

Phase equilibrium engineering of jojoba oil extraction with mixed- CO_2 + propane solvent

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ABSTRACT

Jojoba oil is an important ingredient of many cosmetic and hair care products, which is composed of high-molecular weight monounsaturated esters. It is a liquid wax extracted from the seeds of Jojoba plant (*Simmondsia chinensis*) by mechanical pressing, followed by hexane extraction of the pre-pressed jojoba meal. Health and environmental concerns associated with the use of solvents like hexane have placed new demands on the cosmetic and pharmaceutical industry to invest in clean technologies such as Supercritical Fluid Extraction. Jojoba oil is partially miscible with CO_2 in the liquid and supercritical states. On the other hand, liquid propane has better solvent characteristics, since it shows complete miscibility with jojoba oil below 343 K. The main drawback of propane is its flammability; any percentage of it in a propane/air mixture above 2.15 vol.% will be enough to burn the propane. However, a 30 vol.% of CO_2 in the vapor phase can be used to turn the mixture propane/ CO_2 /air non-flammable. In this work, the phase equilibrium engineering of jojoba oil extraction with mixed- CO_2 + propane solvents has been carried out in order to select appropriate operating conditions.

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1. Introduction

Jojoba oil and its derivatives have a wide range of industrial uses, mainly in cosmetics, and are common in formulations for skin-care, such as lotions, moisturizers, massage oils, and soothing creams [1]. It is a liquid wax composed by monounsaturated esters of high molar mass. Industrial seed oils are generally obtained by mechanical pressing followed by a solvent extraction. The process normally employs hexane as solvent which is harmful for human health and the environment. The current worldwide regulatory requirements on the use of chemicals solvents have prompted the need for research on new clean technologies such as supercritical carbon dioxide (scCO_2) extraction [2].

Carbon dioxide (CO_2) is an inert, inexpensive, easily available, odorless, tasteless, environment-friendly, and GRAS (Generally Recognized As Safe) solvent. The supercritical extraction of jojoba oil by scCO_2 has been studied previously in the literature [3–5]. For instance, Stahl et al. [3] reported the dependence of jojoba oil solubility in CO_2 with temperature and pressure in the range of 293–353 K and 100–2600 bar, respectively. The data show that a pressure above 300 bar is required to achieve good solubility and extraction yields. On the other hand, Salgın [4,5] reported the extraction of jojoba oil by scCO_2 and co-solvents. A maximum

extraction yield of 50.6 wt.% was obtained using only scCO_2 working at 363 K and 600 bar. He also has shown that the addition of hexane as co-solvent (5 vol.%) allows operation under milder conditions (333 K and 300 bar). According to this author, working with ethanol as co-solvent increased the solubility of jojoba oil (JO), thus it was feasible to extract from 0.015 to 0.03 g JO/kg of CO_2 working at 343 K and 350 bar [4]. However, these co-solvents remain in the oil after the depressurization for CO_2 removal, and a complete removal from the oil is difficult, thus requiring a high vacuum step to purify the product at low temperatures to avoid thermal degradation.

To sum up, the system of vegetable oils + CO_2 is heterogeneous over a wide range of conditions, both under sub- and supercritical conditions. High pressures are required to obtain good oil extraction yields because the oil solubility in CO_2 is very low even at pressures as high as 300 bar. Therefore, the extraction of jojoba oil from its seed with CO_2 is still not an attractive alternative from an economic point of view.

Propane and carbon dioxide mixtures have been extensively studied in previous works as supercritical or high-pressure liquid solvents for lipids and oils [2,6,7]. Like any supercritical solvent, both can be easily removed from the oil after the extraction by depressurization. In general, vegetable oils are completely miscible with liquid propane at temperatures lower than ~343 K (LCEP). However, at higher temperatures propane presents liquid–liquid immiscibility with triglycerides, like tripalmitin [8] and sunflower oil [9] (from the lower to the upper critical end point around

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Table 1
Values of GC-EoS pure group parameters (from [11,13]).

Group	T^* (K)	Q	g^*	g'	g''
CO ₂	304.2	1.261	531,890	−0.5780	0.0
Propane	369.8	2.236	436,890	−0.4630	0.0
CH ₃	600	0.848	316,910	−0.9274	0.0
CH ₂	600	0.540	356,080	−0.8755	0.0
CH=CH	600	0.867	403,590	−0.7631	0.0
CH ₂ COO	600	1.42	831,400	−1.0930	0.0

343–370 K, respectively). Its solvent power is much greater than that of CO₂, requiring lower solvent to feed ratios and operating pressures. The main drawback of propane is its flammability; a propane+air mixture with a content of propane higher than 2.15 vol.% will be enough to burn the propane [10]. This suggests that solvent mixtures of propane and CO₂ offer convenient properties regarding solvent power (greater affinity with the substrate than that of CO₂), selectivity, and safety (30 vol.% of CO₂ in the vapor phase can be used to turn the propane/CO₂/air mixture non-flammable [10]).

In previous works [6,7], the phase equilibrium and the extraction of different vegetable oils with mixed solvent (propane and CO₂) were studied. On the other hand, Espinosa et al. [11] upgraded the group contribution equation of state (GC-EoS) to predict phase behavior in highly asymmetric mixtures [11], which was later used to set the proper operating conditions for triglycerides extraction with mixed solvent (propane + CO₂). Also, based on this model and the experimental data, the effect of a liquid phase split on the extraction yield was studied [7].

In this work, the GC-EoS model, together with experimental observations, was used to study the phase equilibrium of CO₂ + propane + jojoba oil mixtures in order to choose operating conditions for the extraction process. Experimental observation of phase equilibria of the ternary system has been obtained to support thermodynamic model predictions. The phase behaviors of binary and ternary systems were studied at different temperatures, pressures and compositions to determine conditions of good solvent power and non-flammable solvent mixtures.

2. Thermodynamic model

The GC-EoS model is based on the two classical contributions to the Helmholtz energy that takes into account the intermolecular forces through a repulsive or free volume term and an attractive or residual term. The attractive term has a group contribution nature while the repulsive term depends on a molecular parameter [12]. The model has been described in detail elsewhere [11–14]. In this work, the parameters for the attractive term proposed by Espinosa et al. [11] and Cismonti et al. [13] were used to evaluate the phase equilibria of solvent mixtures (propane + CO₂) and jojoba oil (Tables 1 and 2). The jojoba oil was represented in this work by the major ester of the extracted oil (C₄₂, see Table 3). In fact, the mixture

Table 2
Values of GC-EoS group–group interaction parameters (from [11,13]).

I	j	k_{ij}^*	k_{ij}'	α_{ij}	α_{ji}
CO ₂	CH ₃	0.980	0.15	3	3
CO ₂	CH ₂	0.930	0.15	3	2
CO ₂	Propane	0.875	0.0	3.369	3.369
CO ₂	CH=CH	0.948	0.0	0.0	0.0
CO ₂	CH ₂ COO	1.000	0.15	0	1
CH ₃	CH ₂	1	0.0	0.0	0.0
CH ₂ COO	CH ₃ /CH ₂	0.869	0.0	0.0	0.0
CH ₂ COO	CH=CH	1.006	0.0	−0.876	−0.876
CH=CH	CH ₃ /CH ₂ /propane	1	0.0	0.0	0.0

Table 3
Jojoba oil (wax esters) composition extracted in this work.

Components	wt.%
Fatty esters	
C-34	0.096
C-36	1.610
C-38	7.840
C-40	31.33
C-42	46.64
C-44	8.682
C-46	0.912
C-48	0.078
Fatty acids	1.789
Sterols	0.377

is formed mainly by three esters (C₄₀, C₄₂ and C₄₄) whose effects on the system topology do not differ substantially. Moreover, a correlation based on the van der Waals volume (r_{vw}) [11] was used to determine the oil critical diameter (d_c) required for the repulsive contribution (C₄₂H₈₀O₂, $r_{vw} = 28.642$, $d_c = 10.661$). The critical properties of C₄₂ wax ester were estimated with the group contribution method developed by Marrero et al. [15] ($T_c = 906.9$ K and $P_c = 4.5$ bar). Finally, the phase diagrams of the binary systems were calculated with the software GPEC [14].

3. Materials and methods

Table 3 shows the composition of the jojoba oil used in this work for experimental observation of phase equilibrium. It was extracted to exhaustion from the grounded seeds with technical grade hexane in a Soxhlet apparatus during 10 h. Afterwards, the solvent was recovered in a rotary evaporator operating under vacuum. The oil used in the experiments was analyzed by GC according to a method proposed by Van Boven et al. [16]. CO₂ (99.9%) was purchased from Linde AG, and propane (99%) was supplied by a Gas Co. (TGS, Argentine).

Fig. 1 shows a schematic diagram of the experimental setup. It consists of a constant volume cell (32 mL capacity) with two sapphire windows and a maximum operating pressure of 250 bar and temperature of 623 K. The cell has been described in detail elsewhere [17]. In a typical experiment, the cell was flushed out with the solvent at low pressure to remove residual gases. Then, it was loaded with a given amount of jojoba oil (~4 g, determined gravimetrically). The solvent mixture of CO₂ + propane in a given mass ratio (analyzed by GC) was fed to the cell from a stainless steel sample cylinder by a manual pressure generator. The amount of solvent (between ~12 g and ~30 g ± 0.1 g) charged to the cell was also determined gravimetrically by weight difference of the sample cylinder. After loading the cell, the temperature was increased up to the desired value (298 K, 313 K and 353 K). Moreover, the pressure was controlled according to the amount of solvent fed to the cell by the manual pressure generator. A camera (Mitsu Ciber-eye) was placed in front of the cell to record the visual observation of its contents.

4. Results and discussion

4.1. Phase behavior CO₂ + propane binary system

The solvent mixture of CO₂ + propane depicts a “type I” behavior following the classification proposed by van Konynenburg and Scott [18]. Fig. 2 shows GC-EoS predictions of propane + CO₂ mixtures under liquid–vapor equilibrium at different temperatures (294 K and 323 K). Good agreement between the experimental data and predicted curves is obtained. It is clear that the mixed-solvent

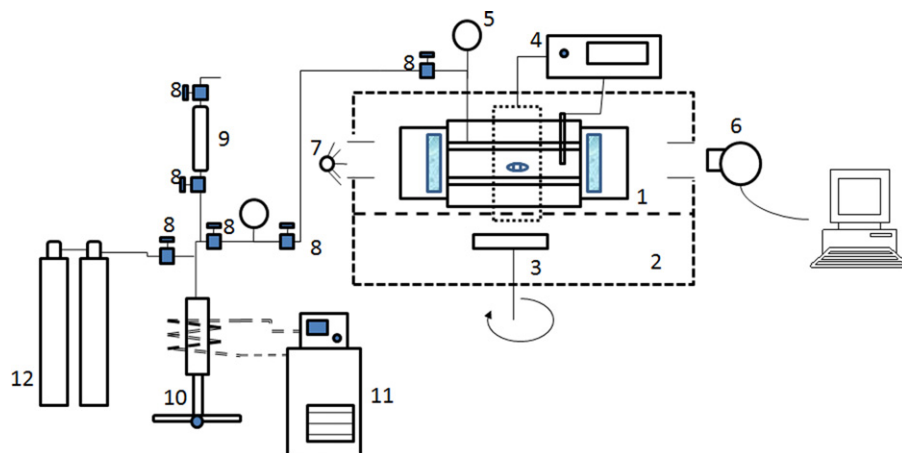


Fig. 1. Schematic diagram of the experimental setup. 1 – Equilibrium cell with heating aluminum jacket. 2 – Isolated fiberglass box. 3 – Magnetic stirrer. 4 – Heating controller and temperature recorder. 5 – Pressure gauge (Aschcroft 7500). 6 – Camera PC. 7 – Cold light source. 8 – Valves (HiP). 9 – Gas stainless steel sample cylinder. 10 – Manual pressure generator (HiP). 11 – Low refrigerated circulator. 12 – CO₂ and propane tube cylinder.

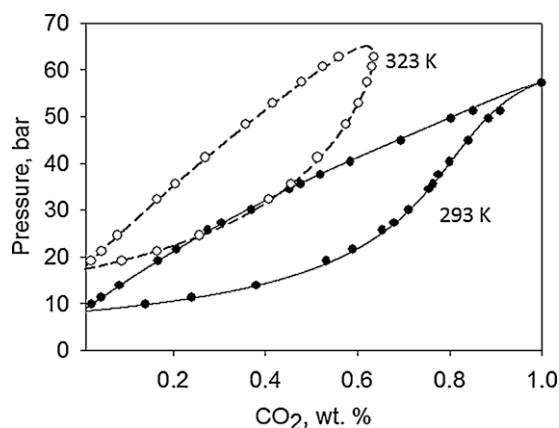


Fig. 2. Liquid–vapor equilibrium of CO₂ + propane binary system. Symbols and solid lines are experimental data [19] and GC-EoS predictions, respectively.

presents homogeneous phase behavior for all CO₂–propane proportions at pressures higher than the CO₂ critical pressure (70 bar).

4.2. Phase behavior of CO₂ + jojoba oil binary system

Fatty esters and jojoba oil (wax esters) present similar molecular structures, only differing in the number of methylene groups (CH₂) that constitute the molecule. Fig. 3 shows the phase equilibria of CO₂ + methyl oleate (C₁₉H₃₆O₂) and CO₂ + docosahexaenoic

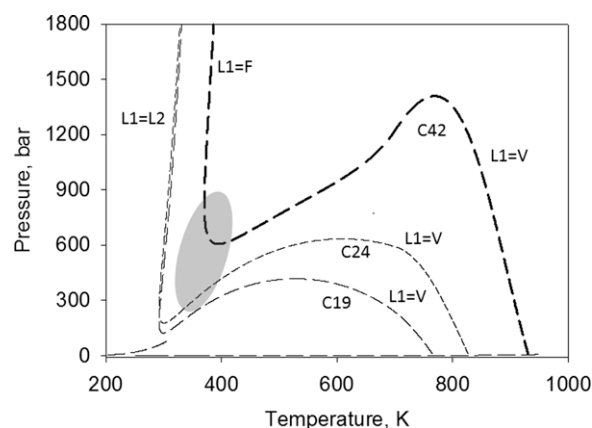


Fig. 4. GC-EoS predictions of the global phase behavior of fatty oils and CO₂ binary mixtures. Diagram calculated with GPEC [14].

acid ethyl ester (DHA) at temperatures that range between 313 and 343 K. There is also good agreement between the experimental data [20,21] and GC-EoS predictions. According to Fig. 3, at 313 K it is possible to get complete miscibility between methyl oleate and CO₂ at pressures higher than 130 bar, while it is necessary to increase the pressure above 200 bar for DHA.

Fig. 4 shows GC-EoS predictions of the global phase behavior of different alkyl chain length fatty esters from C₁₉ up to C₄₂. Jojoba oil is mainly formed by C₄₀ and C₄₂ (Table 3). The model predicts

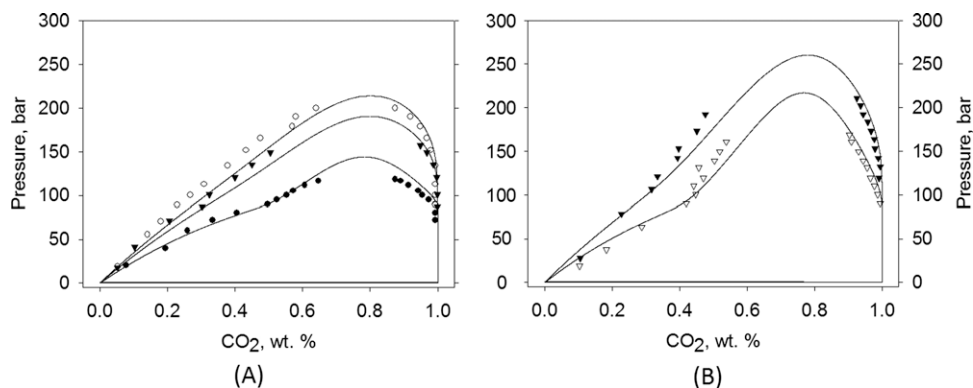


Fig. 3. Phase behavior of CO₂ + fatty esters binary systems. (A) CO₂ + methyl oleate at 313 K (●), 333 K (▼) and 343 K (○), experimental data from [20]. (B) Docosahexaenoic acid ethyl ester (DHA) + CO₂ at 313 K (△) and 333 K (▼), experimental data from [21]. Lines: GC-EoS predictions.

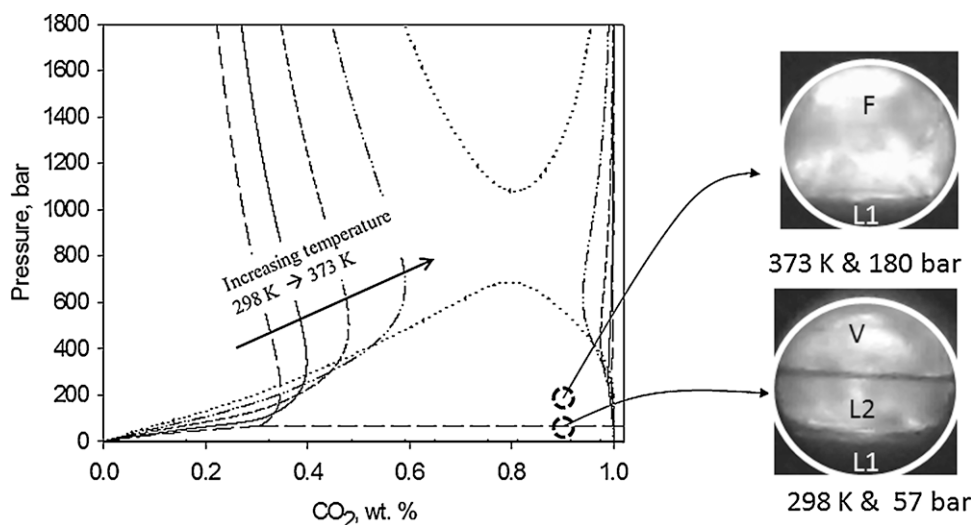


Fig. 5. GC-EoS predictions of CO_2 + jojoba oil binary system at 298 K, 313 K, 333 K, 353 K, and 373 K. Experimental observations in binary systems with 90 wt.% of CO_2 : LLVE and LVE at 298 K and 373 K, respectively.

that the binary systems of CO_2 and fatty esters exhibit Type III phase behavior, where homogeneous phase behavior can be found at temperatures higher than the critical temperature of CO_2 and pressures higher than 200 bar for C_{19} . Similarly, GC-EoS predictions also depict a type III behavior for the binary system of the jojoba oil and CO_2 . However, this mixture exhibits heterogeneous behavior over a wider range of pressure and temperature.

The jojoba oil + CO_2 system (curve C_{42} in Fig. 4) shows liquid immiscibility up to 363 K. In order to achieve homogenous conditions for an efficient oil extraction, the unit has to operate at higher temperatures and pressures above 600 bar. The shadowed region indicated in Fig. 4 sets the milder conditions for a feasible operation that has been reported in the literature [4,5].

Fig. 5 shows the GC-EoS prediction of the isothermal behavior of the CO_2 + jojoba oil binary system. It also shows experimental evidence of the phase behavior for the binary system jojoba oil and CO_2 in the pressure and temperature range of interest in the present work. In agreement with the model predictions, the cell content shows liquid–liquid–vapor equilibria (LLVE) at 298 K and 57 bar and liquid–vapor equilibria (LVE) at 373 K and 180 bar.

At temperatures lower than 370.2 K, the minimum temperature of the liquid–dense fluid critical curve (see $\text{L1} = \text{F}$ in Fig. 4 for C_{42} ester), the immiscibility of jojoba oil in liquid and supercritical CO_2 persists up to pressures as high as 1000 bar. However, the liquid immiscibility can be overcome at higher temperatures, for instance at 373 K and pressures higher than 600 bar (Fig. 5). Moreover, according to the model predictions the immiscibility would reappear at pressures higher than 1100 bar due to the positive slope of the critical line $\text{L1} = \text{F}$, described on Fig. 4. The model predictions above 200 bar are presented but were not experimentally tested since these are out of the operating region of the extraction process under study in this work.

On the other hand, the solubility of jojoba oil in dense CO_2 was studied by Stahl et al. [3]. According to the authors, the oil solubility increases from 300 bar to 1100 bar, and it is particularly more significant at temperatures higher than 323 K. This solubility behavior is in agreement with the model predictions of the jojoba oil + CO_2 system described in Figs. 4 and 5. Even though it is beyond the scope of this work to model quantitatively the solubility of jojoba oil in CO_2 , the GC-EoS predictive capacity was checked to assure that the

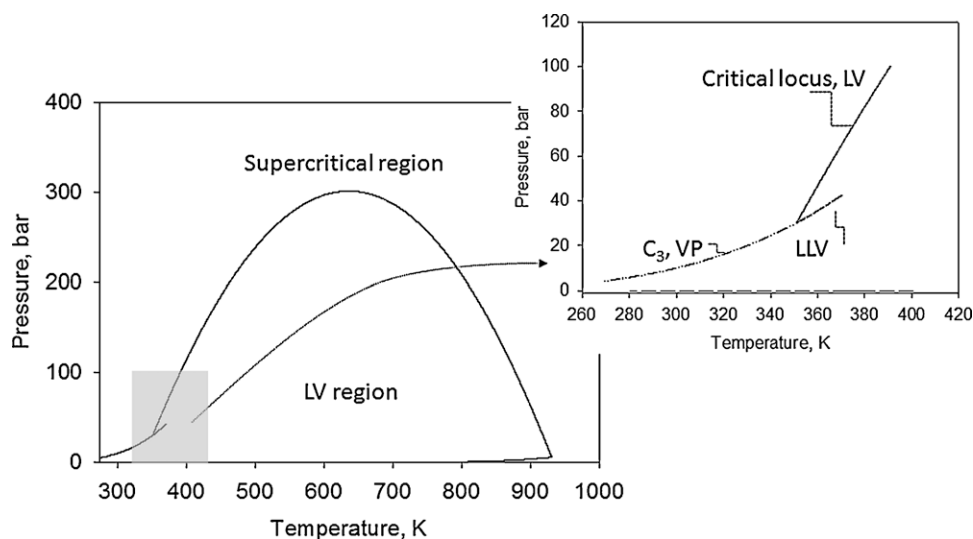


Fig. 6. GC-EoS prediction of the global phase behavior of the jojoba oil and propane binary system. Diagram calculated with GPEC[14].

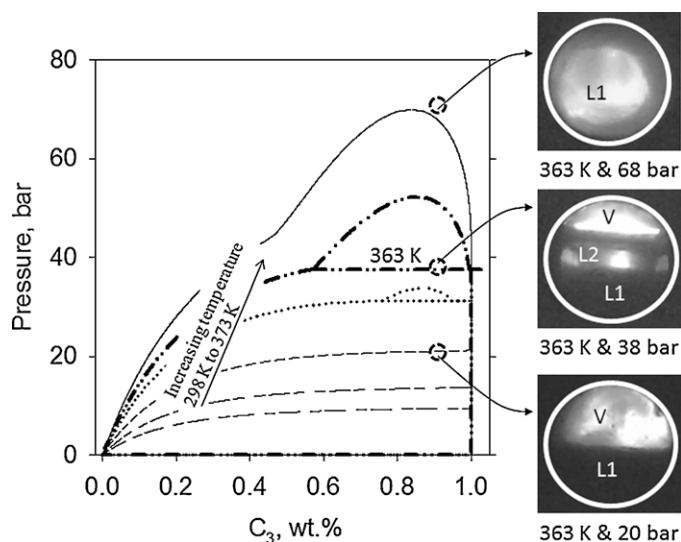


Fig. 7. GC-EoS predictions of propane + jojoba oil at 298 K, 313 K, 333 K, 353 K, 363 K and 373 K. Experimental observations for the jojoba oil + propane system at 363 K (90 wt.% of propane): LVE at 20 bar, LLVE at 38 bar and homogenous condensed phase at 60 bar.

global phase behavior is correctly predicted. Stahl et al. [3] reported that the solubility of jojoba oil in CO₂ is 2.5–5 g JO/kg CO₂ between 293–353 K and 150–300 bar, which is well predicted by the GC-EoS (4 and 8 g JO/kg of CO₂).

4.3. Phase behavior of propane + jojoba oil binary system

Fig. 6 depicts GC-EoS predictions of the global phase behavior of the jojoba oil and propane binary system in a pressure–temperature diagram. The model reports type V phase behavior, i.e., the system presents liquid–liquid equilibrium at high concentrations of propane (~95 mol%), with the upper critical end point, near the propane critical temperature (370 K). According to the model, temperatures higher than 360 K should be avoided in order to prevent a liquid phase split between propane and the jojoba oil mixture, assuring good solvent power. In addition, Fig. 7 shows the isothermal phase behavior predicted for this binary in the temperature range of 298–373 K. As it was mentioned before, at 360 K this system depicts partial liquid miscibility. The phase transitions observed in the laboratory for the binary propane + jojoba oil at 363 K agree with the model predictions (see cell pictures in Fig. 7).

The phase behavior of the propane + jojoba oil binary system presents similarities to the binary of propane + triglycerides. For instance, Coorens et al. [8] have determined that the lower critical end point of the system propane + tripalmitin, where the liquid partial miscibility begins, is at 349 K and 28.8 bar. According to various authors [8,22,23], the liquid phase split of propane with triglycerides exists within the temperature range of 349–370 K. Similarly, in the case of jojoba oil, the GC-EoS predicts that the binary system exhibits liquid–liquid partial miscibility in the range of 350.9–370.3 K.

Propane has an excellent solvent power for the extraction of fatty esters and wax. According to the phase behavior of the binary propane + jojoba oil, an extraction process that employs pure propane as solvent should be carried out at low temperatures in order to prevent the liquid phase split, and pressures barely higher than the vapor pressure of the solvent can be used in the process.

4.4. Phase behavior CO₂ + propane + jojoba oil ternary system

Fig. 8 shows the phase behavior of the ternary mixture CO₂ + propane + jojoba oil at 313 K and different pressures (40, 50, 60 and 70 bar) predicted by the GC-EoS. The solvent mixture exhibits liquid–vapor equilibria at 40 bar, as does the binary CO₂ + jojoba oil. The ternary system presents liquid–vapor equilibria for solvent mixtures with CO₂ concentrations greater than 35 wt.% at low pressure. It is important to note that the solvent is in the limit of non-flammability under this concentration of CO₂. An increase of pressure up to 50 bar shrinks the vapor–liquid region, and a mixed-solvent with ~40 wt.% of CO₂ still depicts complete liquid miscibility with jojoba oil. However, solvent mixtures with CO₂ concentrations between 45 and 70 wt.% present partial liquid miscibility at 50 bar and 313 K, consequently a three-phase region is predicted by the GC-EoS (bold triangles in Fig. 8). The ternary mixture also shows liquid–liquid–vapor equilibria at 60 bar and 313 K in a narrower range of CO₂ composition, between 65 and 75 wt.%. At pressures higher than 60 bar and CO₂ concentrations above 60 wt.%, the system exhibits liquid–liquid equilibria.

To confirm the model predictions, jojoba oil was put into contact with a solvent mixture with 48 wt.% of CO₂ concentration at 313 K operating temperature in the high pressure cell. Table 4 summarizes the results obtained in the experimental observations. Liquid–vapor equilibrium was observed for the ternary mixture at 40 bar. Increasing the amount of solvent, liquid–liquid–vapor equilibria was determined at 50 bar and liquid–liquid equilibrium at 60 bar and 313 K. Finally, homogenous conditions are achieved after further increases of solvent content in the cell at the same temperature and 70 bar.

Operation at higher temperatures increases the heterogeneous region, as depicted in Fig. 9 which shows the GC-EoS predictions for the ternary CO₂ + propane + jojoba oil at 353 K and the same pressures of the previous example (40, 50, 60 and 70 bar). An extraction temperature of 313 K allows working with a CO₂ concentration of 40 wt.%. However, it is necessary to increase the propane concentration to 85–90 wt.% when the working temperature is raised to 353 K. Accordingly, a solvent mixture with 12 wt.% of CO₂ was used to evaluate experimentally the operating conditions at 353 K for the extraction of jojoba oil (see Table 4). The ternary mixture showed liquid–liquid–vapor equilibria at 353 K and 40 bar. Moreover, injecting more mixed-solvent into the cell to raise the liquid level, the vapor phase collapsed at 44 bar, and a liquid–liquid equilibrium was observed even at 50 bar. Finally, under the operating conditions, a single phase was observed for the ternary system at 60 and 70 bar.

4.5. Phase equilibrium engineering of the extraction process

The extractor can be designed to operate with liquid propane + CO₂ mixed-solvent basically in two practical ways. An extraction carried out by percolation, where the solvent that percolates through the ground seeds coexists with a vapor phase within the extractor. On the other hand, it can be designed as an accelerated solvent extraction process with the liquid solvent pumped at high pressure through the extractor (see Fig. 10). In any case, the solvent is in excess respect to the oil being extracted; thus, the extractor operating region is in the lower part of the ternary diagrams previously discussed (near C₃–CO₂ axis), where low concentrations of jojoba oil coexist with the liquid solvent. Moreover, as it was showed in a previous work [7], the liquid partial miscibility must be avoided in the extraction process in order to make an efficient use of the mixed-solvent.

As discussed in previous sections, a liquid phase split can be prevented at temperatures lower than 353 K by adding propane to the mixture solvent. However, the concentration of CO₂ should also be

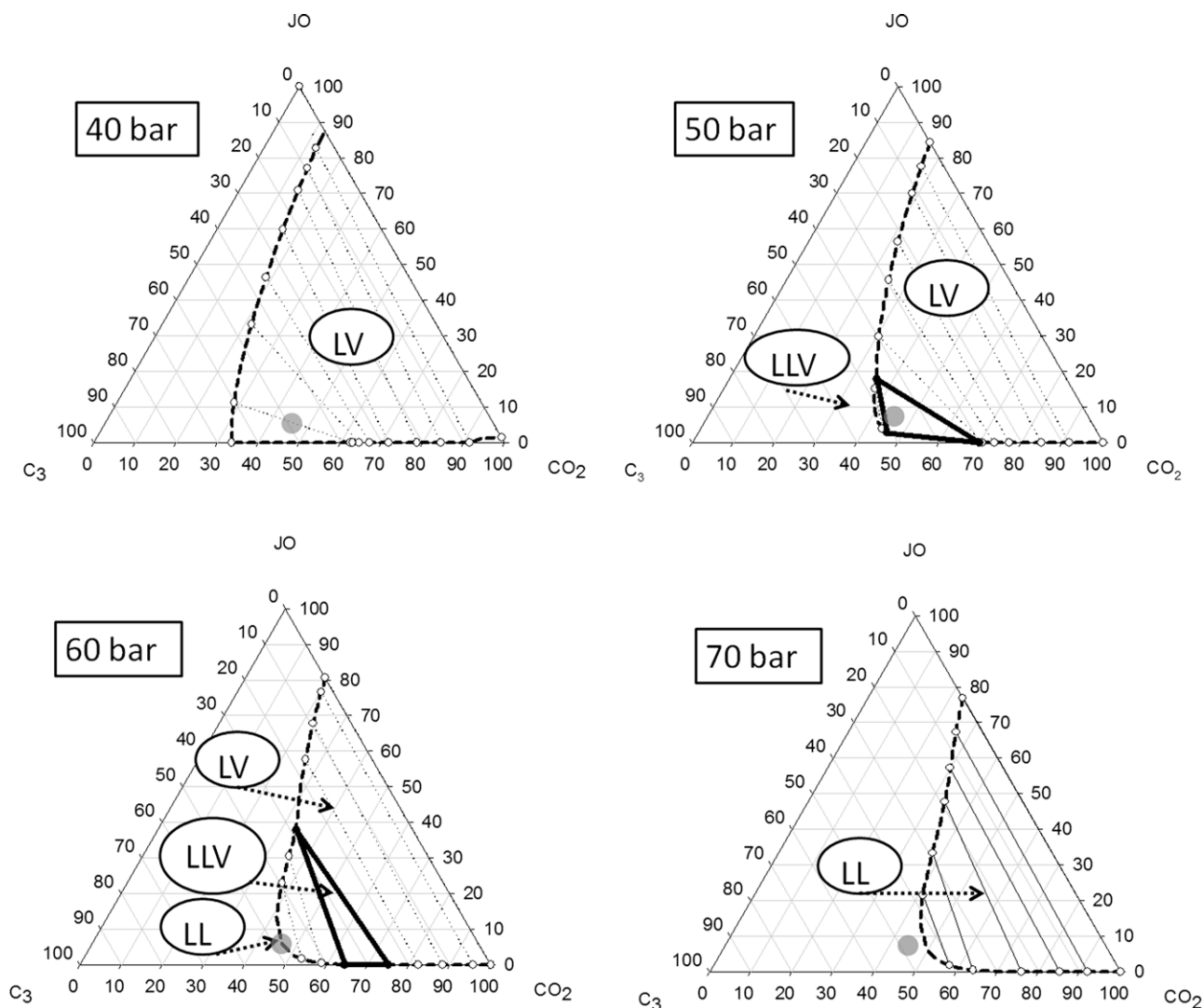


Fig. 8. GC-EoS predictions of CO_2 + propane (C_3) + jojoba oil (JO) phase behavior at 313 K and different pressures (compositions in wt.%). Bold triangle corresponds to LLVE regions and gray dots to the location of the system experimental observations reported in Table 4.

Table 4

Phase transitions of ternary system CO_2 + propane + jojoba oil.

Pressure			
40 bar	50 bar	60 bar	70 bar
<i>313 K and 48 wt.% of CO_2 in the mixed solvent</i>			
Liquid-vapor	Liquid-liquid-vapor	Liquid-liquid	Liquid
<i>353 K and 12 wt.% of CO_2 in the mixed solvent</i>			
Liquid-liquid-vapor	Liquid-liquid	Liquid	Liquid

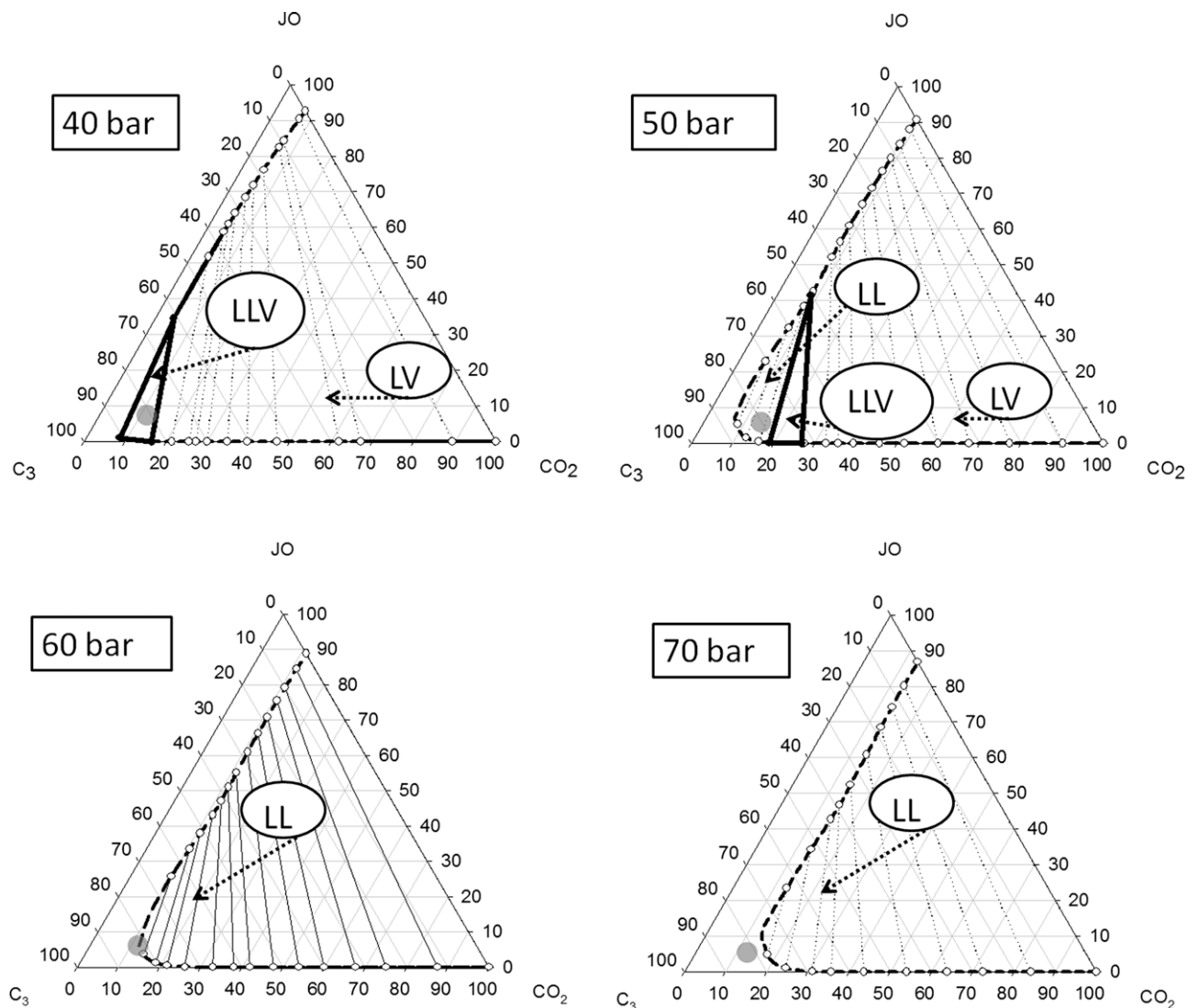


Fig. 9. GC-EoS predictions of CO_2 + propane (C_3) + jojoba oil (JO) phase behavior at 353 K and different pressures (compositions in wt.%). Bold triangle corresponds to LLVE regions and gray dots to the location of the system experimental observations reported in Table 4.

high enough to guarantee a non-flammable solvent and safe operation of the entire process, i.e. the extractor, the flash separators and the recycle solvent loop. A minimum of 30 wt.% of CO_2 is necessary to turn propane non-flammable in contact with air.

According to the phase rule, a ternary system in the three-phase region (LLV) and at a given temperature has only one degree of freedom; therefore, once the pressure of the system is set, there is a unique condition for the phase equilibrium composition. This

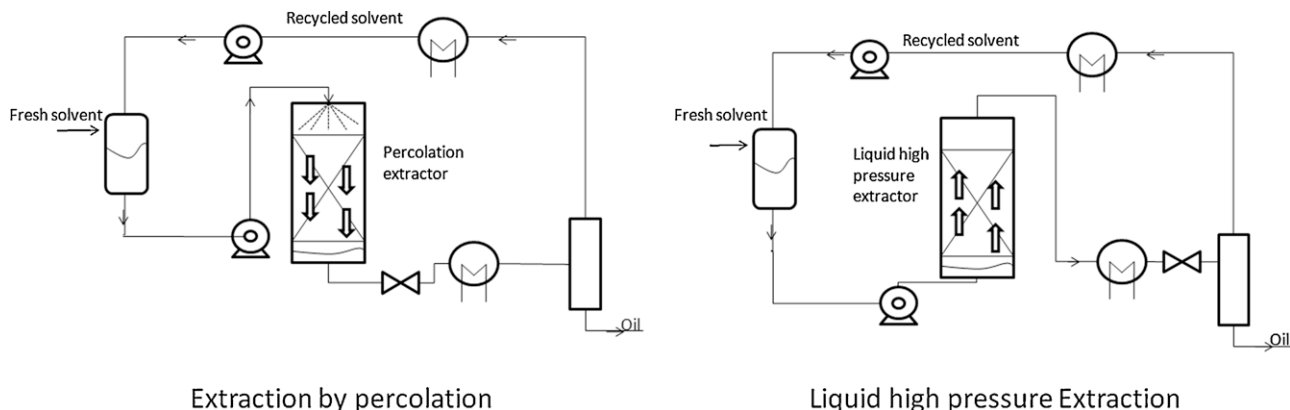


Fig. 10. Schematic diagrams of the two extraction operating modes.

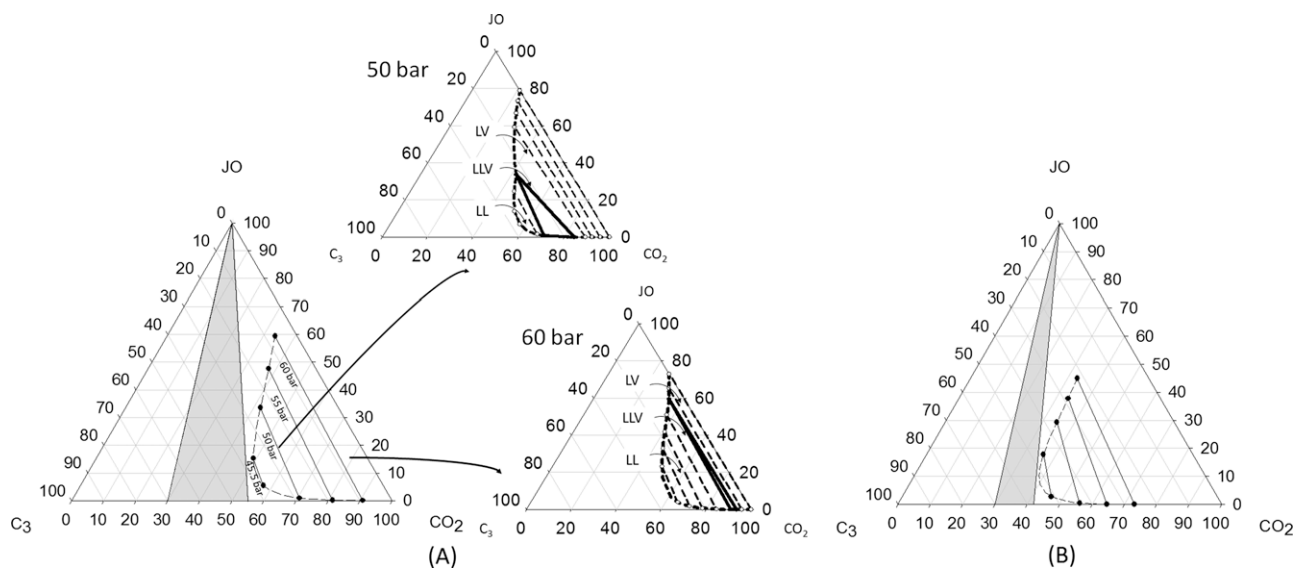


Fig. 11. Feasible operating regions of the jojoba oil extraction process (shadowed region). (●) Projection of the liquid–liquid tie lines of the three phase equilibria at different pressures for two isotherms: (A) 298 K and (B) 313 K.

property allows drawing a binodal curve on a triangular diagram that limits the three-phase LLV equilibria, as a function of pressure, with tie lines indicating the two liquid phase compositions. Fig. 11 shows the binodal curves for the ternary CO_2 + propane + jojoba oil that limit the LLV equilibria at 298 K and 313 K. These curves are useful to design the extraction process because clearly identifies the unfeasible region. The boundaries of the feasible region are given by the liquid partial miscibility on one side and the non-flammability of the solvent on the other, which set constraints to the maximum and minimum permitted CO_2 concentration in the solvent, respectively (shadowed region in Fig. 11).

The feasible operating region is more comprehensive at the lowest temperature (298 K) in which 55 wt.% CO_2 is admitted in the solvent without having partial liquid miscibility, while at 313 K the allowed concentration is 42 wt.%. In comparison with previous works [6,7], where a similar analysis has been carried out for vegetable oils like sunflower or soy oil, the feasible operating region is wider in the jojoba oil extraction process, which can be explained by the higher solubility of jojoba oil in the mixed-solvent compared to that of triglycerides.

The feasible operating region identified in Fig. 11 guarantees a good solvent power and a non-flammable solvent for the two extraction operating modes, percolation and high pressure liquid extraction. However, the constraints are conservative for the latter because, as is shown in Fig. 12, the CO_2 concentration can increase up to 50 wt.% at 313 K or even higher concentrations at pressures over 70 bar. The amount of CO_2 in the mixed-solvent can be increased up to 70 wt.% at the expense of higher extractor operating pressure that should be raised in order to keep the good solvent power.

Knowledge of the ternary system phase behavior is required to perform phase equilibrium engineering of the extraction process. According to the GC-EoS predictions and experimental observations carried out in the present work, it is possible to operate a jojoba oil extractor at 70 bar and 298 K with a mixed CO_2 + propane solvent containing 40 wt.% of CO_2 . In this way, partial liquid miscibility is avoided, and a non flammable solvent with good capacity is ensured. Downstream, the operating temperature can be increased up to 353 K in order to obtain partial liquid miscibility in the ternary system (see Fig. 9) to separate the extracted oil and recover an important fraction of the recycling solvent without depressurization.

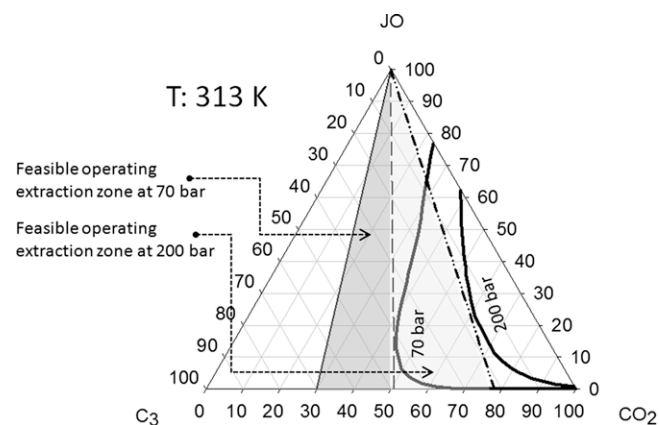


Fig. 12. Feasible operating region of high pressure liquid extraction of jojoba oil at 313 K and 70 or 200 bar according to GC-EoS prediction of the LLE region.

5. Conclusions

The phase equilibria of binary and ternary mixtures with CO_2 , propane and jojoba oil have been studied. GC-EoS predictions show that it is possible to carry out the extraction of jojoba oil from its seeds with a non-flammable liquid mixed- CO_2 + propane solvent with good solvent power. Experimental observations of the phase behavior of jojoba oil extracted from ground seeds with different solvent mixtures (CO_2 concentration from 12 to 48 wt.%) were carried out at 313 and 353 K in a pressure range of 40–70 bar to evaluate potential operating conditions. Partial liquid miscibility can be avoided operating at 313 K and 70 bar with solvent mixtures containing 40 wt.% of CO_2 . Higher operating pressures can also reduce the amount of propane in the solvent required to get a single phase. Moreover, after the extraction, it is possible to separate the solvent and the extracted oil by increasing the temperature to 353 K. In this way, a solvent mixture with 40 wt.% of CO_2 would split into two liquid phases at 70 bar, a dense liquid phase rich in jojoba oil (45–55 wt.% of oil) and a light liquid phase rich in solvent that can be recycled to the extractor without depressurization.

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