

FRACTIONATION OF FATTY ESTERS AND ACYLGLYCEROLS BY CO₂ LIQUID-LIQUID EXTRACTION

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Abstract. Oleochemistry is gaining importance due to its wide range of applications in the energy, food and pharmaceutical industries. The production of biodiesel or fatty acid methyl esters (FAMES) is of great interest due to their use in diesel engines, blended with petroleum fuels. Also, acylglycerols (ACs) are employed in the food and pharmaceutical industries as emulsifiers. Alternative technologies have been proposed in the last decade to improve the conventional process of biodiesel production from unrefined oils and fats. One process of high interest is non-catalytic continuous supercritical methanolysis (scMeOH), which can process raw materials with high free fatty acids (FFA) and water contents. The vegetable oil is treated with an excess of alcohol (40:1 methanol to oil molar ratio) at 593 K and 150 bar to achieve complete conversion. However, working under milder conditions, ACs could also be obtained (543 K to 573 K). In this work, a method for the fractionation of FAMES + ACs mixtures with liquid CO₂ was studied. A CO₂ liquid-liquid extraction technique was implemented to fractionate the products obtained in a scMeOH process. Working at 298 K and 64 bars, a 98 wt% of FAMES was obtained in the extract phase and almost pure acylglycerols in the raffinate phase.

Keywords: Fatty esters, acylglycerols, CO₂, liquid-liquid extraction

1. Introduction

Biodiesel is produced by transesterification of vegetable oils with methanol to obtain glycerol (a byproduct) and the biofuel, which is a mixture of fatty acid methyl esters (FAMES). The global price of crude grade glycerol is going down due to an oversupply from the biodiesel industry. However, new applications are being developed for this byproduct in the food/beverage as well as pharmaceutical sector [1,2]. Acylglycerols (ACs) and mixtures of mono and diglycerides (MG and DG) are glycerol derivatives that are also produced as intermediate products in the transesterification of vegetable oils. MG and DG have applications as emulsifiers in the food industry and, because of the excellent skin compatibility of monoglycerides sulfates, ACs are relevant in the elaboration of personal care products [1].

Alternative technologies have been proposed to improve the conventional process of biodiesel production from unrefined oils and fats [3]. One of the most studied is non-catalytic supercritical methanolysis (scMeOH), which can process raw materials with high free fatty acids (FFA) and water contents [4]. The scMeOH process is carried out at temperatures higher than 325 °C and pressures higher than 150 bar, using a 40:1 molar ratio of methanol to oil (MeOH/Oil). Under these conditions, it is possible to produce biodiesel in specification (96.5 wt.% FAMES) in 30 min. of reaction time [5]. Nevertheless, it is also possible to obtain ACs if the process is carried out at milder operating conditions. It was determined that, working with a lower molar ratio of 20:1 MeOH/Oil at 300 °C and 130 bar, a complete conversion of triglycerides was obtained in 20 min. of reaction time, but the reaction product contains a high concentration of MGs and DGs [6]. These reaction products can be separated in order to obtain FAMES, MGs and DGs of higher added value.

Supercritical CO₂ extraction and fractionation is a green technology that has been widely studied, and some applications, like the extraction of specialty lipids and the fractionation of tocopherols from deodorizer distillate, have reached commercial scale [7]. In a previous work [6] it was shown that FAMES and ACs can

be effectively fractionated using CO₂ under liquid or supercritical state. A group contribution thermodynamic model (GCA-EOS), revised for asymmetric mixtures, was implemented to adjust experimental data on the ternary CO₂+FAMES+ACs system under liquid-liquid and liquid-vapor equilibria.

In this work, FAMES + ACs mixtures obtained by supercritical methanolysis were fractionated in a modified high pressure Soxhlet apparatus by liquid-liquid (L1-L2) crosscurrent extraction using liquid CO₂. The process was based on the results of experimental liquid-liquid-vapor (L1-L2-V) equilibrium measurements carried out on mixtures of CO₂, fatty esters and acylglycerols (80 wt.% MG and 20 wt.% DG) obtained by supercritical methanolysis of sunflower oil. Thermodynamic modeling, combined with reliable experimental information, is applied to study the crosscurrent extraction process.

2. Experimental

2.1 Materials

FAMES and ACs products used in this work were obtained by supercritical methanolysis of commercial high oleic sunflower oil (87 wt.% oleic acid). Methanol (99.8 wt %) and CO₂ (99.9 %) were purchased from Anedra and Linde AG, respectively. Methyl heptadecanoate (99.9 wt. %), methyl oleate (99.9 wt. %), and monopalmitin (99.9 %), from Sigma-Aldrich, were used as analytical standards in the gas chromatographic (GC) analysis.

Batch reactions were carried out at 300 °C and 130 bar using a MeOH:oil molar ratio of 30:1 during 20 minutes of reaction time. After methanol evaporation and glycerol decantation, a final oily product with the following composition (GC analysis) was obtained: FAMES 77 wt%, MGs 18 wt%, DGs 5 wt%. This mixture was enriched with methyl oleate or ACs compounds during the phase equilibrium measurements performed to evaluate the influence of the global composition on liquid-liquid equilibria.

2.2 Liquid-liquid-vapor equilibria of CO₂+FAMES+ACs

Phase equilibrium measurements on the system FAMES + ACs + CO₂ were carried out in a variable volume equilibrium cell, described elsewhere [6,8]. The maximum cell volume is 80 cm³ and equilibrium data can be obtained at temperatures and pressures of up to 420 K and 20 MPa, respectively. A movable piston is used to control the cell pressure through volume changes and to keep a constant pressure 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 is monitored with a pressure transducer (Ashcroft PT Indicator).

Under liquid-liquid-vapor equilibrium conditions, a direct sampling technique was used to determine the composition of each liquid phase. The experimental procedure was described previously [6]. Sampling of each liquid phase was performed through manually operated valves (Reodyne). Two liquid samples were collected in glass vials (1.5 mL) from the L₁ and L₂ liquid phases (300 mg of L₁ and 100 mg of L₂) and gaseous CO₂, obtained by depressurization, was quantified volumetrically (150 mL and 3000 mL from L₁ and L₂, respectively). The composition of each liquid sample was determined by GC, according to the procedure describe elsewhere [5,6].

The experimental temperature was fixed at 298 K ± 0.2 °C. The pressure was very close to the vapor pressure of CO₂ at this temperature (64 bar ± 0.5 bar). Oscillations in pressure due to differences on the initial global composition loaded to cell were not significant with respect to the uncertainty associated with the experimental procedure. Replicates of the experiments were performed to determine errors in the composition of both liquid phases. The uncertainties in the CO₂ compositions were estimated to be equal to 3 wt% and 0.5 wt% for the heavy and light liquid phases, respectively. Uncertainties in FAMES and ACs concentrations are related to GC analyses. Average standard errors of 1 wt% FAMES and 0.5 wt% FAMES were determined for the heavy and light liquid phases, respectively.

2.3 Experimental fractionation of FAMES and ACs components

Figure 1.A shows a schematic diagram of the equipment used in the fractionation of FAMES and ACs. It consist of a high pressure vessel (4000 mL capacity, I.D: 100 mm) with a quick clamp closure system and a flat end vessel head, assembled with a type B Polypack seal. Tube lines are used to load the solvent and fatty mixture, as well as to obtain the purified products. An external electrical heating element at the bottom and

an internal cooling system at the top of the apparatus allows for the internal recirculation of the solvent. A modified Soxhlet type glass extractor was placed inside the vessel to perform CO₂ liquid-liquid extractions of FAMES from FAMES+ACs mixtures.

In a typical experiment, a given amount of the fatty mixture (17 g) was first loaded into the extraction chamber of the modified Soxhlet apparatus and it was introduced inside the high-pressure extraction vessel. After closing this vessel, a gentle CO₂ gas stream was flushed through an internal line, to purge the air. About 750 g of CO₂ was then loaded to pressurize the vessel. Afterwards, liquid CO₂ (about 300 g) was charged into the vessel to start the fractionation experiment. By activating the cooling and heating systems, the solvent was recycled through the Soxhlet apparatus. The CO₂ vapors from the bottom distillation flask rise up through the vessel reaching the top cooling system. The drops of the condensed solvent fall into the extraction chamber and blend with the fatty mixture, producing two liquid phases: a heavy L₁ and a light L₂ phases. When the extraction chamber is almost full, the upper CO₂+FAMES liquid phase is siphoned back to the boiler through the side arm designed to avoid the reflux of the heavy phase L₁, rich in ACs. Solvent vapors from the boiling distillation flask continue to rise up to the condenser and fresh solvent drops fall into the extraction chamber, repeating the cycle. A thermocouple located in the extraction chamber at the siphon-arm level allows establishing the number of cycles that take place in the process. The thermocouple registers a slight temperature difference (about 1 K) between the rising vapors and the L₂ liquid phase.

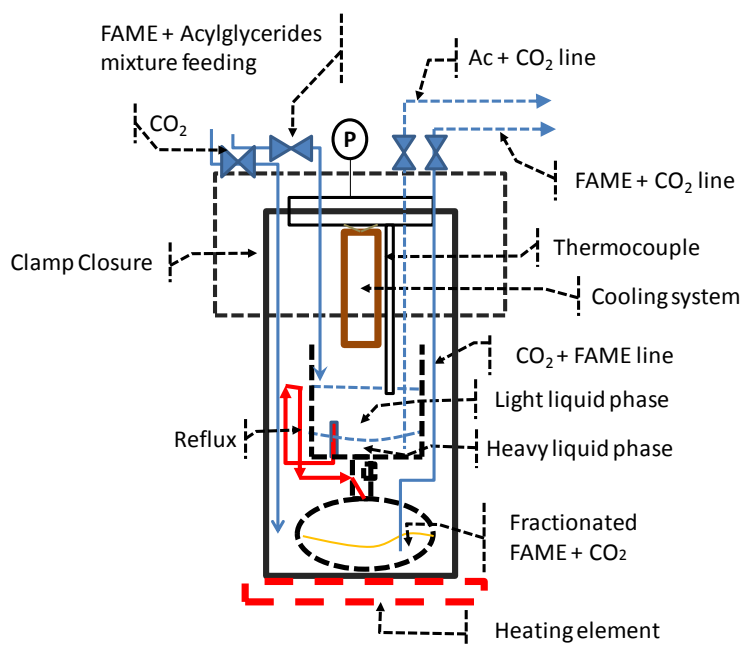


Figure 1. High-pressure extraction vessel used in the fractionation experiments.

3. Results and discussion

3.1 Liquid-liquid-vapor equilibria of CO₂ + fatty mixtures

Figure 2 shows the experimental results obtained in the L₁-L₂-V equilibrium measurements at 298 K and 64 bar, on mixtures of CO₂ with the FAMES + ACs products obtained by supercritical methanolysis of high oleic sunflower oil. Also shown in this figure are the phase equilibrium predictions by the GCA-EOS model. The parameters used in the calculations were previously reported [6].

According to the experimental results, the light liquid phase (L₂) was composed mainly of CO₂ and FAMES. Minor quantities of MGs (lower than 0.16 wt%) were also detected in this phase. The heavy L₁ phase contained all components. As expected, no significant quantities of FAMES or ACs were detected in the vapor phase.

In agreement with the experimental data, the GCA-EOS model predicts a maximum concentration of 8.5 wt% of FAME in the binary CO₂+FAME. This concentration decreases with the presence of ACs in the light liquid phase. The modeling results for the heavy liquid phase presents some discrepancies with respect to the

experimental data. This can be ascribed to greater experimental uncertainties in the direct sampling of this dense liquid phase. On the other hand, the liquid-liquid-vapor phase behavior predicted by the model is based on a mixture having a single MG (monoolein), while the real mixture is composed of MGs and DGs. The amount of CO₂ dissolved in this heavy liquid phase can be affected by the presence of DGs.

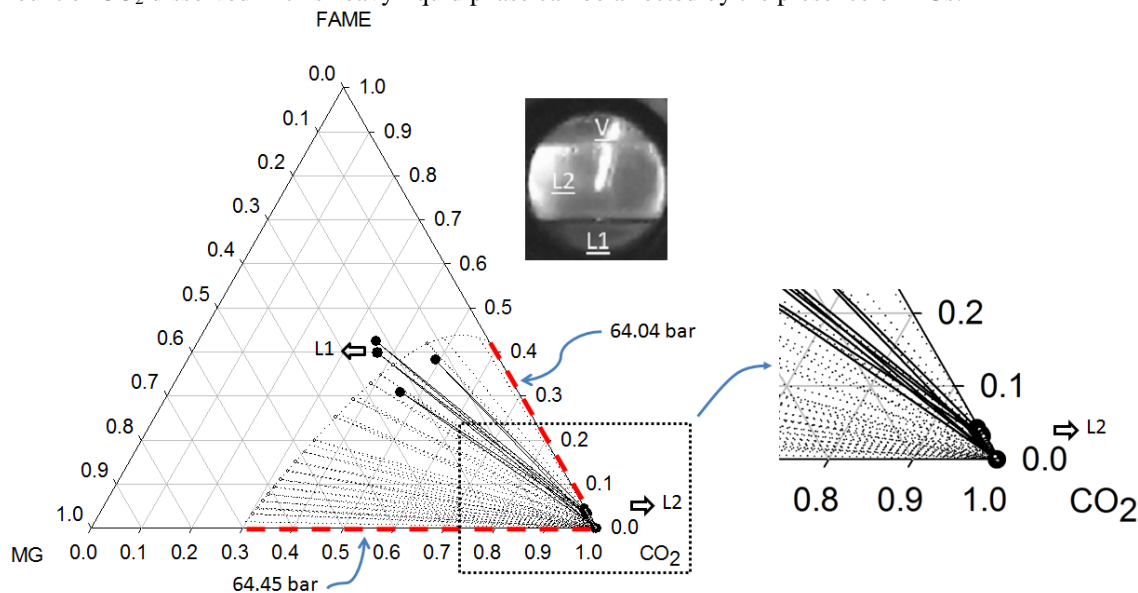


Figure 2. Liquid-liquid-vapor (L₁-L₂-V) equilibria of the system CO₂+FAMES+ACs at 298 K. Symbols: experimental data measured in this work. Dotted lines: liquid-liquid tie lines predicted by the GCA-EOS for the ternary system CO₂ + methyl oleate + monoolein under L₁-L₂-V equilibria. Red dashed lines: mutual liquid solubility of the binary systems.

The binaries CO₂+FAMES and CO₂+ACs exhibit liquid-liquid-vapor equilibrium conditions at 298 K or temperatures lower than CO₂ critical temperature. A binary system under liquid-liquid-vapor equilibria has only one degree of freedom according to the phase rule. Thus, there is only a single pressure where it is possible to obtain the three phase behavior at a fixed temperature. The GCA-EOS predictions of the liquid-liquid-vapor equilibria of both binary systems (CO₂+FAMES and CO₂+ACs) indicates a small difference between the pressures of both three-phase binaries (64.04 bar and 64.45 bar, respectively). Both values are very close to the vapor pressure of CO₂ at 298K, due to the low volatility of FAMES and ACs with respect to CO₂.

Inomata et al. [9] measured the phase equilibria of CO₂ + methyl oleate and showed that this binary system presents complete miscibility at 313 K and pressures higher than 150 bar. GCA EOS predictions [6] are in good agreement with these data. A single liquid phase is predicted at ambient temperature, for pressures higher than 100 bars. Prediction of the liquid-liquid-vapor equilibria at 298 K indicates 8.5 wt% FAME solubility in the light liquid phase.

The solubility of monoolein and diolein in supercritical CO₂ was studied by Nilsson et al. [10]. According to these authors the solubility of monoolein and diolein is quite similar at pressures lower than 250 bar. For example, at 323 K, monoolein solubility is only 0.2 wt% at 150 bar and 0.7 wt.% at 241 bar. Previous work [6] shows that these solubilities are very well predicted by the GCA-EOS model. Under L₁-L₂-V equilibria, the model predicts a monoolein solubility of 0.06 wt% in the light liquid phase.

Experimental visual observations carried out in this study at 298 K showed that two liquid phases will rapidly appear when the FAMES+ACs mixture is put in contact with liquid CO₂. This was independent of the initial overall composition charged into the cell. Also, the pressure in the cell remained almost constant at 64 bars under L₁-L₂-V equilibria. However, the composition of each liquid phase in the system changed with the overall cell composition. According to the phase rule, a three phase ternary system has two degrees of freedom. Thus, the compositions of each phase should remain constant once temperature and pressure have been fixed.

GCA-EOS predictions of the CO₂ + methyl oleate + monoolein system under liquid-liquid-vapor equilibria show effectively that there are small pressure changes in the system for each L₁-L₂ tie line between both binaries under three phase equilibria. This phenomenon could not be observed in the experiments due to

an experimental uncertainty (0.5 bar) in the pressure measurements, greater than the expected pressure changes.

3.2 Fractionation of FAMES+ACs components by crosscurrent extraction

The results on liquid-liquid-vapor equilibrium conditions of CO_2 + FAMES + ACs mixtures show that it is possible to fractionate FAMES and ACs by a cross-current extraction process, because the ACs solubility in the light liquid phase remains very low compared to the FAMES concentration.

As an example, a methanolysis reaction product having 80 wt% FAMES shows partial liquid miscibility with liquid CO_2 . The light liquid phase, rich in solvent, will contain about 5 wt% of FAMES and an ACs content lower than 0.01 wt%. The heavy liquid phase presents a 30 wt% of ACs on a solvent-free basis, and should be re-extracted to obtain a new ACs rich liquid phase.

In the first cross-current experimental extractions carried out in the modified high-pressure Soxhlet apparatus, small fatty samples (~17 g) containing 77 wt% of FAMES and 23 wt% of ACs were processed. Two replicates were carried out operating the high-pressure vessel at 323 K at the bottom and 278 K at the top. Four solvent cycles were completed after 30 minutes of continuous operation, obtaining two liquid products. From the extract phase, 11.1 g of a FAMES product with 98.1 wt% purity was recovered. The raffinate phase, on the other hand, gave a FAMES+ACs mixture with 61.4 wt% ACs.

Figure 3A shows the composition of the two liquid phases under liquid-liquid-vapor equilibria, on a solvent-free basis. The diagram was built from the GCA-EOS predictions of the ternary system CO_2 + FAME + MO at 298 K. The red lines in the diagram represent schematically the cross-current extraction stages which were estimated from a mass balance, according to the volume of the extraction chamber (340 mL) and the volume of L_2 phase recycled on each stage. The calculations were carried out assuming ideal mixing and using the liquid density of the pure solvent and components of the fatty mixture. In the first cycle 250 g of solvent were mixed with the original FAMES + ACs mixture, obtaining point M_1 on the diagram. M_1 lies on a tie line joining a raffinate and an extract phases having a weight fraction of FAMES equal to $X_1=0.531$ and $Y_1=0.981$ respectively. The total amount of FAMES + ACs in the extract phase was $E_1=4.5$ g. The amount of fresh CO_2 fed to the next cycles (123 g) was lower than that used in the first one, because the extract phase L_2 was not completely recycled to the boiler (see level differences in Figure 3B). This implies a global FAMES concentration in the extraction chamber higher than that of the raffinate phase. On the second cycle, the fresh solvent was mixed with a fatty mixture having 0.69 wt fraction of FAMES, obtaining $E_2=3.1$ g of an extract phase with a FAMES composition $Y_2=0.978$. After four extraction stages the final FAMES compositions in the raffinate and extract phases were 38.6 wt% and 97.6 wt% respectively.

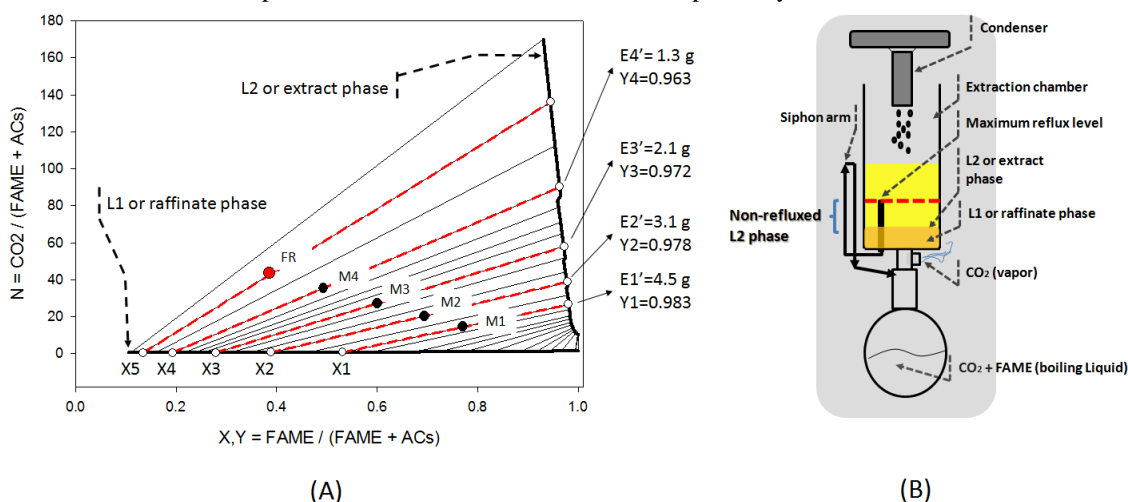


Figure 3. Crosscurrent extraction process for the fractionation of FAMES and ACs with liquid CO_2 . (A) L_1 - L_2 equilibria in a solvent-free basis diagram for the ternary CO_2 +FAME+Monoolein under liquid-liquid-vapor equilibria at 298 K. (B) Diagram of the modified Soxhlet apparatus developed to carry out the separation of the solvent-rich liquid phase (L_1) in equilibrium with the fatty liquid phase (L_2).

The compositions of the extract and raffinate phases obtained in the experimental tests agree well with the modeling results. Indeed, the FAMES concentrations measured in the extract phase were slightly higher than

the calculated values, pointing out a model over-prediction of the ACs concentration in the light liquid phase. Clearly, a most effective separation process could be obtained if a greater volume of the L₂ phase is recycled to the boiler. In this way the global FAMES concentration in the extraction chamber would be closer to that of the raffinate phase. The efficiency can be increased by processing higher amounts of sample, which provides a higher volumetric level of the L₁ phase.

Besides the beneficial properties of CO₂ (non-flammable, inert and relatively cheap solvent) the separation method proposed in this work presents other interesting advantages: i) high-selectivity towards FAMES; ii) low operating temperatures (25 °C to 40 °C) which is important when processing thermo-labile components; iii) moderate operating pressures, compared to the pressure applied in supercritical fluid technology; iv) there is no need for further purification steps of the products to remove the solvent after extraction.

Coupling the CO₂ fractionation with an adsorption process can produce an effective technology for the separation/purification of polar and non-polar components (fatty esters, monoglycerides, diglycerides, fatty acids, glycolipids and phospholipid derivatives) in the oleochemical industry.

4. Conclusions

Experimental observations show that two liquid phases rapidly arise when a biodiesel sample containing FAMES + ACs is mixed with liquid CO₂. The LLV equilibrium of the system CO₂+FAMES+ACs was studied at 298 K and a nearly constant pressure of 64 bars. The compositions of the two liquid phases were measured. The light liquid phase had a concentration of up to 5 wt% FAMES, with a minor ACs content of 0.01 wt%. Thus, it is possible to perform a liquid-liquid extraction to purify FAMES from a biodiesel mixture, obtaining also a raffinate phase enriched in ACs compounds.

Experiments on a liquid-liquid crosscurrent extraction of FAMES from biodiesel samples containing 23 wt% ACs were carried out in this work, using a modified high-pressure Soxhlet apparatus. After four extraction cycles almost 85 wt% of the FAMES initially present in the sample were separated with a concentration of 98 wt%. The GCA-EOS model was a useful tool to study the liquid-liquid-vapor equilibria of the ternary system and to evaluate the liquid-liquid separation process.

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