Supercritical Fluid Extraction of Jojoba Oil

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ABSTRACT: Supercritical fluid extraction of jojoba oil from *Simmondsia chinensis* seeds using CO_2 as the solvent is presented in this study. The effects of process parameters such as pressure and temperature of extraction, particle size of jojoba seeds, flow rate of CO_2, and concentration of entrainer (hexane) on the extraction yield were examined. Increases in the supercritical CO_2 flow rate, temperature, and pressure generally improved the performance. The extraction yield increased as the particle size decreased, indicating the importance of decreasing intraparticle diffusional resistance. The maximum extraction yield obtained was 50.6 wt% with a 0.23-mm particle size and a 2 mL/min CO_2 flow rate at 90°C and 600 bar. Use of an entrainer at a concentration of 5 vol% improved the yield to 52.2 wt% for the same particle size and also enabled the use of a relatively lower pressure and temperature, i.e., 300 bar and 70°C.

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KEY WORDS: Jojoba oil, supercritical CO_2, supercritical fluid extraction.

The word "jojoba" refers both to the plant (*Simmondsia chinensis*) and to the extract of its seeds. The total oil content of mature jojoba seeds generally ranges from 50 to 54 wt%. The jojoba oil extracted from the seeds is not a TG, but a liquid wax (m.p. 7°C) composed mostly of esters of monounsaturated C_{20}–C_{22} FA (MUFA) and long-chain monounsaturated alcohols. Jojoba also contains trace quantities of palmitoleic acid, oleic acid, hexacosanol, alcohols of lower M.W., and α-, δ-, and γ-tocopherols. The oil can be isomerized, hydrogenated, sulfurized, chlorinated, or transesterified. Jojoba oil and its derivatives have a wide range of industrial uses, mainly in cosmetics, and are incorporated in formulations for skin-care preparations such as lotions, moisturizers, massage oils, and soothing creams. It is also widely used in hair-care products, such as shampoos, gels, and mousses, and is a very good base for cosmetics and nail products (1–7).

Different methods, similar to those applied to other oilseeds, have been used to extract jojoba oil from the seeds. Those methods are mainly mechanical pressing, mechanical pressing followed by solvent extraction (leaching), or solvent extraction only (1,8).

Abu-Arabi *et al.* (3) investigated the extraction of jojoba oil by pressing and solvent extraction. They investigated the effects of some organic solvents used in the leaching process, including hexane, petroleum ether, benzene, chloroform, isopropanol, toluene, carbon tetrachloride, tetrachloroethylene, and heptane, on extraction yield and found that the maximum yield of leached oil, achieved with hexane, was 52 wt%.

The past 20 yr have witnessed an intense interest in the use of supercritical fluids (SCF) in separation science. Supercritical fluid extraction (SFE) is an alternative extraction method whereby SCF instead of organic solvents are used as extraction media. SFE and fractionation have been applied to natural materials to separate the desired components from solid/liquid matrices in the food, perfumery, cosmetics, and pharmaceutical industries. Most of the work has been devoted to determining the composition of the extracts or application to new materials.

Stahl *et al.* (9) investigated SFE of jojoba seed using supercritical CO_2 (SC CO_2). They reported that the solubility of jojoba oil changes with temperature and pressure in the range of 20–80°C and 100–2600 bar. The solubility of jojoba oil in SC CO_2 increases from 300 to 700 bar, and then falls off at pressures >700 bar.

The extraction yield depends strongly on the process temperature and pressure conditions and the pretreatment of seeds. Del Vella and Uquiche (10) investigated the effects of particle diameter on the SC CO_2 extraction of rosehip seeds at 40°C and 300 bar. Oil solubility, extraction rate, and yield were increased with decreasing particle size. Fattori *et al.* (11) compared the influences of different seed pretreatment processes on the extraction yield and oil solubility of canola seeds treated with SC CO_2 at temperatures between 25 and 90°C and pressures between 10 and 360 bar. The oil solubility in SC CO_2 was found to be strongly dependent on pressure and weakly dependent on system temperature; the maximum oil solubility obtained was 11 g/kg CO_2 at 55°C and 360 bar. Snyder *et al.* (12) investigated the effects of moisture and particle size on the extractability of oils from soybeans, peanuts, and cottonseeds with SC CO_2 at 50°C and 537 bar and found that oil composition was not influenced by moisture and particle size. Extraction rate and yield were influenced by the particle diameters of the seeds.

In this work, the extraction of jojoba oil from jojoba seeds by SC CO_2 in a semicontinuous system was studied. The extraction rate of jojoba oil was investigated as a function of CO_2 flow rate, temperature, pressure, particle diameter, and entrainer concentration.

EXPERIMENTAL PROCEDURES

Plant materials. The jojoba seeds used were a sun-dried product received from ALATA Agricultural Research Institute (Mersin, Turkey). First, dirt and other impurities were separated from the seeds; the seeds were then washed with deionized distilled water and dried under ambient conditions. The moisture content of the oilseeds, which was determined according to AOCS Method Ca 2c-25 (13), was 2.1 wt%. The dried seeds were packed in polyethylene bags and stored at ambient temperature. The clean and dried seeds were rotary milled, and the fractions were separated according to particle size: 0.21 < 0.25 mm, 1 < 1.18 mm, 2 < 2.36 mm. Particle diameters of each fraction

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were given the arithmetical averages of 0.23, 1.09, and 2.18 mm. The fractions were stored in glass bottles in a desiccator until used for extraction experiments.

SFE. Jojoba oil was extracted from seeds of *S. chinensis* with SC CO_2. Experiments were performed using a semicontinuous SFE system (SFX^{TM} System 2120; all components manufactured by Isco Inc., Lincoln, NE) consisting of a supercritical fluid extractor (Model SFX 220), two syringe pumps (Model 100 DX), with a controller unit (Model SFX 200) and a temperature-controlled restrictor (Model SFX 220).

In each experiment, about 4.5 g dry milled seeds were put into a 10-mL fixed-bed extraction column (57 × 20 mm i.d. stainless steel extraction cell; Isco Inc.), and 0.5-μm filters were placed at both ends of the extraction column to prevent any particle carryover. Care was taken to ensure that the air was purged using CO_2. The extraction column was then placed into the temperature-controlled chamber of the supercritical fluid extractor. CO_2 was then charged into the high-pressure syringe pumps from a CO_2 tank. The SC phase at the outlet of the extractor was passed through the automatic valves to slowly reduce the pressure. The temperature of the restrictor was kept at 80 ± 5°C. The extract was collected in vials containing glass wool. To obtain extraction profiles over time, the collection vials were changed every 10 min for the first 60 min and then every 30 min. The water and hexane (entrainer) co-extracted with jojoba oil were removed by vacuum at 100°C, and then the mass of each extract was gravimetrically determined. Each experiment was repeated at least three times. SE of the data was about ±3%. Therefore, the arithmetical average of the repeated experiment data was used in all figures.

The SFE runs were carried out at 0.5–2 mL/min CO_2 flow rates, 70–90°C, 200–600 bar, and 0–10 vol% entrainer hexane concentrations.

Soxhlet extraction. To compare the extraction efficiencies of SFE with organic solvent extraction (OSE), exhaustive Soxhlet extraction was used, with hexane as the solvent. OSE treatment took about 6 h. The extracted phase (jojoba oil and solvent) was then distilled in two stages to separate jojoba oil from solvent, using simple distillation followed by use of a rotary evaporator (Laborota 4000 Model; Heidolph Instruments, Schwabach, Germany). Organic solvent extraction of jojoba seeds yielded 51.8 wt% of hexane-extractable material.

RESULTS AND DISCUSSION

Effect of particle size. Effect of particle size on the SFE yield (weight of the extracted jojoba oil divided by the weight of the original seed sample of jojoba oil vs. extraction time at a flow rate of CO_2 of 2 mL/min, 600 bar, and 90°C) is shown in Figure 1. As the extraction time increased, higher yields were observed. After the first few minutes of extraction, the effect of particle size could be seen very clearly; i.e., small particles provided higher yields. Halving particle sizes from 2.18 to 1.09 mm caused appreciable improvement in the extraction yield. Further decrease in the particle size by a factor of *ca.* ¼ to 0.23 mm did not bring as much incremental increase in the yield. The effect of intraparticle diffusion seems to gain importance in larger particles, causing an appreciable decrease in the extraction yield. Data from Figure 1 also indicate that an extraction time of about 100 min is sufficient to reach the highest possible yield with the smaller particles (0.23 and 1.09 mm) under the specified conditions.

Effect of temperature. The effect of temperature on the extraction yield for 1.09 mm particles at 400 bar with a 2 mL/min CO_2 flow rate is shown in Figure 2. The extraction increased from 45.8 to 47.3 wt% when the temperature was increased from 70 to 80°C, but the increase to 47.4 wt% when temperature was raised to 90°C was not an appreciable improvement.

Effect of pressure. Figures 3 and 4 show the effects of pressure on extraction yield for 1.09-mm particles with a 2 mL/min CO_2 flow rate at 70 and 90°C, respectively. Figure 3 indicates that extraction at pressures less than 200 bar are not feasible at 70°C. This may be because jojoba oil has a very low solubility in CO_2 below 200 bar (9). The extraction yields obtained under isothermal and isobaric conditions increased with pressure during the first 40 min (equivalent to 0.05–007 kg total CO_2) but were similar at 400–600 bar after 120 min (equivalent to 0.17–0.23 kg total CO_2). The yield obtained at 70°C was maximal at 400 bar but fell off at lower and higher pressures, whereas at 90°C the yield increased monotonically from 300 to 600 bar (Fig. 4). Furthermore, the time required to reach maximal yields was shortened with increasing pressure: 90°C and 600 bar provided the best initial extraction rate and solubility of jojoba oil for the 1.09-mm particles. However, the extraction yield at 400–600 bar was similar after 120 min.

Effect of SC CO_2 flow rate. The extraction rate is affected significantly by increases in SC CO_2 flow rates (Fig. 5). This increase in extraction with time is almost linear during the first 50 min of extraction.

The data in Figure 6 show the variation of extraction yield with the amount of CO_2 used per kg of dry seeds. The data points for all the flow rates fall on a single curve, indicating the accuracy and consistency of the data. The observed extraction yield, 47.2 wt%, was obtained by using 0.20 kg CO_2/kg dry seed at 2 mL/min and 120 min. Therefore, solubility and intraparticle diffusion, not external mass transfer resistance, control the

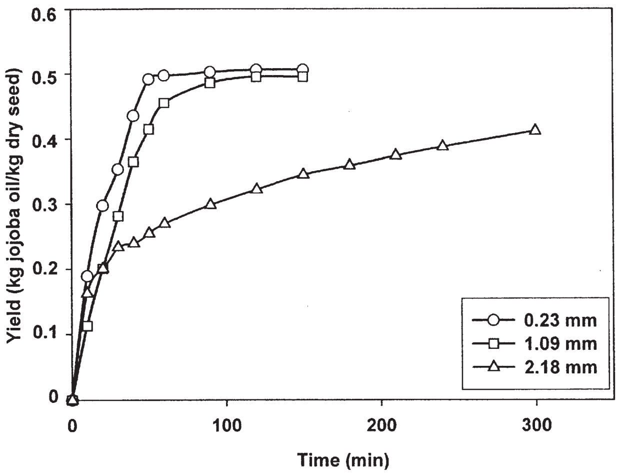

FIG. 1. Effect of particle size on the extraction yield of jojoba oil with time at a 2 mL/min CO_2 flow rate, 90°C, and 600 bar.

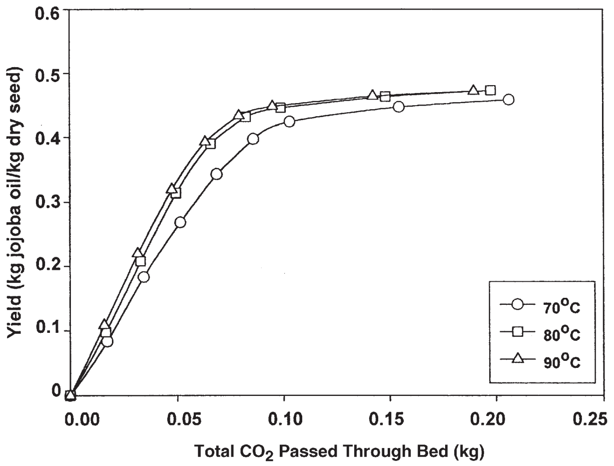

FIG. 2. Effect of temperature on the extraction yield of jojoba oil with total CO_2 used for 1.09-mm particles at 400 bar with a 2 mL/min CO_2 flow rate.

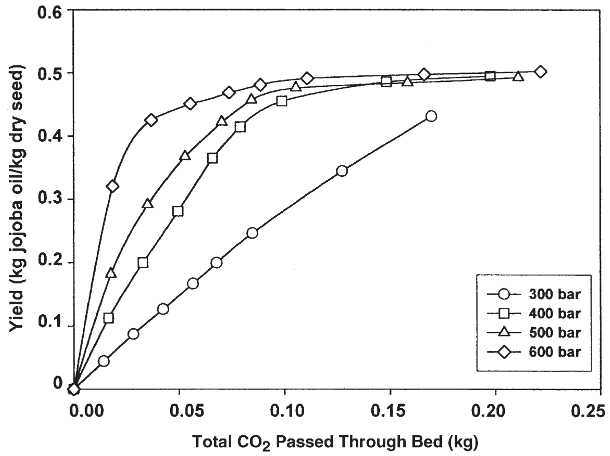

FIG. 4. Effect of pressure on the extraction yield of jojoba oil with total CO_2 used for 1.09-mm particles with a 2 mL/min CO_2 flow rate at 90°C.

extraction process over the range of experimental conditions investigated here, as others have observed (14–17).

Effect of entrainer concentration. The use of the smallest particle size, i.e., 0.23 mm, resulted in SFE yields as high as those obtained from hexane extraction in a Soxhlet extraction (51.8 wt%). The highest yield for medium particle size, 1.09 mm, was 47.2 wt% at 600 bar and 90°C. Consequently, we decided to see whether yield could be increased by using hexane as entrainer together with CO_2 under more moderate conditions.

Experiments were performed with 1.09-mm particles and 2 mL/min of CO_2 at 300 bar and 70°C, with hexane added at 2.5, 5, and 10 vol% concentrations. The results in Figure 7 indicate an entrainer improved the yield and shortened the time required to reach the highest possible extraction efficiencies. The optimal concentration of entrainer was 5 vol% hexane.

The use of 5 vol% hexane improved the extraction yield by almost 100 wt% during the first 60 min according to SC CO_2 exprimental data. Under otherwise identical conditions, the presence of entrainer at a concentration of 5 vol% enabled higher final extraction yields at 120 min; 52.2 wt% was reached with 5% entrainer vs. 43.1 wt% without entrainer. This 52.2 wt% yield was better than the highest value obtained with CO_2 alone at the highest temperature and pressure, and was slightly better than the 51.8 wt% obtained with organic solvent extraction.

An analysis of the operating cost of SFE indicated that use of SFE with entrainer is much less expensive than conventional organic solvent extraction (Fig. 8). Considering the cost of hexane and the extraction time required to reach the highest possible yield, one can conclude that SC with entrainer is the best extraction process for jojoba oil.

The next objective was to determine the possibility of improving the extraction yield for the largest particle size, i.e., 2.18 mm, by the use of an entrainer in SFE; experiments performed at 300 bar showed that use of hexane (5 vol%) as an entrainer indeed improved the SC extraction yield by 30–50%. The improvement with 5 vol% hexane was 40% with 1.09-mm particles.

Experiments were performed with 2.18 mm particles at 400 and 600 bar and at 70°C with and without 5% entrainer. The use of 5% entrainer had practically no effect on extraction yield at 600 bar, but yield was improved slightly at 400 bar. Thus, one may conclude that although entrainer may make a small

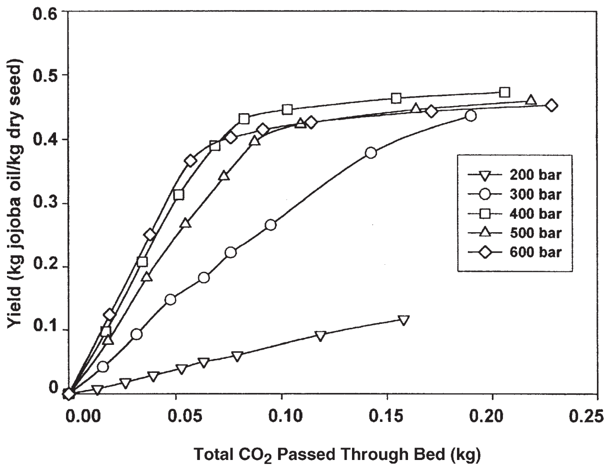

FIG. 3. Effect of pressure on the extraction yield of jojoba oil with total CO_2 used for 1.09-mm particles with a 2 mL/min CO_2 flow rate at 70°C.

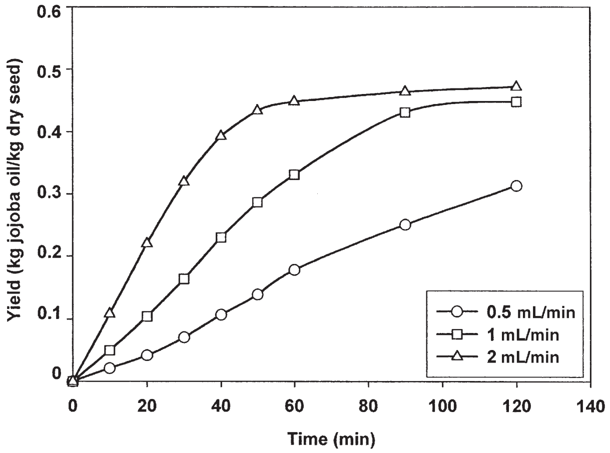

FIG. 5. Effect of CO_2 flow rate on the extraction yield of jojoba oil with time for 1.09-mm particles at 600 bar at 90°C.

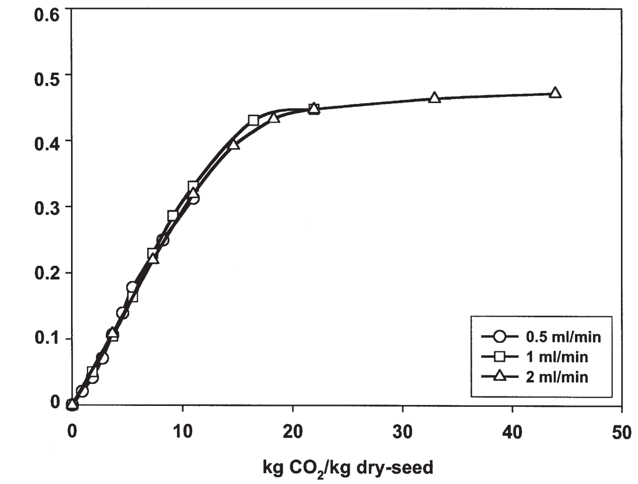

FIG. 6. Variation of extraction yield with the amount of CO_2 used per kg of seed for 1.09-mm particles at 600 bar and 90°C.

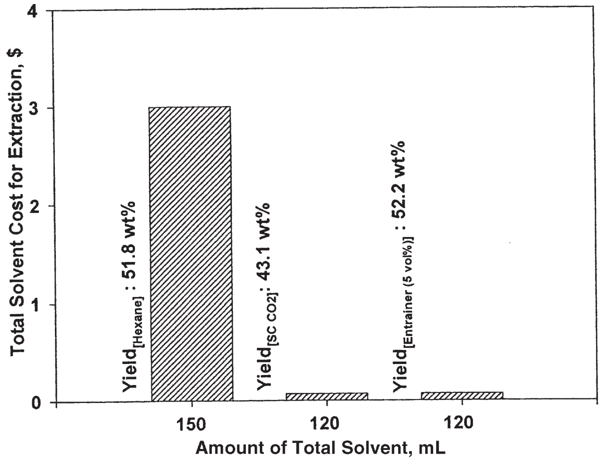

FIG. 8. Comparison of the costs of various extraction methods considering the yields as well (1.18-mm particles, 300 bar, and 40°C).

contribution to SFE efficiency, it is not enough to justify the recommendation to use a 2.18-mm particle size.

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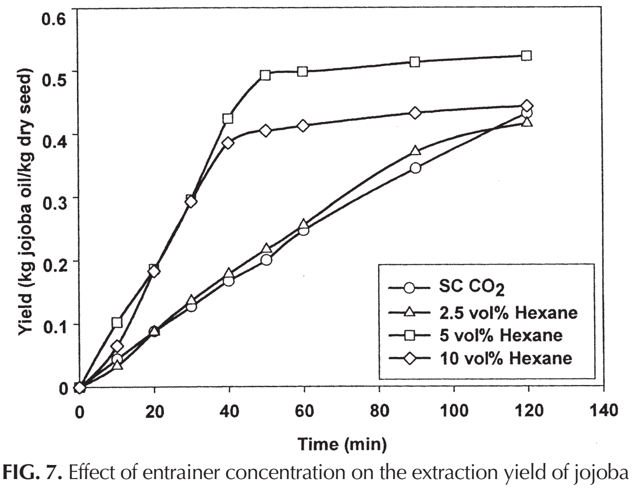

FIG. 7. Effect of entrainer concentration on the extraction yield of jojoba oil with time for 1.09-mm particles at 300 bar and 70°C. SC, supercritical.