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Extraction of Soybean Oil Using Supercritical Carbon Dioxide and Its Characteristics

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Abstract

Extraction of soybean oil from full fat soybean flour was performed using a supercritical carbon dioxide extraction system. Extraction pressure and temperature of the process were 3,000-7,000 psig and 40-70℃, repectively. For the extraction of 1g of soybean oil, 25*l* of carbon was consumed at 7,000 psig and 60℃, whereas more than 250*l* of carbon dioxide was consumed at 3,000 psig and 60℃. The solubility of soybean oil in supercritical carbon dioxide decreased with the increase in temperature below 6,000 psig, and the reverse trend was observed above 6,000 psig. At 6,000 psig the solubilities were shown to be constant regardless of extraction temperature. Soybean oils extracted with supercritical carbon dioxide were lighter in color and contained less phosphorus than those extracted with hexane.
Keywords: supercritical carbon dioxide, soybean oil, extraction kinetics, phosphorus content, color

Introduction

Most vegetable oils have conventinally been obtained from oilseeds by either pressing and/or organic solvent extraction methods. Because of some disadvantages and limitations of conventional organic solvent extraction methods, several alternative extraction methods have been developed, and one of them is supercritical fluid extraction method[1]. Supercritical fluid extraction is a rapid extraction process compared to organic solvent extraction due to higher diffusivity, and lower density and viscosity of supercritical fluid than organic solvent[2].

In the current supercritical fluid techniques, supercritical carbon dioxide ($SCCO_2$) is most widely used since it has relatively low critical temperature (31.1 ℃) and critical pressure (73 bar)[3]. Furthermore carbon dioxide is non-toxic, non-corrosive, non-flammable, cheap, and readily available in large quantity and in high purity[3]. $SCCO_2$ extraction has been practically and successfully applied to the decaffeination of coffee[4], extraction of hop resin, spices and tobacco[5], concentration of aroma compounds[6], extraction of oils from oil-bearing materials[7-12], and fraction of lipids materials[13].

As described earlier, $SCCO_2$ extraction system of soybean oil was well established, and the effects of extraction conditions on the properties of soybean oil were also determined in a limited range of operation pressure and temperature[7,14,15].

The objectives of the pressent study are (i) to observe the effects of extraction pressure and temperature, and SCCO consumption on the degree of extraction of soybean oil, (ii) to access the kinetics of extraction process, and (iii) to determine the effects of extraction conditions on the characteristics of SCCO extracted soybean oil with the comparision of hexane-extracted soybean oil, in the wide range of extraction pressure and temperature.

Materials and Methods

Materials

Full fat soybean flour (100-120 mesh) was purchased from a local market in Korea. Gaseous carbon dioxide (CO_2) was of commercial grade. All reagents used were of analytical grade unless otherwise specified.

Equipment

The extraction equipment was assembled in our laboratory and the system was basically the same as Autoclave Engineers supercritical extraction screening system manufactured by Autoclave Engineers, Inc. (Erie, Pennsylvania, U.S.A.) as shown in Fig. 1[16]. Pressurized CO_2 from cylinder was fed to a liquid pump (Model 110, Haskel Engineering Corp.) through a check valve, 5μ particulate filter, and cooling

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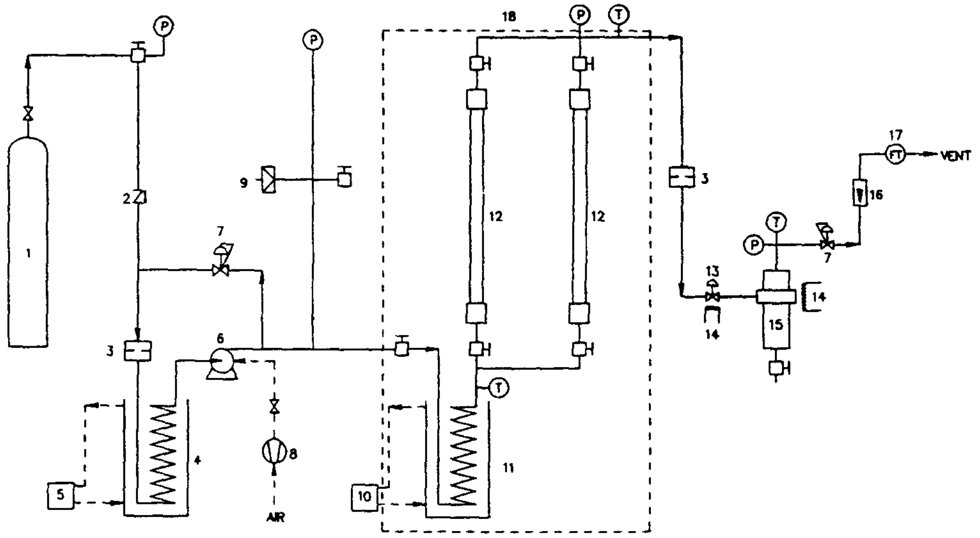


1. CO_2 cylinder
2. Check valve
3. Filter
4. Subcooler
5. Refrigerated Circulator
6. Pump
7. Back pressure Regulator
8. Air compressor
9. Rupture
10. Heating circulator
11. Preheater
12. Extracter
13. Metering valve
14. Electric heater
15. Separator
16. Rotameter
17. Flow totalizer
18. Air bath
P: Pressure gauge
T: Thermocouple

Fig. 1. Supercritical carbon dioxide extraction equipment

apparatus. Pressure of Co_2 was maintained constant by a back pressure relief valve. After the compressed Co_2 is heated up to desired supercritical temperature by heating apparatus, it was introduced to an extractor. The extractor was mounted vertically in a temperature-controlled oven. Pressure and temperature of the system were determined by pressure gauges and thermocouples, respectively. Gas leaving the extractor passed through a micrometering valve to a separator. Micrometering valve was heated by attached heating element in order to prevent freezing of the valve. The instantaneous flow rate of Co_2 through the extractor was monitored by a rotameter, while total flow was measured by a totalizer before being vented to the atomosphere[16].

Extraction

Full fat soybean flour (20g) was filled in the extractor and stamped down carefully. The extractor containing the sample was inserted into the extraction module, and extraction was carried out at different pressures of 3,000, 4,000, 5,000, 6,000 and 7,000 psig, and temperatures of 40, 50, 60 and 70℃ according to the slightly modified procedure of Friedrich et al. [14]. Average flow rate of CO_2 gas at atmospheric pressure was 10l/min. The amount of soybean oil extracted with $SCCO_2$ was determined gravimetrically. Soybean oil extract was collected into four fractions (F1, F2, F3 and F4) according to the progressive extraction at 50℃ and 7,000 psig. The degree of extraction was expressed in extraction yield calculated as weight percentage of soybean oil obtained from one gram of dry full fat soybean flour[14]. Soybean oil was also extracted by hexane in a Soxhlet apparatus for 6 hrs.

Analyses

Phosphorus contents of oil samples were determined by AOCS method[17]. Fatty acid composition of oil samples were analyzed by gas-liquid chromatography according to AOCS method using a gas chromatographys (Hewelet-Packard, HP 5890)[17]. Color of oil samples was measured by Lovibond Tintometer (Model E) with a 5¼ inch cell.

Results and Discussion

In order to evaluate the solventing power of $SCCO_2$ for soybean oil from full fat soybean flour, extraction yields were determined at different extraction condi-

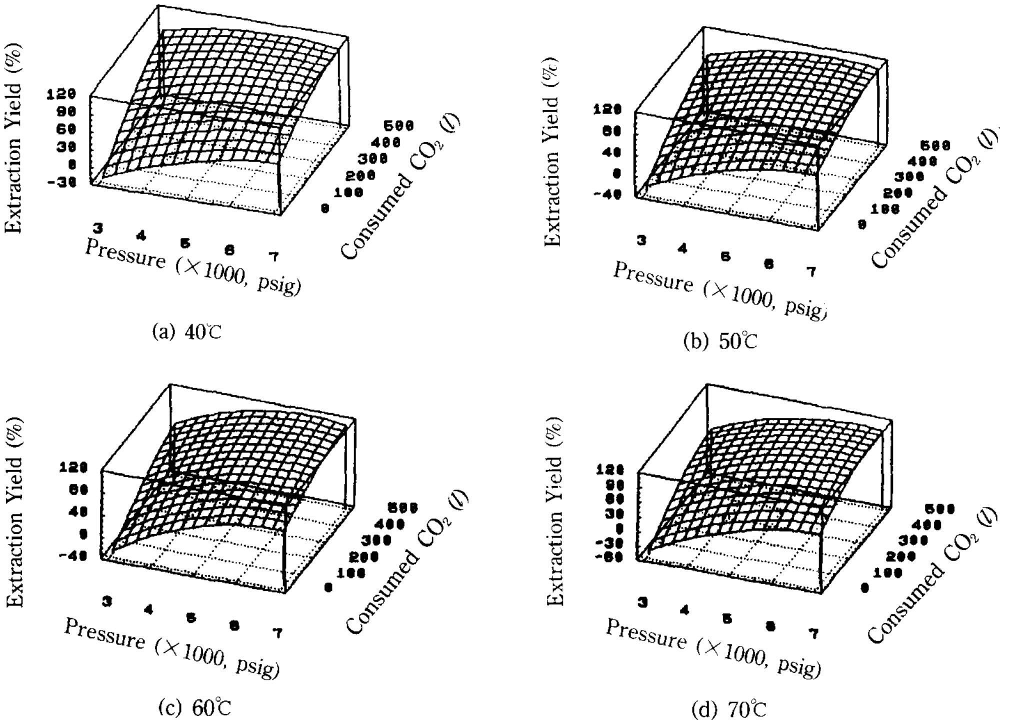


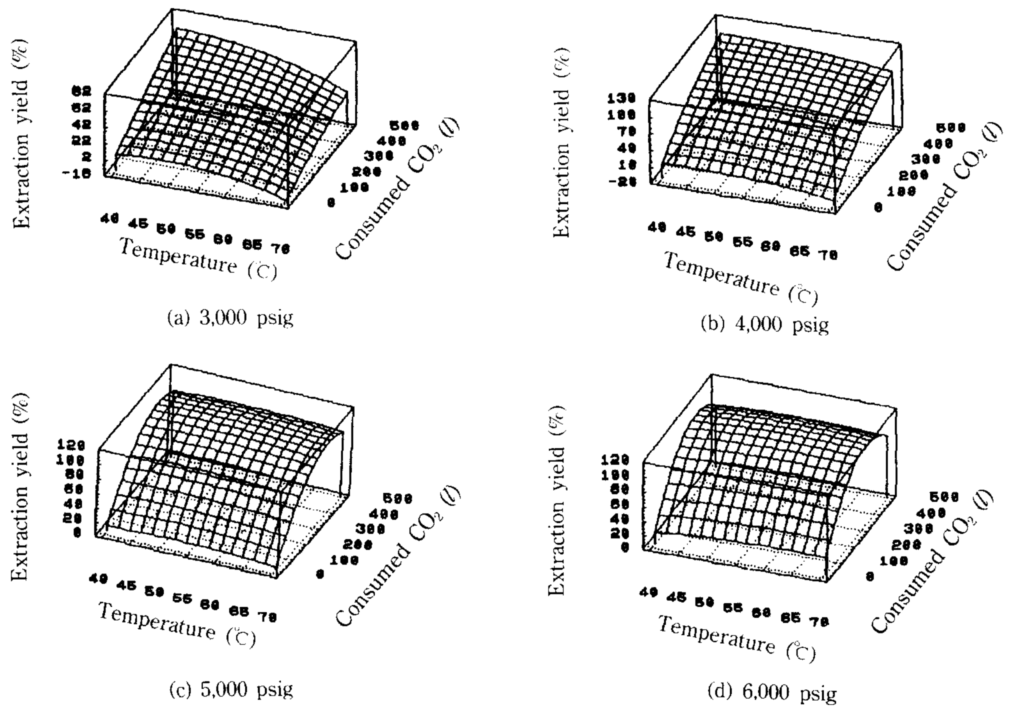
Fig. 2. Effects of extraction pressure and carbon dioxide consumption on the extraction yield of different temperatures

tions. Fig. 2 shows the effects of extraction pressure and carbon dioxide consumption on the extraction yield of soybean oil at different temperatures. Data obtained were statistically analyzed by stempwise variable selection method of regression analysis, and were shown in response surface plotting[18]. Extraction yield increased obviousely with the increase of pressure and the amount of consumed carbon dioxide at all temperatures tested. Maximum extraction yield was 95%. Extraction yield remained relatively constant regardless of the increase in pressure at 40 ℃ and 500*l* of carbon dioxide, whereas extraction yield increased with the increase in pressue at 70℃ and 500*l* of carbon dioxide.

Effects of extraction temperature and carbon dioxide consumption on the extraction yield of soybean oil at different pressures are shown in Fig. 3. At low extraction pressures such as 3,000, 4,000 and 5,000 psig, extraction yield decreased with the increase in temperature with a same amount of carbon dioxide, whereas the reverse trend was observed at 7,000 psig. However, extraction yield was constant with the change in temperature at 6,000 psig. At 7,000 psig and 70℃, the extraction of 50% soybean oil from full fat soybean flour required 50*l* of carbon dioxide, whereas about 1,000*l* of carbon dioxide was required for the extraction of same amount of oil at 3,000 psig and 70℃.

Fig.4 shows the effects of extraction pressure and temperature on the solubility of soybean oil. The solubility was constant (0.026g oil/*l* CO_2) at 6,000 psig regardless of temperatures tested. Above the pressure of 6,000 psig, the solubility increased as temperature increased, in contrast the reverse trend was observed below 6,000 psig. The solubility at 7,000 psig and 70℃ was 0.052g oil/*l* CO_2, which was 25 times higher than that at 7,000 psig and 40℃. However, the solubilities of soybean oil in supercritical carbon dioxide decreased from 0.034 to 0.007g oil/*l* CO_2 when the temperatures increased from 40℃ to 70℃ at 3,000 psig.

It is reported that the solvent power of supercritical carbon dioxide for soybean oil is highly dependent on pressure and temperature[14,15]. At the pressure below 6,000 psig, solvent power decreases with increasing temperature because the density of SCO_2 decreased, which reduced solvent power of $SCCO_2$. Density of carbon dioxide changes rapidly between



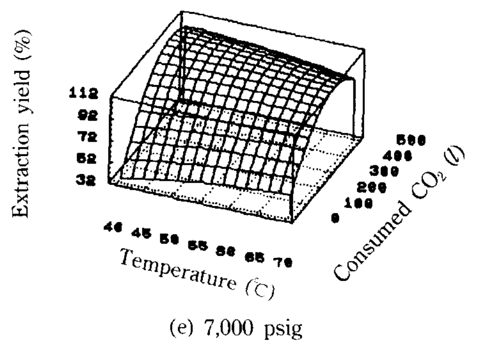


Fig. 3. Effects of extraction temperature and carbon dioxide consumption on the extraction yield of soybean oil at different pressures

1,070 psig (critical pressure) and 6,000 psig, wherea above 6,000 psig the density does not change rapidly. Therefore, at pressure below 6,000 psig, the solubility of soybean oil in supercritical carbon dioxide was influenced strongly by pressure. However, at pressures higher than 6,000 psig, solvent power increased as temperature increased. The density of $SCCO_2$ was not majorly affected by the change in temperature above 6,000 psig, and higher temperature enhanced the solubilization of oil in $SCCO_2$

Phosphorus conten, color and fatty acid composition of $SCCO_2$ and hexane-extracted soybean oil are shown in Table 1. Oil was extracted at 50℃ and 7,000 psig. Phosphorus contents in $SCCO_2$ -extracted soybean oils were extremely low (4-22 ppm) compared to 520 ppm in hexane-extracted soybean oil. List et al. reported that the extremely low solubility of phospholipids in $SCCO_2$ -extracted soybean oil resulted more neutral lipids in oils and this is one of the advantages for refining, i.e., skipping the degumming process[8,12].

Color of initial fractions, F1 and F2, of $SCCO_2$ -extracted soybean oil showed less red and yellow color intensities, and ranged from 0.7 to 1.0 red (R) unit compared to 3.0 unit of hexan-extracted oil. Final fraction (F4) showed 3.3 red unit which was slightly more red than hexane-extracted oil. Yellow color of $SCCO_2$ -extracted soybean oil ranged from 19 to 30.4 and that of hexane-extracted soybean oil was 30. Yellow color of soybean oil was less affected by extrac-

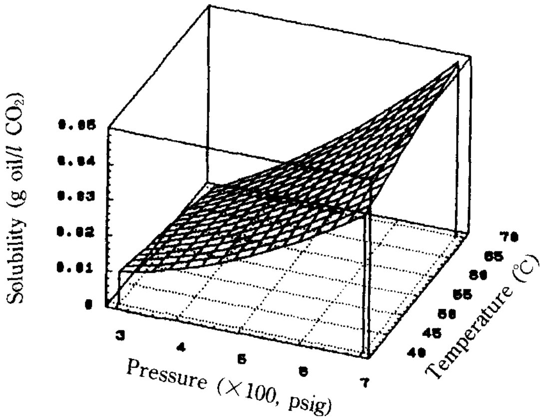


Fig. 4. Effects of extraction pressure and temperature on the solubility of soybean oil

Table 1. Phosphorus content, color and fatty acid composition of $SCCO_2$, and hexane-extracted soybean oil

Analytical item		$SCCO_2$ fractions F1	F2	F3	F4	Hexane
Yield(%)		35	70	84	95	96
Phosphorus(ppm)		4	4	12	22	516
Color	R	1.0	0.7	2.5	3.3	3.0
	Y	19.0	25.0	30.0	30.4	30.0
Fatty acid composition (%)						
Palmitic acid		11.9	11.9	10.3	10.1	11.7
Stearic acid		3.5	3.5	4.7	5.3	4.0
Oleic acid		20.4	20.4	23.1	24.3	21.6
Linoleic acid		54.3	54.3	52.9	51.8	53.4
Linolenic acid		9.3	9.4	8.8	8.2	8.8
Others		0.6	0.5	0.3	0.3	0.5

tion solvent than red color. Color of total $SCCO_2$-extracted soybean oil was less than that of hexane-extracted oil and this result can be applied to bleaching process.

Fatty acid composition of hexane-extraced soybean ranged within the typical values of soybean oil (Table 1). In $SCCO_2$ -extracted soybean oil, the contents of oleic acid and stearic acid increased gradually from F1 to F4, and the contents of palmitic, linoleic and linolenic acid decreased. This is due to the differences in solubility of individual fatty acids in $SCCO_2$[13].

The results conclusively showed that $SCCO_2$ extraction was effective in obtaining soybean oil under mild thermal condition, and the $SCCO_2$ -extracted oil contained much less phospholipids and color than hexane-extracted oil. $SCCO_2$ extraction can be used for rapid extraction, to simplify degumming and bleaching processes.

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초임계 탄산가스를 이용한 대두유의 추출과 추출대두유의 성질

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초임계 탄산가스를 추출용매로 사용하여 대두유를 추출하였다. 추출압력과 온도의 범위는 각각 3,000-7,000 psig와 40-70℃였다. 1g의 대두유를 추출하기 위하여 7,000 psig, 60℃에서는 25 l의 탄산가스가 필요하였으나, 3,000 psig, 60℃에서는 250 l가 소요되었다. 추출압력 6,000 psig 미만에서는 온도가 증가할수록 추출율이 감소하였고, 6,000 psig에서는 온도에 관계없이 추출율이 일정한 반면, 6,000 psig를 넘어서는 온도가 증가할수록 추출율도 증가하였다. 초임계탄산가스로 추출된 대두유는 핵산으로 추출한 대우유보다 색도가 약하였으며 인지질의 함량도 매우 적었다. 지방산조정은 초임계 추출이 진행됨에 따라 변화하였다. 초임계탄산가스를 이용하여 대두유를 추출할 경우, 신속한 추출이 이루어지며, 탈검과 탈색의 정제공정을 삭제내지는 축소하여 정제유를 만들 수 있다.