

RESEARCH NOTES

Phase Transitions in a Biodiesel Reactor Using Supercritical Methanol

Pablo Hegel, Guillermo Mabe, Selva Pereda, and Esteban A. Brignole*

*Planta Piloto de Ingeniería Química, (Universidad Nacional del Sur—CONICET),
CC 717-8000 Bahía Blanca, Argentina*

Recent experimental studies on noncatalytic 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 methanol. Although it is generally agreed that temperatures of > 550 K and high methanol/oil ratios are required to obtain high conversions and high reaction rates, there is disagreement in the literature regarding the operating pressure, the assumed phase conditions, the use of co-solvents, and the justification of the sudden increase of 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 methyl esters is measured. From direct observations and the modeling of the phase behavior, a better understanding of the supercritical methanol transesterification process is obtained.

1. Introduction

The production of methyl and ethyl esters of fatty acids is of great industrial interest, considering the direct application of these esters as biodiesel. The conventional way of producing fatty acid esters is via catalytic transesterification of vegetable oils (such as soybean or rapeseed oil) with methanol or ethanol. The main products of the reaction are fatty acid esters and glycerin.

When acidic or basic catalysts are used at moderate temperatures, the reaction is slow and, generally, the removal of the catalyst and saponification products from the fatty acid esters + glycerin mixtures complicates the purification of the biodiesel and glycerol. Several proposals have been made to obtain the biodiesel without the use of a catalyst, to simplify the separation of the reaction products, as well as to obtain faster reaction rates by working at higher temperatures. Recent experimental studies of noncatalytic transesterification by Saka and Kusdiana¹ have shown that the reaction rates justify a commercial application if the conditions are similar to the critical properties of methanol.

1.1. Phase Equilibrium Engineering of Noncatalytic Supercritical Transesterification. When the reaction between the oil and methanol is performed with basic or acidic catalysts at moderate temperatures, the oil + methanol immiscibility cannot be avoided, and this effect hinders the rate of reaction. A motivation behind operation at higher temperatures and pressures has been to obtain complete miscibility between the methanol (the most studied alcohol for this reaction) and the vegetable oil. However, complete miscibility, even with methanol, is attained at temperatures well below the critical temperature of methanol (512 K).

Different operating conditions have been proposed for noncatalytic transesterification. Diasakou et al.² performed the reaction of soybean oil with methanol at temperatures close to 510 K and 6 MPa. The methanol/oil molar ratio ranged from 6

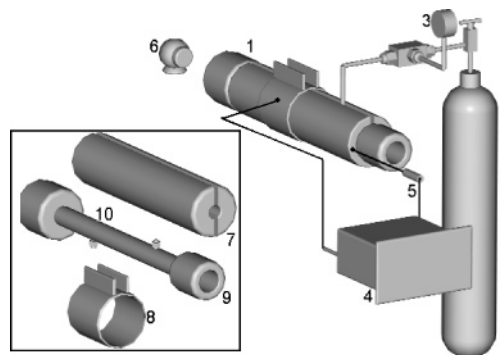


Figure 1. Schematic of the experimental apparatus. Legend: 1, windowed reactor; 2, propane tank; 3, pressure gauge; 4, temperature controller; 5, temperature sensor; 6, camera; 7, aluminum jacket; 8, heating tape; 9, windows; and 10, stainless steel reactor.

to 27. Under these conditions, the rate of reaction was slow and only partial conversion was obtained. Saka and Kusdiana¹ used a small (5 cm³) batch reactor that was charged with rapeseed oil and methanol to study the reaction at ~ 620 K and 45 MPa. Under these rather extreme conditions, the conversion of oil was completed in < 6 min. In a follow-up work, the same authors³ studied the reaction kinetics, and they reported a drastic change in the reaction rate at temperatures in the range of 540–570 K. This effect was attributed to the decrease of methanol hydrogen bonding with temperature, which facilitates the solvation of the triglycerides in the methanol supercritical phase.

Recently, Cao et al.⁴ proposed the use of propane as a co-solvent, to facilitate the operation under single-phase supercritical conditions and, therefore, to reduce the operating pressure and temperature of the reaction process. Their results indicate that it is possible to operate under milder conditions, while simultaneously keeping a high reaction rate, using a propane:methanol molar ratio in the range of 0.05–0.1 and working at 540 K and pressures of ~ 12 MPa. The conditions proposed by these authors are quite different from those of Saka and Kusdiana.¹ Although the reaction kinetics can be highly dependent on the conditions of homogeneity of the reaction

* To whom correspondence should be addressed. Tel.: 54 291 4861700. Fax: 54 291 4861600. E-mail address: ebrignole@plapiqui.edu.ar.

Table 1. Experimental Conditions of the Soy Oil^a Supercritical Transesterification Reactions, Showing the Effect of the Global Density, as Well as the Oil Concentration and Propane Addition

run	Composition (wt %)			global density (g/cm ³)	pressure, <i>P</i> (MPa)	temperature, <i>T</i> (K)	phase conditions	yield (%)
	oil	methanol	propane					
Effect of Global Density								
1	53.93	45.88	0.19	0.8051	14.3	573.1	L	96.0
2	48.28	47.56	4.16	0.5696	8.9	560.9	LV	
3	28.20	67.18	4.62	0.5132	12.6	588.1	SC	
Effect of Oil Concentration								
4	20.16	74.33	5.51	0.4307	11.6	566.3	SC	97.2
5	28.20	67.18	4.62	0.5132	8.8	543.1	LV	
6	48.28	47.56	4.16	0.5696	7.0	543.1	LV	
Effect of Propane Addition								
7	29.57	70.43		0.4895	9.6	560.9	LV	99.0
8	28.20	67.18	4.62	0.5132	10.2	560.9	LV	98.5
9	25.63	61.02	13.35	0.5649	10.9	543.1	SC	96.7
10	22.44	53.45	24.11	0.6450	21.1	560.9	SC	93.7

^a Soy oil molecular weight = 885.

Table 2. Experimental Transition Temperature, According to the Methanol/Oil Molar Ratio and Propane Composition

run	methanol/oil molar ratio	propane addition (wt %)	transition temperature (K)
3	65.88	4.62	588.1
4	102.0	5.51	566.3
9	65.84	13.35	543.1
10	65.87	24.11	516.0

mixture, it seems that operating under supercritical conditions enhances the rate of reaction. Recently, He et al.⁵ proposed a high methanol/oil ratio, a pressure of 35 MPa, and a temperature of 583 K as conditions to achieve high conversion with 25 min of residence time in a continuous reactor. Varma and Madras⁶ proposed operating at 573 K and 20 MPa to obtain a high rate of reaction and conversion.

The purpose of the current work is to determine how the phase conditions, homogeneous or heterogeneous, influence the kinetics and conversion of the supercritical methanol transesterification process. To accomplish this task, an experimental study of the boundaries of the single- and multiple-phase regions of the reacting system vegetable oil + methanol, under different pressures and temperatures, with and without the use of propane is presented in this work. A related problem was investigated by Pereda et al.^{7,8} and applied to the hydrogenation of vegetable oils with solid catalysts, and guidelines for determining feasible conditions for homogeneous fluid phase reactor operation were developed. Baiker⁹ has stressed that overlooking the phase equilibrium analysis of supercritical reacting systems may lead to incorrect conclusions regarding the experimental results.

With the exception of the work of He et al.,⁵ all of the reported studies on supercritical methanol + oil transesterification have been conducted in constant-volume reactors without windows. Therefore, direct observation of the phase behavior during the reaction process has not been possible. On the other hand, the exact mass of reactants and co-solvent charged into the reactor has not been reported, so the global density of the reacting system cannot be calculated. However, by fixing the temperature, the reactor volume, and the amount of each component charged into the reactor, there are no degrees of freedom left for the system and, consequently, the reactor pressure is fixed. Thus, in most cases, the pressure under which the reaction occurs can be measured or calculated, but it is not controlled. Therefore, in the present work, the evolution of phase behavior with temperature during the noncatalytic transesterification process, with and without co-solvent (propane), was

observed under a controlled reactor global density and composition. For this purpose, transesterification experiments were performed in a see-through, two-window cylindrical reactor and the conversion that was achieved under different reaction conditions was measured.

2. Experimental Section

Commercial refined soybean oil was used as vegetable oil. Methanol (99.7% purity) was purchased from Anedra. The propane that was used as the co-solvent had 98.9% purity, as analyzed via gas chromatography (GC). The experimental phase behavior observations were conducted in a fixed-volume reactor. Figure 1 shows a schematic diagram of the equipment used in this study. The reactor is a stainless-steel cylindrical device. It has two windows and a capacity of 32 cm³. A camera (Mitzu Cyber-eye) that has been connected to a personal computer (PC) and placed in front of one of the windows records the visual observation of the reactor contents. Brass screws are used to hold the glass windows against the body of the reactor. A pair of Teflon and Viton O-rings are used as a sealing system. The reactor has an aluminum jacket that is externally heated by two 450 W electrical resistances connected to a temperature controller. The temperature is measured using a 100 Ω platinum resistance thermometer that has been placed in the aluminum jacket and is controlled to within ±2 K for a set time. The pressure inside the reactor is measured by a Bourdon manometer (to within ±0.3 MPa). The reactor has a feed line to load a fixed amount of co-solvent independently. The entire system is isolated with a fiberglass mat, to maintain better temperature control.

The experimental procedure is as follows. The reactor was charged with a given amount of soybean oil (4.5–8 g) and liquid methanol (9–11 g), in different molar ratios. The reactor then was evacuated for 30 min, using a vacuum pump. Part of the methanol evaporated and was collected in a liquid trap at 250 K and weighed, using an analytical balance. A known amount of propane was then added to the reactor as a co-solvent. After the reactor was charged, the temperature was increased up to the desired values as follows. At the beginning of the heating period, the power was adjusted to give a heating rate of 10 K/min up to 423 K, and then it was set to a heating rate of 20 K/min, up to the desired temperature. The experimental conditions studied in this work are shown in Table 1. The desired temperature was controlled for a constant period of 10 min in all the experiments, except in runs 1, 3, and 4. These were

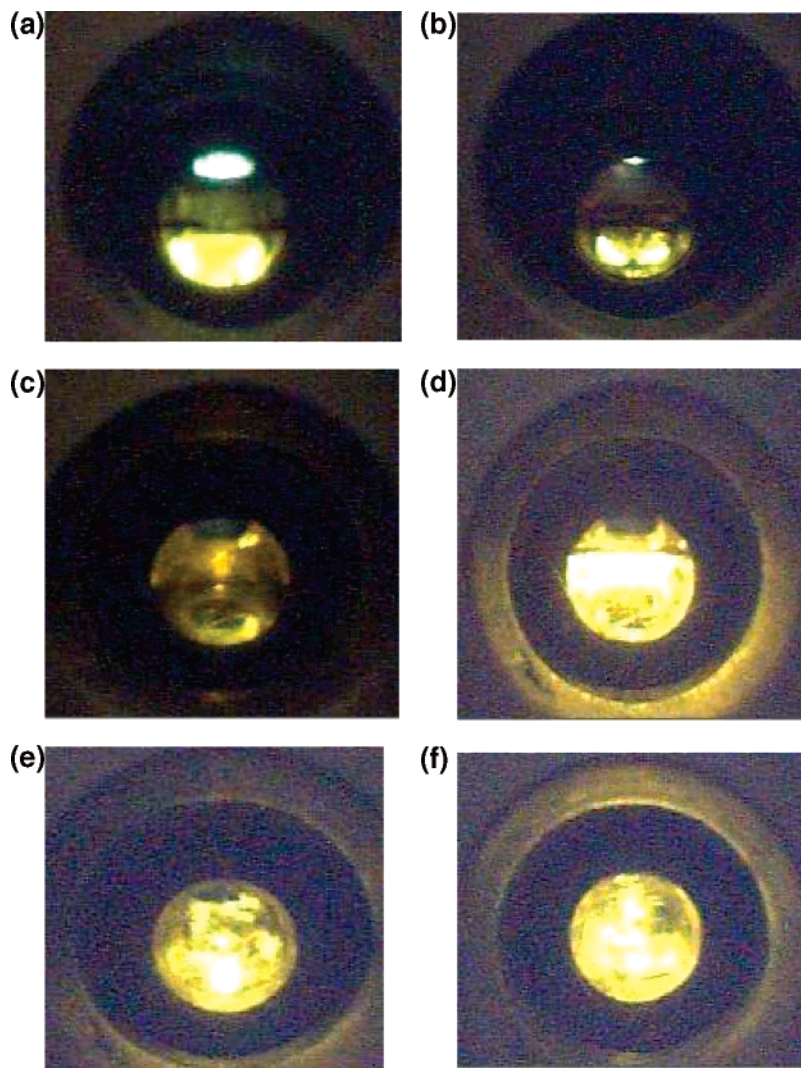


Figure 2. Phase behavior evolution during the heating process of the reacting mixture (run 1): (a) three-phase equilibria (LLV), 298 K, 0.86 MPa; (b) three-phase equilibria (LLV), 413 K, 1.38 MPa; (c) two-phase equilibria (LV), 453 K, 2.76 MPa; (d) two-phase equilibria (LV), 473 K, 3.45 MPa; (e) two-phase equilibria (LV), 513 K, 6.2 MPa; and (f) one liquid phase (L), 563 K, 10.34 MPa.

preliminary runs devoted to study the phase behavior for which the yield of fatty acid methyl ester (FAME) was not measured. Thereafter, the reactor was air-cooled, to quench the reaction. After the experiment, the reactor was evacuated and the oil samples were analyzed via GC, to evaluate the degree of conversion of triglycerides to esters. The analysis of the reaction products was made via GC analysis (GC-Varian Star 3400 CX), using a capillary column (J&W Scientific, model DB-5HT; length = 15 m, inner diameter (ID) = 0.32 mm, film thickness = 0.1 μm) and a flame ionization detector (FID). Hydrogen was used as the carrier gas at a flow rate of 5 mL/min, measured at a temperature of 25 $^{\circ}\text{C}$. The injector and detector temperatures were 320 and 380 $^{\circ}\text{C}$, respectively. Tetradecane was used as an internal standard. A stock solution of pyridine with a known amount of tetradecane was prepared. Samples were prepared by adding ~ 0.05 g of the oil phase to 2 mL of pyridine. A reaction mixture that consisted of 0.1 mL of sample, 0.2 mL N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA), 0.1 mL trimethylchlorosilane (TMCS), and 0.1 mL of internal standard solution was prepared in a 5-mL screw-cap vial with Teflon-faced septa. This mixture was heated at 70 $^{\circ}\text{C}$ for 20 min. Five microliters of the reaction mixture were injected into the GC system. The reactions were performed two times, and two injections were made per reaction (AOCS Official Method Cd 11b-91). The oven temperature program consisted of starting

at 40 $^{\circ}\text{C}$, a ramp from 2 $^{\circ}\text{C}/\text{min}$ to 50 $^{\circ}\text{C}$, and a ramp from 10 $^{\circ}\text{C}/\text{min}$ to 370 $^{\circ}\text{C}$ (15 min).

3. Results

The experimental conditions studied in the present work are given in Table 1. The temperatures reported in this table are those at the end of each run. The temperatures where the transition to the supercritical state was observed were generally different and are reported in Table 2. In the first experimental run, the global density (ρ_G , defined as the total mass charged into the reactor divided by the reactor volume), as well as the oil mass fraction (x_1), were greatest at $\rho_G = 0.8051$ g/cm 3 and $x_1 = 0.5393$, respectively. Figures 2a and 2b show that the system exhibits LLV equilibria at moderate temperatures. At higher temperatures (such as 453 K) (Figure 2c), LV equilibria is observed, because the liquid phase becomes completely miscible. This behavior is also noticed at supercritical methanol temperatures. However, at 563 K (Figure 2f) and higher temperatures, a single-phase system can be observed. At temperatures of >563 K, a high increase in pressure with increasing temperature is observed. This steep increase in pressure is typical of a liquid phase isochoric (constant volume) increase of pressure with temperature. This liquid phase is a homogeneous liquid mixture of fatty acid esters, glycerin, methanol, and propane.

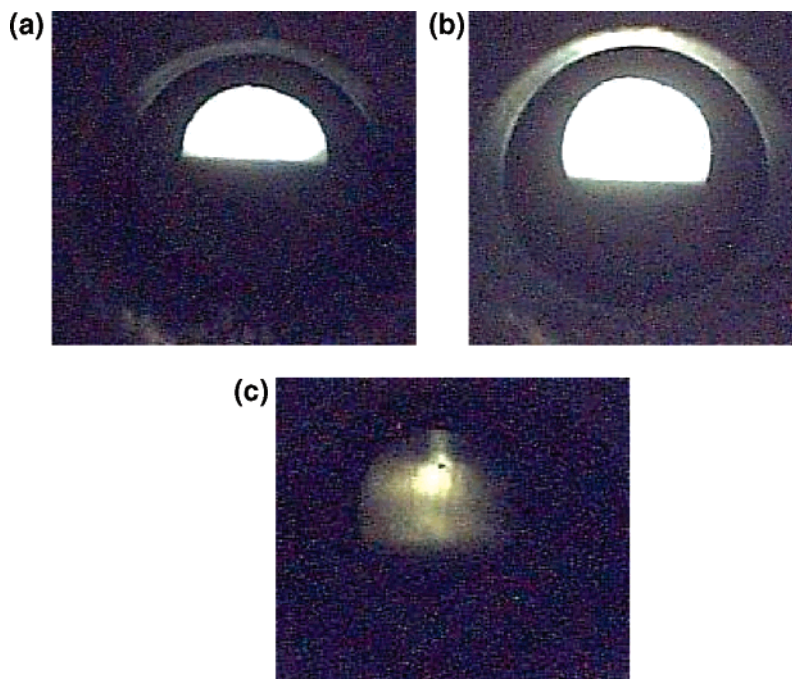


Figure 3. Phase behavior evolution during the heating process of the reacting mixture (run 3): (a) two-phase equilibria (LV), 443 K, 9.31 MPa; (b) two-phase equilibria (LV), 563 K, 11.0 MPa; and (c) transition to supercritical phase behavior (588 K, 12.6 MPa).

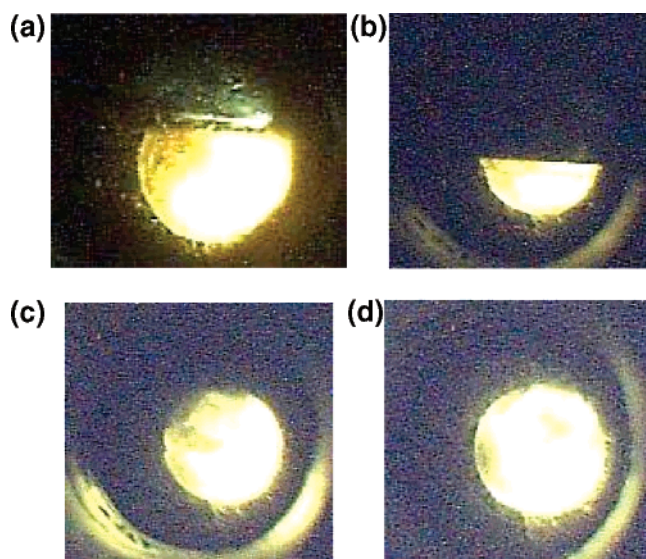


Figure 4. Phase behavior evolution during the heating process of the reacting mixture (run 10): (a) two-phase equilibria (LV), 433 K, 4.83 MPa; (b) two-phase equilibria (LV), 478 K, 6.9 MPa; (c) transition to supercritical phase behavior (516 K, 11.7 MPa); and (d) supercritical behavior (560.9 K, 21.1 MPa).

In run 2, the oil mass fraction and the methanol/oil ratio were similar to those used in the first run, but a smaller mass of reactants was charged into the reactor and the global density was 0.569 g/cm^3 . The concentration of propane in this case was higher than that in run 1. Under these conditions, LV equilibria prevails in the high-temperature range and the homogeneous phase behavior is not achieved. In run 3, the volume of methanol and oil charged to the reactor was less than that in run 1 and the ratio of methanol/oil was greater, which resulted in the reactor composition and global density given in Table 1. A smaller global density was chosen in runs 2 and 3, to prevent the expansion of the liquid phase from filling the entire reactor volume with the consequent isochoric increase in pressure. In run 3, once again, LLV equilibria become LV equilibria at ~ 430

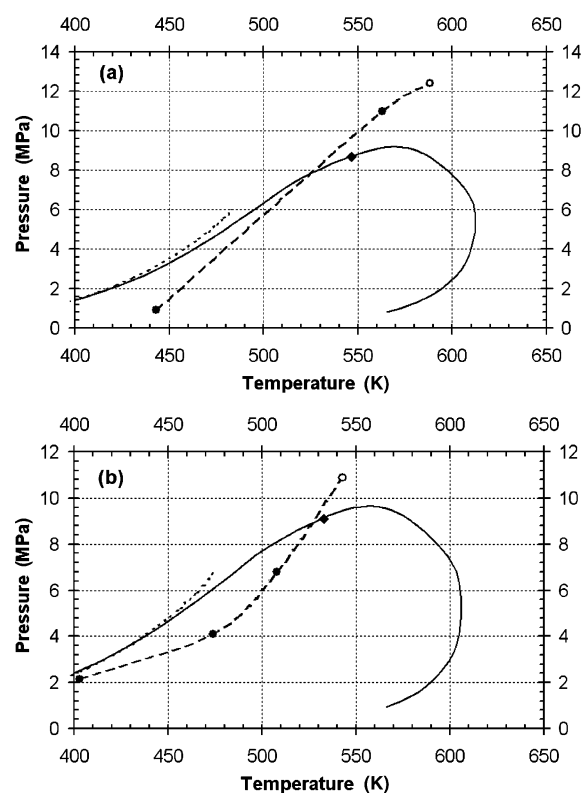


Figure 5. Reaction trajectory (represented by the dashed line) on a pressure–temperature (PT) diagram for (a) run 3 and (b) run 9; the unfilled point corresponds to the final conditions of the reaction. The dotted line represents the GCA–EoS prediction for reactive mixture bubble points (soy oil + methanol + propane), the solid line represents the GCA–EoS prediction for the reaction products phase envelope (methanol + propane + FAME + glycerin). The filled diamond symbol (◆) denotes the critical point.

K and this behavior is observed up to a temperature of 561 K (Figure 3). However, if the temperature is further increased to 588 K, a single opaque fluid phase typical of a supercritical fluid can be observed.

The effect of oil concentration on phase behavior is studied in runs 4–6. In run 4, the mass of methanol and oil charged to the reactor was the smallest, yielding the lowest global density and the greatest methanol/oil ratio. In this case, as in previous runs, there is a transition from LLV to LV equilibria and, at 566.3 K, a single supercritical opaque phase is observed. In this run, the supercritical condition is achieved at a lower temperature than in run 3, using a lower initial fraction of oil in the reactor. In runs 5 and 6, the LV phase behavior prevails up to the end of the reaction period, because of the higher oil concentration and lower final temperatures.

Finally, the effect of propane concentration on the phase behavior is studied in runs 7–10. In Figure 4 (run 10), a supercritical condition can be observed at 516 K for the highest propane concentration. Run 7 was performed without co-solvent. In this case, the observed phase behavior was similar to that observed at low propane/methanol ratios. In runs 8–10, the propane/methanol molar ratios were 0.0507, 0.159, and 0.328, respectively. In each of these experiments, a single-phase supercritical condition was achieved at temperatures that were decreasing as the propane concentration increased: 588, 543, and 516 K (see Table 2).

Table 1 shows the yield of biodiesel obtained in the experimental runs at the reported temperatures and pressures. It can be observed that high conversions were obtained in all cases when the final temperature was 543 K or higher. The lowest yield (88.3%) was obtained in run 6 for this temperature; in this case, the relatively low yield can be explained by the low methanol/oil ratio.

4. Discussion of Results and Conclusions

All previous works have assumed that the role of the supercritical state of methanol was to avoid the two-liquid-phase nature of vegetable oil/methanol mixtures. However, our experiments show that the liquid phase becomes completely miscible at temperatures well below the critical temperature of methanol.

In the first run, the transition from LLV equilibria to LV equilibria occurred at 453 K. In this run, the system exhibited LV equilibria in the methanol supercritical range of 512–563 K, and at higher temperatures, the liquid phase completely filled the volume of the reactor. Thereafter, a steep increase in pressure with temperature was observed. This behavior is observed when the reactor operates at high global densities. This is the case for the Saka and Kusdiana¹ pioneering experiments, where very high pressures are obtained (35–40 MPa) when the reactor temperature is increased from room temperature to the temperature range of 570–620 K. In run 2, when working with a methanol/oil ratio similar to that of run 1, but with a smaller global density, the LV equilibrium condition prevails up to 561 K and the pressure increase with temperature is moderate, even with the use of a co-solvent (propane).

Runs 3 and 4 were performed with higher methanol/oil ratios than those used for runs 1 and 2. In these experiments, it was possible to achieve a homogeneous supercritical phase by increasing the system temperature while working at moderate pressures of 10–15 MPa. Figure 3 shows how the fraction of the light phase increases with temperature, ending up in a supercritical phase. An increase in the methanol/oil ratio decreases the critical temperature of the system (see Table 2), and a similar effect occurs when increasing the propane concentration (runs 7–10). The increase in propane concentration drastically decreases the temperature required to bring the system into a supercritical phase. In run 7 (without propane)

and run 8, similar yields of FAME were obtained; however, using a shorter reaction time and faster quenching conditions, a difference between runs 7 and 8 can be observed.

In each experimental run, the reactor has a particular initial and final composition, constant global density, and thermal history. The reaction system for the final compositions, in each case, results in different pressure–temperature (P – T) phase envelopes, which limit the mixture bubble and dew points, on which the trajectory of the P – T history of each experiment can be drawn. In this sense, we have observed phase transitions that end in either a homogeneous supercritical fluid, a dense liquid phase, or a heterogeneous vapor–liquid system. The fluid mixtures, which are characteristic of supercritical transesterification processes, are asymmetric mixtures of vegetable oils, derivatives, and near-critical solvents. These mixtures have been studied in previous works using the GCA–EOS model (see the work of Espinosa et al.¹⁰ and Ferreira et al.¹¹). Phase envelopes of the transesterification reaction mixtures and their critical points were predicted based on the GCA–EOS model. Figure 5 gives phase envelopes and critical points of the fatty acid ester (methyl oleate) + methanol + glycerin + co-solvent (assuming 100% yield) of runs 3 and 9 (Figures 5a and 5b, respectively). On these diagrams, the reactor thermal history of runs 3 and 9 are also plotted; the predictions agree with the experimental observations of the phase conditions. In addition, a decrease of the critical temperature when increasing propane concentration is clearly shown.

With regard to the effect of heterogeneous phase conditions on biodiesel production, we have observed that a high conversion has been obtained in most cases, even when operating in the two-phase region. In these cases, the oil transesterification possibly occurs mainly in the light supercritical phase, where the oil and the monoglycerides and diglycerides are partially soluble and the concentration of methanol is high. Moreover, the light-phase transport properties favor a higher reaction rate. Also, as suggested by Saka and Kusdiana,¹ the fraction of nonassociated methanol may be higher in the light phase. Finally, as has been observed in the present work, the effect of propane in obtaining high reaction rates at 550 K and 12 MPa reported by Cao et al.⁴ can be explained by an increase in the fraction of light phase, because of a reduction of the system's critical temperature.

Additional experimental work on continuous reactors, with an independent control of pressure, temperature, and residence time is needed to determine the optimum operation conditions of supercritical methanol transesterification reactors.

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