



# Supercritical production and fractionation of fatty acid esters and acylglycerols



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## ABSTRACT

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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>. The simulation of the extraction process working with CO<sub>2</sub>, 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<sub>2</sub>) as a green solvent. CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>. Thus, all the acylglycerides 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<sub>2</sub> 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<sub>2</sub> (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 <sub>2</sub> | 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 Agrosiences, 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<sub>2</sub> (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/cm<sup>3</sup> and 0.6 g/cm<sup>3</sup>. 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                 |

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