

BIODIESEL PRODUCTION USING SUPERCRITICAL ALCOHOLS IN BATCH AND CONTINUOUS REACTORS

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Abstract. Recent experimental studies on non-catalytic transesterification have shown that high reaction rates, which justify the commercial application of this process, can be obtained if the operating conditions are above the critical pressure and temperature of the alcohol. Even though it is generally agreed that temperatures above 550 K and high alcohol/oil ratios are required to obtain high conversions and high reaction rates, there is disagreement among the different authors regarding the operating pressure, the assumed phase conditions, the use of co-solvents and the justification of the sudden increase of the rate of reaction with temperature. In the present work, the reactor phase transitions are directly observed in a double windowed cylindrical reactor and the conversion to ethyl esters is measured. Also studies on a continuous reactor are carried out to obtain a better control of operating conditions and reactants residence time. In these studies different oils, crude and refined, are studied. Also the effect of using methanol or ethanol on the rate of reaction and efficiency of conversion are considered. 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 reactants residence time, temperature, pressure and molar ratio of ethanol/oil. The present results confirm preliminary studies that indicate that high conversions can be obtained at pressures of 10-15 Mpa at temperatures between 570 and 600 K using a molar ratio of 39. From direct observations and the modeling of the phase behavior, a better understanding of the supercritical ethanol transesterification process is obtained as well as the confirmation of the phase equilibrium predictions based on the GCA-EOS model.

Keywords: Biodiesel, supercritical methanol, continuous reactor

1. Introduction

Nowadays biofuels play an important role due to the increasing worldwide energy problems. The production of methyl and ethyl esters is of great industrial interest because of their direct use as biodiesel. Most of the biodiesel currently produced uses soybean oil, methanol and an alkaline catalyst. The main products of the reaction are fatty esters and glycerin. The high value of soybean oil as a food product makes production of a cost-effective fuel very challenging. 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. The conventional alkaline process and acid catalyst process are very sensitive to these components in vegetable oil. Most industries use pre-treatment steps to reduce the free fatty acids and water contents that hinder the efficient use of waste cooking oils, animal fats and crude oils as feedstock for biodiesel production. Besides, when acid or basic catalysts are used at moderate temperatures the reaction is slow and, in general, the removal of the catalyst and saponification products from the fatty esters + glycerin mixtures turns biodiesel and glycerin purification difficult. The transesterification of vegetable oils using supercritical alcohols is an alternative for biodiesel industrial production. The pioneering experimental studies of non-catalytic transesterification by Saka and Kusdiana (2001) 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.

1.1. Phase equilibrium engineering of non-catalytic supercritical transesterification

In a previous work (Hegel et al., 2007) it was determined how the phase condition, homogeneous or heterogeneous, influences the kinetics and efficiency of the reaction of transesterification using supercritical methanol. The evolution of the phase behavior with temperature, during the non-catalytic transesterification reaction, with and without propane as a co-solvent, was observed in a see-through, two window cylindrical reactor, at controlled reaction cell global densities and initial methanol / soybean oil composition. Cell global density (ρ_g = defined as the total mass charged into the reactor divided by the reactor volume) was an important factor from a phase equilibrium engineering point of view. 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 ($\rho_g < 0.55 \text{ g/cm}^3$) the liquid-vapor (LV) equilibrium conditions prevailed up to 563K. However, it was observed that high efficiencies were achieved at temperatures over 550K and 10 minutes of reaction, even in the LV phase regions [3]. This result partially explains why different operating conditions have been proposed for non – catalytic supercritical transesterification reactions.

Saka and Kusdiana (2001) used a small 5 cm^3 batch reactor, charged with rapeseed oil and methanol. Therefore, high global densities were used by the authors to study the reaction at around 620 K, resulting in very high pressures ($\approx 45 \text{ MPa}$). Under these rather extreme conditions the conversion of oil to biodiesel was completed in approximately 5 minutes.

Recently Cao et al. (2005) proposed the use of propane as a co-solvent to reduce the critical point of the system and facilitate the operation in a single-phase supercritical condition. Their results indicate that it is possible to operate at milder conditions, keeping a high reaction rate, using a propane to methanol molar ratio in the range of 0.05 to 0.1, and working at 540 K and pressures around 12 MPa. The conditions proposed by these authors are quite different from those of Saka and Kusdiana (2001) and Kusdiana and Saka (2004). Hegel et al. (2007) observed in their experiments that the increase of propane concentration drastically reduces the critical temperature of the system, leading to a single supercritical phase at lower temperatures. According to them, the low pressures obtained by Cao et al. (2005) are probably also due to the use of lower cell global densities than Saka and Kusdiana (2001).

In the present work, a phase equilibrium engineering analysis, from direct observations and modeling of the phase behavior is applied to the transesterification of *Raphanus sativus L.*

oil (a non-edible vegetable oil) in supercritical ethanol, in order to find feasible homogeneous operating conditions at moderate pressures. Then, the different variables affecting the non-catalytic transesterification reaction are evaluated to set the best operating conditions. The optimum values of the variables in the experimental range studied are determined by applying a three variable Doehlert design of experiments and response surface methodology. Different vegetable oils (crude sunflower oil and commercial soybean oil) are also tested. The optimum operating conditions are being implemented in a continuous reactor.

2. Experimental

Raphanus sativus L. oil extracted by cold press, commercial soybean oil, and crude sunflower oil were used as vegetable oils. Ethanol (99.5%), methanol (99.7%) and heptane (99.%) were purchased from Anedra. Methyl heptadecanoate (> 99%) was purchased from Sigma-Aldrich.

Supercritical biodiesel reactions were carried out in batch and continuous mode. A stainless steel tubular reaction cell of 32 cm³ (15 cm of internal diameter) was used to carry out the transesterification of crude *Raphanus sativus L.* oil in supercritical ethanol in batch mode to determine the phase behavior of the reaction. Figure 1 shows a schematic diagram of the experimental equipment. Basically, it has two adapted 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 450W connected to a temperature controller (Novus N480D) were used to heat the reaction cell. It also has an external aluminum jacket to obtain a more uniform reactor heating process. A PT-100 platinum resistance thermometer placed in the external aluminum jacketed measures the temperature with an error of ± 2 K. The pressure inside the reaction cell is measured by a gauge pressure for high temperature (Dynisco PG4 series). The entire system is isolated by a fiberglass mat to reduce the loss of energy and allow a better temperature control. The reactor has also a feed line to load a given amount of co-solvent.

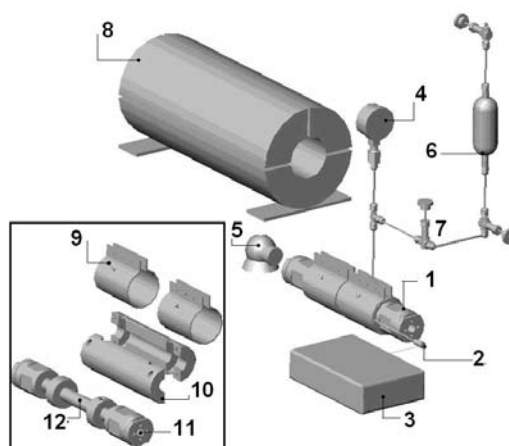


Figure 1 Equipment used in this work to analyze the phase behavior and the efficiency of a high pressure biodiesel reaction. 1. Reaction cell. 2. Temperature sensor. 3. Temperature controller. 4. Pressure sensor. 5. Camera. 6. Co-solvent reservoir. 7. Valve. 8. Fiber mat. 9. Electric resistance. 10. Aluminum jacket. 11. Windows. 12. Stainless steel reactor.

The best conditions obtained in batch mode were tested in a continuous reactor. Figure 2 shows a schematic diagram. As it can be seen the reaction system basically consists of a feed cylinder where the reactants are loaded, a membrane compressor that pumps the reactants up to the desired pressure, a recycle line that was assembled to control the reactants flow rate, The coiled reactor ofdiameter and length(dimensions) is placed in an electric oven at the desired reaction temperature. The stainless steel tubular reactor has 185.64 ml internal volume (4.5 mm inside diameter), and cooling system and a back pressure regulator valve at the outlet. The temperature of the mixture is sensed by two PT-100 temperature sensors directly connected at the inlet and outlet of the reactor and the pressure is measured by a pressure gauge for high temperature at the reactor inlet.

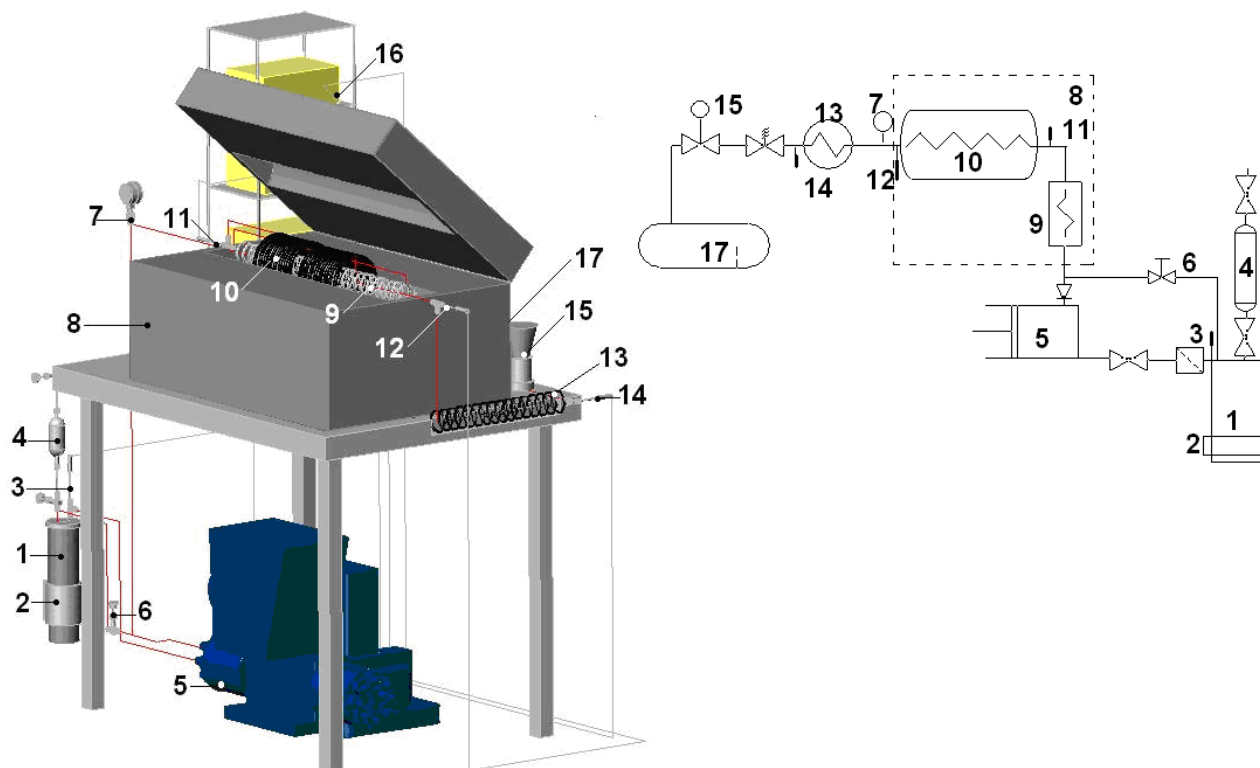


Figure 2 Continuous Transesterification reactor by supercritical alcohol 1. Suction tank. 2. Heating device. 3. Temperature sensor (PT-100). 4. CO₂ purges system. 5. Membrane compressor. 6. Needle valve. 7. Pressure gauge. 8. Oven. 9. Heating coil system. 10. Tubular reactor. 11. Temperature sensor (PT-100). 12. Temperature sensor (PT-100). 13. Cooling system. 14. Temperature sensor (PT-100). 15. Back pressure regulator. 16. Temperature Control system. 17. Discharge recipient.

2.1. Experimental Procedure

The experimental procedure of the batch mode experiences is as follows. The reactor was charged with a given amount of oil and liquid alcohol. Different molar ratios of the reagents were studied. The residual air was evacuated from the reaction cell by flushing low pressurized nitrogen gas. After the charge of reagents the entire system was assembled, and the temperature was raised up to the desired value as follows. At the beginning, the temperature

controller was adjusted to give a heating rate of 15 K/min up to 493 K. Then, the system was let at 493 K for six minutes 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 minutes. The phase behavior of the system at different temperature and pressure conditions was recorded by a video camera. When the reaction finished, the temperature controller was turned off and the reactor was air-cooled to quench the reaction.

In the continuous reactor the mixture of ethanol and oil were loaded to the feed cylinder. The reactive mixture was heated at 120°C to avoid liquid partial miscibility. The membrane compressor pumped the reactants up to the desired pressure set by the back pressure regulator at the reactor outlet. A recycle line was assembled to control the reactants flow rate, which is measured volumetrically at the reactor outlet. Then the reactive mixture flow through the reactor after which was cooled at ambient temperature before being expanded at atmospheric pressure and stored for analysis. Three samples were periodically collected in a glass recipient placed at the reactor outlet after the steady state conditions was reached. After the reaction the entire system was cleaned and purged with CO₂.

2.2. Analytical method

The amount of alcohol present in the products of the reactions was separated in a vacuum oven at 70 °C and 25 mmHg. Without the presence of methanol or ethanol, the biodiesel and glycerin become practically immiscible and can be easily recovered. The biodiesel samples were analyzed by gas chromatograph (GC – Varian Star 3400 CX) to determine their ester contents. 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 selected chromatograph 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 °C and 270 °C, respectively. The oven temperature program consisted of starting at and maintaining 120 °C for six minutes, 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 to 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 solution (2mg/ml of methyl heptadecanoate and 10mg/ml of reaction products).

2.3. Statistical analysis

The synthesis of ethyl esters by transesterification of *Raphanus sativus L.* oil using supercritical ethanol was carried out by a Doehlert design of experiments (Doehlert, 1970). This experimental design is very useful and offers advantages in relation to other designs. Doehlert designs are easily applied to optimize variables and they need fewer experiments in relation to central composite and Box-Behnken designs (Ferreira et al., 2004).

The response selected was the ethyl esters contents in the biodiesel samples, $Y_{\text{ester}}\%$. The variables or factors investigated were the reaction temperature, X_T , reaction time, X_t , and

the initial alcohol to oil molar ratio, X_M . They were selected on the basis of a preliminary factorial design. The reagent to reactor volume ratio was fixed at 75%, in order to reach a global density of load of approximately 0.61 g/cm^3 and working pressures no higher than 18 MPa. Under these operating conditions, the pressures varied from 9,5 to 15 MPa.

The selection of levels for each variable was carried out on the basis of a previous work [3] and results obtained in preliminary studies in our lab. The lowest temperature value was set at 568 K and the highest was chosen as 598 K. The reaction time varied between 15 and 29 minutes, and the initial alcohol:oil molar ratio was studied in the 32:1 to 52:1 range. Once these levels were selected, the Doehlert desing of experiments was applied. The Doehlert matrix and the experimental conditions studied in this work are presented in Table 1. The first three columns of data show factor levels on a natural scale, and the next three 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.

Tabla 1. Biodiesel production by transesterification of *Raphanus sativus* L. oil in supercritical ethanol. Experimental conditions studied in this work. Doehlert matrix and experimental results.

Run Number	Real Values			Coded Values			$Y_{\text{ester}}(\%)$
	T K	t min.	RM	X_T	X_t	X_M	
1	598	22	42	1	0	0	93.08
2	590.5	29	42	0.5	0.866	0	95.51
3	590.5	24.3	52	0.5	0.289	0.8166	76.06
4	568	22	42	-1	0	0	91.70
5	575,5	15	42	-0.5	-0.866	0	72.32
6	575,5	19.7	32	-0.5	-0.289	-0.8166	91.37
7	590.5	15	42	0.5	-0.866	0	94.80
8	590.5	19.7	32	0.5	-0.289	-0.8166	92.32
9	575,5	29	42	-0.5	0.866	0	93.47
10	583	26.7	32	0	0.577	-0.8166	94.19
11	575,5	24.3	52	-0.5	0.289	0.8166	74.46
12	583	17.3	52	0	-0.577	0.8166	66.27
13	583	22	42	0	0	0	91.57
14	583	22	42	0	0	0	95.15
15	583	22	42	0	0	0	92.10

3. Results and discussion

3.1. Experimental phase behavior

The ester contents in all the experiments are also presented in Table 1. In all cases, a single-phase system at the end of the reaction was observed. Figure 3 shows a typical evolution of the phase behavior during the non-catalytic transesterification reaction, at the reported operating conditions.

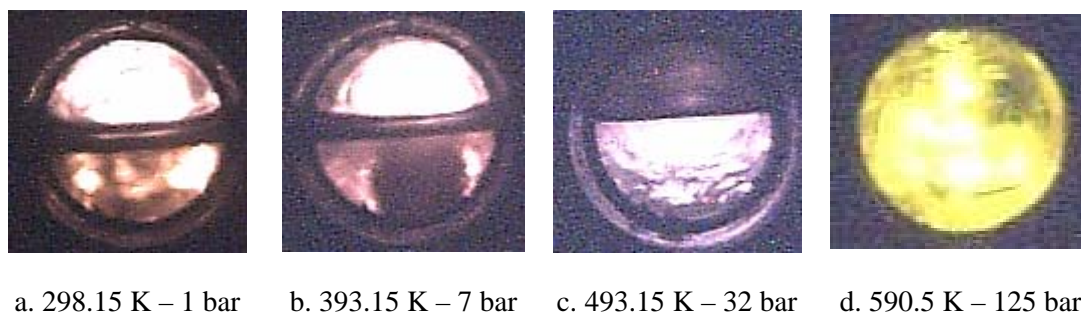


Figure 3 Phase behavior evolution during the heating process of the reacting mixture (run #2)

Figure 3a and 3b show that the system exhibits liquid-liquid-vapor (LLV) equilibria at moderate temperatures. Figure 3c shows that at higher temperatures (such as 493 K) the liquid phases become completely miscible and liquid-vapor (LV) equilibria can be observed. However, the system changes to a single-phase condition (Figure 3d) at temperatures over 573 K, the pressure increase with temperature was moderate in all cases. According to Hegel et al. [3], this behavior is probably due to the global density of load that in this work was set around 0.615 g/cm^3 .

The application of a group contribution equation 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. (2004) and (2005) and more recently by Andreatta et al. (2007). In a previous work (Hegel et al., 2007) experimental observations of the multiple phase behavior between the reactants and products of the transesterification of vegetable oils (triglycerides, fatty esters, methanol and glycerin) were compared with modeling predictions using GCA-EOS. Phase envelope prediction in agreement with experimental trajectories of the reactive system. Andreatta et al. (2008) measured LL and LLV equilibria data for the system methyl oleate-methanol-glycerin, and used GCA-EOS to represent these experimental data. The model showed a good predictive capability. Hence, it can be applied to explore the operating conditions in the reactor. Figure 4 shows the liquid-supercritical phase behavior predicted by the GCA EOS for the methanol – methyl laureate mixture at 493 K, 523 K and 543 K in a pressure – molar concentration diagram. As it can be observed the model agrees well with the experimental data reported for the system (Shimoyama et al., 2007)

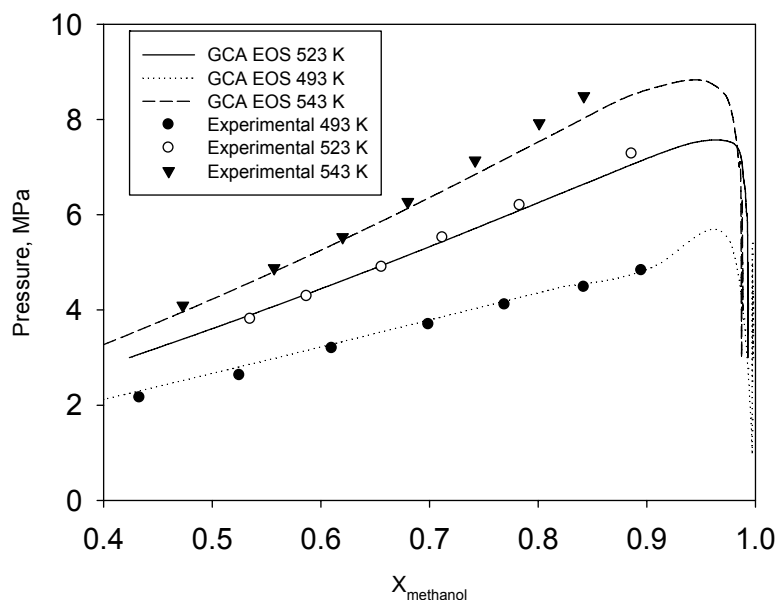


Figure 4 Liquid-vapor phase equilibria in a pressure vs. molar concentration of methanol diagram for the methanol + methyl laureate mixture. (Lines) GCA – EOS prediction, (symbols) Equilibrium data reported by Shymomaya et al.

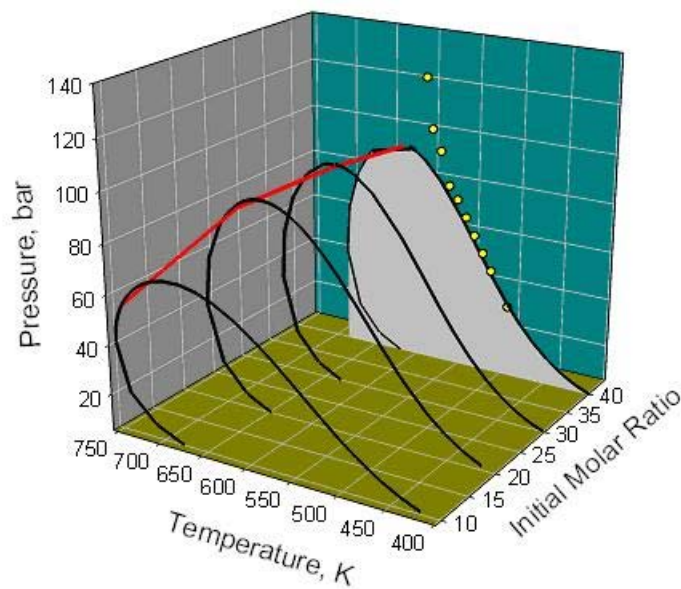


Figure 5. Phase equilibrium analysis of the transesterification of *Raphanus sativus*L. oil using supercritical ethanol. Reaction trajectory (○) on a pressure-temperature (PT) diagram for a reactive mixture with 42:1 initial EtOH:oil molar ratio. The solid line represents the GCA-EOS prediction for the liquid-vapor phase envelope for the products of the reaction (ethanol + ethyl esters + glycerin) at different initial molar ratios. The red line denotes the critical point of the reaction products.

The critical parameters of the ester (methyl laureate and ethyl eicosapentanoate) were predicted by a group contribution method (Constatinou and Gani, 1994). The GCA-EOS group energy and interaction parameters for non-associating groups are those of Espinosa et al. (2001)- For self associating groups or groups with cross-association the parameters reported by Ferreira et al. (2005) and Gros et al. (1997) are used. The alcohol, glycerin and esters interaction specific parameters are those of Hegel et al. (2008).

Figure 5 gives the phase envelopes and critical points of the system composed by ethyl oleate + ethanol + glycerin. Here, the ethyl eicosapentanoate represents the ethyl esters produced by the transesterification of *Raphanus sativus*, L oil. Phase envelopes and the critical points were predicted based on the GCA-EOS model. Figure 5 also shows the thermal history of an experimental run with the same initial ethanol:oil molar ratio (42:1). It can be observed that the predictions agree with the experimental observations of the phase conditions. In fact, a liquid single-phase condition is predicted at the end of the reaction, when almost all the vegetable oil has been converted to fatty ethyl esters, and a near supercritical state can be observed.

3.2. Model fitting and analysis of response

The data multivariable analysis 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 (Barros et al., 2003). Response surface methodology has also been used for biodiesel production optimization (Domingos et al., 2007). In this work, response surface methodology was performed on experimental data and, as a result, a lineal regression quadratic model was obtained as shown in Eq. (1):

$$Y_{\text{ester}\%} = 92.943 + 3.729X_T + 6.369X_t - 12.465X_M - 0.553X_T^2 - 5.040X_t^2 - 14.333X_M^2 - 11.801X_TX_t + 4.572X_TX_M + 3.115X_tX_M \quad (1)$$

The error and *p-value* associated to each coefficient of this model can be seen in Table 2. According to Montgomery (2005) the *p-value* can be understood as the minimum significance level of a group of data or variable in a statistical hypothesis test.

Table 3 shows the analysis of variance – ANOVA of the lineal regression quadratic model resulted. This statistical technique subdivides the total variance of the data in groups of different sources of variance, for the purpose of statistical hypothesis tests (Barros et al., 2003). According to *p-values*, it can be observed that the model has a good adjustment with experimental data and is also statistically significant. The coefficient of determination R^2 approaches to unity (0.92) indicating that the regression model has a good prediction capacity.

Tabla 2. Coefficients of the lineal regression quadratic model and their respective error and *p-value* associated.

	Coefficients	Error	<i>p-value</i>
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

Tabla 3. Analysis of variace (ANOVA) of the lineal regression quadratic model

	Degree of Freedom	Sum of Squares	Mean Squares	* Calculated value of F	<i>p-value</i>
Model	9	1258.2	139.8	6.672	0.025
Residue	5	104.8	20.95		
Lack of adjustment	3	97.3	32.44	8.708	0.105
Pure error	2	7.4	3.72		
Total	14	1363			

* The value of F is determined by the ratio between mean squares

Figure 6 plots of experimental versus predicted values for biodiesel production from *Raphanus sativus L.* oil. It can be observed that there are no tendencies in the linear regression fit; hence the model explains the experimental range studied adequately.

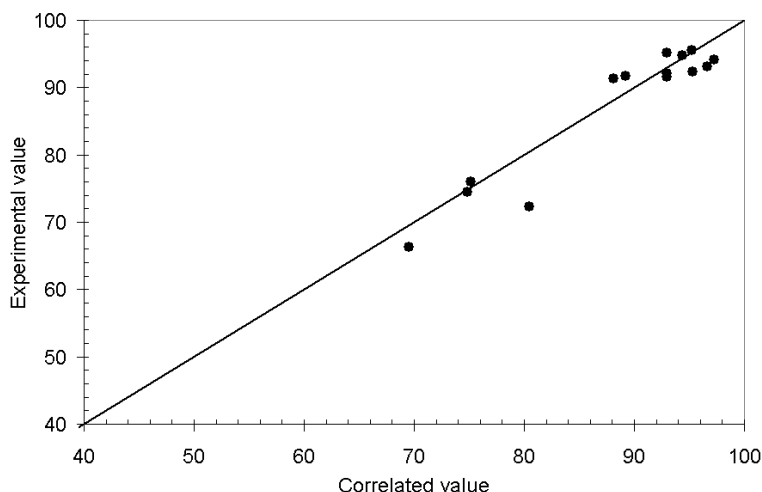


Figure 6. *Raphanus sativus L.* oil transesterification in supercritical ethanol. Experimental values vs. correlated values.

According to *p-values* in Table 2, 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 *Raphanus sativus L.* oil, followed by time and temperature of the reaction, respectively.

To aid visualization and help to identify the type of interaction between the variables on the reaction conversion, within the studied range, the response surface for ester contents (Esters%) in biodiesel samples is shown in figure 7.

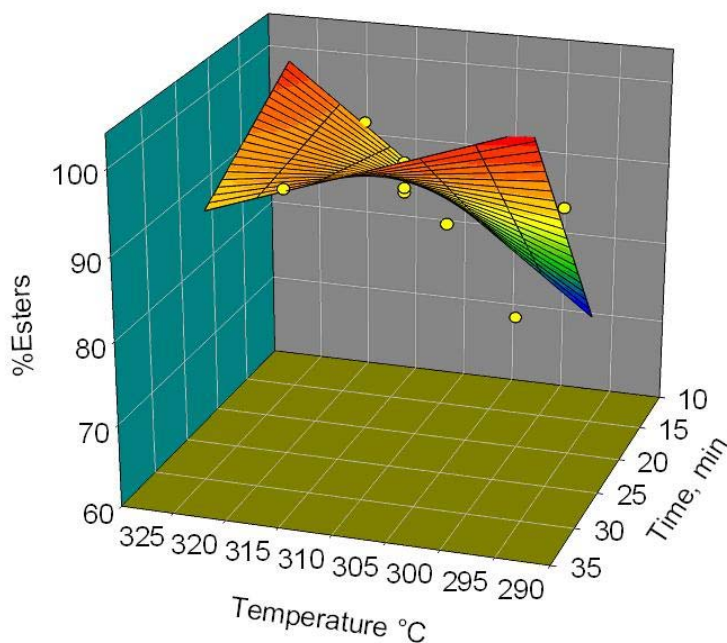


Figure 7 Biodiesel production from *Raphanus sativus L.* oil in supercritical ethanol. Response surface for Ester% vs. temperature for a given reaction time. EtOH:oil molar ratio 42:1. (○) Experimental data reported in table 1.

Figure 7 shows the plot of ester% versus temperature and reaction time with EtOH:oil molar ratio maintained at its zero level. According to the statistical model, there is an expected increase in ester % as temperature increases for reaction times between 15-25 minutes. For reaction times over 25 minutes, the model predicts a decrease in esters% with an increase in temperature, but we have no experimental results to confirm the observed tendency. From figure 8, it can be observed that biodiesel with ester contents higher than 95% can be obtained in 15 minutes, at 591 K.

3.3. Checking results

To check the model adequacy for predicting the maximum ester%, one additional experiment using optimal operating conditions was carried out under the conditions described in Table 4. 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 results derived from this study indicated that the Doehlert design is a powerful tool for optimizing the conditions for biodiesel production in supercritical alcohols.

Tabla 4. Values for testing the best conditions of maximum biodiesel production from *Raphanus sativus* *L. oil* in supercritical ethanol

Parameters	Optimum value
Esters%	97.5%
Global density of load, g/cm ³	0.61
Temperature, K	592
EtOH:oil molar ratio	39
Time, minutes	15

3.4. Transesterification of commercial soybean oil and crude sunflower oil in supercritical alcohols

Additional experimental work was carried out to test different vegetable oils. The transesterification of crude sunflower as well as soy oils was performed in supercritical ethanol using operating conditions slightly different from that reported in Table 4 (591 K, 37:1 EtOH:oil and 25 minutes). The products of these reactions were analyzed by gas chromatography in three replicates, according to AOCS Official Method Cd 11b-91, and the contents of ethyl esters in all of the chromatograms was greater than 96%. These results confirm a previous work [3], where high conversions were achieved in the synthesis of methyl ester by transesterification of soybean oil using supercritical methanol at lower temperatures (563 K)

and 10 minutes of reaction time. Preliminary analysis seems to indicate that ethanol is less reactive than methanol in the experimental range considered.

3.5. High pressure continuous reactor for production of biodiesel in supercritical ethanol

In order to allow an independent and better control of pressure, temperature and residence time during biodiesel production in supercritical alcohols, the assembly proposed in Figure 6 was constructed in our lab. The best conditions obtained in this work in batch mode (reported in table 4) were applied in this continuous process. Soy oil was used to carry out the experiences with supercritical ethanol.

The results confirm previous results obtained in batch studies. For an initial molar ratio of 40:1 ethanol / soy oil and a flow rate of 3.2 g/min, 60 % of esters was obtained a 320°C and 130 bars for a reactor volume was of 93 cm³. According to the global density of the reactive mixture measured at the operating conditions (0.431 g/cm³) the residence time was 12 min. The global density is a key variable in the continuous process because it determines the residence time. This variable depends on the substrate that is being used in the process. In case of *Raphanus sativus L.* oil the global density for the same operating conditions was 0.61 g/cm³.

An increased of the reactor volume to 186 cm³ produced a biodiesel with 81.5% of ester content. Studies on continuous biodiesel production by supercritical alcohols are being carried out in our lab.

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. A global density of 0.615 g/cm³ was set to reach a single-phase system and moderate reaction pressures at the final transesterification temperatures. High ester contents in the reaction products were obtained. Design of experiments was applied to optimize the synthesis of ethyl esters from crude *Raphanus sativus L.* oil. A three variable Doehlert design has proved to be effective in the study and optimization of the variables affecting the process. A lineal regression quadratic model was obtained to predict the ester contents as a function of the variables. Analysis of the residues showed that the model predicted adequately the ester% over the experimental range considered. According to these results, in the experimental range studied, a high yield of ester (97,5%) can be obtained, working in the following conditions: approximately 592 K, EtOH:oil molar ratio of 39:1 and 15 minutes of reaction time. Different vegetable oils were tested at similar conditions and high efficient reactions were achieved. An assembly for continuous transesterification in supercritical alcohol is being prepared to confirm the best conditions obtained in bath mode reaction, as well as to reach a better and independent control of the variables that affect the reaction of transesterification in supercritical alcohols. *Raphanus sativus L.* and other oils will also be used in the continuous processes for biodiesel production.

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