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Effect of Temperature and Pressure on the Extraction Yield of Oil from Sunflower Seed with Supercritical Carbon Dioxide

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Abstract: Sunflower seed oil was extracted using supercritical carbon dioxide in a semi-continuous flow extractor with the temperature range 313-343 K and the pressure range 20-40 MPa. The extraction rates increased with pressure at each temperature, but decreased with temperature increase up to about 28 MPa. After this pressure, higher temperature favored the extraction rate because of the competitive effects of solvent density change and solute vapor pressure change with the variation of temperature and pressure, resulting the crossover effect of solubility of oil in supercritical carbon dioxide. The fatty acids composition of the extracted oil was similar to that of soybean and tomato seed oil with high content of oleic acid.

Key words: Supercritical carbon dioxide, extraction, vegetable oil, fatty acid compositions, yields of oil, solubility

INTRODUCTION

Sunflower is now commercially widely cultivated to produce vegetable oils in the countries around the East-South Asia. It represents an important role as a potential source of edible oil as well as proteins for human consumption[1]. Since sunflower oil is good as edible oil, for cosmetic and pharmaceutical products and for use in the varnish industry, developing an extraction technology and characterizing its compositions is important.

Extraction of vegetable and essential oils from plant materials (seed, leaves and herbs) with supercritical carbon dioxide is an alternative process to the conventional process such as solvent extraction or steam distillation. In the last two decade, supercritical carbon dioxide extraction of vegetable oil has been extensively studied because of its large consumption for edible purpose and in other industries as an important raw material for various products. The hexane extraction has been used conventionally to extract soybean oil, but extraction with supercritical carbon dioxide was lighter in color and contains less iron as well as phosphorous[2].

Vegetable oils are very complex compounds while basic component are fatty acid triglycerides. Sunflower seed contains 32-53% oil[3], consisting of 7-12% saturated acids (palmitic and stearic), 30-80% oleic acid, 10-60% linoleic acid and less than 2% other acids. The composition of vegetable oils varies with the variety of plantation.

The conventional production methods of oils such as steam distillation or solvent extraction can lead to degradation of heat sensible compounds and partial hydrolysis of water sensible compounds. In solvent extraction process, another separation process is required to separate the solute from the solvent which is usually expensive and some times solvent residual problem is observed.

Supercritical fluid extraction is an effective alternative process to the conventional methods that has received increasing attention in a variety of fields due to the following factors: (i) supercritical fluids provide solubility and mass transfer rates; (ii) operation can be manipulated by changing the pressure or temperature and (iii) the ease of separation of the extracted solute from the supercritical solvent by simple expansion. Supercritical fluid has liquid-like density, low surface tension and viscosity and high diffusivity. The diffusivity of supercritical fluid is one to two orders of magnitude than those of other liquids, which permits rapid mass transfer, resulting in a larger extraction rate than that obtained by conventional methods.

Supercritical extraction has been applied to a large number of natural solid materials, especially in food industries[4]. Carbon dioxide is mostly used as supercritical

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fluid for the extraction of vegetable oils and essential oils from natural materials because of its low critical temperature that prevents the thermal degradation, no residual problem, odorless and colorless properties. It is also non-toxic and is generally accepted as a harmless ingredient of foods and beverages and easily available. Carbon dioxide has also been tested for corn, soybean, peanut, rape seed and tomato seed.

The effects of milling of tomato seed and the flow rate of carbon dioxide on the extraction behavior of oil from tomato seed have been studied and the extraction rate was analyzed by models containing mass transfer process parameters in both the solvent and solid phases[5]. Solubility is one of the most important parameters in the supercritical fluid extraction process; it is influenced by the temperature and pressure and allows variation of extraction rate and also extraction rate (quantity and quality). The compositions of vegetable oils are also important for utilization in several applications in the food industry, pharmacy and cosmetics.

In this study, oil was extracted from sunflower seed with supercritical carbon dioxide in a semi-batch flow extractor (where flow of carbon dioxide was continuous and sample inside the extractor was batch). The objectives of this study were (i) to determine the effects of temperature and pressure and degree of extraction on yield, compositions of oil extracts, (ii) characterize the chemical composition differences for effective utilization.

MATERIALS AND METHODS

Materials: Sunflower seed used was a sun-dried Japanese product. The clean and dried seeds were milled to the desired size 0.27 mm, stored in a glass bottle in a desiccator and used within two days for extraction. The initial oil content was about 41%.

Experimental apparatus: A schematic diagram of the experimental apparatus is shown in Fig. 1. Oil was extracted with supercritical carbon dioxide in a semi-continuous-flow extractor. Liquid carbon dioxide from a cylinder with a siphon attachment is passed through a cooling head (about 268 K) of high pressure pump and compressed to the operating pressure by back-pressure regulator. The temperature at the cooling head is maintained by circulating ethylene glycol from a chiller at the temperature of 265 K. Compressed carbon dioxide flows through the heat exchanger into the extraction column (21×5 cm inside diameter) placed in a thermostat oven where the experimental temperature is maintained. The exit fluid from the extractor is expanded at collection tube that placed in an ice pot. Dry gas meter measures the exit flow rate of carbon dioxide. The pressure in the extractor is controlled by the back-pressure regulator.

Experimental procedure: A known weight (about 5 g) of the milled seed (0.27 mm) was placed between glass beds in the extractor for the uniform distribution of the solvent flow at a flow rate 3.78 g/min measured at the exit with a dry gas meter. The extraction column was placed vertically in the thermostat oven and extraction was conducted for the temperature range 313-343 K and pressure range 20-40 MPa. After attaining the chiller temperature of 265 K and the experimental temperature at the thermostat oven, pump was started to flow the carbon dioxide at a rate of 3 mL min^{-1} while the pressure was gradually increased in the extraction column to experimental pressure that was controlled by back-pressure regulator.

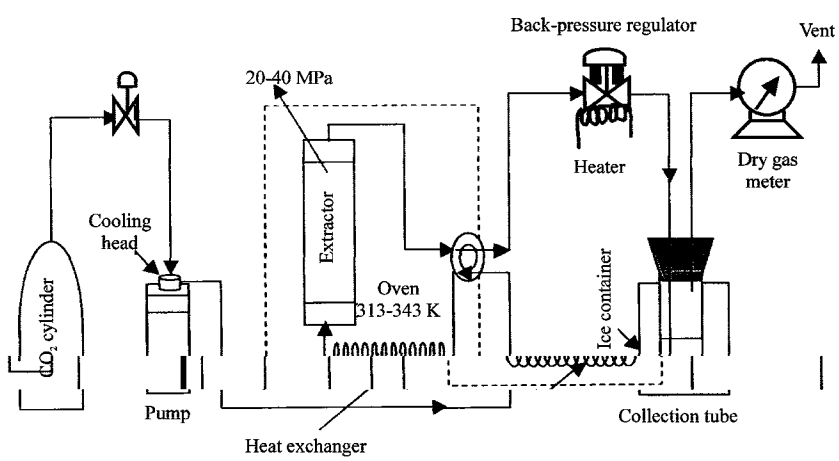

Fig. 1: Schematic of experimental set-up

At the experimental pressure, carbon dioxide was passed through the extraction column to start the extraction and the exit fluid (carbon dioxide with oil) was expanded at ambient pressure in a collection tube where oil was collected and the gas was vented through the dry gas meter. The extraction was carried out for about 5 h and at constant flow rate of carbon dioxide for all the experimental runs at our studied temperatures and pressures. The maximum yield of oil (41%) was obtained at the conditions of 343 K and 40 MPa while the weight variation of the extract for the last 3 h was less than 0.01%.

The extracts were fractionated into eight fractions for each run at definite interval of times and weighted

Gas Chromatography-FID analysis: The GC-FID analysis was performed using a Shimadzu GC-14A instrument (Shimadzu Inc., Tokyo, Japan) equipped with a J&W DB5-fused silica capillary column (15 m×0.25 mm i.d×0.25 μm film) with He carrier gas: 380 kPa, H_2:120 kPa, air: 150 kPa, column pressure: 80 kPa, oven temperature 503 K, injection and detection temperatures: 553.

The extracted fractions were analyzed as free fatty acids after hydrolysis with 1 N KOH in chloroform for 30 sec at 373 K, followed by addition of 4-5 mL of NaCl saturated with 1 N HCl and hexane extraction (3×6 mL); the combined extract used as sample for GC analysis. The reproducibility was confirmed with 2-3% variation by repeating the same analysis for three times.

RESULTS AND DISCUSSION

Effect of temperature: Figure 2a-c show the plots of the oil yield against the amount of CO_2 consumed per unit mass of sample, the yield being defined as the mass of extract per unit mass of sample. Extraction yield increased with an increase in temperature at 40 MPa and decreased with an increase in temperature at 20 MPa (Fig. 2a-c). However, the temperature effect on the extraction yield at 30 MPa is very smaller than that of other two pressures, as all the curves lie almost close to each other.

This crossover effect has been observed in solubility[6,7]. This behavior was explained by the competing effects of the reduction of solvent density and the increase of solute vapor pressure with an increase in temperature[8]. Same characteristic was observed in the extraction of ginger oil[6]. At lower pressure, the change of solvent density is more effective than the solute vapor pressure, as extraction yield increased with a decrease in temperature. However, the extraction yield does not increase any more with solvent density and starts to decrease and after certain pressure, the extraction yield depends on solute vapor pressure and it increased with an increase in temperature.

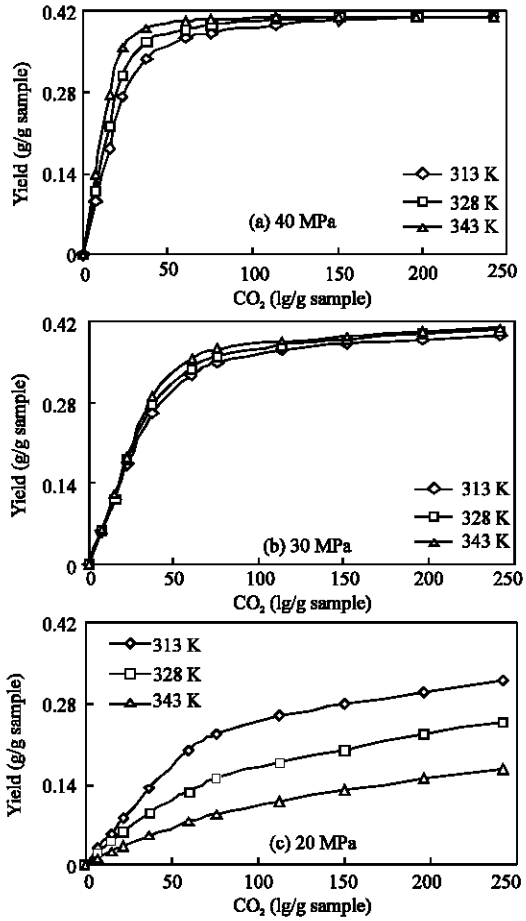

Fig. 2: Effect of temperature on the extraction yield of sunflower seed oil at 40 MPa (a), 30 MPa (b) and 20 MPa (c)

Table 1: Densities of carbon dioxide under the experimental conditions

P (MPa)	T (K)	ρ (g L^{-1})
20	313	841.2
	328	756.3
	343	661.7
30	313	911.2
	328	851.36
	343	789.0
40	313	957.3
	328	908.0
	343	857.6

P = Pressure, T = Temperature, ρ = Density

Effect of pressure: The density was calculated from Adachi correlation[9]. At constant temperature, the density of the solvent increased with an increase in pressure (Table 1), causes the higher extraction yield at higher pressure. The pressure effect was observed greater at higher temperature of 343 K and smaller at

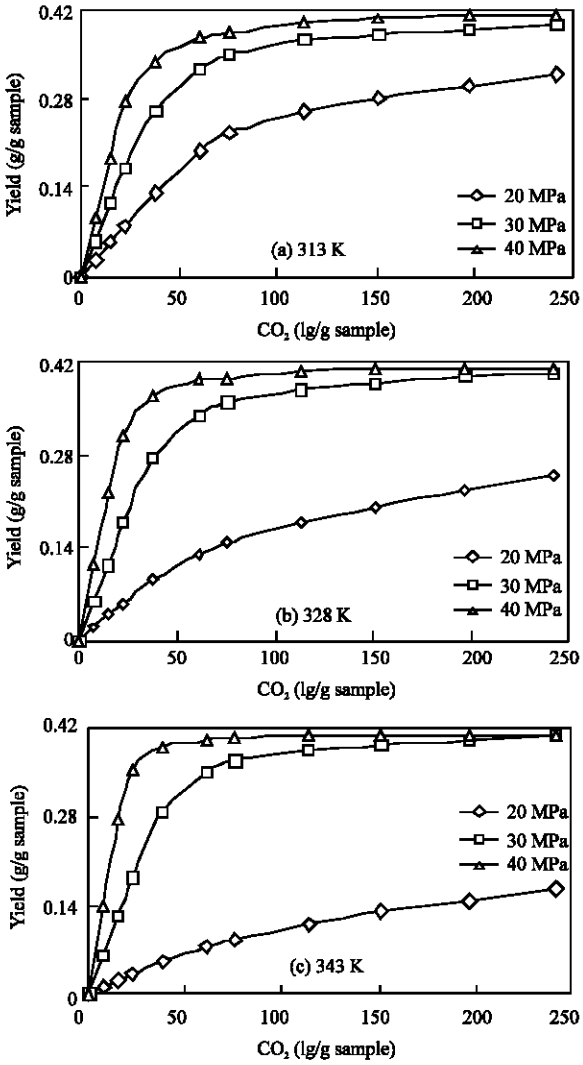

Fig. 3: Effect of pressure on the extraction yield of sunflower seed oil at 313 K (a), 323 K (b) and 343 K (c)

313 K (Fig. 3a-c). This property due to the solubility is controlled by a balance between solvent density and solute vapor pressure changes with the change of pressure and temperature.

Solubility: The extraction curves in the initial part of the extraction increased linearly with a slope corresponding to the solubility of oil (CO_2 g g^{-1}). The experimental solubility of the oil, obtained from the slopes in Fig. 2 is plotted as a function of pressure in Fig. 4. The crossover effect of solubility of sunflower oil was observed at around 28 MPa as in Fig. 4 where all the studied temperatures show the same solubility. The solubility increased with pressure at each temperature as a result of the increase in density of CO_2, but decreased with

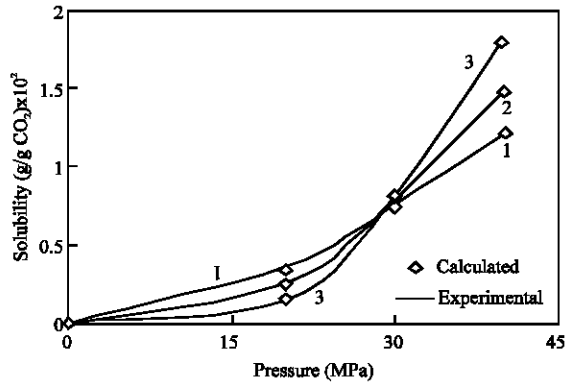

Fig. 4: Solubility of sunflower seed oil with respect to pressure and at temperatures: 313 K (1), 323 K (2) and 343 K (3)

increasing temperature up to 28 MPa. Around this pressure, the magnitude of such a density change becomes smaller[10] and the solute vapor pressure change becomes more effective that can easily overcome the effect of solvent density change on the solubility. Due to this fact, the opposite behavior of solubility of oil in respect of temperature was observed with an increase in pressure after about 28 MPa, (Fig. 4). This solubility behavior of sunflower seed oil in carbon dioxide is similar to that of tomato seed oil up to 25 MPa[11]. Del Valle and Aguilera[12] proposed the following equation to predict solubility of vegetable in supercritical carbon dioxide.

$$C_r = [(40.361-18708/T+2186840/T^2)x(0.001\rho)^{10.724}\pm2.7]/\rho \qquad (1)$$

Where, C_r is the solubility (g/g CO_2), T is the temperature in (K) and ρ is the density of carbon dioxide (g L^{-1}). The calculated values of solubility of this oil were obtained using the Eq. 1 those were very close to experimental values (Fig. 4).

Compositions analysis: The extracted fractions of the sunflower seed oil at 328 K and 40 MPa were analyzed for free fatty acids by GC-FID and the compositions of the fatty acids (Table 2). The yield 27.3-99.5%) in Table 2 was obtained by dividing the weight of extract at a definite time by the total oil content in the sample based on 41% and the composition (% w/w) of fatty acids in Table 2 was calculated on the basis of total fatty acids peak areas.

The major fatty acids in sunflower oil are palmitic, stearic, oleic and linoleic acids together account for 98% or more of the total fatty acids[3], those are almost the same as tomato seed oil[11] and as soybean oil[13]. Apart from these major fatty acids, there are some lower carbon content saturated fatty acids in trace amount less than 2% in sunflower seed oil which are extracted in the initial 50%

Table 2: Composition (% w/w) of fatty acids in sunflower oil extracted with supercritical carbon dioxide at 328 K and 40 MPa

Time (min)	Yield (%)	C (12:0)	C (13:0)	C (14:0)	C (16:0)	C (18:0)	C (18:1)	C (18:2)	C (18:3)
10	27.3	0.48	0.36	0.65	4.12	3.18	70.82	19.35	1.04
20	54.2	0.14	0.16	0.26	4.32	3.40	71.90	19.32	0.50
30	75.5	---	---	---	4.58	3.80	72.50	19.00	0.12
50	89.5	---	---	---	4.98	4.35	72.78	17.89	---
80	95.0	---	---	---	5.67	5.12	73.51	15.70	---
100	96.5	---	---	---	6.60	5.75	73.93	13.72	---
150	99.5	---	---	---	7.30	6.55	75.13	11.02	---

Major fatty acids are: (C 16:0) = Palmitic acid; (C 18:0) = Steric acids; (C18:1) = Oleic acid; (C 18:2) = Linoleic acid

of the extraction. The composition of individual fractions remained almost the same until the final 50% of the extraction. Linoleic and linolenic decreased while oleic, stearic and palmitic acids increased. This change of composition may be because of differences the solubility of fatty acids in supercritical carbon dioxide where soluble components can be extracted first. Fatty acids with shorter chain length and higher degree of unsaturation have higher solubility[14]. The same behavior was observed in the extraction of soybean oil[13] and also in the extraction of tomato seed oil[11].

CONCLUSIONS

The effects of variation in temperature and pressure on the extraction yield of oil from sunflower seed using supercritical carbon dioxide suggests use of higher pressure and lower temperature to increase the solvent density, while solubility depends on solvent density. The experimental solubility values were similar to the values estimated from the equation reported for vegetable oils. The composition of the extracted oil was similar to that of soybean and tomato seed oil.

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