BIODIESEL PRODUCTION USING SUPERCRITICAL ALCOHOLS AND DIFFERENT VEGETABLE OILS 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. In these studies different oils, crude and refined, as well as the effect of water and free fatty acids, are studied. Also the effect of using methanol or ethanol and different co-solvents 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 alcohol/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.

INTRODUCTION

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. 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 [1] [2] 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.

In a previous work [3] it was determined how the phase condition, homogeneous or heterogeneous, influences the kinetics and efficiency of the reaction of transesterification using supercritical

methanol, at controlled reactor charge global densities and initial methanol / soybean oil composition. 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-commercial 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.

MATERIALS AND METHODS

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 mode in a see through, two window stainless steel tubular reaction cell of 32 cm^3 (15 cm of internal diameter). Details of the experimental apparatus and technique are given by [3]. The biodiesel samples were analyzed by gas chromatograph (GC – Varian Star 3400 CX) to determine their ester contents. The chromatograph conditions were selected according to BS EN 14103:2003. The synthesis of ethyl ester by transesterification of *Raphanus sativus L.* oil using supercritical ethanol was carried out according to a Doehlert design of experiments [4]. This experimental design is very useful and offers advantages in relation to other designs [5]. The response selected was the ethyl esters contents in the biodiesel samples, Y_{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 reactor charge global density of approximately 0.61 g/cm^3 and working pressures no higher than 18 MPa. Under our 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 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.

Table 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_{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

RESULTS

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. The system exhibits liquid-liquid-vapor (LLV) equilibria at moderate temperatures. 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 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 reactor charge global density 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. [6] [7] and more recently by Andreatta et al. [8]. Andreatta et al. [9] 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 1 gives the bubble points of the initial reactive mixture of ethanol and oil with a molar ratio of 42:1, as well as the phase envelopes and critical points of the system composed by ethyl oleate + ethanol + glycerin. Here, the ethyl oleate represents the ethyl esters produced by the transesterification. Phase envelopes and the critical points were predicted based on the GCA-EOS model. Figure 1 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.
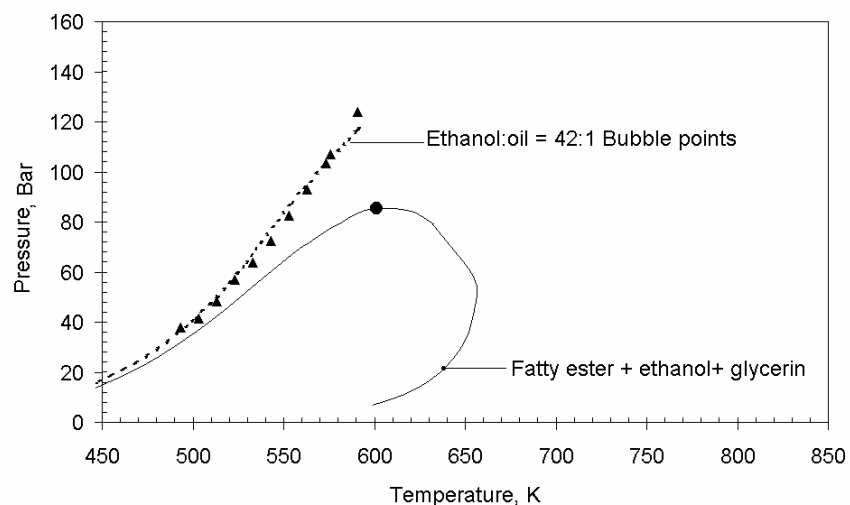
Figure 2. Phase equilibrium analysis of the transesterification of *Raphanus sativusL.* oil using supercritical ethanol. Reaction trajectory (▲) on a pressure-temperature (PT) diagram for a reactive mixture with 42:1 initial EtOH:oil molar ratio. The dotted line represents the GCA-EOS prediction for reactive mixture bubble points. The solid line represents the GCA-EOS prediction for the liquid-vapor phase envelope for the products of the reaction (ethanol + ethyl esters + glycerin). The dark dot symbol (●) denotes the critical point.

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 [10] [11] [12] [13]. Response surface methodology has also been used for biodiesel production optimization [12] [13]. In this work, response surface methodology was performed on experimental data and, as a result,

a lineal regression quadratic model, based on the coded values of the variables, was obtained as shown in Equation (1):

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

From the analysis of variance – ANOVA – a lineal regression quadratic model resulted.   The model has good agreement with the 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.

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.

The response surface for ester contents (Esters%) in biodiesel samples are shown in Figure 3. From these figures we can identify the type of interaction between the variables that influence the reaction, within the range studied. Each plot represents the effect of two variables, while the third one is set at its zero level (i.e. 22 min. in Figure 3a, 583 K for temperature in Figure 3b and 42:1 EtOH:oil in Figure 3c).

a).   b).   c).
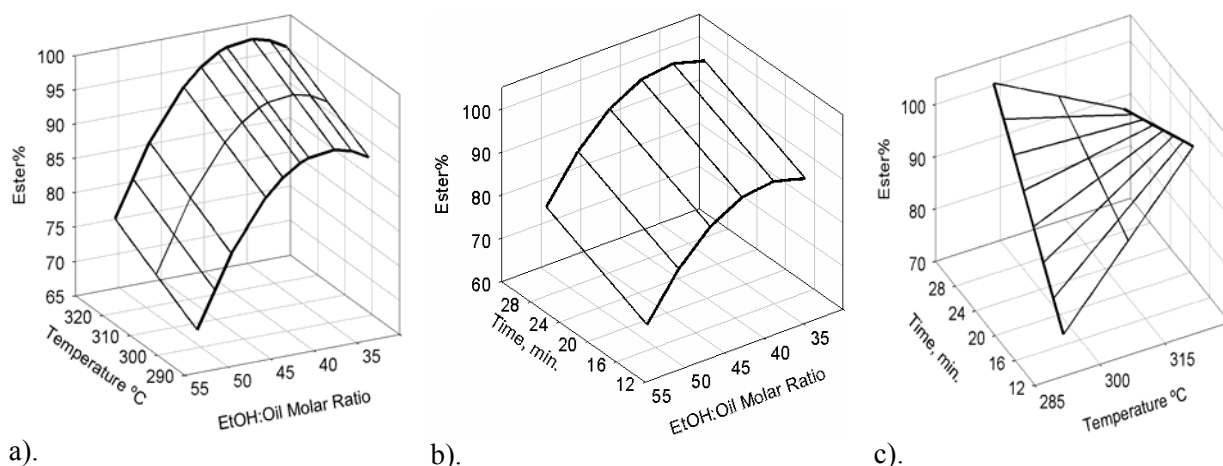
Figure 3. Biodiesel production from *Raphanus sativus L.*oil in supercritical ethanol. A).Response surface of ester% vs. temperature and ethanol:oil molar ratio. Reaction time: 22 minutes. B). Response surface of ester% vs. EtOH:oil molar ratio and time. Temperature: 583 K. C). Response surface of ester% vs. time and temperature. EtOH:oil molar ratio 42:1.

Figure 3a shows the surface plot of ester% versus temperature and EtOH:oil molar ratio. The maximum ester% is achieved at the maximum temperature level. In the 32-39 range, there is an increase of ester% as the EtOH:oil molar ratio increases. However, an increase in EtOH:oil molar ratio beyond the optimal region (EtOH:oil = 39) resulted in a decrease of the expected ester%. Figure 3b shows the surface plot of ester% for a fixed temperature (583 K). As can be seen in this plot, the maximum ester% is obtained at the maximum level for reaction time and at an EtOH:oil molar ratio of 39. Although the temperature is the least statistically significant variable among the three factors researched, it has a positive influence in the experimental range considered.

Figure 3c 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 3, it can be observed that biodiesel with ester contents higher than 95% can be obtained in 15 minutes, at 591 K.

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.

Table 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

Additional experimental work was carried out to test different vegetable oils. The transesterification of commercial soybean oil, crude sunflower as well as *Raphanus sativus L.* 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 99%. These results confirm previous works [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.

In order to allow an independent and better control of pressure, temperature and residence time during biodiesel production in supercritical alcohols, a continuous supercritical biodiesel reactor is being constructed in our lab.

CONCLUSIONS

In the present work, from a phase equilibrium engineering analysis, using the GCA-EOS model a global density of 0.615 g/cm^3 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 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 close to the following conditions: 590 K, EtOH:oil molar ratio of 39:1 and 15 minutes of reaction time. Different vegetable oils were tested at similar conditions and high yields of esters were achieved. An apparatus for continuous transesterification in supercritical alcohol is being built to confirm the best conditions obtained in batch 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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