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Method for Separating Fatty Acid Ethyl Ester Mixtures

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Abstract

The aim of the present study is to identify the preferred region of the thermodynamic surface for the separation of a mixture of ethyl esters of oleic and palmitic fatty acids within the framework of the authors' original method. This method is based on the concept of the dual nature of the mass transfer mechanism in supercritical fluid extraction processes for systems exhibiting type I and II phase behavior. Results are presented for the separation of a binary mixture of ethyl oleate and ethyl palmitate. The process was carried out in asymptotic proximity to the critical point of the CO_2–ethyl oleate system. As a result, in one of the extract samples, an ethyl oleate concentration of 94 wt.% was achieved within a 20-minute process duration, starting from an initial content of 25.28 wt.% in the feed mixture. A comparison with the separation results obtained for the same mixture under asymptotic proximity to the critical point of the CO_2–ethyl palmitate system revealed the superiority of the aforementioned conditions. The proposed separation method is not limited to the specific mixture discussed here and is proposed for the first time.

1. Introduction

Bioenergy, represented by major energy carriers such as biogas, bioethanol, and biodiesel, is of particular importance for countries that possess limited or no natural reserves of gas, oil, coal, or other hydrocarbons [1–3]. For example, in several African countries, including Benin, Ghana, and Togo, the shea butter tree is widely cultivated [4–6]. While a significant portion of shea butter oil is exported for use in the cosmetics industry, the remaining fraction could potentially be utilized as a feedstock for biodiesel production [7, 8].

However, the relatively high content of saturated fatty acids in shea butter oil, primarily stearic, palmitic, and arachidic acids, and their derivatives, which exhibit higher viscosity than unsaturated fatty acids such as oleic, linoleic, and linolenic acids, results in increased viscosity of the biodiesel produced from this feedstock (i.e., a mixture of fatty acid esters). For example, studies on the ethanolysis of shea butter oil under supercritical fluid (SCF) conditions (T = 623 K, P = 30 MPa, τ = 30–60 min, alcohol/oil ratio = 30:1–42:1) reported biodiesel viscosities of 8.06–11.71 mm^2/s [9], which significantly exceed the limits specified by international standards (ASTM D-6751-02: ν = 1.9–6.0 mm^2/s; EN 14214: ν = 3.5–5.0 mm^2/s).

One possible approach to addressing the high viscosity of the resulting esters is the fractionation of the fatty acid ethyl ester mixture by SCF extraction, which would enable the removal of high-viscosity saturated fatty acid esters. Such fractionation may be implemented using an original approach based on the concept of the dual nature of the mass-transfer mechanism in SCF extraction processes for binary systems exhibiting type I and II phase behavior [10], a concept first formulated in [11].

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Concerning the aforementioned concept of the dual mass transfer mechanism and the resulting prerequisites for developing an original separation method, the following should be noted.

First, the dual nature of mass transfer in SCF extraction processes for systems with a continuous critical curve implies that mass transfer occurs both under equilibrium solubility conditions and via non-equilibrium macro-transfer. The latter can also take place in the subcritical region for systems exhibiting type I and II phase behavior.

Second, the physicochemical basis of non-equilibrium macro-transfer, which significantly enhances the efficiency of SCF extraction, is associated with an anomalous change in the excess volume of the "target component–extractant" mixture in the near-critical region. This effect promotes the transition of the system from a two-phase (liquid–vapor) to a three-phase (liquid–liquid–vapor) state [12]. Under such conditions, a highly extractant-saturated, swollen liquid phase of reduced density is formed and can undergo non-equilibrium transfer.

Third, creating optimal conditions for non-equilibrium macro-transfer of a single component in SCF extraction forms the basis of the proposed approach to the separation of liquid-phase mixtures with different physicochemical properties.

The results of a considerable number of publications attempting to estimate the solubility of ethyl oleate (EO) and ethyl palmitate (EP) in carbon dioxide within the near-critical region, including [13–17], often lack consistency and may not represent true equilibrium parameters, due to the absence of the concept regarding the dual nature of the mass transfer mechanism in extraction processes for systems of type I and II phase behavior [11]. In such a situation, only the concentration values of ethyl oleate and ethyl palmitate in their mixtures with carbon dioxide, calculated from the characteristics of the vapor branches of the binodal curves for the "CO_2–ethyl oleate" and "CO_2–ethyl palmitate" systems (the subcritical region of these binary mixtures, see Table 1), can be considered sufficiently reliable.

The supercritical CO_2 extraction process investigated in this study was carried out using a model mixture consisting of ethyl palmitate (saturated) and ethyl oleate (unsaturated). The binary systems "CO_2–ethyl palmitate" and "CO_2–ethyl oleate" exhibit type I and II phase behavior with a continuous critical curve (Fig. 1) [18, 20, 21].

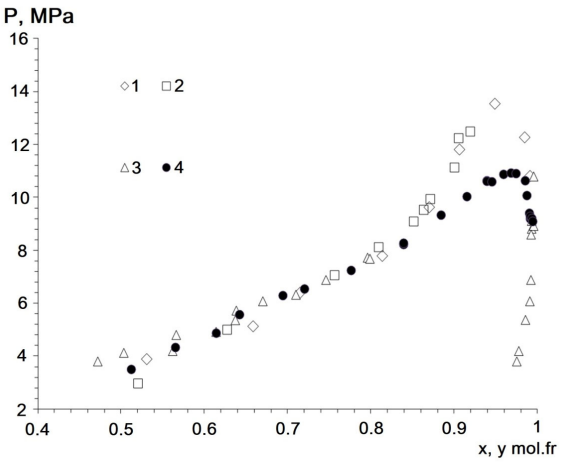

Fig. 1. Phase equilibrium diagrams (T = 313.15 K) for binary systems: "CO_2–ethyl oleate" at T = 313.15 K: 1 – [18], 2 – [21], 3 – [21]; "CO_2–ethyl palmitate": 4 – [20].

Table 1. Concentration of fatty acid ethyl esters in their mixtures with CO_2 based on phase equilibrium studies of the vapor branches of the binodal curves for the corresponding binary systems at T = 313.15 K

"CO_2–ethyl oleate" [18]		"CO_2–ethyl palmitate" [19]		"CO_2–ethyl palmitate" [20]	
P, MPa	1-y, mol. fr.	P, MPa	1-y, mol. fr.	P, MPa	1-y, mol. fr
13.55	0.0515	10.93	0.032	11.07	0.0372
12.28	0.0157	10.91	0.026	10.43	0.0192
10.82	0.0093	10.64	0.015	9.64	0.087
–	–	10.08	0.013	–	–
–	–	9.41	0.010	–	–
–	–	9.20	0.009	–	–
–	–	9.29	0.009	–	–
–	–	9.21	0.007	–	–
–	–	9.10	0.006	–	–

y – mole fraction of carbon dioxide on the vapor branch of the binodal according to the respective experimental studies

As shown in Fig. 1, the pressure range of 11–14 MPa at T = 313.15 K corresponds to the subcritical vapor–liquid equilibrium region for the CO_2–ethyl oleate system. In contrast, for the CO_2–ethyl palmitate system, this range represents the supercritical gas region of complete miscibility. Extraction performed near the critical point of the CO_2–ethyl palmitate system (P = 11.5 MPa, T = 313.15 K) is inevitably influenced by the significant presence of ethyl oleate in the extract. This effect arises because, according to several estimates [15, 16], mass transfer under equilibrium solubility conditions is several times higher for ethyl oleate than for ethyl palmitate, which hinders the concentration of the latter. The higher solubility of ethyl oleate in CO_2 is attributed to its double bond and lower crystallinity.

Thus, the aim of this work is to concentrate ethyl oleate in the extract by conducting supercritical CO_2 extraction near the critical point of the ethyl oleate–CO_2 system (P_c ~14.0 MPa, T_c = 313.15 K).

2. Experimental section

Materials. The following materials were used for the separation of a mixture of ethyl esters of oleic and palmitic fatty acids by supercritical CO_2 ($scCO_2$) extraction:

– Carbon dioxide (≥ 99.0% purity, GOST 8050-85);

– Ethyl oleate (analytical grade; Sisco Research Laboratories Pvt. Ltd, n_D^{20} = 1.450, ρ^{20} = 870 kg/m^3);

– Ethyl palmitate (≥ 97.0% main substance content).

Methods. Supercritical CO_2 extraction was performed using the experimental system shown in Fig. 2. The system allows extraction at temperatures of 300–373 K and pressures of 8–25 MPa. It consists of four main modules: a pressure generation and stabilization unit, a temperature control block, an extraction cell, and a system for measuring and recording the mass of the recovered extract.

The pressurization system includes a 10 L CO_2 cylinder (1) and a “Supercritical 24” high-pressure pump (Teledyne SSI, Newark, USA) (3), capable of delivering liquid CO_2 at flow rates from 0.01 to 24 mL/min at pressures up to 10,000 psi (689.48 bar). Temperature control is provided by an electric heater (10), a Type K Chromel–Alumel thermocouple, and a TRM-1 precision temperature controller. The extract mass is measured using an OKB “Vesta” electronic analytical balance (OKB Spectr, Saint Petersburg, Russia) with automated data acquisition (readability 0.001 g), interfaced with a personal computer (15).

Research Procedure. The pre-cleaned extractor (5) was evacuated to remove residual solvent vapors and atmospheric air. A predetermined volume of the liquid sample was introduced into the extractor through the outlet regulating valve (6) using a dispenser, while the inlet valve (4) remained closed. The mass of the loaded liquid phase was determined gravimetrically.

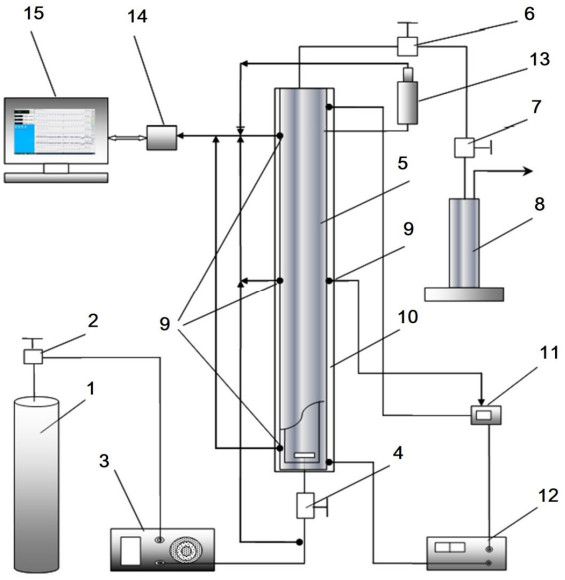

Fig. 2. Schematic diagram of the experimental setup for supercritical CO_2 extraction. Component designation: 1 – carbon dioxide cylinder; 2 – gas shut-off valve; 3 – high-pressure liquid pump; 4 – extractor inlet valve; 5 – extraction cell (extractor); 6 – outlet valve; 7 – needle regulating valve; 8 – separator; 9 – thermocouple (temperature sensor); 10 – electric heater; 11 – temperature controller; 12 – power supply unit; 13 – strain-gauge pressure transducer; 14 – analog-to-digital converter (ADC); 15 – personal computer.

Carbon dioxide was used as the extractant. CO_2 was delivered from cylinder (1) to the high-pressure pump (3), where it was preliminarily liquefied, and subsequently fed into the extractor at a specified flow rate in the supercritical state, at a pressure slightly below the target experimental value. The thermostating system, comprising a TPM-1 precision temperature controller ("Oven", OKB Spectr, Saint Petersburg, Russia), a thermocouple, and an electric heater (10), was then activated to bring the cell to the required temperature. The external surface of the extractor was thermally insulated to minimize heat losses.

Once the set temperature was reached, the system was pressurized to the planned experimental pressure by additional pumping of CO_2. During CO_2 delivery, intensive mixing of the cell contents was ensured by reciprocating rotation of the cell at an amplitude of ±45° about its vertical axis. After phase saturation and pressure stabilization, the system was maintained under static conditions for 30 minutes. Thermodynamic equilibrium was assumed when no further pressure changes were observed. Mixing was terminated once equilibrium had been established.

Pressure was monitored using a strain-gauge transducer (13), and temperature uniformity was verified using Chromel–Alumel thermocouples (9). Signals were recorded via an analog-to-digital converter interfaced with a personal computer (15).

Subsequently, valves (6) and (7) were opened to direct the supercritical fluid into the separator (8), where gas–liquid phase separation occurred. A constant flow rate was maintained by fine adjustment of the needle valve (7). The separator was placed on the platform of an electronic balance equipped with automated data acquisition connected to a personal computer. Analysis of the mass accumulation kinetics enabled identification of the time interval corresponding to the equilibrium dissolution regime. The final mass of the extract was determined by reweighing the extractor using a "CAS CUX-4200H" (CAS Corporation, Seoul, South Korea) analytical balance.

The composition of the obtained extract was analyzed by gas chromatography using a Chromatec-Crystal 5000 system (SC SDO "Chromatec", Yoshkar-Ola, Russia) equipped with a flame ionization detector. Component separation was achieved on a capillary column, and peaks were identified by comparing retention times with those of certified ethyl oleate and ethyl palmitate standards. Quantification of the target esters was performed using the internal normalization method.

3. Results and discussion

The experiments were conducted at a temperature of 313.15 K and a pressure of 14 MPa, with an extractor loading degree of 30% and CO_2 flow rates ranging from 0.5 to 1.0 ml/min. The process duration extended up to 60 minutes. The obtained data were interpreted within the framework of the dual nature of mass transfer, a concept applicable to systems exhibiting type I and II phase behavior.

Figure 3 shows representative mass accumulation kinetics in the separator during supercritical fluid extraction of a binary ethyl oleate/ethyl palmitate mixture with a composition of 25.28/74.72 wt.% (equivalent to 25/75 vol.% or a 1:3 volumetric ratio). As evident from Fig. 3, the mass transfer rate in the non-equilibrium macro-transfer regime is significantly higher than in the equilibrium solubility regime. Consequently, SCF extraction of systems with type I and II phase behavior under non-equilibrium macro-transfer conditions is substantially more efficient than processes relying solely on equilibrium solubility. This includes processes for systems with type V phase behavior, for which macro-transfer is absent due to the lack of a critical point and a near-critical fluid state for the binary "target component–extractant" system.

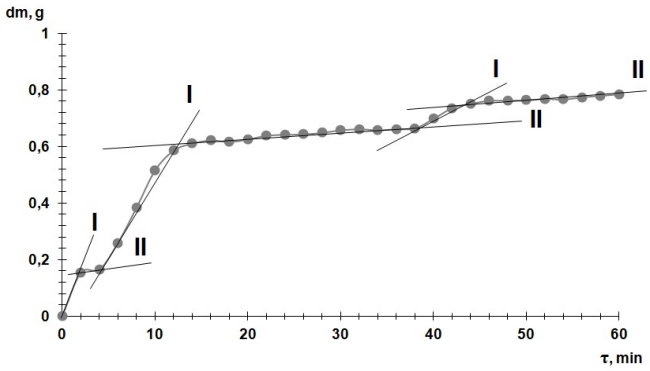

Fig. 3. Kinetics of separator mass during $scCO_2$ extraction of ethyl oleate/ethyl palmitate (25.28/74.72 wt.%). Conditions: 60 min, 313.15 K, 14 MPa, V_{vol} = 30%, V_{CO2} = 1 mL/min. I – non-equilibrium macro-transfer; II – mass transfer in the equilibrium solubility regime.

Figure 4 shows a photograph of the separator's aqueous medium after the $scCO_2$ extraction process. Flask A (Fig. 4) corresponds to a previously conducted experiment performed under asymptotic proximity to the critical point of the CO_2–ethyl palmitate system, whereas flask B corresponds to the present study carried out under asymptotic proximity to the critical point of the CO_2–ethyl oleate system.

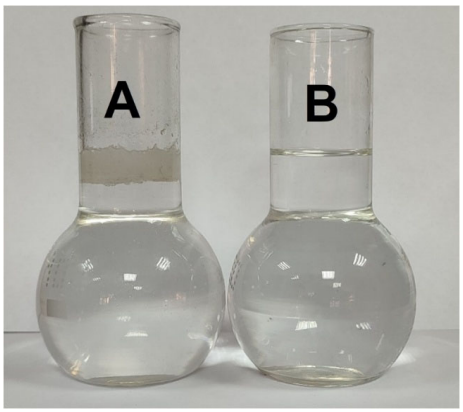

Fig. 4. Appearance of the separator medium following the SCF extraction process: A – corresponds to the experiment carried out under conditions of an asymptotic relationship to the critical transport system "CO_2–ethyl palmitate"; B – corresponds to the present study under conditions of an asymptotic structure to the critical transport system "CO_2–ethyl oleate".

In the experiment conducted near the critical point of the CO_2–ethyl palmitate mixture, ethyl palmitate — preferentially extracted under these conditions and readily crystallizing at household refrigerator temperatures — formed a clearly visible solid-phase ring in the neck of flask A. In contrast, flask B, containing the extract obtained near the critical point of the CO_2–ethyl oleate mixture, shows no visible indications of ethyl palmitate.

Selected results of the $scCO_2$ extraction separation for the studied binary mixture, obtained from chromatographic analysis performed under asymptotic proximity to the critical point of the CO_2–ethyl oleate system, are presented in Table 2.

For a 20-minute separation process of the initial mixture containing 25.28 wt.% ethyl oleate, extract sample No. 3 contains 94 wt.% ethyl oleate. This result is significant and may serve as a basis for applying this method to assess the quality of the resulting fuel based on its kinematic viscosity.

Table 2. Conditions and results of $scCO_2$ extraction separation of the binary mixture composed of ethyl oleate and ethyl palmitate

#	T, K	P_c, MPa	P, MPa	Initial composition EO/EP, wt.%	V_{vol}, %	V_{CO2}, ml/min	τ, min	C_{EO}, wt.%	C_{EP}, wt.%
1	313.15	~14.0	14.0	25.28:74.72	30	1.0	16	90	10
2	313.15	~14.0	14.0	25.28:74.72	30	1.0	17	90	10
3	313.15	~14.0	14.0	25.28:74.72	30	0.5	20	94	6
4	313.15	~14.0	14.0	25.28:74.72	30	0.5	16	89	11

P_c – critical pressure of the "CO_2–ethyl oleate" mixture; V_{vol} – initial packing degree of the extractor with the ethyl oleate/ethyl palmitate mixture; V_{CO2} – extractant flow rate; τ – duration of the SCF extraction process; CEO, CEP – concentrations of ethyl oleate and ethyl palmitate in the extract, respectively.

4. Conclusion

The concept of the dual nature of the mass transfer mechanism served as the basis for the development of the proposed separation approach. In the present study, an ethyl oleate concentration of 94 wt.% was achieved within 20 min in one of the extract samples obtained from a mixture of ethyl palmitate and ethyl oleate with a composition of 74.72/25.28 wt.%, corresponding to an initial ethyl oleate content of 25.28 wt.% in the feed mixture. The separation process exhibited rapid kinetics.

The preference for conducting the separation process in asymptotic proximity to the critical point of the CO_2–ethyl oleate binary mixture is justified by the fact that, under these conditions, the primary mass transfer of ethyl oleate occurs in the non-equilibrium macro-transfer regime. In contrast, the absence of macro-transfer for ethyl palmitate, combined with its lower solubility in CO_2 compared with that of ethyl oleate, contributes to the higher ethyl oleate purity of the extract.

The obtained results suggest that the proposed method is promising and has strong potential for further development. It should also be noted that these results were achieved using a batch apparatus with a single loading of the mixture into the extractor. The process may also be implemented in continuous-feed mode, which represents an important direction for future research.

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