EXPERIMENTAL RESEARCH INTO THE SUPERCRITICAL CARBON DIOXIDE FLUID EXTRACTION FOR SOYBEAN SEED OILS

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Abstract

Supercritical fluid CO_2 extraction (SCFE) is an environmental friendly technology, and shows an attractive future in separation process. In this thesis, a SCFE set-up with an extraction volume of 1L was established, with which soybean oil was extracted using supercritical CO_2. The experiments show that many factors have impacts on the oil yield, such as extraction pressure, temperature, and extraction time, as well as seed particle size and charge quantity. For the SCFE of soybean oil, the optimum conditions were at a pressure of 30MPa and a temperature of 35? , and the soybean flakes thickness of 0.4mm. The soybean oil obtained from SCFE process contains 16.089% of saturated fatty acid and 83.567% of unsaturated fatty acid. From the changes of oil yield with the extraction time, it can be concluded that the extraction process contains three stages: fast extraction stage (line); transitional stage and the slow extraction stage. At the first stage, 75%-80% of the oil has been extracted out.

INTRODUCTION

The supercritical state is defined that the pressure and temperature of fluid are both exceed critical phase points. The fluid is known as Supercritical Fluid (SCF). Experiments show that SCF is characterized by the following attributes:(a) the density of the fluid is near to a liquid, (b) the viscosity diffusivity and the heat exchange coefficient of the fluid are between a liquid and a gas, but rather a gas. So, the solubility of substances are higher in SCF than in normal solvents, moreover, the higher the solubility, the higher the pressure and the lower the temperature.

Supercritical Fluid Extraction (SCFE) is a kind of unique extraction process in which embodies the above features. So, separation of the extracted substances from the supercritical fluid can be accomplished (in whole or in part) by altering the pressure and/or the temperature of the system. The technology of SCFE differs from conventional solvent extraction because the product from SCFE is purer and the yield is larger. Also, the process of SCFE is more simple and economical than that of distillation. Particularly, as a sanitary generative technology, the extraction with supercritical CO_2 is very popular in the field of purification of materials with high subordinate values.

In the last years, several studies investigating SCFE of lipidic compounds from a wide range of different vegetable matrices (seeds, flowers, leaves, etc.) have been published[1-16]. In most of these studies carbon dioxide is the solvent used because of its relatively low critical temperature (31.1?), non-toxicity, non-flammability, good solvent power, ease of removal from the product and low cost. The high quality of the products obtained by SCFE was pointed out by Friedrich et al [1-4], who observed that the extracted products do not need any particular refining operate as the vegetable material does not undergo any stressing treatments.

The aim of this work to investigate the influence of pressure, temperature, particle size and CO_2 flow rate on the yield and the composition of soybean seed oil obtained from Chinese soybean seed by supercritical carbon dioxide extraction. So, in this paper, the relationship among pressure, temperature, particle size, and CO_2 flow rate with the extraction rate of soybean seed oil was studied. Furthermore, the property of the extraction process (such as extraction control factors) was pointed out based on the changes of oil yield with the extraction time.

I - MATERIALS AND METHODS

Dried and flaked soybean seeds obtained from Dalian Hua-Tai Oil Plant contained 18.5wt% oil and 13.1wt% water. The purity of carbon dioxide supplied by Guangming Gas Plant was better than 99.9%.

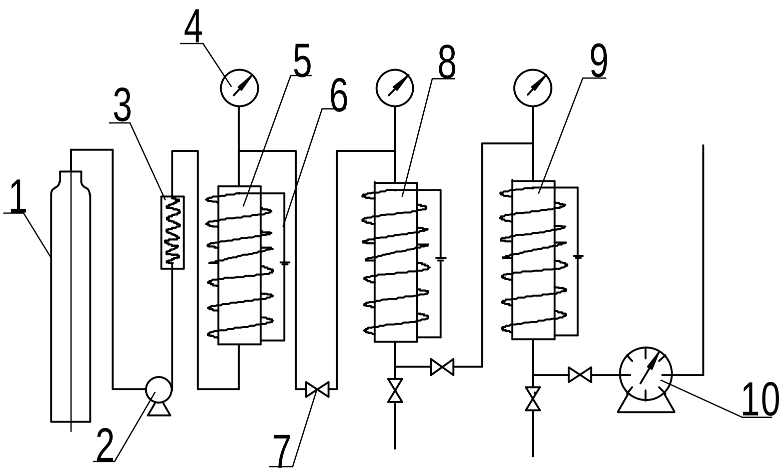
II - APPARATUS AND EXTRACTION PROCEDURE

Extraction measurements were carried out in a semi-batch flow extraction apparatus. Supercritical carbon dioxide was used as solvent. Liquid carbon dioxide from the supply cylinder passes through a cold bath (about 263K) and then is pumped with a two-plugs Pump, model 2JX-40/8 (Hangzhou, P.R.China) and heated by a tubular heat exchanger to the extraction temperatures. The pressure is controlled with a back- pressure regulator (Yancheng, Jiangsu, P.R.China, model number H21X-100P, DW6).

The extractor containing the raw material to be extracted was in a thermostatically controlled by an electrical heating belt bath, the temperature inside the extractor being controlled by a digital controller (Yuyao, Zhejiang, P.R.China, model number TDA-8002) within an accuracy of ±0.1K. The pressure at the exit of the extractor was measured using a pressure gauge with an accuracy of 0.2 MPa. After leaving the extractor, the stream of carbon dioxide loaded with extract flowed through an on/off valve and a sequence of pressure expansion valves (needle valve, Yancheng, Jiangsu, P.R.China, model number WL21H-320P, DW6). The stream pressure was in this way reduced in three successive stages down to atmospheric pressure, and the oily extract was recovered in a glass collector. Water and volatile components were deposited in a second collector. The volume of the carbon dioxide was measured by using of a Wet Test Meter (Changchun Meter Company, Jilin, P.R.China, model number LML-2) with an accuracy of ±0.01 L. The pressure and temperature conditions were measured at the end of assembly. The estimated accuracy of the pressure measurement was ±0.1 MPa and temperature was measured with a mercury thermometer to within ±0.1 K.

III - GC ANALYSIS OF FATTY ACIDS

Extracted oil was analyzsed by GC (HP-4890), the column temperature was increased from 70 to 280? , and the detector temperature was maintained 205? . The samples were pre-treated by means of methyl-esterifies and a 0.6μ l portion was injected into the GC. Analysis was performed under the following conditions; column, a PEG-20M (30m length × 0.25mm I.D.); a carrier gas, Nitrogen. The relative percentage of different compounds of the extracted soybean seed oils, using SCF process and organic solvent extraction method separately, is listed in Table 1. It is noticeable that content of the saturated fatty acid is about 16.089% and unsaturated fatty acid is about 83.567%. The GC spectrums of soybean seed oils are listed in Fig.2.

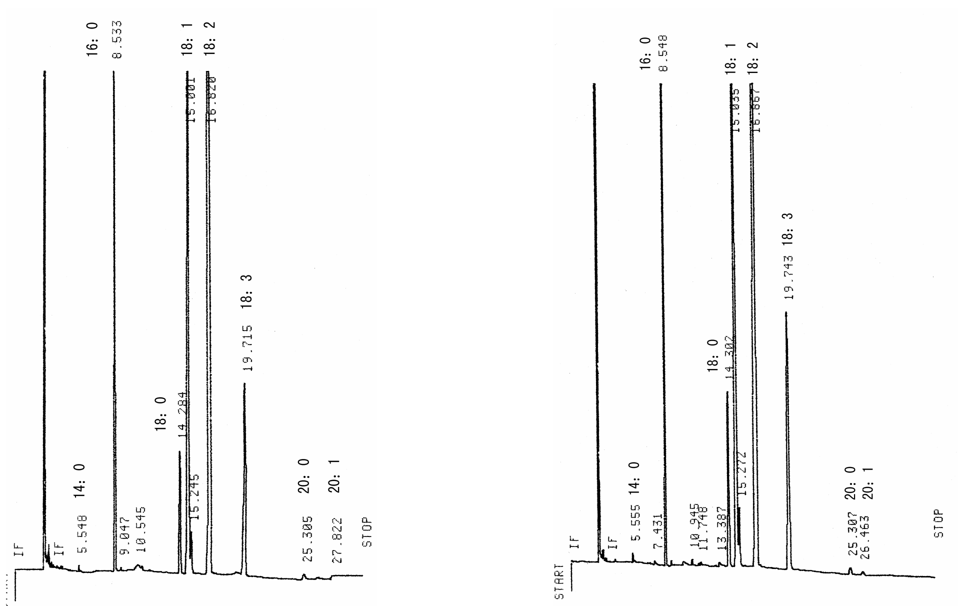


1.CO_2 cylinder; 2.pump; 3.pre-heater; 4. pressure gauge; 5.extractor
6.electric heating belt; 7.reductor; 8,9.separator; 10.wet test meter

Figure 1 Schematic Diagram of Experimental Apparatus

Table 1 Fatty Acids Composition of The Seed Oil Extracted By SCFE (%)

Chemical compositions		C_{14}^{0}	C_{16}^{0}	C_{16}^{1}	C_{18}^{0}	C_{18}^{1}	C_{18}^{2}	C_{18}^{3}	C_{20}^{0}	C_{20}^{1}
Extraction method	Solvent extraction	0.073	11.169		3.937	21.632	53.454	8.153	0.422	0.200
	SCFE	0.081	11.547	0.146	4.107	22.118	53.105	7.993	0.354	0.205



(a) Solvent Extraction　　(b) SCFE

Figure 2 Gas Chromatograms of Soybean Oils

IV- RESULTS AND DISCUSSION

In order to find the optimum operating conditions, the effects of various process parameters such as extraction pressure, temperature, extraction time and particle size, as well as filling fraction, were investigated on the oil yield.

IV-1 Temperature effect

The effect of extraction temperature on the oil yield was illustrated in Fig.3. It can be seen that the oil yield first increased with the temperature rise , and attained the maximum value at the temperature of 40? , then decreased with the further increasing of temperature. Such a change of oil yield with the temperature is due to the coupling effect of temperature and pressure. On one hand, the increasing of temperature resulted in the decrease of solvent density, thus decrease the solubility of seed in SCF. On the other hand, the saturation pressure of solute in SCF increased with the temperature increase, which improved the solubility.

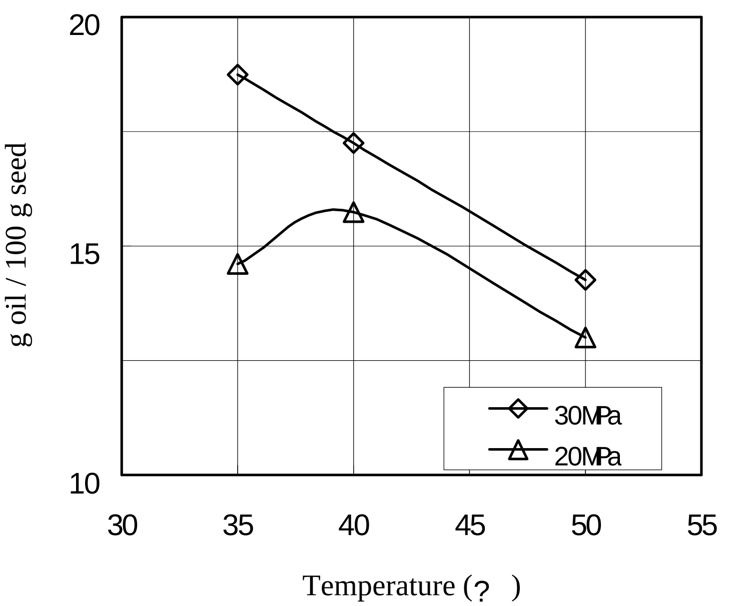


Fig.3 Effects of Temperature on the Extraction Efficiency

IV-2 Pressure effect

The effect of extraction pressure on the oil yield is shown in Fig.4. The experiments were performed at four different temperatures and various pressures. The particle size is fixed at 0.4mm in flakes and the CO_2 flow rate is fixed to 0.2m^3/h. It is clear that with the increase of pressure, the oil yield increased. It is well known that with the increase of pressure, the density of SCF CO_2 increased, and the solubility of solute increased. Furthermore, according to the P-R equation of state (EOS), the variation of density with pressure become significant between 5~ 25MPa . For the practical application, we propose that 25MPa should be employed.

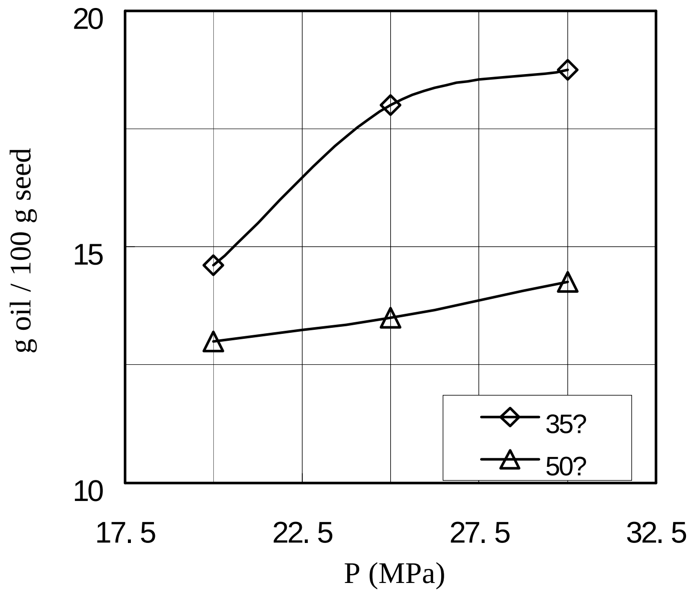


Fig.4 Effects of Pressure on the Extraction Efficiency

IV-3 Time effect

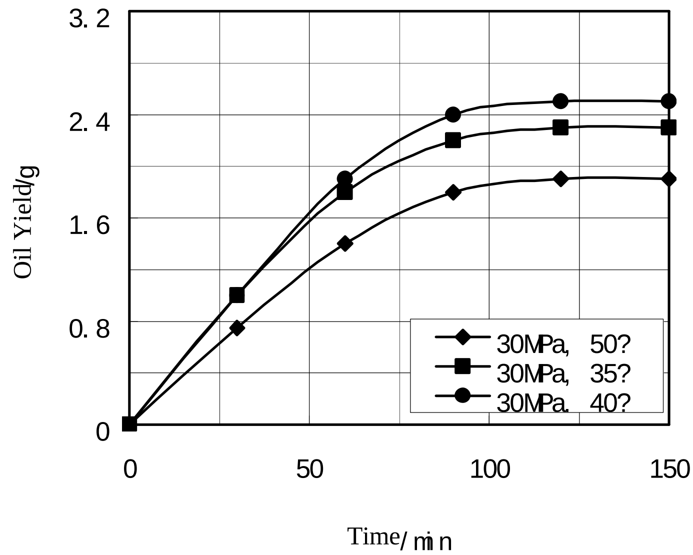


Fig.5 Effects of Operating Time on the Extraction Efficiency

Fig.5 shows the yield-vs-time curves under the different operating conditions at the fixed flow rate of $0.2m^3/h$? From Fig.5, it can be seen that the extraction process is composed of three stages: rapid extraction of free solute, transitional stage of surface and internal diffusion and slow extraction mainly based on the internal diffusion [6,8,17,18]. The time consumed in the first extraction stage depends both on the solute solubility in SCF CO_2 and on the particle size. Under our experimental conditions, most parts of seed oil was extracted in the first stage during 90~ 100 min.

V-CONCLUSION

The experimental results show that the process parameters have important effect on the extraction efficiency. The optimum condition for the extraction of soybean seed oil is as follows: the extraction pressure of 25MPa, the temperature of 40? ? When the solvent flow rate is 0.2m^3/h, the extraction time is 1.5~ 2h? The soybean seed oil extracted with SCF CO_2 has a high quality. The content of the saturated fatty acid is about 16.089% and unsaturated fatty acid is about 83.567%.

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