Extraction of fatty oil from rose hip seed using supercritical carbon dioxide

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Abstract
Extraction of fatty oil from rose hip seeds was studied using supercritical carbon dioxide at various operating conditions. Extraction yield decreased with increase in pressure, but slightly increased with increase in temperature and dramatically increased with decreasing particle. The change of CO_2 flow rate didn't affect to extraction yield. About 19.94 g oil/100 g seed was obtained at 330 bar of pressure, 70°C of temperature, 3 ml/min of CO_2 flow rate and 0.556 mm of particle size. As determined by GC-FID, linoleic acid was the most abundant followed by linolenic, palmitic and stearic acid. Generally the composition of fatty oil extracted was almost independent on the extracting condition. The apparent solubility of oil in SC-CO_2 was calculated and correlated with the density using Chrastil equation.

Keyword: rose hip seed, supercritical carbon dioxide extraction, fatty oil

INTRODUCTION

Supercritical carbon dioxide (SC-CO_2) has been proposed as a nontoxic alternative of light petroleum fractions for vegetable oil extraction [1, 2]. Extraction with conventional organic solvents produces low quality oil that requires extensive refining, whereas expression is appropriate only for seeds containing ≥20% oil [1]. Previous work on SC-CO2 extraction of oil-containing seeds has been reviewed recently [2]. An interesting substrate for SC-CO2 extraction is rose hip (*Rosa canina L.*) seed, which is an inexpensive source of unsaturated fatty acid-rich oil used in cosmetics and other high-value applications [1-7]. The composition of unsaturated fatty acid-rich oil of rose hip seed has been observed [3, 8], but the changes of oil composition as function of changes in the SC-CO_2 extraction conditions has not been investigated so far.

Extraction of oil from crushed seeds has been claimed to be divided in two stages [9, 10]. "Free oil" is extracted initially from the surface of seed particles at constant rate that is partially determined by external mass transfer mechanisms. A plot of cumulative yield (g oil/g oil-free substrate) produces a straight line with a slope that corresponds to the apparent solubility of the oil in SC-CO_2. In the second stage, when free oil is depleted from the particles, the extraction rate is determined by internal mass transfer mechanisms of "tied oil", and the aforementioned plot approaches an oil yield value asymptotically. Illes et al. [5] reported that at high extraction temperature (55°C), the increase of apparent solubility of rose hip seed oil as a function of increasing pressure was higher than that observed at lower temperature (35°C). For instance, at 350 bar the values of apparent solubility were 1.24 and 1.36 g per 100 g at 35 and 55°C, respectively. Eggers et al. [6] reported that the apparent solubility of rosehip seed oil was virtually unaffected by seed pretreatment, extraction temperature (40-80°C), extraction pressure (≥ 500 bar), or solvent ratio (the mass of solvent utilized per unit time and unit mass of substrate loaded in the extraction vessel, 8.6-28.6 g CO2/(g substrate h)), but increased as a result of an increase in extraction pressure from 300 to 500 bar. Reverchon et al. [6] reported that the apparent solubility in SC-CO_2 of oil in milled rosehip seeds increased from 0.5g/kg at 40^{o}C and 103.4 bar, to 40 g/kg at 40^{o}C and 689.5 bar, and was also unaffected by process temperature and solvent ratio.

The purpose of this work was to study the effect of extraction conditions, such as pressure, temperature, CO_2 flow rate and particle sizes on the yield and oil composition. The apparent solubility of oil in SC-CO_2 was also calculated and correlated using the Chrastil equation.

EXPERIMENTAL

I - MATERIALS AND CHEMICALS

Sample of dry rose hip (fruits including seeds) was obtained from Sanoflore Co., France. Prior to processing, the dry rose hip fruits were separated from the seeds. Seeds were ground in a coffee grinder and sieved into several grades (0.556; 0.688; 2.112 mm). Standard fatty acids (linoleic, linolenic, stearic and palmitic acid), hexane, sodium chloride, potassium chloride, and hydrochloric acid, used for GC analysis and esterification of oil extracted were purchased from Wako Pure Chemical Industries, Ltd., Japan. CO_2 was obtained from Uchimura Co., Japan.

II - SC-CO_2 EXTRACTION

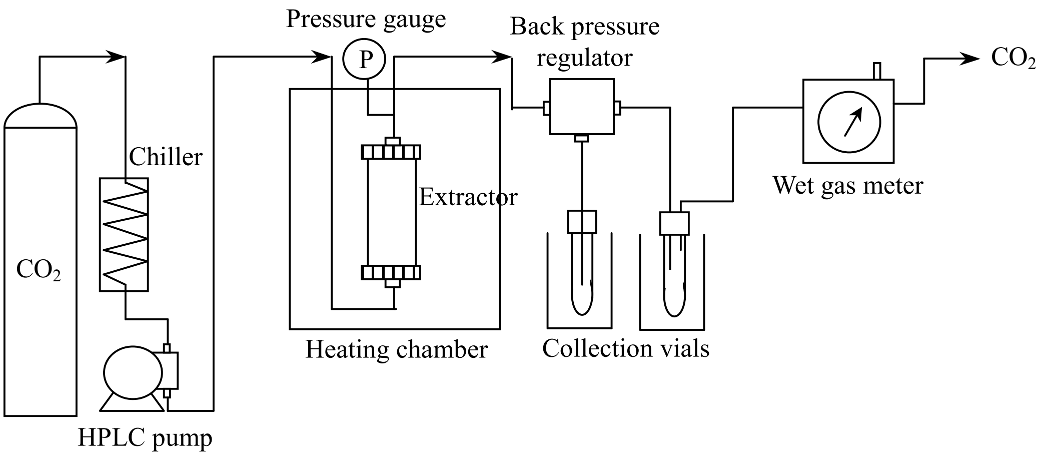

Figure 1 : Schematic diagram of supercritical CO_2 extraction system.

Figure 1 shows a schematic diagram of SC-CO_2 extraction apparatus. The apparatus includes a chiller (Cooling Unit CLU-33, Iwaki Asahi Techno Glass, Japan), a pump for CO_2 (Intelligent Prep. Pump. PU-2086 Plus, Jasco, Japan), a heating chamber (ST-110, ESPEC Corp., Japan), an extraction vessel (Thar Tech, Inc., USA, 10 ml in volume), back pressure regulator (SCF-Bpg, Jasco, Japan), collection vials, and a wet gas meter (Sinagawa Co., Japan). Fatty oil was extracted from rose hip seeds, under various pressures (200 – 450 bar), temperatures (50 – 80^{o}C), CO_2 flow rates (2 – 4 ml/min) and particles sizes (0.556 – 2.112 mm) to determine the effect of these factors on the total fatty oil extracted and fatty oil composition, and to perform the apparent solubility of oil in SC-CO_2. In each experiment, approximately 3.5 grams of samples were loaded into a 10 ml extraction vessel and the remaining volume was filled with glass beads in the bottom and upper of the cell. The cell was placed in the heating chamber to maintain the operating temperature. The extract was collected in the vial at every 10 to 40 min for 3 hours, and weighed immediately after the collection.

III - ANALYSIS

Fatty acid composition was identified by gas chromatography-flame ionization detector (GC-FID). Prior to injection the extracted oils were pretreated by methyl esters according to the following method [11]. 2 ml of 5% solution of hydrochloric acid and methanol was added to the oils, and then esterified for 2 hours at 80^{o}C. After 2 hours, the esterification was terminated by adding 5 ml of 5% NaCl solution, and then mixed with 5 ml of hexane. And then 4 ml of 3% KCl was added to hexane layer and washed. The methyl esters dissolved in hexane layer were separated by a 30 ml funnel and analyzed by GC-FID (Gas Chromatography GC-14A, Shimadzu, Japan) equipped with a DB-5 capillary column (15 m x 0.250 mm x 0.25 μm). The oven temperature was increased from 70 to 320^{o}C at interval of 5^{o}C/min and the detector temperature was maintained at 300^{o}C. The injection volume was 0.6 μl and tricaprin was used as internal standard.

RESULT AND DISCUSSION

I – EXTRACTION YIELD

Yield of the extract was studied at various pressures (200 – 330 bar), temperatures (40 – 60^{o}C), CO_2 flow rates (2 – 4 ml/min) and particle sizes (0.556 – 2.112 mm). Yield of the extract was defined as weight of oil extracted in 100 g of sample.

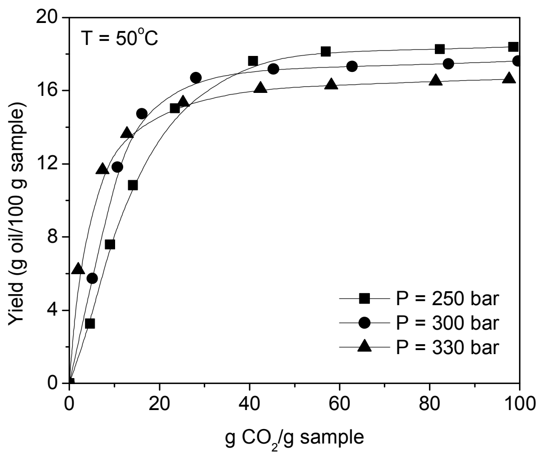

Figure 2: The effect of pressure on extraction yield of fatty oil.

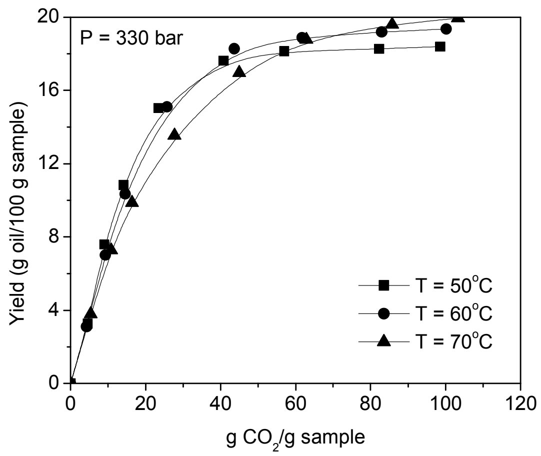

Figure 3: The effect of temperature on extraction yield of fatty oil.

The effect of pressure on the extraction yield was studied at 50^{o}C of temperature, 3 ml/min of CO_2 flow rate and 0.556 mm of particle size for 3 hours. Figure 2 shows the effect of pressure on extraction yield of fatty oil. Extraction yield decreased with increasing extraction pressure, although the solubility of oil in SC-CO_2 increased. It can be explained that at elevated pressure, the magnitude of such density change become smaller and the solute vapor pressure change becomes more effective and can easily overcome the effect of solvent density change on the total extraction rate. Due to this fact, Figure 2 reveals that the lower pressure favored the extraction yield of fatty oil where vapor pressure of solute is dominant in this extraction process. However Figure 2 also shows that at low solvent ratio (g CO_2/g sample) the extraction yield of fatty oil increased with increasing pressure where the density of solvent is dominant.

Figures 3 shows the effect of temperature on the extraction yield of fatty oil. The effect of temperature was examined at 330 bar, 3 ml/min and 0.556 mm of particle size for 3 hours.

From the figure it is evident that extraction yield of fatty oil slightly decreased with the increase in temperature at low solvent ratio then increased as increasing temperature for higher solvent ratio. This crossover effect has been observed in solubility [12]. King and Bott [12] explained the competing effects of the reduction in solvent density and the increase in solute vapor pressure with increasing temperature. In this condition, the extraction rate is dependent on solute vapor pressure and it increased with an increase in temperature for larger CO_2 consumed.

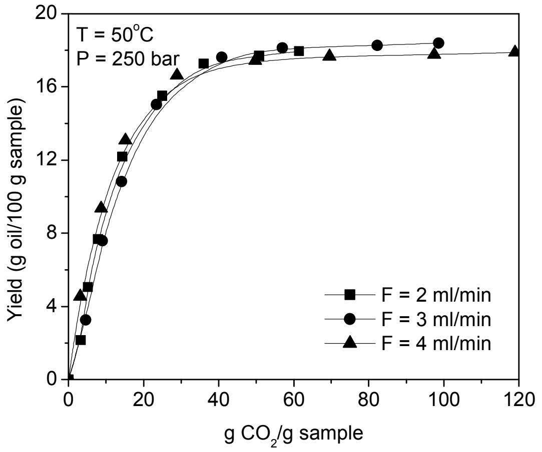

Figure 4: The effect of CO_2 flow rate on extraction yield of fatty oil.

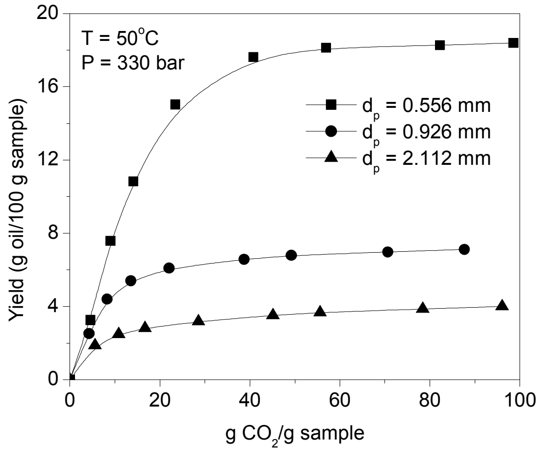

Figure 5: The effect of particle size on extraction yield of fatty oil.

For various CO_2 flow rate, extractions were studied at smallest particle size (0.556 mm), 250 bar and 50°C. Figure 3 shows the effect of CO_2 flow rate on extraction yield of fatty oil. As shown in Figure 3 extraction yield of fatty oil is not affected by CO_2 flow rate as the various flow rates yield almost in the same values. The small effect of flow rate on the extraction process may be caused by the fact that at these rates, the CO_2 could not be distributed evenly through out the extractor. Furthermore the extraction may be highly influenced by the solubility limitation. Increasing the mass transfer by increasing the CO_2 flow rate may not enhance the extraction rate significantly.

The effect of particle size on extraction yield of fatty oil, as shown in Figure 5, was studied at 330 bar, 50°C and 3 ml/min of CO_2 flow rate. In the figure extraction yield dramatically increased with decrease in particle size. Mass transfer in SC-CO_2 extraction from solid particles in most cases depends heavily on the transport rate in the solid phase, and generally the extraction rate increases with decreasing particle size [12]. It can be explained that the reduction of particle size can open the plant cells and increase the surface of the solid to contact with solvent.

Based on the experimental result, the highest extraction yield was 19.94 g oil/100 g seed obtained at 330 bar of pressure, 70°C of temperature, 3 ml/min of CO_2 flow rate and 0.556 mm of particle size.

II – COMPOSITION OF FATTY OIL

Based on the analytical result, fatty oil extracted from rose hip seed mainly contains linoleic acid as the most abundant followed by linolenic, palmitic and stearic acid. Generally the composition of fatty oil extracted was independent on the extracting condition. Maximum linoleic, linolenic, palmitic and stearic acid extracted were 11.8, 7.8, 0.76 and 0.70 mg/g rose hip seeds obtained at 300 bar and 50°C.

III – APPARENT OIL SOLUBILITY

Figure 6 shows the apparent solubility of rose hip seed oil in SC-CO_2 as function of density at 50, 60, 70 and 80°C. As shown in this figure the apparent solubility of oil in SC-CO_2 is increased by increasing its density particularly at high temperature due to increased solubility. At lower temperature higher solvent density is required to reach the same solubility value obtained at high temperature.

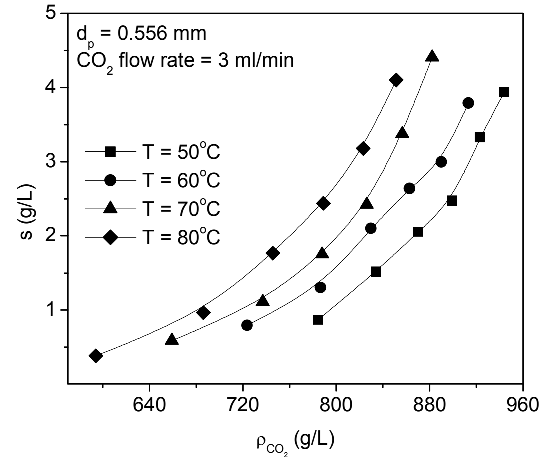

Figure 6: Apparent solubility of rose hip seed oil in SC-CO_2 as function of solvent density at different temperatures.

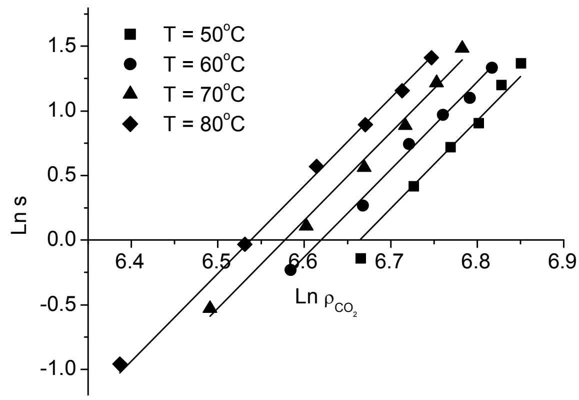

Figure 7: Chrastil plot of rose hip seed oil solubility in SC-CO_2 at different temperatures.

Figure 7 shows the apparent solubility of the solute according to the Chrastil equation [13]. This equation relates the solubility of a solute to the density of the supercritical fluid based on the assumption that the association of a solute (S) with the k molecules of supercritical solvent (C) produces a solvato complex (SC_k), which is in equilibrium with the gas. The Chrastil equation can be written as

$$\ln(s) = k\ln(\rho) + a/T + b \qquad (1)$$

where $a = \Delta H / R$ and $b = -\ln[M_C^k/(M_S + kM_C)] + q$

s is solubility, ρ is the solvent density, T is the temperature, k is the association number, ΔH is the total heat of reaction (i.e., heat of solvation plus heat of vaporization of the solute), q is a constant and M_S and M_C are the molecular weights of solute and solvent, respectively. The association constant k is the slope of the linear correlation and represents the average number of solvent molecules in the solvato complex. The log s is a linear function of $1/T$ at constant density and has a slope given by a. The value of constant b can be chosen to minimize the deviation of the equation from experimental data [14].

From the above mentioned experimental data, the estimated values of constants are: k=6.788; a =-3254; b=-35.17. Isotherm calculated from Chrastil equation by using the aforementioned constants coincided with the experimental points (see Figure 7).

CONCLUSION

Fatty oil from rose hip seed has been extracted using SC-CO_2 at various operating conditions. The highest extraction yield was 19.94 g oil/100 g seed obtained at 330 bar of pressure, 70°C of temperature, 3 ml/min of CO_2 flow rate and 0.556 mm of particle size. Fatty oil extracted mainly contains linoleic acid as the most abundant followed by linolenic, palmitic and stearic acid. Maximum linoleic, linolenic, palmitic and stearic acid extracted were obtained at 300 bar and 50^oC.

The apparent solubility of oil in SC-CO_2 was calculated and correlated with the density using Chrastil equation.

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REFERENCES :

[1] J.M. del Valle, E.L. Uquiche, Particle size-effects on supercritical CO_2 extraction of oil-containing seed, J. Am. Oil Chem. Soc., Vol. 79, **2002**, p. 1261.

[2] J.M. del Valle, O. Rivera, M. Mattea, L. Ruetsch, J. Daghero, A. Flores, Supercritical CO_2 processing of pretreated rosehip seeds: effect of process scale on oil extraction kinetics, J. Supercrit. Fluids, Vol. 31, **2004**, p. 159.

[3] K. Szentmihalyi, P. Vinkler, B. Lakatos, V. Illes, M. Then, Rose hip (*Rosa canina L.*) oil obtained from waste hip seeds by different extraction methods, Bioresource Technology, Vol. 82, **2002**, p. 195.

[4] E. Reverchon, A. Kaziunas, C. Marrone, Supercritical CO2 extraction of hiprose seed oil: experiments and mathematical modeling, Chem. Eng. Sci., Vol. 55, **2000**, p. 2195.

[5] V. Illes, O. Szalai, M. Then, H. Daood, S. Perneczki, Extraction of hiprose fruit by supercritical CO_2 and propane, J. Supercrit. Fluids, Vol. 10, **1997**, p. 209.

[6] R. Eggers, A. Ambrogi, J. von Schnitzler, Special features of SCF solid extraction of natural products: deoiling of wheat gluten and extraction of rose hip oil, Braz. J. Chem. Eng., Vol. 17, **2000**, p. 329.

[7] J.M. del Valle, S. Bello, J. Thiel, A. Allen, L. Chordia, Comparison of conventional and supercritical CO_2-extracted rosehip oil, Braz. J. Chem. Eng., Vol. 17, **2000**, p. 335.

[8] M.D. Zlatanov, Lipid composition of Bulgarian chokeberry, black currant and rose hip seed oils, J. Sci. Food Agricult., Vol. 79, **1999**, p. 1620.

[9] H. Sovova, Rate of the vegetable oil extraction with supercritical CO2. I. Modeling of extraction curves, Chem. Eng. Sci., Vol. 49, **1994**, p. 409.

[10] H. Sovova, Mathematical model for supercritical fluid extraction of natural products and extraction curve evaluation, J. Supercrit. Fluids, Vol. 33, **2005**, p. 35.

[11] H-J. Kim, S-B. Lee, K-A. Park, I-K. Hong, Characterization of extraction and separation of rice bran oil rich in EFA using SFE process, Separation and Purification Technology, Vol. 15, **1999**, p. 1.

[12] M.B. King and T.R. Bott, Extraction of Natural Products Using Near-Critical Solvents, 1st edition, Chapman & Hall, Glasgow, **1993**.

[13] J. Chrastil, Solubility of solids and liquids in supercritical gases, J. Phys. Chem., Vol. 86, **1982**, p.3016.

[14] Y. Yamini, M.R. Fat'hi, N. Alizadeh, M. Shamsipur, Solubility of dihydroxybenzene isomers in supercritical carbon dioxide, Fluid Phase Equilibria, Vol. 152, **1998**, p. 299.