximum biodiesel production from fodder radish oil in supercritical methanol.

Parameters	Optimum value
Esters (%)	97.0%
Global density of load (g/cm ³)	0.52
Temperature (K)	590
Methanol:oil molar ratio	39
Time (min)	27

ence of temperature (b_{XT2}) and time (b_{Xt2}) in the methyl ester content were not significant with P -value much greater than the $\alpha = 0.055$ significance level. The results are suggesting that in experimental range studied both, temperature and time, have a linear influence in the transesterification reaction with supercritical alcohols.

The results derived from this study indicated that the Doehlert design is a powerful tool for optimizing the conditions for biodiesel production in supercritical alcohols.

4. Conclusions

In the present work, a phase equilibrium engineering analysis, using the GCA-EOS model, was performed to explore the operating conditions in the reactor. Global densities of reactants in the cell of 0.55 g/cm³ and 0.52 g/cm³ were chosen for ethanol and methanol studies, respectively. In this way it was possible to reach a single-phase system at moderate pressures over the range of reaction temperatures studied. High ester contents in the reaction products were obtained.

A Doehlert design has proven to be effective in the study and optimization of the variables affecting the supercritical ethanol and methanol transesterification process. For both alcohols studied lineal regression quadratic models were obtained to predict the ester content as a function of the variables. Analysis of the residues showed that the models predicted adequately the ester% over the experimental range considered.

Optimal operating conditions (initial molar ratio of 39:1, a reaction temperature of 592 K and 22 min of reaction time) were selected from the lineal regression quadratic model derived from the three-variable Doehlert design applied to ethanol studies.

Based on ethanol studies and other previous works, an initial molar ratio of 39:1 alcohol/oil was used in the methanol studies. A two variable Doehlert design was used to find the optimum conditions. Similar results to those of supercritical ethanol transesterification were obtained.

The non-catalytic transesterification of fodder radish oil with supercritical alcohols can be performed with molar ratios of alcohols to oil in the range of 30:1 to 40:1 and temperatures of 583–590 K.

A homogenous phase with the advance of the reaction can be obtained at pressures of 11 and 14 MPa, for supercritical ethanol and methanol, respectively, depending on the global density of the initial reactants used in the batch reaction process.

Reaction times higher than 20 min are required to obtain high ester contents (greater than 96% by weigh fraction) even when the reaction takes place in homogeneous phase conditions. Present results are important regarding the continuous process because in this case the residence time is directly related to the global density of the reaction mixture.

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