HIGH-PRESSURE EXTRACTION OF JOJOBA OIL WITH MIXED-CO_2/PROPANE SOLVENTS

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Abstract. Previous studies on the phase equilibria of jojoba oil and CO_2+propane mixtures have shown that this solvent mixture is a good separation agent for the extraction of jojoba oil from seeds. High solvent load capacities can be obtained using a solvent mixture with CO_2 concentrations up to 70 wt%, working at 313 K and 200 bars. In this work the extraction of jojoba oil with high pressure liquid CO_2/propane solvent mixtures was studied experimentally. First, jojoba oil was extracted at 313 K using different liquid solvent concentrations (30 wt%, 50 wt% and 70 wt% CO_2) at pressures of 70 bars and 200 bars, to assess the influence of the solvent composition and phase behavior on extraction rate. A great influence of the phase condition on the extraction rate was determined. Similar results were obtained when the high-pressure liquid extractions of jojoba oil from milled seeds were carried out using solvent mixtures containing 30 wt% and 50 wt% CO_2 at 313K and 70 bars. A mixed CO_2 + propane liquid solvent with 30 wt% CO_2 exhibits good solvent power. An oil extraction yield of 90 % was obtained at 313 K and 70 bar, by applying a solvent to oilseed mass ratio of 8 g solvent / g oilseed to jojoba flour (milled seeds having diameters lower that 0.84 mm) preheated at 343 K.

Keywords: Phase equilibria, Solubility, Jojoba oil, Extraction, Carbon dioxide, Propane

1. Introduction

Nowadays, the vegetable oil industry is one of the main manufacturing areas that demands novel economical and green technologies. Many conventional processes to extract oil from oil-seeds require the use of organic solvents such as hexane, which are considered harmful to human health and environment [1]. An interesting alternative is to use dense gases or supercritical fluids. Particularly, carbon dioxide has been extensively studied [2], because it is an inert, inexpensive, easily available, odorless, tasteless, environmentally friendly, and GRAS (Generally Recognized As Safe) solvent. As an additional advantage CO_2 can be easily removed from the oil by depressurization, after extraction.

In the particular case of jojoba oil, its many and diverse uses have motivated some research on alternative extraction processes. Jojoba oil and derived products have a wide range of industrial applications. In the cosmetic industry it is used in formulations for skin-care, such as lotions, moisturizers, massage oils, and soothing creams [3]. It is also used in specialized lubricants, antifoaming agents, detergents, driers, emulsifiers, fibers, plasticizers, protective coating, resins and surfactants, among others [1].

The extraction of jojoba oil using supercritical CO_2 ($scCO_2$) has been studied by Stahl et al. [4] and Salgın et al. [1,5]. These last authors also studied the addition of co-solvents to increase the oil solubility in CO_2. The results obtained in the aforementioned works show that the system jojoba oil + CO_2 is heterogeneous over a wide range of both, 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 bars. Therefore, the CO_2 extraction of jojoba oil from the seeds is still not an attractive alternative from an economical point of view. On the other hand, although the process performance can be improved by the use of ethanol as cosolvent, a

further step is required in this case to remove the alcohol. In general, a complete removal of the co-solvent from the oil is difficult. In order to avoid thermal degradation, a vacuum step is required to purify the product at low temperatures.

An alternative method for the extraction of oil seeds involves the addition of propane to carbon dioxide as solubility modifier. In general, vegetable oils are completely miscible in liquid propane at temperatures lower than 343 K (lower critical end point LCEP). Its solvent power is much greater than that of CO_2, requiring lower solvent / feed ratios and operating pressures. Also, propane can be easily removed from the oil after extraction, by simple depressurization. The main drawback in the use of propane is its flammability. Propane will burn in any propane/air mixture having more than 2.15% by volume of propane [6]. This inconvenient can be overcome by using a CO_2 + propane solvent mixture having a sufficient amount of CO_2 to turn the propane/CO_2/air mixture non-flammable [6]. Previous studies of vegetable oil extraction with propane and CO_2 mixed solvents report good results [7-9].

In earlier work [10], a process was proposed for the extraction of jojoba oil using a high-pressure liquid solvent. The GC-EOS group contribution thermodynamic model, combined with reliable experimental observation, were used to study the phase equilibrium scenario of CO_2 + propane + jojoba oil mixtures, in order to select the best operating conditions for the extraction process. The phase behavior of binary and ternary mixtures was studied at different temperatures, pressures and compositions, in order to determine conditions with good solvent power, for non-flammable solvent mixtures. It was found that it is possible to avoid partial liquid miscibility if the extractor is operated at 70 bars and 313K, with CO_2 + propane solvent mixtures containing between 30 wt% and 50 wt% CO_2. It is also possible to increase the CO_2 concentration in the solvent up to 70 wt% and keep a good solvent power, at the expenses of increasing the extractor operating pressure up to 200 bars [10].

In order to corroborate these previous results [10], experimental extractions of jojoba oil from ground oilseeds were carried out in this work, using CO_2 + propane solvent mixtures. The influence of the phase behavior and solvent composition on the extraction rate was analyzed. The solubility of jojoba oil in CO_2 + propane mixtures was also determined from the experimental data. During the extraction experiments, a special focus was placed on the effect of certain properties (i.e. phase conditions, thermal pre-treatment, particle size) in the extraction process. [1,5,11-13]. Therefore, one innovative aspect of the present contribution is the application of phase equilibrium engineering to the extraction of jojoba oil using a green solvent mixture.

2. Materials and methods

2.1 Materials

The jojoba seeds (*Simmondsia chinesis*) used in the experiments were cultivated and harvested in La Rioja (Argentina). The oil composition has been detailed in a previous work [10]. The moisture content of the oilseeds, which was determined according to AOCS Method Ca2c-25 [14], was 3.8%. The clean seeds were ground in a rotary mill to produce particles with a diameter smaller than 2.83 mm. The sieved fraction containing particle diameters smaller than 0.84 mm is identified in the text as jojoba flour. The oil content of the seeds was determined by 10 hours Soxhlet extraction using technical grade hexane, followed by solvent removal under vacuum in a rotary-evaporator. The oil content in the ground material and the flour was 50 wt%.

The CO_2 (99.9 %) was purchased from Linde AG and propane (99 %) was provided by a local supplier (TGS, Argentina).

2.2 Experimental apparatus and operational procedure

Experimental runs were performed in a high-pressure extraction apparatus (Fig. 1) described in detail elsewhere [15]. The experimental procedure was slightly modified from the previous one [15] to accomplish the objectives of this work.

Propane + carbon dioxide liquid mixtures were used as solvent. These mixtures were prepared gravimetrically in a stainless steel sample cylinder (500 mL capacity) at a given mass ratio, and the final composition was determined by gas chromatography. The range of solvent compositions studied was from 30 wt% to 70 wt% CO_2, covering conditions from complete to partial oil/solvent miscibility.

The extraction experiments were carried out to study both, the oil solubility in the solvent mixture and the oil extraction from ground seeds. The experimental procedure was as follows. A given amount of jojoba oil (1.5 g - 2.5 g) or milled seeds (6 g) were mixed with glass spheres (d = 1 mm) and loaded into the extraction cell. After the entire system has been assembled, a gentle solvent stream was flushed through the cell to remove residual air. The extractor was then pressurized with the solvent mixture and allowed to reach equilibrium conditions under constant temperature and pressure. The solvent was then continuously pumped to the cell to carry out the oil extraction. After depressurization of the extract, the jojoba oil was collected in glass "U" tubes and weighed in a precision balance. The solvent flow rate was set at 0.5 g/min to assure equilibrium conditions or maximum solvent load capacity at the extractor outlet. The residence time in the cell was between 10 and 25 minutes, depending on the solvent mass density. The extraction experiments were carried out at 313 K and 333 K and pressures of 70 bars and 200 bars.

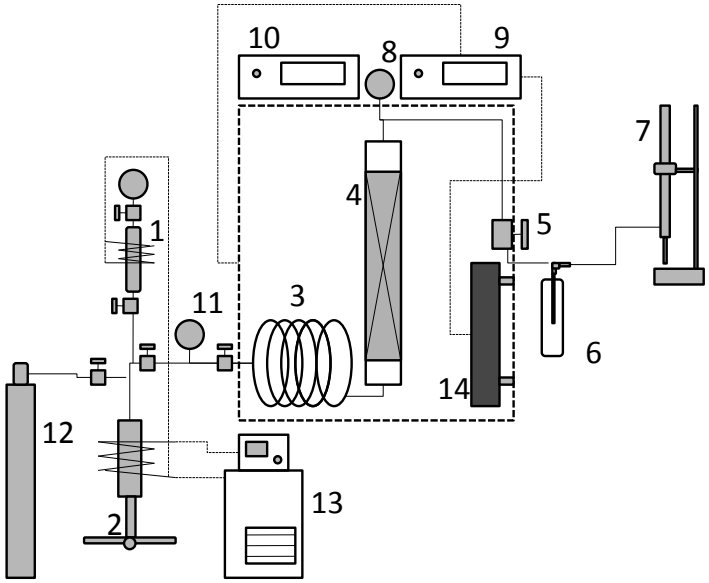

Figure 1. High pressure extractor: 1. Gas stainless steel sample cylinder, 2. Pressure generator, 3. Heat exchanger element, 4. Extraction cell, 5. BPR valve, 6. Liquid trap, 7. Flow-meter, 8. Temperature sensor, 9. Temperature controller, 10. Extractor temperature indicator, 11. Pressure sensor, 12. Gas cylinder, 13. Low refrigerated circulator, 14. Heating element.

3. Results and discussion

3.1 Extractions of Jojoba oil with CO_2 + propane solvent mixtures

These experiments were conducted at 313K, loading the extraction cell with glass spheres coated with jojoba oil. Figure 2 shows the influence of the solvent composition (30 wt%, 50 wt% and 70 wt% CO_2) on the cumulative extraction yield of jojoba oil as a function of time for both, the 70 bar (Figure 2A) and 200 bar (Figure 2B) experiments. Solvent mixtures having 30 wt% and 50 wt% CO_2 were able to extract nearly all the oil after 80 min, independently of the operating pressure.

Figure 2A shows an initial steep rise and a final plateau in both, the 30wt% and 50wt% curves. On the other hand, the 70wt% curve depicts a linear kinetic. In this case, only about 20% of the oil was removed after 112 minutes of operation. This is in agreement with previous results [10], which indicate that the last conditions correspond to an oil + solvent liquid-liquid (LL) heterogeneous region, associated with a poor solvent power.

Figure 2B shows the influence of the solvent composition in the extractions carried out at 200 bar and 313K. At this high pressure the three solvent mixtures achieved good solvent power. The final oil extraction obtained by the 30 wt%, 50 wt% and 70 wt% CO_2 solvent mixtures was 97.4%, 93.2% and 87.4 %, respectively. The difference on the final extraction yields are certainly related to solvent transport properties such as density and diffusion coefficients.

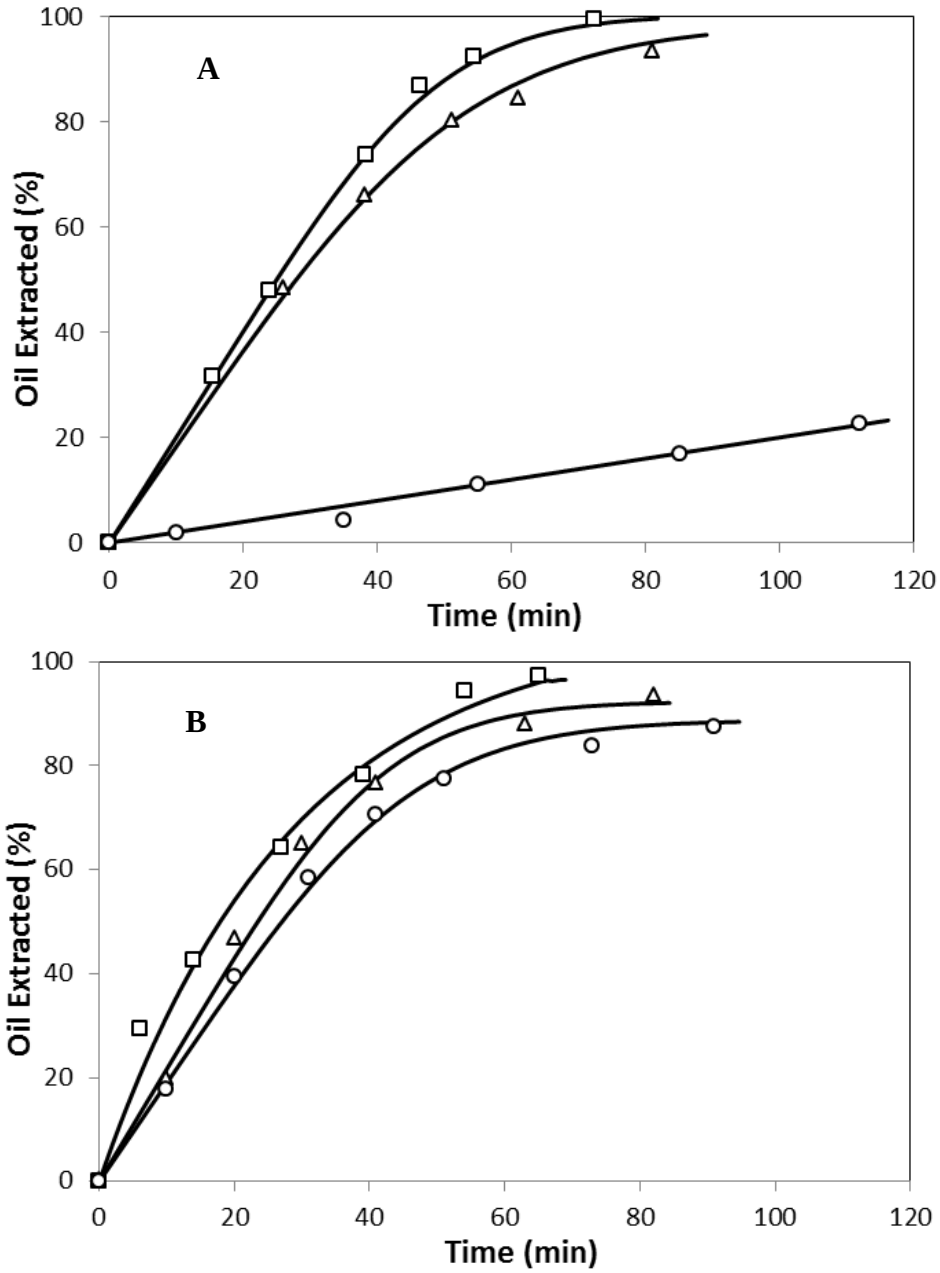

Fig. 2- Extraction of jojoba oil with CO_2+propane solvent mixtures of different composition at 313 K, for a solvent flow rate of 0.5 g/min and 70 bar (A) or 200 bar (B) pressure.

Figure 3, on the other hand, shows the effect of pressure on the cumulative extraction yield of jojoba oil, as a function of the solvent mass used in the extractions. The curves in Figure 3A correspond to the 30 wt% CO_2 solvent mixture, while those of Figure 3B were obtained from the experiments with the 50wt% CO_2 mixture. It should be pointed out that the solvent + oil system exhibits a single phase for these two solvent concentrations. However, for both solvent compositions the results indicate a greater solvent load capacity at the highest pressure. This can be related to an improvement of the transport properties, associated with the increase of the solvent mass density.

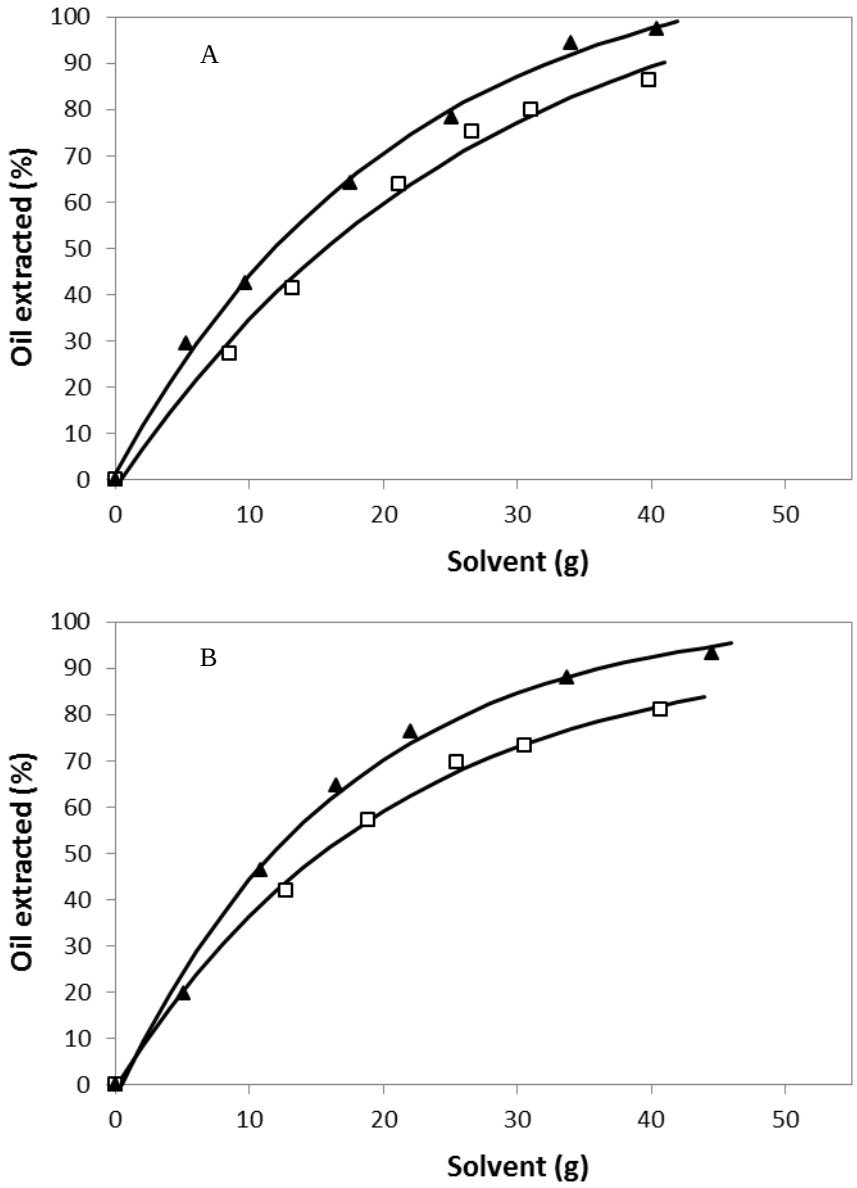

Figure 3. Jojoba oil extraction with CO_2 + propane solvent mixtures at 70 bar (□) and 200 bar (▲). Extraction conditions: 313 K, solvent flow rate 0.5 g/min. A) 30 wt% CO_2, and B) 50 wt% CO_2.

From these experiments we can conclude that extraction conditions under the homogeneous region produces the highest extraction yield of jojoba oil. The best results were obtained using the solvent mixture with the lower CO_2 concentration.

In this study, also the solubility of jojoba oil in the 70wt% CO_2/propane mixed solvent was studied at 313 K. As it was mentioned, this ternary system exhibits liquid partial miscibility. The value of the solubility was determined from the slope of the initial linear portion of the curve relating the cumulative oil yield vs. the solvent mass (extracted oil / solvent, g/g). Under heterogeneous liquid-liquid conditions the value of this slope corresponds to the oil solubility in the solvent, while under single fluid conditions it represents an apparent solubility given by the solvent load capacity, whose value is related to transport properties.

Figure 4 illustrates the effect of the operating pressure on the oil solubility at 313 K, for a solvent mixture having 70 wt% CO_2. As it can be observed, the solubility increases with pressure in the range of 70 bar to 130 bar. Beyond this point, it decreases gradually with a pressure rise. Under liquid-liquid equilibrium conditions, the increase of the solvent density with pressure allows a higher dissolution of the jojoba oil in the solvent;

hence, solubility increases with pressure. On the other hand, at pressures beyond 130 bar the oil is completely soluble in the mixed solvent. Under these homogeneous conditions, the increment of the solvent density with pressure implies a higher mass of solvent in the extractor cell. For the same amount of oil initially present in the extractor, this means a decrease in the apparent solubility. From the results depicted in Figure 4, we found that, at 313K, the highest solubility of jojoba oil in the 70wt% CO_2 solvent mixture (66.2 g jojoba oil/kg solvent) is reached when the extractor is operated at 130 bar. At 110 bar this solubility drops to a value of 30 g jojoba oil / kg solvent.

Stahl et al. [4] measured a value of 11 g jojoba oil/kg CO_2 for the jojoba oil solubility in pure CO_2 at 350 bar and 333 K. On the other hand, Salgin et al [1,5] determined a similar value (15 g jojoba oil /kg CO_2) at 350 bar and 343 K. With the addition of 8 vol% of ethanol as co-solvent, these authors found the solubility to increase up to 25 g jojoba oil / kg CO_2. In comparison with pure CO_2 or CO_2+ethanol mixtures, the results obtained in this study point out that greater extraction efficiency can be obtained with CO_2/propane solvent mixtures, because it is possible to reach higher solubility operating the extractor at lower pressures.

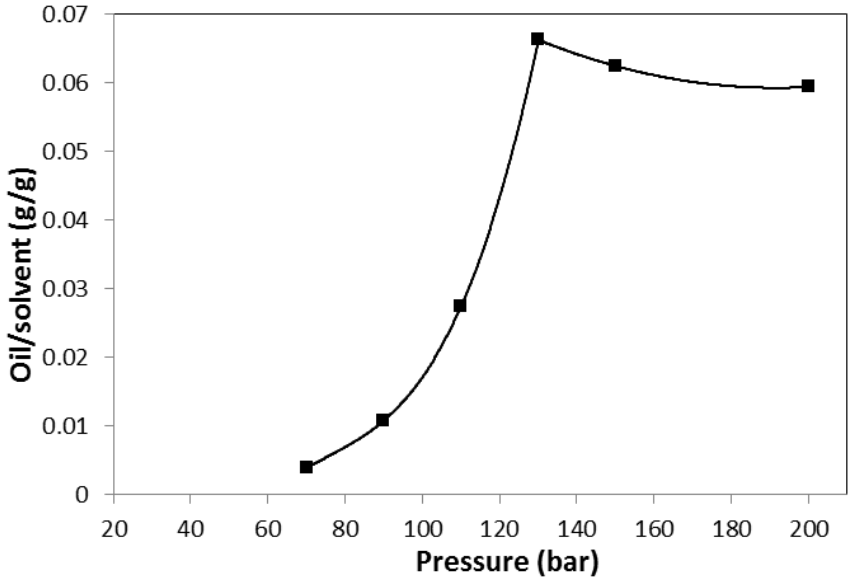

Figure 4. Effect of pressure on the Jojoba oil solubility in a solvent mixture with 70 wt% CO_2 at 313 K.

3.2 Extractions of jojoba oil from milled seeds using CO_2/propane solvent mixtures

This section presents the results found in the extraction of jojoba oil from the milled seeds. The operating conditions were selected according to the results obtained in the jojoba oil extractions, as shown in the previous section. The extractions were carried out under homogeneous oil/solvent conditions, using 30 wt% CO_2 and 50 wt% CO_2 solvent mixtures. The extraction temperature and pressure were set at 313K and 70 bar, respectively. As shown in Figure 3, there is no major increase in the oil yield by working at higher pressures. This lower pressure entails lower process costs and safer operating conditions. Different pre-treatments of the seeds were analyzed in order to maximize extraction yields. The results are given as a percentage of extracted oil with respect to the total oil content of the milled seeds (50wt%), as measured by Soxhlet extraction.

Effect of solvent composition. Figure 5 shows the curves of cumulative oil extraction yield versus solvent mass. As it can be seen, no-substantial difference was observed in the final extraction yield when using the 30wt% or 50wt% CO_2 solvent mixture. This was not the case in the extraction of rosehip oil from oil-seeds by percolation with liquid CO_2/propane mixtures, as shown in previous work [9]. In this case, lower mass transfer rates were obtained for the solvent mixtures having higher concentrations of CO_2. The results were explained by a reduction of the mass diffusivity, caused by the higher non-ideality of the mixed solvent + oil system, as measured by the value of the oil activity coefficient in the mixture. The difference between the results of previous work [9] and those obtained in this study could be related to the experimental procedure. The operating temperature and, particularly, the type of flow used in both experiments were different. In the previous work [9] the extraction was carried out by percolation of liquid solvent mixtures at

room temperature (293 K / 298 K), while in this study a compressed liquid solvent mixture was pumped through the extractor at a temperature higher than the critical temperature of CO_2. Also, the chemical nature of the solutes is different. Jojoba oil is a mixture of wax esters, while rosehip oil is a mixture of triglycerides. Further studies are necessary to elucidate this difference and to evaluate the effect of the mixed solvent composition on the extraction.

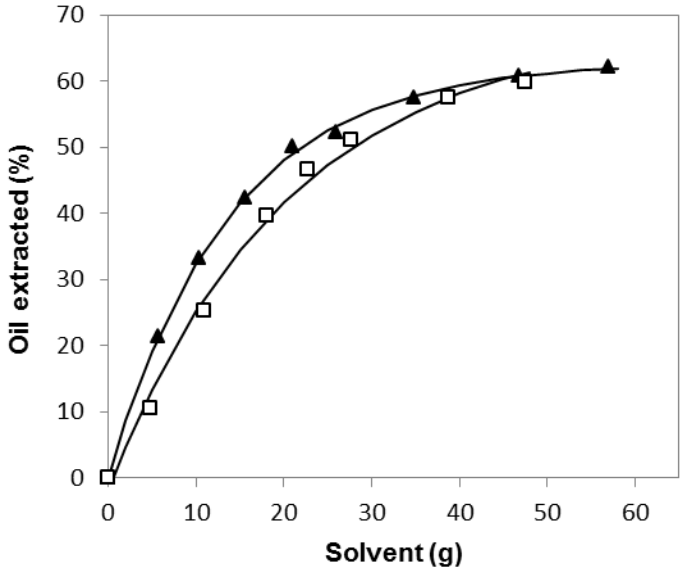

Figure 5. Effect of solvent mixture composition on the percentage of jojoba oil extracted from ground seeds with particle diameters d < 2.8 mm. Symbols are experimental data for (□) 50 wt% CO_2 and (▲) 30 wt % CO_2 mixed solvents. Experimental extraction condition: 313 K, 70 bar and solvent flow-rate = 0.05 g/min. Lines: sketched for better visualization of experimental data.

In these experiments about 6 g of milled jojoba seeds were extracted using a specific solvent mass of 8 g CO_2 / g seeds. The final oil yield was just about 60 %. However, at these homogenous working conditions, the apparent solubility of the oil in the solvent, determined from the extraction curves, was higher in the extraction of milled seeds than in the extraction of oil. This increment of the apparent solubility is related to the greater amount of oil loaded to the extractor (1.5 g of jojoba oil versus 3 g of jojoba oil present in the milled seeds) for the same solvent mass capacity per unit of extractor volume.

Effect of particle size and thermal pre-treatment. The effect of the size and pre-heating treatment of the milled seeds on the extraction yield was studied. In order to increase the extraction yield, the milled jojoba seeds were heated prior to extraction. It is expected that this pre-heating treatment coagulates proteins, causing the coalescence of oil droplets and making the seeds more permeable to the flow of oil. Also, the affinity of oil for the solid seed surfaces would decrease [11].

A series of extractions were carried out on ground jojoba seeds of two different sizes (milled seeds with diameters lower than 2.8 mm and a sieved fraction with diameters lower than 0.84 mm) with and without pre-heating at 343K and 363K during 120 minutes. All extractions were performed at 70 bar and 313K, with a 30wt% CO_2 solvent mixture flowing at a rate of 0.05 g/min. A set of experiments were also carried out on jojoba flour (sieved fraction of ground seeds having diameters lower than 0.84 mm) at 333K.

Figure 6 shows the results of these extractions. As it can be seen in this figure, the final percentage of extracted oil increased from 62% to 69.9% when the jojoba seeds were pre-heated at 343K. Increasing the pre-heating temperature to 363K didn´t produced any significant increase in the extraction yield.

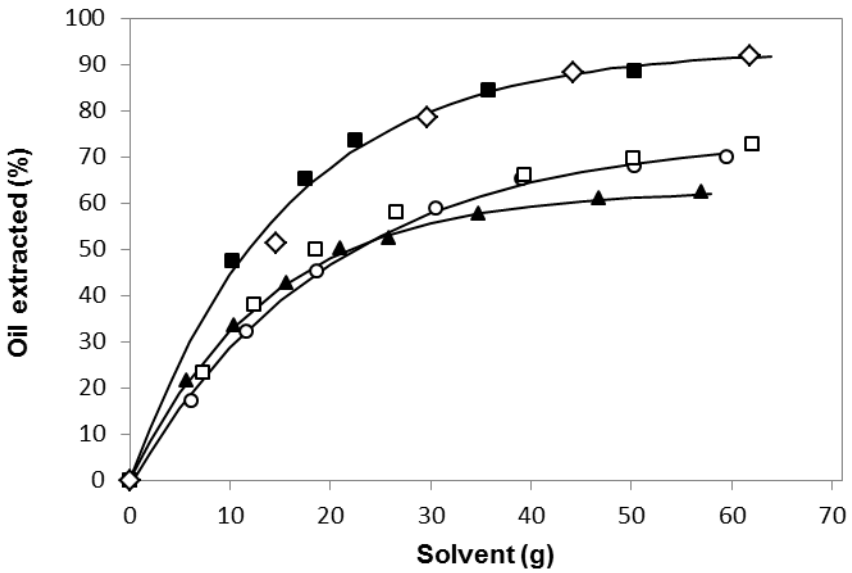

Figure 6. Effect of thermal pre-treatment on the percentage of jojoba oil extracted from milled seeds. Experimental extraction conditions: 313 K, 70 bar, 30 wt% CO_2 and solvent flow-rate of 0.05 g/min. Symbols are experimental data: (▲) ground seeds (d < 2.8 mm); (O) ground seeds pre-heated at 343K; (□) ground seeds pre-heated at 363K; (■) Flour (d < 0.84 mm) pre-heated at 343 K; (◊) Flour pre-heated at 343 K and 333K extraction temperature. Lines: sketched for better visualization of experimental results.

Regarding the effect of particle size on oil yield, the extraction of jojoba flour (i.e. sieved fraction having diameters lower than 0.84 mm) showed significantly higher yields than those of the milled seeds having diameters up to 2.8 mm. A 90% final yield was reached in the extractions of pre-heated jojoba flour. The effect of particle size on supercritical CO_2 extraction performance has been discussed in previous work [1,5,12]. Salgin et al. [5] suggest that the effect of intraparticle diffusion seem to gain importance in larger particles, causing an appreciable decrease in the extraction yield. In addition, Reverchon et al. [12] attributes this behavior to the reduction of the seed - solvent contact area when bigger particles are used.

Any temperature increase will reduce the oil viscosity, which, in turn, should increase the mass transfer rate [16]. However, extraction yields achieved at 333K showed negligible changes with respect to the results obtained at 313 K (see Figure 6). These results may suggest that most of the oil present in the seeds was released during pretreatment (heating and milling), reducing internal mass resistance and increasing intra-particle diffusion.

Pretreatment of jojoba seeds showed a remarkable effect on the efficiency of oil extraction. A 90% oil yield could be achieved using a specific solvent mass of 10 g solvent / g seed. This result represents a noticeable improvement with regard to previous work [1,4,5], showing the potentiality of CO2/propane solvent mixtures for the extraction of jojoba oil.

4. Conclusions

In this work, high pressure liquid extractions of jojoba oil were carried out in order to analyze the effect of solvent composition (30 wt% to 70 wt% CO_2), pressure (70 bars and 200 bars) and phase behavior on solvent power. It was concluded that operating under liquid-liquid equilibrium conditions reduces the extraction yields because the solvent load capacity is regulated by oil solubility limits. It is possible to operate the extractor at 70 bars under homogeneous conditions, by using CO_2 + propane solvent mixtures having up to 50 wt% CO_2. Higher CO_2 concentrations, such as 70 wt%, require pressures higher than 130 bar in order to reach single liquid phase oil + solvent conditions. Results obtained in the oilseed extractions with mixed solvents having 30 wt% CO_2 and 50 wt% CO_2 showed similar results of the cumulative extraction curves. After thermal pre-treatment and reduction of the ground seed particle size, it was possible to extract up to 90 % of the total oil content of the seeds, using 10 g solvent / g seeds. The use of CO_2 + propane solvent mixtures

shows to be an efficient green alternative technology to extract oils from ground seeds, meeting solvent power, selectivity and safety goals.

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