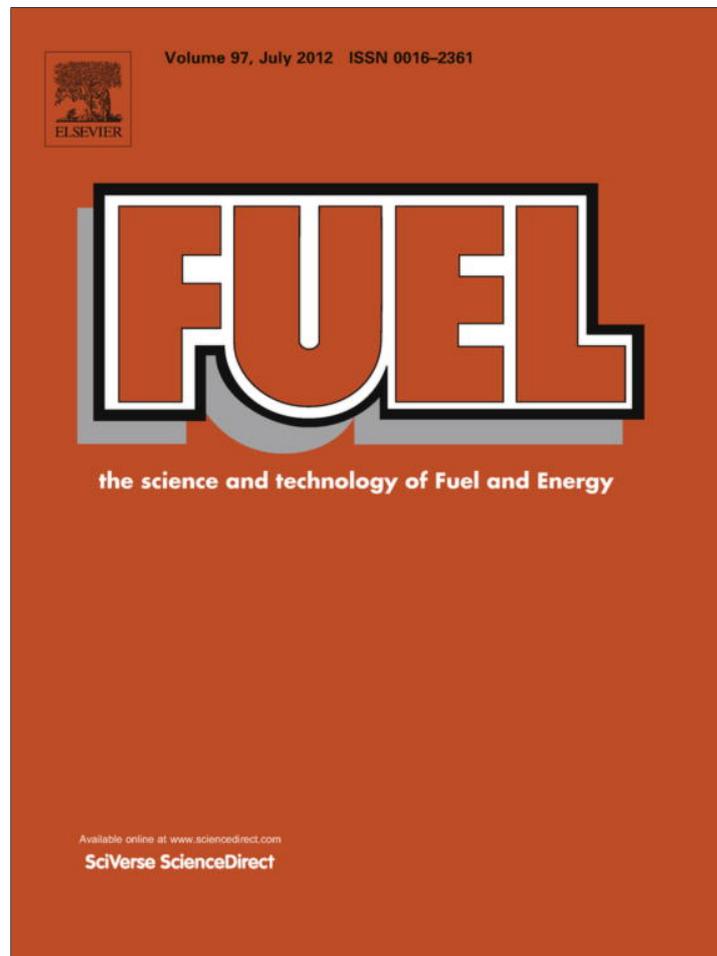


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Continuous production of fatty acid ethyl esters from sunflower oil using supercritical ethanol

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ABSTRACT

The production of first generation biofuels has increased in the last few years because of the rising price of fossil fuels and environmental policies. Biodiesel process alternatives have been proposed in order to achieve higher yields, non-catalytic and more environmentally friendly processes, a greater profit from by-products and particularly the possibility of using low quality and cheaper feedstocks. In this regard, one of the most studied technologies has been the non-catalytic supercritical transesterification of fats and raw vegetable oils.

This work reports results on the continuous production of fatty acid ethyl esters (FAEEs) from the non-catalytic supercritical ethanolysis of sunflower oil. The reaction was carried out in the following range of operating conditions: (i) ethanol-to-oil molar ratio of 40:1; (ii) temperature and pressure range, 573–618 K and 165–200 bar and (iii) mass flow rates varying from 3 to 16 g/min. Given the high sensitivity of the specific density in supercritical mixtures, the mixture residence time in the reactor was estimated based on experimental data of the reactive mixture density. Moreover, we show here that overlooking the use of this experimental data and assuming ideal solution behavior for density calculation, which is usually done, may lead to important deviations in the kinetic model parameters. The mixture densities were correlated with the Peng–Robinson equation of state (PR-EoS). In the range of operating conditions studied in this work, up to 90% by mass fraction of fatty ester was obtained.

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1. Introduction

Biodiesel production has grown rapidly over the past decade because it is an attractive replacement or additive for petroleum diesel. It is compatible with existing diesel engines, reduces GHG emissions, and is biodegradable. Biodiesel is a mixture of fatty acids alkyl esters commonly derived from the transesterification of refined vegetable oils with methanol or ethanol in the presence of an alkali or acid catalyst [1]. For example, Argentina produced in 2009/2010 about 2.6 million tons of biodiesel from refined soybean oil and a 20% increase was estimated for 2011.

Recent interest in using alternative feedstock, as crude vegetable oils or waste cooking oils, has grown considerably because of the high cost of using refined edible vegetable oils [2]. However, the processing of low cost non-edible feedstock is not feasible by the conventional catalytic process due to the presence of water and free fatty acids (FFAs) that form soaps with the catalyst hindering the process yield [3,4]. The non-catalytic supercritical alcohol technology for the processing of low quality feedstocks, has been under study during the last decade and has shown to be a feasible alternative for biodiesel economic production [5]. The supercritical

transesterification of lipids is a viable technology that presents less impact on the environment, uses less amount of water in the purification steps after the reaction, and allows the processing of low cost oils since it is not affected by the presence of water and FFAs [4].

Most of the studies of supercritical transesterification of oils have been carried out in batch reactors. In these studies the reactor is first heated up to a certain temperature to initiate the reaction, the temperature is kept constant for a given period of time to allow the transesterification reaction to take place and then a quenching is carried out to stop the reaction. It has been found that the reaction takes place in the 553–623 K temperature range. At temperatures lower than 553 K the fatty esters content in the reaction products is lower than 40 wt.%, even at long residence times ($t_r > 100$ min) On the other hand, at temperatures higher than 623 K degradation of the reaction products has been found [5,6]. Several authors in the literature recommend an alcohol to oil molar ratio of 40:1 as a near optimum value to conduct the supercritical ethanolysis. It was observed that changing alcohol-to-oil ratio from 10:1 to 40:1 the reaction conversion increases; however, from 40:1 to 70:1 has no significant effects [7]. One important drawback of the studies in batch reactor is that heating and cooling periods introduce a significant uncertainty on the reaction time.

Processing biodiesel by the supercritical technology requires a large scale production volume for a well establish market. This fact

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together with the extreme operating conditions and the absence of catalyst promotes the selection of continuous tubular reactors. However, compared to the batch type studies, research on the continuous transesterification of vegetable oils by the non-catalytic supercritical technology is still limited. Also only a few bench scale studies on continuous supercritical methanolysis of coconut oil [8], soybean oil [9] and rapeseed oil [10] have been carry out.

Methanol has been the most used alcohol to perform the transesterification in the conventional catalytic process as well as in the supercritical technology [5,6] because with this alcohol complete conversion can be achieved. However, in order to move forward second generation biofuels, ethanol should be used for biodiesel production because it comes from renewable resources. Silva et al. [11] studied the continuous production of biodiesel from soybean oil with supercritical ethanol. They found the highest conversion at 623 K and 200 bar, working with an ethanol-to-oil molar ratio of 40:1 and a residence time of 15 min. Vieitez et al. [12] also studied the biodiesel production with supercritical ethanol–water mixtures in a continuous process. The authors concluded that the process efficiency is comparable in the presence of water to that of the anhydrous processes.

The residence time in a continuous reactor depends on the volumetric flow rate over the reactor volume. In this sense, the reacting mixture specific volume at the operating pressure, temperature and composition plays a very important role in supercritical reactors. This parameter has been overestimated in most cases in the open literature [5]. Recently, Velez et al. [13,14] measured the molar density of reacting mixtures of sunflower oil with methanol and ethanol in the 553–618 K temperature range, 100–400 bar pressure range and alcohol to oil molar ratio from 25 to 40. These data can now be applied to the evaluation of the reacting mixture residence time and for general process design needs.

In this work we studied the continuous supercritical ethanolysis of a commercial sunflower oil to produce fatty acids ethyl esters (FAEEs). Even though the supercritical technology is interesting regarding its application on vegetable oils with high free fatty acids content, we selected a refined oil in order to validate the use of previously measured experimental data on molar density [13,14] of sunflower oil transesterification mixtures. With this data we calculated the reactive mixture residence time and evaluated the inaccuracy in the reaction kinetic parameter if this variable is overlooked in a continuous supercritical reactor.

The reaction kinetics was studied over a temperature range of 553–618 K at pressures higher than 150 bar. The effect of the temperature and pressure on the specific density of the reacting mixture was considered in the determination of the reactor residence time.

The reaction was carried out under the following operating conditions: (i) ethanol-to-oil molar ratio of 40:1; (ii) temperature and

pressure range, 573–618 K and 165–200 bar, respectively and (iii) mass flow rates varying from 3 to 16 g/min. The mixture residence time in the reactor was estimated from experimental data on molar volumes of the reactive mixtures, which were correlated with the Peng–Robinson equation of state (PR-EoS).

2. Materials and experimental methods

2.1. Materials

The vegetable oil studied in this work was commercial sunflower oil with a fatty acid composition of 85 wt.% of oleic acid, 14 wt.% of palmitic acid, and 1 wt.% of stearic acid. Analytical grade ethanol (Fisher) and azeotropic ethanol (96 wt.%) were used with no further purification.

2.2. Apparatus and experimental procedure

Fig. 1 shows the experimental tubular reactor. It consists of a 260 cm³ reactor tube equipped with an electric pre-heater, a condenser and a separator. An electric thermostat is used to control the temperature of the pre-heater that is composed by a single line (SS-316 tubing of 1/8-in. o.d., 0.035-in. thickness, and 14-m length) coiled over an aluminum solid rod and heated by eight electric resistances of 250 W. The tubular reactor consists in a 316 SS Swagelok tubing (6 mm outer diameter (o.d.) - 0.711 mm wall thickness) placed in an electric oven (3 kW of electric power) with temperature control. The reaction temperature is monitored by two PTs-100 directly connected at the inlet and outlet of the tubular reactor allowing to control the desired temperature with a precision of 5 K.

The heater and the electric oven were pre-heated at the desired reaction temperature. The alcohol and oil, in a molar ratio of 40–1, placed in a Parr Reactor (2 L capacity) were mixed and heated up to 400 K to obtain a single liquid phase [14]. The reactants were pumped by a high-pressure plunger pump (Dosivac, DE7/700, double head) at pressures higher than 150 bar, in order to obtain a single phase in the process. The reactants were heated at the reaction temperature in the pre-heater. The fluid product exiting from the reactor was cooled down by an external water-cooling bath and depressurized using a back-pressure regulator.

Steady state operation is achieved after a residence time had elapsed at least two times. Afterwards, ca. 50 mL of liquid product was collected in a glass beaker placed at the reactor outlet. Excess of ethanol was evaporated until constant weight of the samples.

2.2.1. Gas chromatography

The liquid products obtained after ethanol evaporation split up in two phases: glycerol and biodiesel. Fatty esters, monoglycerides,

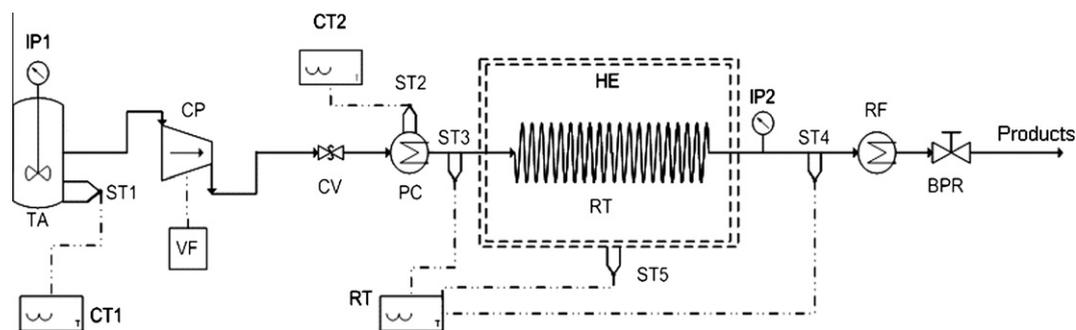


Fig. 1. Experimental setup of the transesterification of high oleic sunflower oil by continuous supercritical ethanol process. TA: pre-mixer tank, CT1: temperature control of pre-mixer tank, IP1: pressure indicator, ST1: temperature sensor of pre-mixer tank, CP: high pressure plunger pump, VF: frequency drive, CV: check valve, CT2: temperature control of heater, ST2: temperature sensor of heater, PC: coiled heater, RT: temperature register, ST3, ST4 y ST5: temperature sensor of reactor, HE: coiled reactor and oven, IP2: pressure indicator, RF: cooler, BPR: back pressure regulator.

and diglycerides are highly immiscible with glycerine; therefore, they are all found in the biodiesel phase.

The biodiesel phase was analysed by gas chromatography by GC – Varian Star 3400 CX with a flame ionization detector (FID) and capillary column (J&W Scientific, model DB-5ht, 15 m length, 0.32 mm inner diameter, and 0.10 μm film thickness). The chromatographic conditions were selected according to BS EN 14105:2003, modified to analyse FAEE, fatty acids, mono, di and triglycerides. Tetradecane was used as internal standard, and purified ethyl esters (99%) were used as reference of fatty esters for a calibration curve. A stock pyridine solution with a known amount of internal standard was prepared (~10 mg/ml). The sample injected to the chromatograph consisted of 2 μL of a solution prepared with 0.05 ml of the internal standard stock solution, 0.1 ml of liquid sample and 0.2 ml of silylating agent solution (BSTFA:TMCS 2:1 v/v).

3. Modeling of the vegetable oil + alcohol global density behavior under reaction conditions

In previous works [13,14] the densities of reacting mixtures of sunflower oil + pure and azeotropic ethanol were measured in a constant volume cell (isochoric method) in a wide range of temperature (553–623 K) and pressure (120–350 bar). Moreover, in those works the conditions where phase transition from the heterogeneous to the homogeneous region occurs were also determined. In the present work the experimental isochoric lines were correlated with PR-EoS [15] in order to have a tool to predict the system density in the continuous reactor at different operating conditions. In a constant volume cell the molar density of the system is invariant because in the transesterification reaction there is no change in the number of moles along the reaction pathway. For this reason, we model the system density considering only the reaction products, FAEE, glycerin, excess ethanol, and water when using azeotropic ethanol. Table 1 summarizes the pure component critical properties and acentric factors used in PR-EoS.

The classic quadratic mixing rule for the energy parameter (*a*) was used in PR-EoS

$$\begin{aligned}
 a &= \sum_i \sum_j y_i y_j a_{ij} \\
 b &= \sum_i b_i y_i \\
 a_{ij} &= \sqrt{a_{ii} a_{jj}} (1 - k_{ij})
 \end{aligned} \tag{1}$$

Eq. (2) shows the temperature dependence used for the binary energy interaction, k_{ij} (T_{ci} and T_{cj} are the critical temperature of component *i* and *j*, respectively).

$$k_{ij} = k_{ij}^0 \left[1 + k_{ij}^1 \ln \left(\frac{T}{0.5(T_{ci} + T_{cj})} \right) \right] \tag{2}$$

k_{ij}^0 and k_{ij}^1 were fitted for a given experimental isochore by minimizing the following objective function:

$$f = \sum_i |P^{\text{exp}} - P^{\text{calc}}| \tag{3}$$

P^{exp} and P^{calc} are the experimental and calculated pressure, respectively. The parameterization was performed using the 0.51 g/cm³ isochore for the reacting system with absolute and azeotropic ethanol. Working with absolute ethanol the parameters for all components but water were set and afterwards, with the isochore corresponding to sunflower oil with azeotropic ethanol the parameters for water were fitted. The rest of the data was used to check the model predictive capacity. Table 2 summarizes the fitted binary energy interaction parameters.

Fig. 2 shows the quality of experimental data correlation (dashed dotted lines) and prediction (solid lines) PR-EoS is capable

Table 1
Pure component critical properties and acentric factor used in PR-EoS.

Component	Tc (K)	Pc (atm)	Ω
Ethanol ^a	513.9	60.7	0.644
Water ^a	647.0	217.1	0.344
Ethyl oleate ^b	730.0	26.0	1.050
Glycerol ^a	850.0	74.0	0.512

^a DIPPR database [16].

^b Marrero and Gani group contribution method [17].

Table 2
Binary energy interaction parameters for PR-EoS.

Comp. <i>i</i>	Comp. <i>j</i>	$k_{ij}^0 = k_{ij}^0$	$k_{ij}^1 = k_{ij}^1$
Ethanol	Ethyl oleate	-0.5453	1.5887
	Glycerine	0.0000	0.0000
	Water	-0.3740	0.0000
Ethyl oleate	Glycerine	0.0000	0.0000
	Water	0.0000	0.0000
Glycerine	Water	0.0000	0.0000

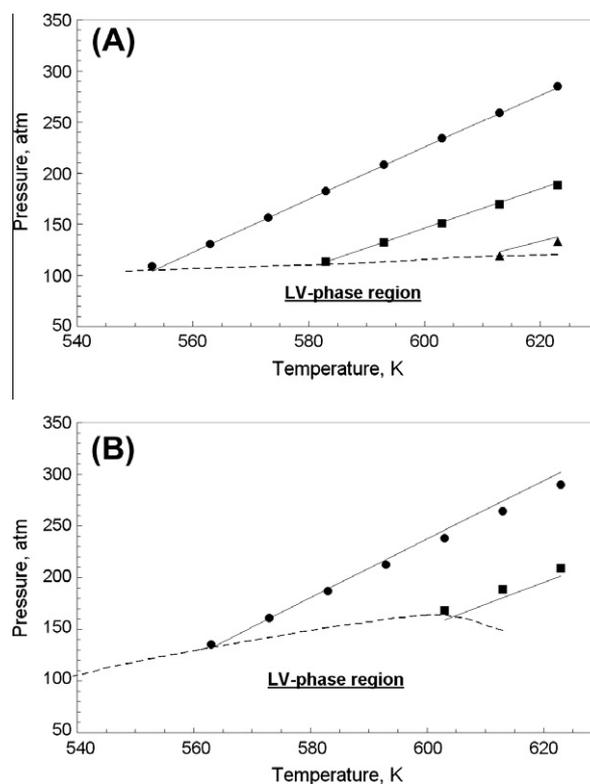


Fig. 2. PR-EoS modeling of PVT data of sunflower oil transesterification with absolute ethanol (A) and azeotropic ethanol (B) using an alcohol to oil molar ratio of 40. Experimental data: isochoric lines [13] at 0.37 g/cm³ (▲), 0.44 g/cm³ (■) and 0.51 g/cm³ (●). Solid lines: PR-EoS correlation for 0.51 g/cm³ and predictions for the other densities. Dashed lines: experimental phase transition line [13].

to describe the isochoric pressure–temperature behavior of the reacting mixtures of ethanol with vegetable oils under reaction conditions.

4. Results and discussion

Tables 3 and 4 show the experimental results obtained in this work for the transesterification of sunflower oil with absolute

Table 3
Operating conditions and final FAEE content for the transesterification of high oleic sunflower oil with supercritical absolute ethanol, feed molar ratio of 40/1.

Exp. No.	T (K)	F (g/min)	P (bar)	ρ (g/ml)	t_r (min)	FAEE (%)
1	573	3.75	195	0.54	38	72
2		7.30	180	0.53	19	45
3		5.06	195	0.54	28	56
4		16.20	175	0.52	8	20
5	593	6.26	190	0.49	20	62
6		10.60	195	0.49	12	42
7		3.90	200	0.5	33	81
8		2.85	195	0.495	45	88
9	618	4.43	160	0.468	28	91
10		2.57	190	0.49	50	90
11		3.40	195	0.5	38	89
12		8.48	165	0.47	14	72

Table 4
Operating conditions and final FAEE content for the transesterification of high oleic sunflower oil with supercritical azeotropic ethanol, feed molar ratio of 40–1.

Exp. No.	T (K)	F (g/min)	P (bar)	ρ (g/ml)	t_r (min)	FAEE (%)
1	593	11.6	190	0.490	11	71
2		8.0	195	0.494	16	81
3		5.63	200	0.498	23	79
4		4.28	195	0.494	30	88
5		3.27	190	0.490	39	89

and azeotropic ethanol, respectively. These tables report the ester concentrations as a function of the mass flow rate and the residence time. A maximum FAEE content of 90% was obtained at 28 min of residence working at 618 K (the highest reaction temperature) and 160 bar. At lower temperature (593 K), 45 min of residence were required to achieve similar conversion.

The pressure of the system was set to control different mass flow but always at values high enough to assure homogenous phase operation. Fig. 2 shows with dashed lines the region of partial miscibility for the sunflower oil + ethanol (Fig. 2A) and sunflower oil + azeotropic ethanol (Fig. 2B) reacting systems. In the range of temperature used in this work it is possible to achieve homogenous phase at pressures higher than 125 bar when absolute ethanol is used as reactant, while pressures above 150 bar are required to obtain a single phase when azeotropic ethanol is used in the reaction (see Ref. [13] for a detailed explanation). In previous works, it has been shown that the effect of pressure on transesterification conversion is negligible at pressures higher than 150 bar [5,6,8,10–14].

4.1. Residence time calculation in supercritical reactors

In previous studies on continuous supercritical transesterification the mixture residence time in the reactor was obtained assuming ideal solution behavior (null mixing volume), using pure component density to calculate the mixture property (Eq. (4)). This approach might be acceptable when dealing with near ideal liquid mixtures. It can even give good estimates for non-ideal liquid solutions, since generally the volume of mixing is negligible. However, assuming ideal solution behavior in supercritical mixtures, which are characterized by having a highly variable density (from gas-like to liquid-like) according to the operating conditions and mixture composition, may lead to important deviations in the calculated residence time and consequently in the kinetic model parameters. In some cases also the change of vegetable oil density from inlet to operating conditions is disregarded [5].

$$t_r = \frac{V}{F_A(\rho_A/\rho_A^S) + F_{VO}(\rho_{VO}/\rho_{VO}^S)} \quad (4)$$

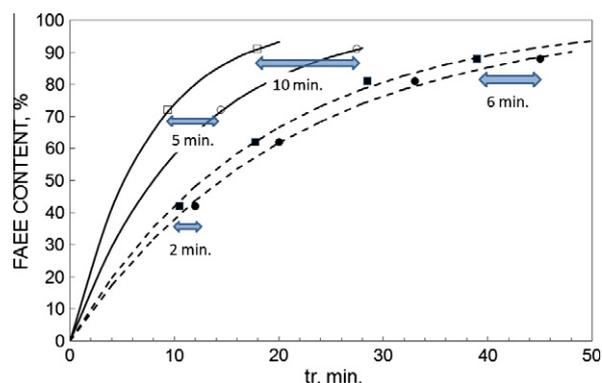


Fig. 3. Non-catalytic continuous supercritical ethanolsis of sunflower oil. Dots: experimental reaction conversion (product FAEE content) at 593 K (dashed lines) and 618 K (solid lines) vs. residence time. Symbols ■ and □: residence time assuming ideal solutions; ● and ○: residence time estimated on the basis of experimental PVT data.

where t_r is the residence time, V the reactor volume, F the volumetric flow-rate at ambient conditions, and ρ/ρ^S the ratio of the density at inlet and operating conditions (A and VO subscript stand for alcohol and vegetable oil, respectively).

In this work, the residence time was estimated according to Eq. (5), where the volumetric properties of the mixture (ρ_M^S) are estimated with PR-EoS fitted to PVT experimental data for transesterification reactive mixtures (see Section 3).

$$t_r = \frac{V}{M/\rho_M^S}, \quad M = \text{mass flow rate} \quad (5)$$

Fig. 3 shows the FAEE content in the reaction product at 593 K and ~200 bar as a function of the residence time calculated rigorously and the result that would be obtained assuming ideal solutions. As can be observed the volumetric properties has a direct influence in the calculation of residence time and therefore in the evaluation of the reaction kinetics.

The absolute errors in the estimation of reaction time assuming ideal solutions at 593 K are between 2 and 6 min at 10 and 45 min, respectively. However, this error increases with temperature and at 618 K almost 50% error is obtained at a residence time of 25 min. Moreover, the lower the mass flow rates the higher the difference in the estimation of residence time.

4.2. Effect of temperature on reaction kinetics

Fig. 4 shows the effect of temperature on the synthesis of biodiesel with supercritical ethanol. The temperature was varied between 573 K and 618 K at a fixed ethanol to oil molar ratio of 40:1. The FAEE content obtained at 573 K after 10 min of reaction time was almost 20%, m/m. On the other hand, working with a temperature of 618 K the reaction rate is much higher achieving more than 50% of FAEE within 10 min, and 90% of FAEE in less than 30 min of reaction time. When the reactor was operated at 593 K it was necessary 50 min to reach a 90% of FAEE content.

Silva et al. [11] and Vieitez et al. [12] studied the transesterification of soybean oil with supercritical ethanol under similar operating conditions. For example, working at 200 bar and 623 K with ethanol to oil molar ratio of 40:1, they achieved a content of ester of 65% by mass in the reaction products for a residence time of 10 min. The ester content obtained by these authors for a given residence time was slightly higher in comparison with results obtained in this work. However, these authors assumed ideal solutions to estimate the residence time in the continuous reactor which gives a difference of ca. 5 min with respect to the residence

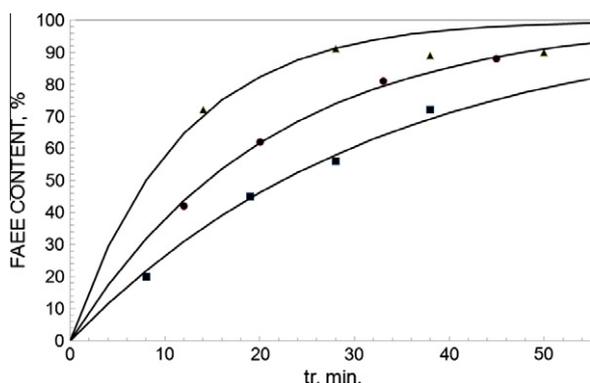


Fig. 4. Sunflower ethanolysis kinetics at operating conditions reported in Table 3: (■) 573 K, (●) 593 K, (▲) 618 K. Solid lines: kinetic model Eq. (6).

time estimated in this work. Therefore, the results obtained in this work are in agreement with those of Silva et al. [11].

A simplified kinetic model, Eq. (6), was proposed to represent the experimental reaction data. The transesterification reaction was considered irreversible due to the large excess of ethanol. Indeed, the concentration of ethanol was considered constant and the rate of reaction was proportional to the concentration of vegetable oil. This assumption was used by other authors [5,6] to model the kinetic data of the supercritical transesterification of vegetable oils in batch and continuous reactors.

$$\text{rate} = \frac{dC_o}{dt} = -kC_o \approx -kC_{nE} \quad (6)$$

The reaction rate can be determined based on the decreased of oil concentration (C_o) or on the non-esterified compounds (C_{nE}) present in the mixture (triglycerides, diglycerides and monoglycerides). Fig. 5 shows the value of kinetic constants (slope of each line) obtained at 573 K, 593 K and 618 K.

If the residence time is evaluated assuming an ideal solution behavior, greater values of k are obtained. At temperatures of 573 K and 593 K the relative errors in the k values are low (~5%). However, an increase of the reaction temperature to 618 K enlarges the error in the estimated residence time and consequently the error in k value also (~18%).

Fig. 4 compares the FAEE content predicted by the kinetic model with the experimental data for the three studied temperatures. The kinetic model demonstrates a good fitting of the experimental data at 573 K and 593 K. On the other hand, it can be observed that for the highest reaction temperature the kinetic model over-predict the FAEE content at residence times higher than 28 min. Many

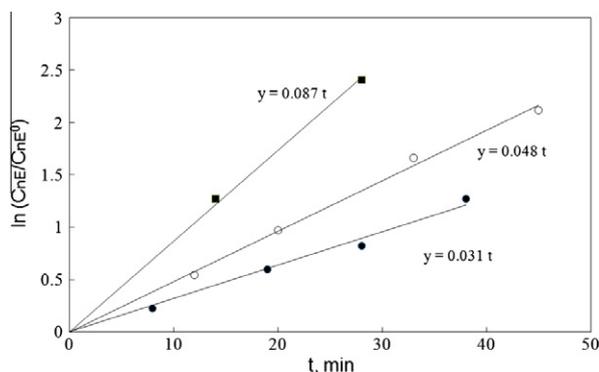


Fig. 5. Experimental values of $\ln(C_{nE}/C_{nE}^0)$ against the reaction time at different temperatures (●) 573 K, (○) 593 K, (■) 618 K. Reaction kinetic constant evaluated at different temperatures according to the integrated Eq. (6).

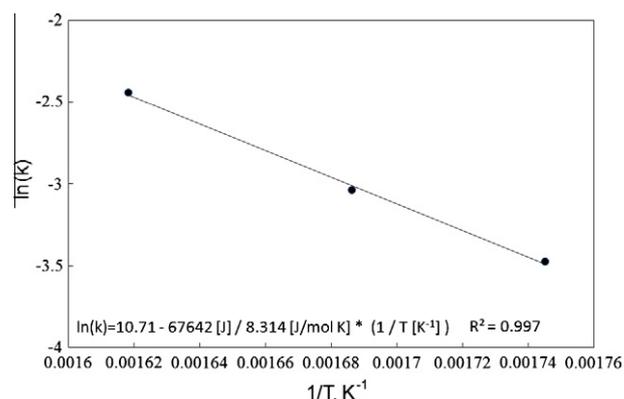


Fig. 6. Arrhenius plot for the supercritical transesterification of sunflower oil. Reaction activation energy: 67.6 kJ/mol of triglyceride.

authors [6,9,12] have shown that a partial degradation of unsaturated esters takes place at high temperatures (>593 K), which could explain the differences between the predicted FAEE content and the data obtained experimentally. However, it was not detected by GC analysis any compound besides FAEE components and other triglyceride derivatives (free fatty acids, monoglycerides and diglycerides). It is important to mention that, even at the highest temperature, the glycerol obtained as by-product was of good quality (high purity and a clear product).

Based on the results shown in Fig. 5, the corresponding Arrhenius plot for this model is presented in Fig. 6, which gives an activation energy of 67.6 kJ/kmol_{triglyceride} for a molar ratio of 40:1 ethanol to oil. If the reaction rate constant is evaluated with the ideal residence time, a higher value of the activation energy is obtained (86 kJ/kmol_{triglyceride}). This means that the effect of temperature would be more pronounced than the real one when ideal solution behavior is assumed to estimate the residence time. Silva et al. [11] reported an activation energy of 78.7 kJ/kmol_{triglyceride} for the reaction under study with the same ethanol to oil molar ratio and assuming ideal solution behavior. However, these authors used different values of the pure component molar volume than the one used here. In this work the pure component densities were estimated with Lo and Stiel [18] experimental PVT data for ethanol and Halvorsen et al. [19] correlation for the oil.

4.3. Transesterification of sunflower oil with supercritical azeotropic ethanol

According to Kusdiana and Saka [4], the presence of water does not slow down the reaction as is the case in conventional catalytic

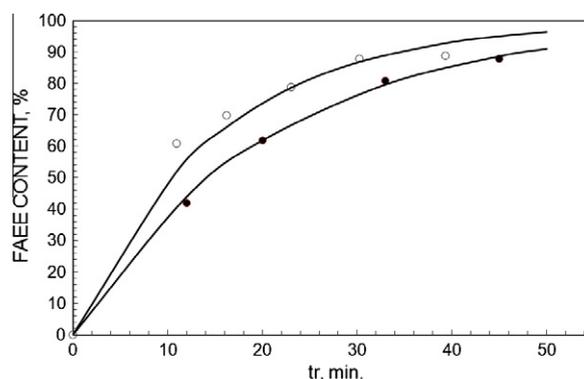


Fig. 7. Ethanolysis of high oleic sunflower oil. FAEE content on the reaction products against the residence time at 593 K and ethanol to oil molar ratio of 40:1. (○) Azeotropic ethanol (4% m/m of water), (●) Absolute ethanol.

processes. The presence of water can hydrolyze the oil and form free fatty acids. This side reaction poses no problem in the non-catalytic supercritical transesterification process because the esterification of the free fatty acids will occur at a rate faster than transesterification [4,12]. Therefore, all free fatty acids will be converted to their corresponding fatty esters.

In this work we evaluate the effect of water in the non-catalytic supercritical ethanolysis using azeotropic ethanol (96 wt.% ethanol and 4% water). Fig. 7 compares the results obtained for the transesterification carried out with azeotropic ethanol with the corresponding with pure ethanol at a reaction temperature of 593 K. This figure shows that, for a given residence time, the FFAE content in the reaction products are greater for the transesterification with azeotropic ethanol. The kinetic constant is greater for azeotropic ethanol ($k = 0.064 \text{ min}^{-1}$) than the one obtained in the transesterification with pure ethanol at 593 K. This observation is

in agreement with results reported by Vieitez et al. [12] in the supercritical ethanol transesterification of soybean oil, where the presence of water (5 wt.% in ethanol) also increased the reaction rate.

The fatty ester content obtained in this study for a given residence time is higher in comparison to previous results obtained by Vieitez et al. [12] for similar operating conditions of temperature, pressure and ethanol to oil molar ratio in the soybean oil transesterification. According to different authors [6,9,12] there is a preferential degradation of polyunsaturated fatty esters at temperatures higher than 573 K. This could explain the difference between the results obtained in this work and those of Vieitez et al. [12]; soybean oil has an important composition of linoleic acid (C18:2, 53 wt.%), while the vegetable oil used in the present study has oleic acid (C18:1, 85 wt.%) as main component, which is less susceptible to degradation.

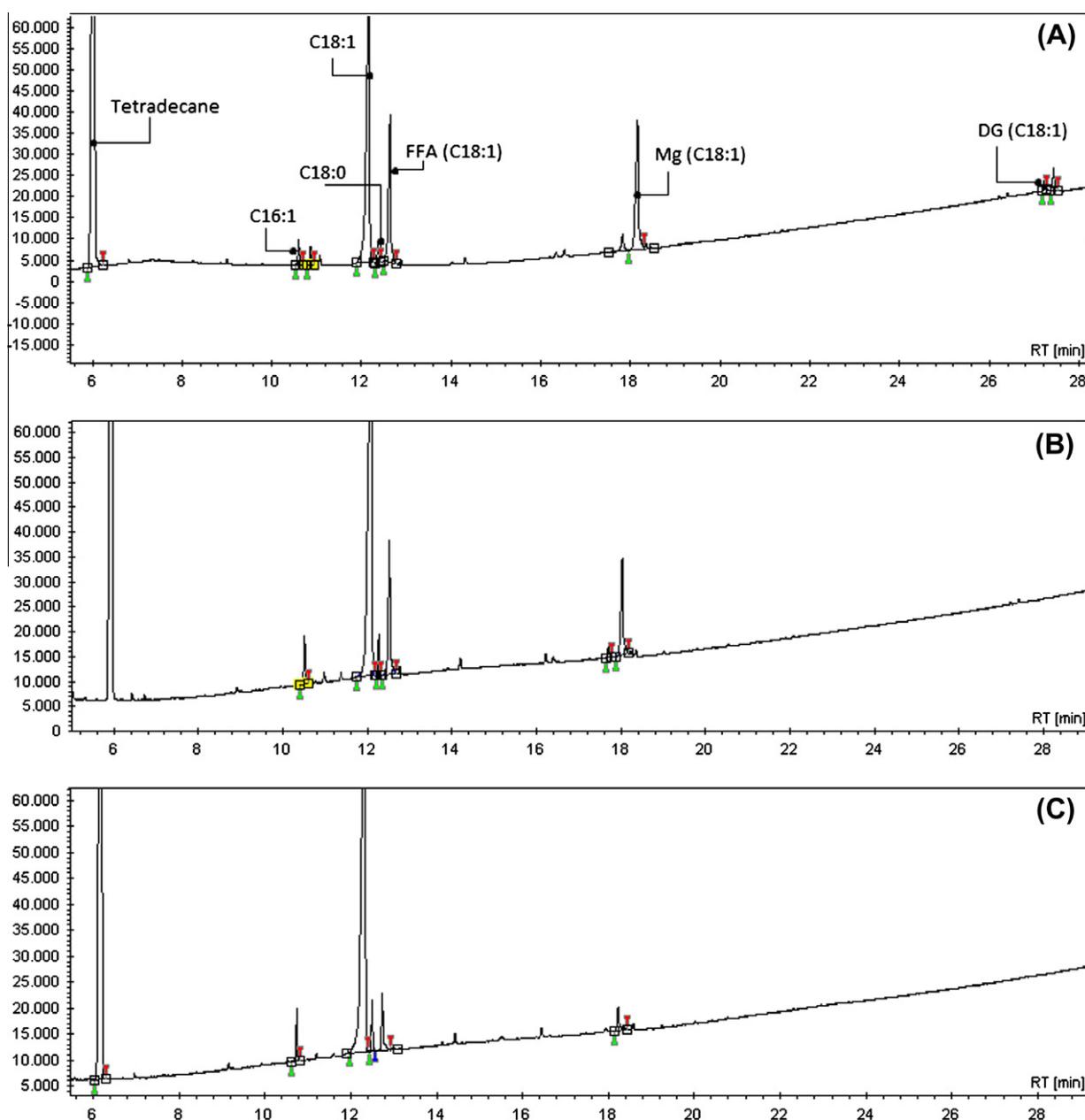


Fig. 8. GC analysis of reaction products in the supercritical transesterification of high oleic sunflower oil with azeotropic ethanol (Run 2, 3 and 4 in Table 4) at different reaction times: (A) 16 min (B) 23 min and (C) 30 min.

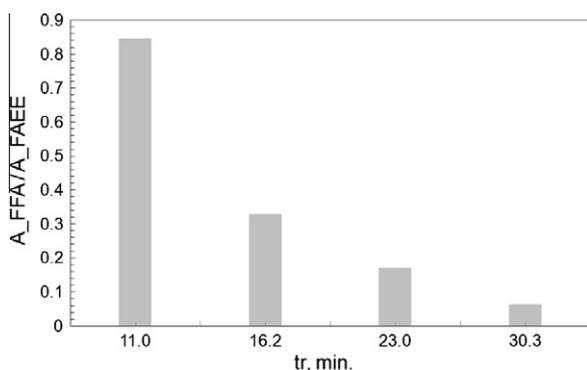


Fig. 9. Chromatographic area of FFA respects to area of FAEE in the reaction products against the residence time.

It is important to mention that when water is present in the system, free fatty acids are detected in the reaction products (see Fig. 8), that were not observed when the reaction was carried out with absolute ethanol. Figs. 8 and 9 show that the FFA content in the reaction products decrease respect to the residence time while there is an increase of the FAEE content in the reaction products. The supercritical ethanolysis is more tolerant to the presence of water; however, the residence time could be a critical variable. Kusdiana and Saka [4] observed a similar behavior in the transesterification of rapeseed oil with supercritical methanol in presence of water. According to these authors, triglycerides were partially hydrolyzed towards fatty acids, which were converted to methyl esters, and after long residence time in the reactor, methyl esters reacted with water again to produce fatty acids. In this work, for the residence times higher than 20 min, it is possible to obtain similar yield towards the fatty esters (90% m/m FAEE in the reaction products), being the fatty acids still present in minor quantities when the reaction was carried out with azeotropic ethanol.

5. Conclusions

In this work, experimental data on the continuous process of supercritical ethanolysis of sunflower oil are presented. The data were obtained for ethanol to oil molar ratio of 40:1 at three different temperatures (573, 593 and 618 K).

Recently measured experimental PVT data of the reactive mixture was modeled with PR-EoS in order to have a tool to predict its specific volume at the different operating conditions. Significant deviations in the calculation of residence time were obtained using the experimental correlation of PVT data with respect to estimations based on assuming ideal solution.

A first-order kinetic model was proposed and a good agreement between experimental and calculated values was observed. The

effect of temperature on the rate coefficient gives an activation energy of 67.6 kJ/mol_{triglyceride} for sunflower oil transesterification with ethanol, which is 27% lower than the one calculated assuming ideal solution volumetric behavior.

The effect of water in the reaction was also studied by using azeotropic ethanol in the transesterification. The final fatty esters content was similar to that of the anhydrous process. However, the rate of transesterification was higher in the case of supercritical transesterification with azeotropic ethanol. This is probably due to a first hydrolysis reaction of triglycerides to produce fatty acids that in the presence of ethanol are readily esterified.

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