Supercritical production and fractionation of fatty acid esters and acylglycerols

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A B S T R A C T

The production of biodiesel or fatty acid esters (FAE) from lipids with supercritical methanol (scMeOH) has gained interest in the last decade because it allows the direct transesterification of crude oils and fats. The reaction should be carried out above 593 K in order to achieve complete conversion. When milder conditions are set, also monoglycerides (MG) and diglycerides (DG), together with glycerol, are obtained as byproducts of the transesterification process. Acylglycerols are common food emulsifiers and surface active agents in many industrial cleaning products.

The main goal of this work is to study the fractionation of FAE and acylglycerols by using CO_2 as a green solvent. Mixtures of FAE, MG and DG were produced by partial transesterification of sunflower oil with scMeOH in a temperature range of 556–605 K and using different methanol to oil molar ratios (between 20 and 50). Then, experimental data on phase equilibria of reaction products + CO_2 were measured at 298 K and 313 K in a variable volume cell with windows. The measured data were used to test the predictive capability of the Group Contribution with Association Equation of State (GCA-EoS). The acylglycerols can be purified by near critical extraction of the FAE with CO_2. The simulation of the extraction process working with CO_2, in liquid or supercritical state, gives a concentration of acylglycerols higher than 99.8 wt.% in the raffinate phase with a concentration of FAE above 97 wt.% in the extract phase.

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1. Introduction

The production of fatty acid esters or biodiesel is of great interest nowadays because of its direct application in diesel engines. If complete conversion is not achieved, besides fatty acid methyl esters (FAME) and glycerin, acylglycerols are obtained as byproducts; i.e. monoglycerides (MG) and diglycerides (DG) [1]. Most of the currently produced biodiesel uses palm or soybean oil, methanol and an alkaline catalyst.

The main drawback of the conventional technology is that it requires a refined vegetable oil with low content of free fatty acids (FFA) and water because these impurities react with the catalyst [2]. Therefore, the non-catalytic supercritical methanolysis is an interesting alternative for biodiesel industrial production because it is free of the above-mentioned problems; with the additional advantage that cheaper raw materials can be used [3]. The supercritical technology requires high excess of methanol and temperatures above 593 K in order to achieve almost complete triglyceride conversion. Under milder conditions the last step of the reaction, i.e.

transesterification of MG to produce glycerol and FAME, does not proceed to completion. MG is a valuable byproduct due to their application in the food industry as emulsifiers [4] and in the pharmaceutical industry [5].

Commercial MG is obtained via an alcoholysis pathway in which either fatty acids or a fat are reacted with an excess of glycerol. The reaction products contain mainly MG, DG, TG and glycerol, but depending on the glycerol/fat ratio the MG content fluctuates between 40% and 60% of MG [6]. A further refined MG up to around 90 wt% purity, also called "high mono", is conventionally obtained by short path distillation of the reaction products at ca. 473 K and 0.01 mbar or less [6]. This process is expensive and recovers only part of the produced MG. Moreover, MG concentration higher than 96 wt.% cannot be achieved by distillation because of interesterification reactions causes degradation of MG toward glycerol and free fatty acids. Peter et al. [7] proposed an interesting alternative to obtain 99 wt.% purity of MG from the acylglycerides mixture by means of supercritical fluid extraction using mixtures of carbon dioxide and propane as extraction solvents. TG, DG and MG were separated in two countercurrent fractionation columns with a mixture of carbon dioxide and propane [7].

The supercritical fluid fractionation of fatty esters and MG mixtures also appears as a promising process with direct application in

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the biodiesel and food industry. The phase behavior of the system under consideration is required as a function of pressure, temperature, and product concentrations to develop a feasible separation process. The main goal of the present work is to study the fractionation of FAME and MG/DG by using carbon dioxide (CO_2) as a green solvent. CO_2 presents complete solubility with fatty acid esters in a wide range of temperature and pressure and exhibits partial miscibility with acylglycerols (both in liquid and supercritical state); therefore, it should be selective for fractionating the partial transesterification products.

In this work high oleic sunflower oil was transesterified with scMeOH in a batch reactor to study the production of FAME, MG and DG mixtures. Different reaction conditions of temperature (543 K, 573 K and 603 K) and methanol to oil molar ratios between 20 and 50 were evaluated to obtain FAME and MG as main reaction products, with minor quantities of DG. Afterward, experimental data on phase equilibria of the transesterification products and CO_2 were measured in a variable volume cell. The multicomponent system was studied at 298 and 313 K and pressures between 75 and 110 bar. Finally, the GCA-EoS [8] (group contribution with association EoS) was used to model the measured data. Phase scenarios suitable for the design of the extraction process, were identified following a phase equilibrium engineering approach.

2. Thermodynamic model

As it was indicated in the previous section, the reaction products studied in this work are complex mixtures of fatty acid esters and acylglycerols (MG and DG) which have hydrocarbons chains of different length and degree of unsaturation. Nevertheless, their molecular structure can be characterized with few functional groups. Moreover, the presence of highly polar groups increases the mixture non-ideality due to the association effects between molecules [8]. Consequently, the Group Contribution with Association Equation of State (GCA-EoS), which is also an adequate model for size-asymmetric mixtures [9], was selected to predict the phase equilibria of the system under study.

The GCA-EoS model is based on a group contribution expression of the configurational Helmholtz function that describes intermolecular forces through three contributions: the two classic repulsive and residual terms and a third expression that quantifies the association forces. Details of model equations can be found elsewhere [10].

In this work, it was assumed that under the studied operating conditions, MG/DG distribute equally between the liquid–vapor, and liquid–liquid phases in equilibrium with CO_2. Thus, all the acyl-glycerides present in the reaction products were modeled as MG. This assumption is based on previous experimental data reported by Nilsson et al. [11] that show a similar concentration of MG and DG in supercritical CO_2 for the range of pressure and temperature studied in this work.

The FAME and MG/DG products were modeled as single pseudo-components following the procedure described by Espinosa et al. [12]. Given that the starting oil has high content of oleic acid, methyl oleate and monoolein reproduced the mean molecular weight and degree of unsaturation of FAME and MG/DG components in the reaction products, respectively.

The model parameters proposed by Espinosa et al. [12], Cismondi et al. [13] and Andreatta et al. [14] were used to evaluate the phase equilibria of mixtures containing FAME, MG/DG and CO_2 (reported in the Appendix). Critical properties of oil derivatives were estimated with the group contribution method developed by Constantinou and Gani [15]. Also, a correlation [12] based on the van der Waals volume (r_{vw}) was used to determine their critical diameter (d_c). All critical properties are given in Table 1. Moreover,

Table 1
Critical properties used in this work.

	T_c (K)	P_c (bar)	d_c
Methyl oleate	767	10.5	7.975
Monoolein	829	10.3	8.500
CO_2	304.1	74.0	3.129

phase diagrams of binary system were calculated with the software GPEC (Global Phase Equilibrium Calculations) [16].

3. Experimental procedure

3.1. Materials

Sunflower oil of high oleic acid content obtained from hybrid seeds (traded by Dow Agrosciences, Bahía Blanca, Argentina) was used to carry out the transesterification reactions. Table 2 reports the major fatty acid profile of the vegetable oil, evaluated according to the AOCS method (see following section). Methanol (99.8 wt.%) and CO_2 (99.9 wt.%) were purchased from Anedra (Buenos Aires, Argentina) and Linde AG (Buenos Aires, Argentina), respectively. Methyl heptadecanoate (99.9 wt. %), methyl oleate (99.9 wt. %), monopalmitin (99.9%) and dipalmitin (99.9 wt.%) from Sigma–Aldrich (Buenos Aires, Argentina) were used as analytical standards. N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) was used as silylating agent.

### 3.2. Gas chromatographic analyses

The oily samples were analyzed by gas chromatography in a GC – Varian Star 3400 CX. The equipment was assembled with a flame ionization detector (FID) and a capillary column (J&W Scientific, model DB-5ht, 15 m length, 0.32 mm inner diameter, and 0.10 μm film thickness). The chromatographic temperature conditions were selected according to the European norm BS EN 14105:2003 which was modified according to the AOCS Official Method (Cd 11b-91), to determine FAME, MG, DG and TG. Tetradecane was used as internal standard, and 99% methyl heptadecanoate was used as reference of FAME for a calibration curve. A stock pyridine solution with a known amount of internal standard was prepared (∼10 mg/ml). The sample solution was prepared by diluting 50 mg of oily phase in 5 mL of pyridine. The sample injected to the chromatograph consisted of 2 μl of a solution prepared with 0.1 ml of the internal standard stock solution, 0.1 ml of sample solution and 0.1 ml of silylating agent (MSTFA).

3.3. Supercritical alcoholysis

The transesterification reactions of sunflower oil of high oleic acid content were carried out with supercritical methanol in a batch reactor of ca. 40 ml (Fig. 1). The equipment and experimental procedure had been explained elsewhere [17]. Briefly, the reactor was first loaded with a given amount of oil and alcohol, previously weighed in a precision balance. The initial charge to the reactor was chosen to obtain a mass global density between 0.45 g/cm³ and 0.6 g/cm³. In this way it was possible to keep the pressure between 130 bar and 200 bar for the selected operating

Table 2
Major Fatty acid profile of the vegetable oil used in this work.

Fatty acids	Mass fraction (%)
C16:0	7
C18:1	87
C18:2	6
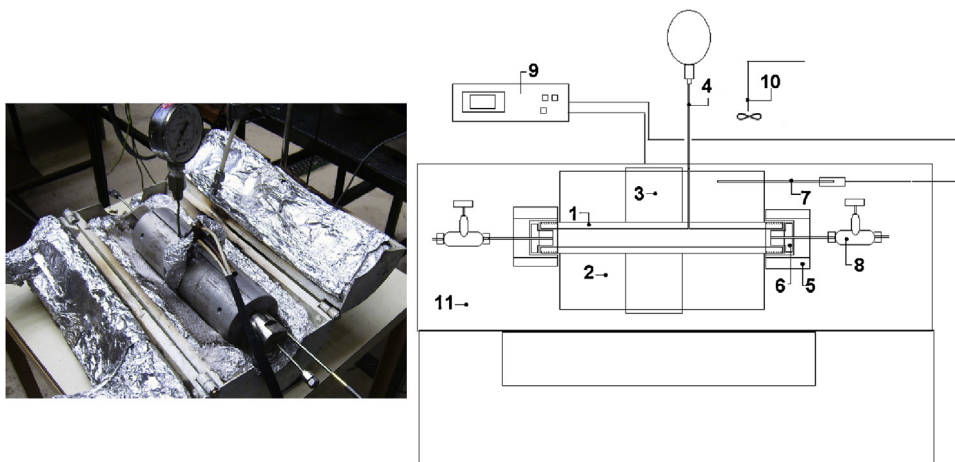
Fig. 1. Scheme of the batch reactor used for supercritical methanolysis of sunflower oil: (1) high pressure stainless steel tube (ca. 40 ml), (2) aluminum jacket, (3) electric heat resistance, (4) pressure gauge, (5) retention screw, (6) seal system, (7) temperature sensor, (8) high pressure/temperature valves, (9) temperature controller, (10) cooling compressed-air line (7 kg/cm^2), and (11) isolated high temperature box.

temperatures. According to previous works [19], under these conditions it is possible to assure that the reactive mixture is in a single phase. The trapped air was evacuated from the reaction cell by flushing it with nitrogen. Afterwards the temperature was raised at a rate of 5 K/min up to the desired value. The reaction time was arbitrarily assumed as the time the reactor was kept at the selected reaction temperature. At the end of each run, the heating was turned off and the reactor was air-cooled to quench the reaction. The system temperature was lowered to 150 °C in 1 min and left ca. 20 min to reach ambient temperature before opening the reaction cell. The methanol excess was removed in a rotary-evaporator under vacuum at 70 °C and glycerol was separated by decantation. The liquid products obtained split up in two phases: glycerol and lipid phases after methanol evaporation. The fatty acid esters, MG, and DG remain in the lipid phase, whose compositions were determined chromatographically. The experimental error obtained in replicated runs was up to 3.5 wt.% in FAME composition and 2.5 wt.% in MG and DG composition.

3.4. Phase equilibria of reaction products with CO_2

The phase equilibria of the system FAME + MG/DG mixtures and CO_2 were determined in a variable volume equilibrium cell, previously described elsewhere [18]. The cell maximum volume is 80 cm^3 and equilibrium data up to 20 MPa and 420 K can be measured. The pressure is controlled through volume changes with a movable piston, which is also used to keep the pressure constant during sampling. The cell has a magnetic stirrer and two windows for internal visual observation. Temperature is controlled inside the cell by a proportional controller and monitored with a platinum RTD probe. The pressure inside the cell was monitored with a pressure transducer (Ashcroft PT Indicator).

Fig. 2 shows a schematic diagram of the experimental set up. The experimental procedure was as follows. The cell was flushed with CO_2 at low pressure to remove the residual air and then evacuated through a vacuum line. A given amount of oil (∼7 g) was fed into the cell from the oil vessel. Then, CO_2 was fed into the cell using a manual pressure generator. The temperature control and the magnetic stirrer were turned on; once the set temperature was reached the pressure was increased up to the desired value by displacement of the movable piston. When the conditions reached steady state (∼2 h) the magnetic stirrer was turned off and the system left to settle overnight before sampling (∼10 h). The samples of the liquid phases were collected into glass vials (1.5 ml)

by depressurization using manually operated valves with external loops (Reodyne). In a typical study, the total amount of the oil phases collected in the glass vials was about 300 and 100 mg for the heavy and light liquid phase, respectively. The liquid samples were weighed in a precision balance with an accuracy of ∼0.1 mg. On the other hand, the CO_2 content in each phase was obtained volumetrically [18]. At ambient conditions, the volume of solvent was about 100–200 cm^3 for the heavy liquid phase and 2000–4000 cm^3 for the light liquid phase. The experimental error of CO_2 concentration in the heavy liquid phase was greater than in the solvent phase. Replicated measurements of liquid/liquid equilibrium showed an error in CO_2 concentration up to 2 wt.% in the heavy liquid phase and 0.2 wt.% in the light liquid or solvent phase. Oily products concentrations (FAE, MG and DG) in both liquid phases presented an error of 0.5 wt.%.

4. Results and discussion

4.1. Production of FAME and MG by methanolysis

Table 3 summarizes the experimental operating conditions studied in this work and the FAME, MG and DG content of the oil products in each case. The reaction was carried out during 40 min in most experiments, with only a few runs of 20 min. Three different temperatures were evaluated in the range of 543–603 K using a methanol to oil molar ratio between 20 and 50. A FAME content above 40% was obtained in all runs. However, in order to minimize the selectivity toward DG and FFA, the reactor should be operated at 573 K, where the FAME content was around 80 wt.%. On the other hand, MG concentration in the reaction products was very low at 603 K at the reactants molar ratios studied in this work. Moreover, evidence of degradation was observed at this temperature in the chromatographic analyses, which was more noticeable for the lower methanol to oil molar ratios (20 and 30). The decomposition of unsaturated FAME has been previously reported in the literature [20–22]. Imahara et al. [21] observed the decomposition of methyl oleate at temperatures higher than 573 K with exposure times higher than 20 min. Depending on the conditions, complete triglyceride conversion was achieved and the main reaction products identified in the chromatographic analyses were FAME, MG, and DG and FFA.

Table 3 also shows that similar quantities of MG and DG were obtained at 543 K and their concentration in the reaction products remained constant independently of the methanol to oil
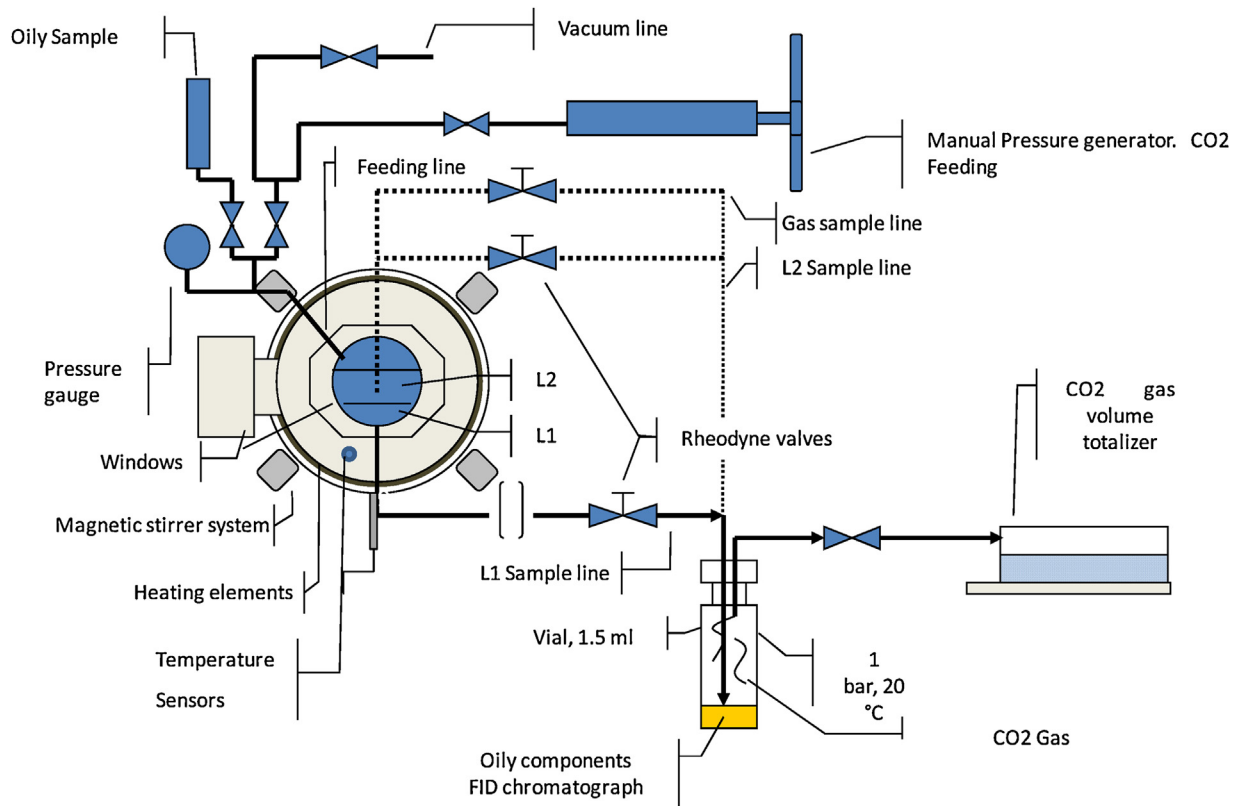
Fig. 2. Schematic diagram of the experimental set up used in the phase equilibria study of mixtures of FAME + acylglycerides + CO_2.

molar ratio. However, high concentrations of free fatty acids and triglycerides were determined in the reaction products at this temperature.

The best experimental response was obtained at 573 K with methanol to oil molar ratios above 30, where DG was present in minor quantities (3–5 wt.%) and a significant amount of MG (11–16 wt.%) was obtained (shadowed rows in Table 3). Also, the content of triglycerides and free fatty acids were negligible in the reaction products obtained at 573 K.

Results shown in Table 3 are in agreement with previous works published in the literature about supercritical methanolysis of

vegetable oils [17,20]. For example, Valle et al. [17] obtained 84 wt.% of FAME content working in a batch reactor with a mixture of methanol and fodder radish oil (40 to 1 MeOH to oil) at 609 K and 16 min of reaction time.

4.2. Phase equilibria of CO_2+reaction products

Before measuring the reaction product phase equilibrium, the behavior of the system was predicted with GCA-EoS. In order to test the model predictive capacity, the binary data available in the literature [11,23] were evaluated first.

Table 3
Results obtained in this work to study the transesterification of high oleic sunflower oil by scMeOH. Reaction time: 40 min and 20 min (MR, molar ratio).

T (K)	MR	ρ (g/cm^3)	P (bar)	FAME (wt%)	MG (wt%)	DG (wt%)	FA (wt%)	TG (wt%)
Reaction time: 40 min								
543	20	0.6	140	51	16	21	3	9
	30	0.6	150	49	14	21	3	13
	40	0.55	135	50	14	22	4	10
	50	0.5	140	44	14	26	4	12
573	20	0.5	160	78	14	6	2	0
	30	0.5	170	77	16	5	2	0
	40	0.5	180	84	11	3	2	0
	50	0.45	180	82	12	4	2	0
603	20	0.45	170	86	4	0	1	0
	30	0.45	180	81	2	0	1	0
	40	0.45	188	90	2	0	1	0
	50	0.45	200	90	2	0	1	0
Reaction time: 20 min								
573	20	0.5	160	70	15	13	2	0
	40	0.5	180	83	12	3	2	0
603	20	0.45	170	81	5	0	1	0
	40	0.45	189	88	4	0	1	0

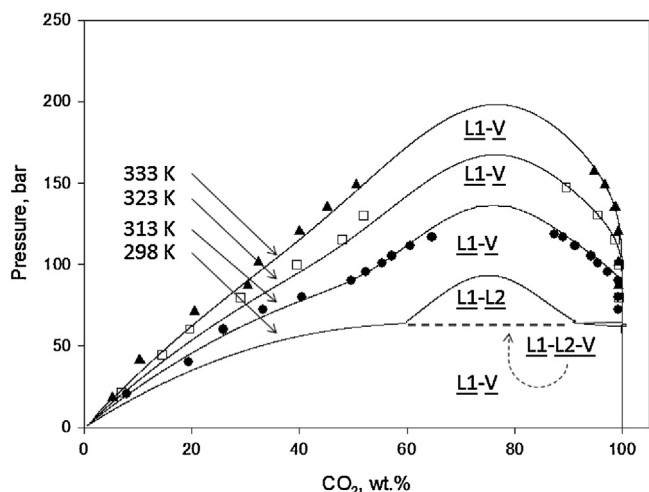**Fig. 3.** Phase behavior of the mixture CO_2 + methyl oleate. Symbols: experimental data reported by Inomata et al. [23]. Lines: GCA-EoS predictions.

4.2.1. Phase behavior of CO_2 + methyl oleate

Fig. 3 shows the phase equilibria of the binary CO_2 + methyl oleate in a pressure – composition diagram at different temperatures (298, 313, 323 and 333 K). GCA-EoS predictions of the system are in agreement with experimental data reported previously by Inomata et al. [23].

According to GCA-EoS predictions, the system presents liquid–liquid–vapor equilibria (L1–L2–V) at temperatures lower than CO_2 critical temperature. For example, at 298 K and 64 bar the system exhibits L1–L2–V phases and the solubility of methyl oleate in the liquid solvent (L2 phase) is approximately ~8.5 wt.%. The vapour phase collapses over 64 bar, and partial liquid–liquid miscibility remains in the system up to ~93 bar. According to GCA-EoS predictions at 298 K, there is an increment of FAME solubility in the liquid solvent phase with pressure. An increase of pressure from 64 bar to 93 bar raises the solubility up to 25 wt.%.

Temperatures higher than the CO_2 critical point show liquid–vapour equilibrium. For example, the system exhibits L1–V equilibrium at 313 K and pressures lower than ~135 bar. In this

case, FAME shows a low solubility in the solvent phase (V) at pressures lower than 90 bar. As usual, higher operating temperatures require higher pressures to avoid partial miscibility between the substrate and solvent.

4.2.2. Phase behavior of CO_2 + monoolein

Carbon dioxide has a rather low dissolving power for many natural products, particularly when these are highly polar or have long hydrocarbon chains, as it is the case of the vegetable oil derived MG. Fig. 4 shows the phase equilibria of the mixture CO_2 + monoolein predicted by the GCA-EoS. The binary system is highly immiscible and exhibit liquid phase partial miscibility at temperatures lower than the critical temperature of CO_2. GCA-EoS predictions indicate that the solubility of MG in the liquid solvent phase (L2) at 298 K and 75 bar is 0.013 wt.%. Moreover, it increases with pressure (0.15 wt.% at 200 bar).

At temperatures higher than the CO_2 critical point, the system presents liquid–vapour equilibria (Fig. 4). The MG solubility in the solvent phase (V) is very low. Nilsson et al. [11] measured monoolein solubility in supercritical CO_2 at 323 K and 333 K. The authors found a MG solubility of 0.22 wt.% at 323 K and 151 bar. Furthermore, it increases with pressure up to 0.7 wt.% at 241 bar. GCA-EoS predictions are in good agreement with the experimental data (see Fig. 4b). Diolein solubility, according to these authors [11], is 0.16 wt.% at 323 K and 151 bar and 0.8 wt.% at 241 bar, showing a similar behavior to MG.

According to the phase behavior associated to these binary systems, it is not convenient to carry out the FAME extraction at pressures higher than 150 bar and temperatures higher than 313 K, to avoid the co-extraction of the MG. However, it should be above 90 bars to ensure FAME extraction with CO_2. Nevertheless, to achieve better FAME solubility, a liquid CO_2 extraction at 298 K might work out at lower pressures since FAME solubility is higher.

4.2.3. Reaction products + CO_2

Fig. 5 shows experimental results obtained in this work at 298 K and 75 bar. The system exhibits liquid phase split (L1–L2) under this condition. For example, a product mixture with 20 wt.% of MG splits in two liquid phases when mixed with near critical CO_2. The extract phase, rich in solvent (L2), has ~9 wt.% FAME (98.5 wt.% on a
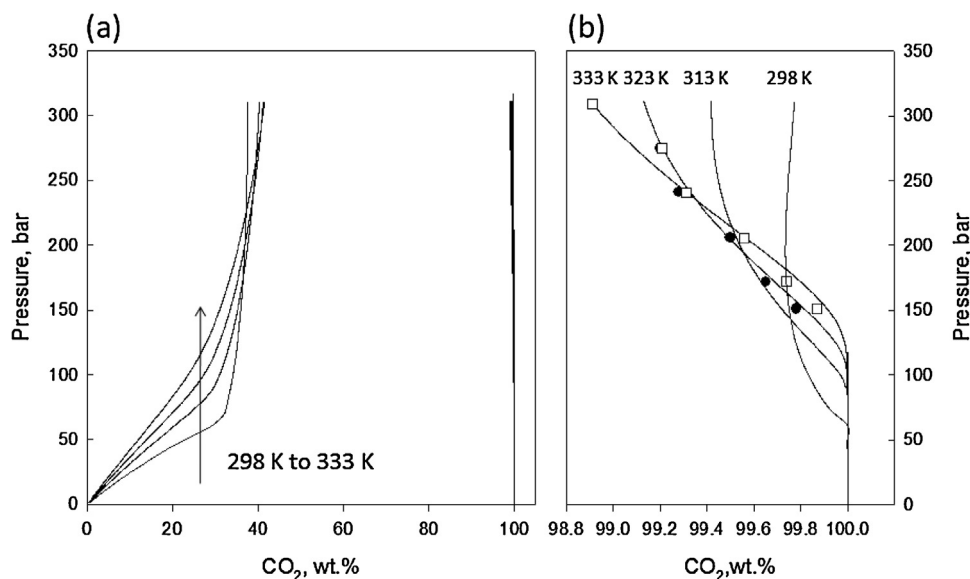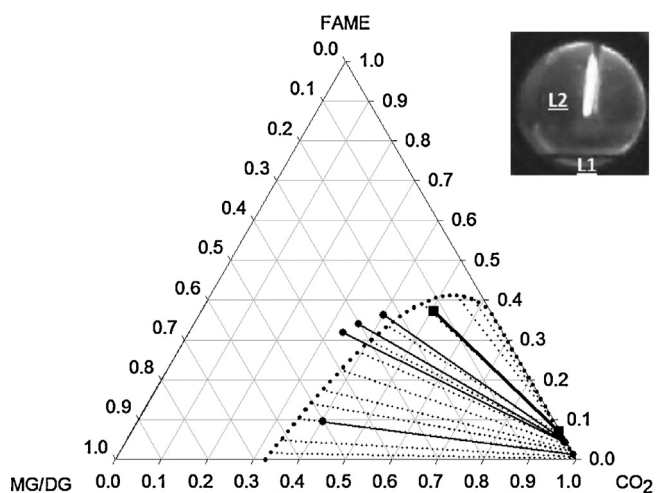

Fig. 4. Phase behavior of the mixture CO_2 + monoolein. Symbols: experimental data reported by Nilsson et al. [11] at 323 K (●) and 333 K (□). Lines: GCA-EoS predictions.
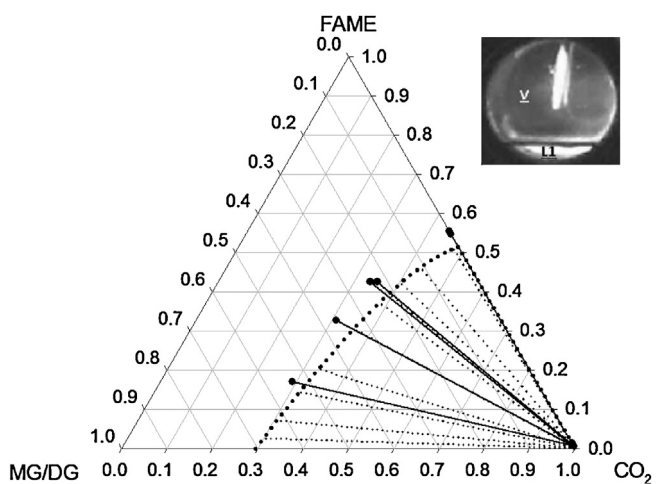
Fig. 5. Phase diagram for the system CO_2 + FAME + MG at 75 bar and 298 K. Symbols and solid tie lines: Experimental data obtained in this work. Dotted lines: GCA-EoS predictions.
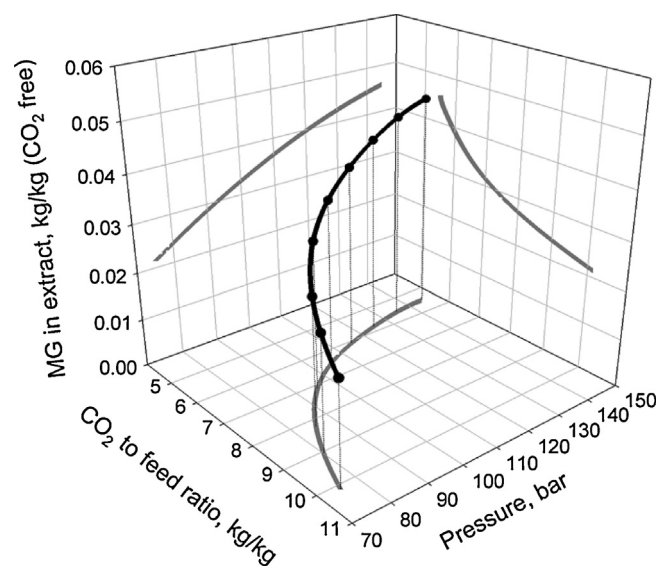

Fig. 7. Seven-stage countercurrent liquid extraction processes for FAME/MG separation using CO_2 at 298 K. MG content in the extract phase (on a CO_2-free basis) as a function of the operating pressure and the feed CO_2 mass ratio.

solvent free basis) and the raffinate phase rich in oily products (L1) with a CO_2 concentration of ~50 wt.% (experimental points shown with squares in Fig. 5).

Fig. 5 also shows that the GCA-EoS liquid–liquid predictions of the ternary system give a good representation of the phase behavior. The dispersion of the experimental data on L1 phase was greater at this pressure in comparison with other measurements. The experimental error associated to these measurements is important because of the high density of the liquid phases to be sampled and the sensitivity of the system to small changes in pressure (~0.5 bar).

Fig. 6 shows the phase equilibria of the system at 313 K and 90 bar. Of course, in this case the system exhibit liquid–vapour equilibria (L1–V). The concentration of CO_2 in the liquid phase is between 30 and 45 wt.%. On the other hand, the solubility of FAME in the solvent phase (V) is very low (<0.5%). From the point of view of the extractive process, it is inconvenient to operate at 90 bar and supercritical temperatures due the very low solubility of FAME in CO_2 under these conditions. Fig. 6 also shows that the GCA-EoS model qualitatively predicts the system behavior with a slight under-prediction of the CO_2 concentration in the raffinate phase.

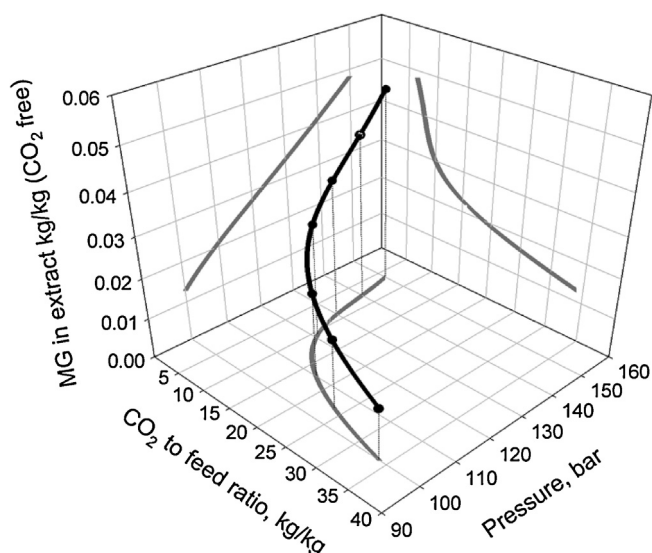### 4.3. Separation process of FAME and MG by liquid and supercritical CO_2

According to the phase behavior of the ternary system the reaction products can be fractionated with CO_2 under liquid or supercritical state. In order to compare operating conditions (temperature, pressure and solvent load) of a counter-current column, a multi-component extraction was simulated based on the GCA-EoS predictions of phase equilibria. The routine is based on the GCEXTRACT program developed by Andersen [24] and more details can be found elsewhere [25,26]. A seven-stage isothermal extractor was assumed for the fractionation of a reaction product containing 80 wt.% of FAME and 20 wt% of MG. Moreover, the solvent load was calculated specifying a FAME concentration of 0.2 wt.% in the refined product.

GCA-EoS predictions showed that the binary CO_2 + FAME exhibits complete miscibility at 298 K and pressures near or higher than 100 bar (Fig. 3). On the other hand, the binary CO_2 + MG depicts partial liquid miscibility with a very low solubility of MG in the solvent phase. The experimental liquid–liquid determinations of the ternary mixture described previously at 298 K and 75 bar are in agreement with these observations indicating that it is technically feasible to carry out a liquid–liquid extraction process.

Fig. 7 shows the simulation of the FAME/MG separation at 298 K in a pressure range of 70–150 bars. This figure depicts the MG concentration in the extract (on a CO_2 free basis) as a function of pressure and the solvent to feed mass ratio required to achieve the specification of 99.8 wt% MG in the refined product. As expected, the solvent load decreases with the extractor pressure; however, above 110 bar, the required load does not substantially decrease (ca. 5.75 kg of CO_2/kg Feed). On the other hand, the MG in the extract increases almost linearly with pressure from about 2.1 wt% to 4.5 wt.% at 75 bar and 145 bar, respectively.

When the separation process is operated at 298 K and 75 bar (experimental conditions, reported in Fig. 5) it is necessary to load 10 kg CO_2/kg Feed to achieve the specification. This high load is mainly due to the partial liquid miscibility between CO_2 and methyl oleate at these operating conditions [23].

Solid–liquid equilibria could be present when the system is operated at low temperatures, due to the high melting point of MG (35 °C). However, the CO_2 solubility in MG lowers the melting point

Fig. 6. Phase diagram for the system CO_2 + FAME + MG at 90 bar and 313 K. Symbols and solid tie lines: Experimental data obtained in this work. Dotted lines: GCA-EoS predictions.

Fig. 8. Seven-stage countercurrent supercritical extraction processes for FAME/MG separation using CO_2 at 313 K. MG content in the extract phase (on a CO_2-free basis) as a function of the operating pressure and the feed CO_2 mass ratio.

of the mixture, based on the eutectic behavior. This is in accordance with the experimental determinations carried out at 298 K, where solid–liquid equilibrium was not observed.

A higher selectivity through the extraction of FAME could be obtained operating the extraction process at 313 K with CO_2 under supercritical conditions. Experimental data reported previously [23] indicate that the pressure should be higher than 90 bar in order to obtain a good solubility of fatty acid esters in the supercritical CO_2 phase. Also, previous results pointed out a lower solubility of MG in the extract phase at a given pressure.

Like the previous study, Fig. 8 shows the simulations of the FAME/MG separation in the same pressure range but at 313 K, i.e. supercritical extraction. The results in this case are quite similar to the liquid–liquid operation. A sharp increase in the required CO_2 load to reach the specified MG content in the refined product at pressures between 100 bar and 120 is observed. However, the MG in the extract phase increases linearly with pressure. The advantage of the supercritical operation is the higher selectivity toward fatty acid esters that allows losing a lower amount of MG in the extract phase for a given pressure. On the other hand, the main drawback in comparison with the operation at 298 K is a higher solvent to feed ratio in order to achieve the refined product specification. For example, according to Fig. 8 at 110 bar the extraction process at 313 K requires ~17 kg CO_2/kg Feed. However, the amount of MG in the extract phase for the supercritical conditions (~2 wt% MG) is lower than that obtained using liquid CO_2 at 298 K (3.6 wt% MG). In contrast, if the amount of MG in the extract phase is specified at 3.5 wt% (on a CO_2 free basis), then it is possible to achieve the 99.8 wt% MG in the refined phase working at 313 K and 130 bar with a solvent to feed ratio of 8.7 kg CO_2/kg Feed.

5. Conclusions

The production of fatty acid methyl esters and acylglycerols by supercritical methanolysis was studied. A reaction product containing FAME, MG and DG (~80, 16 and 4 wt.%, respectively) was obtained feeding the reactor with a 30/1 methanol/oil molar ratio and operating at 573 K.

The partitioning of FAME and acylglycerides with liquid and supercritical CO_2 was determined experimentally in a variable volume equilibrium cell at 298 K and 313 K. The results showed that it

would be possible to separate FAME (98 wt.% purity) from a MG/DG mixture operating under liquid–liquid–vapour and liquid–liquid equilibria at 298 K/64 bar, and 298 K/75 bar, respectively.

The GCA-EoS model shows a good predictive capability of the ternary system FAME + MG + CO_2 multiphase behavior under the studied conditions at 298 K (LLV, LL) and 313 K (LV). Thus, the model is a reliable tool to design a high pressure CO_2 multistage extraction process.

A countercurrent extraction process of seven stages employing CO_2 as solvent in liquid and supercritical state was simulated to obtain a refined product of 99.8 wt% MG. A reaction product mixture with 80 wt.% of FAME can be separated using ~7 kg of CO_2/kg oily products by countercurrent extraction at 298 K and ~110 bar, obtaining an extract phase with only ~3.5 wt% of MG. Operating the extractor at 313 K and similar pressures allows to reduce the MG content in the extract phase (~2 wt% MG), reducing the MG lost from almost 15% to less than 8%. However, higher CO_2 to Feed ratios (17 kg CO_2/kg Feed) are required in order to achieve the MG specification in the refined products.

Acknowledgments

Appendix.

Tables 4–6 summarize the complete set of pure-group and binary interaction model parameters required for predicting the

Table 4
GCA-EoS pure group parameters [12–14].

Group	T^* (K)	q	g^*	g'	g''
CH$_3$	600	0.848	316,910	−0.9274	0.0
CH$_2$	600	0.540	356,080	−0.8755	0.0
CH$_2$COO	600	1.42	831,400	−1.0930	0.0
CH$_2$OH	512.6	1.124	787,954	−0.3654	0
CHOH	512.6	0.904	787,954	−0.3654	0
CH=CH	600	0.867	403,590	−0.7631	0.0
CO$_2$	304.2	1.261	531,890	−0.5780	0.0

g^*, surface energy parameter and its temperature dependence (g' and g''); q, normalized van der Waals surface area; T^*, characteristic reference temperature of each group.

Table 5
GCA-EoS group–group interaction parameters [12–14].

i	j	k_{ij}^*	k_{ij}'	α_{ij}	α_{ji}
CH$_3$/CH$_2$	CH$_2$OH /CHOH	0.987	0	0	0
CH$_3$/CH$_2$	CH=CH	1	0	0	0
CH$_3$	CO$_2$	0.980	0.150	0	0
CH$_2$	CO$_2$	0.930	0.150	0	0
CH$_3$	CH$_2$COO	0.869	0	0	0
CH$_2$	CH$_2$COO	1.500	0.646	0	0
CH$_2$COO	CH$_2$OH/ CHOH	0.905	0	0	0
CH$_2$COO	CH=CH	1.006	0	−0.876	−0.876
CH$_2$COO	CO$_2$	1.115	0.094	−1.615	−1.615
CH$_2$OH	CH=CH	1	0	0	0
CHOH	CH=CH	0.816	0	0	0
CH$_2$OH/CHOH	CO$_2$	0.980	−0.010	0	0
CH=CH	CO$_2$	0.948	0	0	0

k_{ij}^* and k_{ij}': binary interaction parameter and its temperature dependence; α_{ij} and α_{ji}: non randomness parameters.

Table 6
GCA-EoS association parameters [14].

	ε/k (K)	k (cm^3/mol)
Self association OH^{glycerol}	2480	0.7350
Cross association OH^{glycerol}–COOCH$_2$	2200	0.9100

ε/k and k: are the association energy and volume parameters.

phase behavior of binary and ternary mixtures between CO_2, methyl oleate, and monoolein.

Methyl oleate was represented by the following group composition: 1 ester group (CH_2COO) + 1 olefin group ($CH{=}CH$) + 15 paraffin groups ($2CH_3 + 13CH_2$). Monoolein, on the other hand, was represented by the following group composition: 2 alcohol groups (CH_2OH and $CHOH$) + 1 ester group (CH_2COO) + 1 olefin group ($CH{=}CH$) + 15 paraffin groups ($1CH_3 + 14CH_2$). CO_2 was represented by a molecular group.

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