Supercritical Carbon Dioxide Fluid Extraction of Seed Oil For Hippophae Rhamnoides L.

Jianzhong Yin*, Runjie Liu, Yuan Ma, Che Zhu
School of Chemical Engineering, Dalian University of Technology, Dalian 116012, *People 's Republic of China*
Correpondence: yinjzhaq@mail.dlptt.ln.cn

Abstract

In this paper, a SCFE set-up with an extraction volume of 1L was established, with which Hippophae Rhamnoides L. seed 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 fluid flow rate, as well as seed particle size and filling quantity. For the extraction process of Hippophae Rhamnoides L. seed oil, the optimum conditions were as follows: extraction pressure of 20MPa~ 30MPa, extraction temperature of 35? ~ 40? , supercritical CO_2 flow rate of 0.15m^3/h~ 0.3m^3/h, and extraction time of 4-5h. Under such a condition, the oil obtained is very lucid and good quality, and the yield is as high as above 90%. GC analysis shows that the oil contains 12.61% of saturated fatty acid and 86.93% 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.

Keywords : Supercritical fluid extraction; Hippophae Rhamnoides L. Seed;

1. Introduction

Hippophae Rhamnoides L is largely grown in the part of northeastern and northwestern of China. Its main function is often used as shelterbelt so as to protection the environment. On the medical view, its sarcocarps and seeds usually have high pharmacodynamic values. Especially for the Hippophae Rhamnoides L seed oil, it has been widely used to cure the cancer and enhance the immunity of the human body. Therefore, there is a great demand for the Hippophae Rhamnoides L seed oil in the world market. In 1997, Hippophae Rhamnoides L. was listed in pharmacopoeia of People's Republic of China.

Compared with the traditional grinding technique and solvent extraction, supercritical fluid extraction using CO_2 has gained more and more attention due to the high purity of the product oil and free from solvent contamination. In this work, the extraction pressure, extraction temperature, particle size of the vegetable matrix, filling quantities, and solvent flow rate were identified as the parameters that mainly contribute to process optimization, and therefore, their effect on the yield of Hippophae Rhamnoides L. seed oil has been studied in detail.

2. Experimental

Hippophae Rhamnoides L seed (produced in eastern area of Inner Mongolia, China) was milled and sieved to appropriate particle size before use. They contain 18.5wt% oil and 13.1wt% water. The purity of carbon dioxide supplied by Guangming Gas Plant was better than 99.9%.

Extraction measurements were carried out in a semi-batch flow extraction apparatus (see Fig.1.). 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).

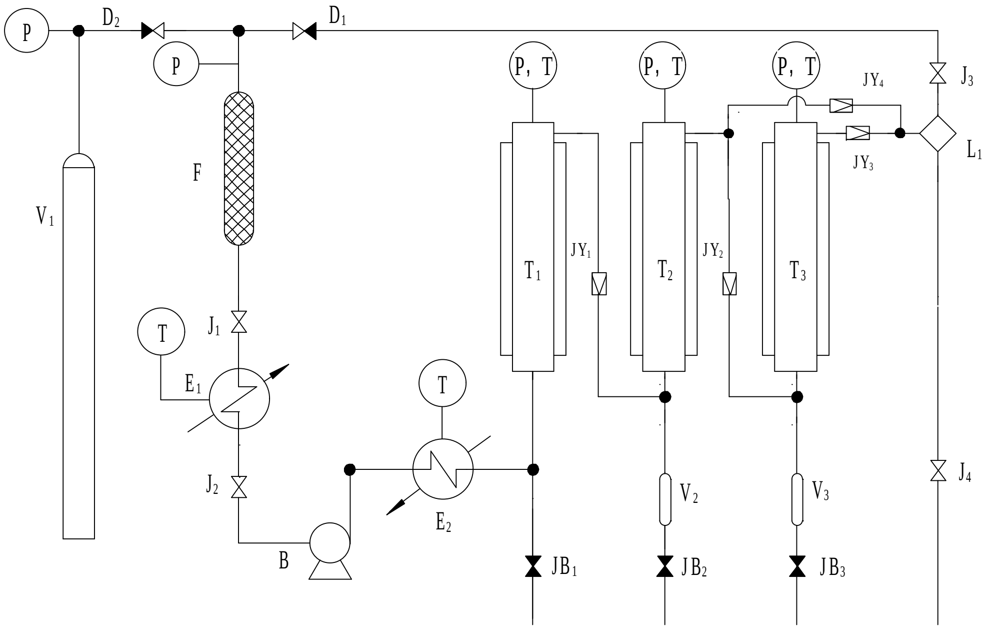

Fig.1 Schematic diagram of the experimental apparatus.

B: Pump, D_{-2}: , E_1: Condenser, E_2: Heat exchanger, F: Filter, J_{1-4}: Valves, JB_{1-3}: Valve(always closed), JY_{1-4}: Reductors, L: Rotameter , P: Pressure gauge, T: Temperature meter, T_1: Extractor, T_{2-3}: Separators, V_1: CO_2 cylinder, V_{2-3}: Sample collectors.

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 ±0.01K. The pressure at the exit of the extractor was measured using a pressure gauge with an accuracy of 0.01 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 carbon dioxide delivered was measured by a Wet Test Meter (Changchun Meter Company, Jilin, P.R.China, model number LML-2) with an accuracy of ±0.001 L. The pressure and temperature conditions were measured at the end of assembly. The estimated accuracy of the pressure measurement was ±0.01 MPa and temperature was measured with a mercury thermometer to within ±0.01 K.

3. Results and discussion

The extraction pressure, extraction temperature, particle size of the vegetable matrix, filling quantities, and solvent flow rate were identified as the parameters that mainly contribute to process optimization, and therefore, their effect on the yield of Hippophae Rhamnoides L. seed oil has been studied in detail.

3.1. Effect of Temperature

The effect of extraction temperature on the oil yield was illustrated in Fig.2. 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.

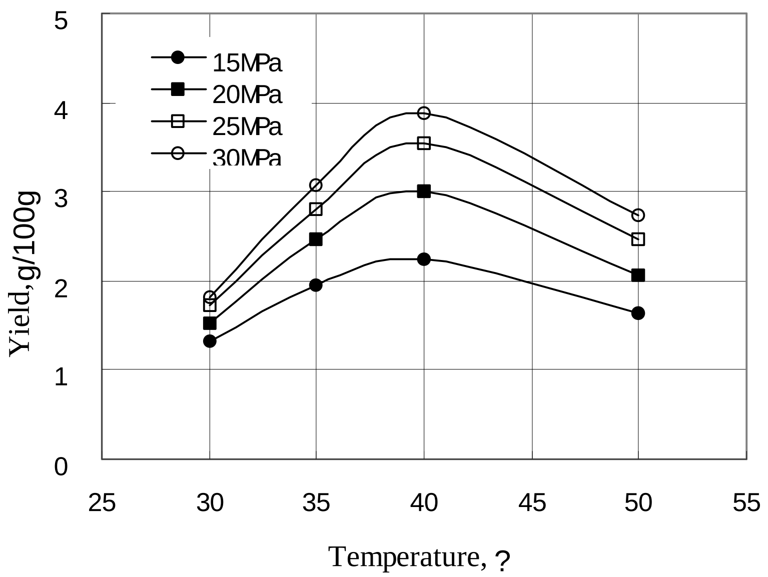

Fig.2. Effects of temperature on the extraction efficiency

3.2. Effect of Pressure

The effect of extraction pressure on the oil yield is shown in Fig.3. 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.

3.3. Effect of Particle sizes

Besides temperature and pressure, the particle size has a critical impact on the extraction efficiency. In the present work, we investigated the particle size effect at the pressure of 30MPa and a temperature of 35? . As shown in Fig.4, the smaller is the particle size, the higher oil yield was obtained. Especially for the particle size between 18~ 36 mesh, the oil yield increased rapidly with the particle size decrease. Decreasing the particle size can improve the mass transfer; meanwhile increase the mass transfer resistance. Therefore, a suitable particle size should be employed.

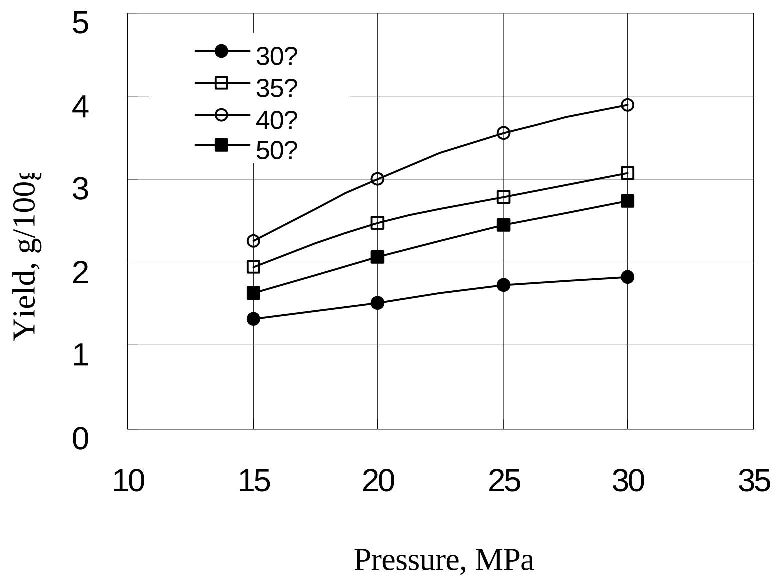

Fig.3. Effects of pressure on the extraction efficiency

3.4. Effect of Filling

Fig.5 shows the filling effect on the oil yield. It can be seen that with a decrease of filling volume, the oil yield increased. This is because the smaller filling volume can enlarge the contact area between the fluid and the solid, so improve the mass transfer. When the filling fraction is about 45%, the oil yield after a 4h extraction is about 4.2%. While when the filling fraction is 75%, the oil yield went down to 3.2% after the same extraction periods. However, from the economic point of view, the filling fraction of 75~ 80% is suitable?

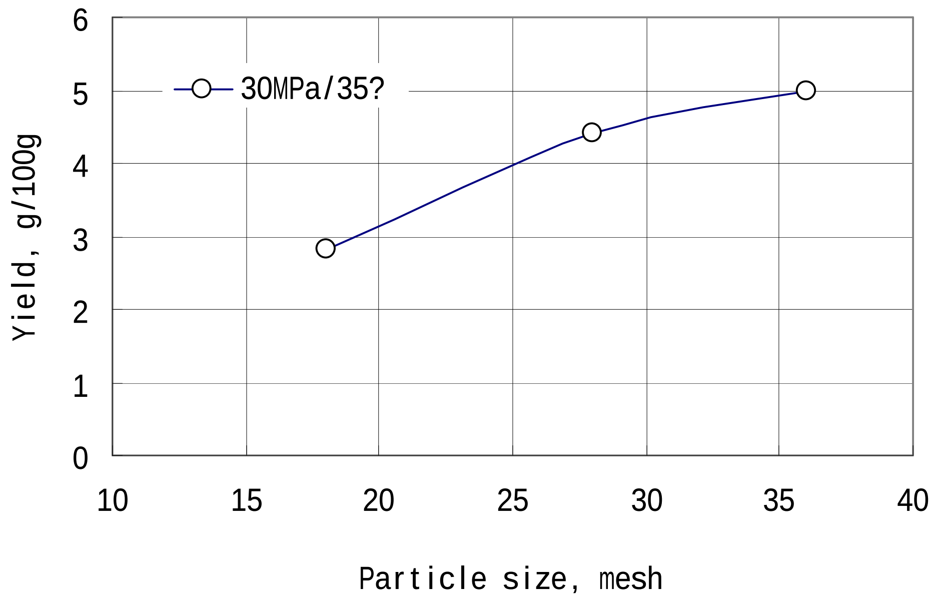

Fig.4. Effects of particle size on the extraction efficiency

3.5. Effect of flow rate

Fig.6 shows the yield-vs-time curves under the different operating conditions at the fixed flow rate of 0.2m^3/h? From Fig.6, 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 [6,8,13-16]. 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.

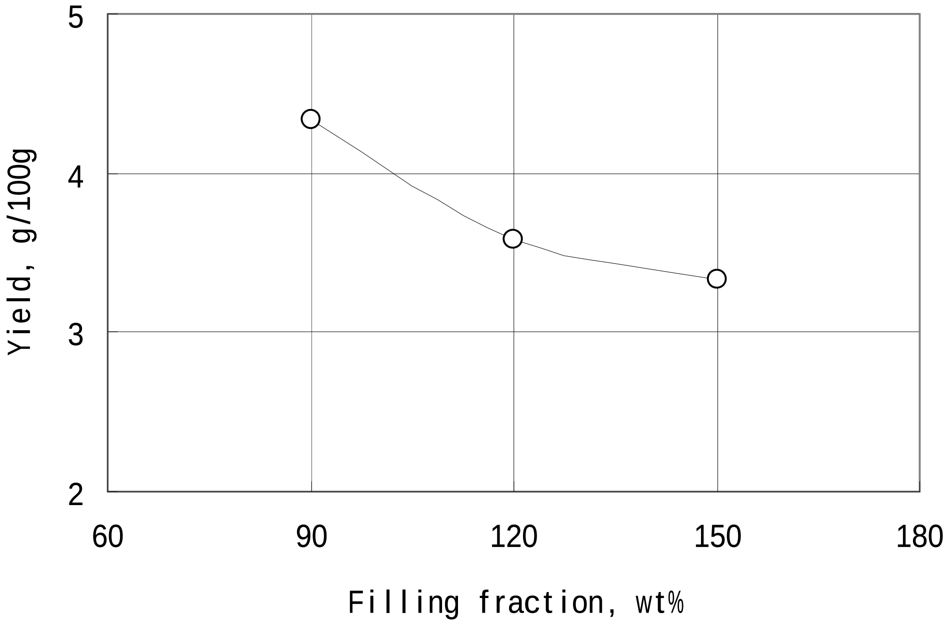

Fig.5. Effects of filling quantity on the extraction efficiency

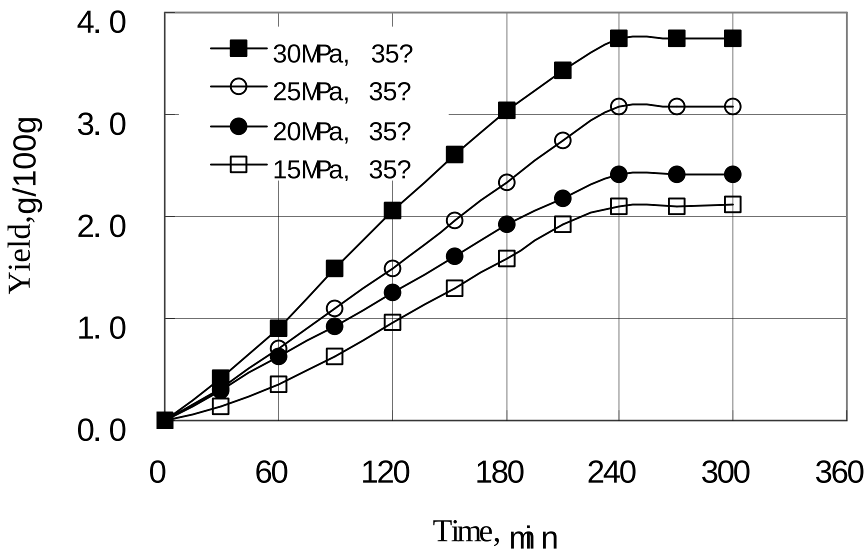

Fig.6. Effects of operating time on the extraction efficiency

3.6 Chemical components analysis

Extracted oil was analyzed 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 Hippophae Rhamnoides L 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 12.3% and unsaturated fatty acid is about 87.7%.

Table 1. Fatty acids composition of the Hippophae Rhamnoides L. seed oil

Saturated fatty acids (12.293%)			Unsaturated fatty acids (87.707%)		
Nutmeg acid	Palmitic acid	Stearic acid	Oleic acid	Linoleic acid	Flaxen acid
0.14	9.7	2.2	23.1	36.6	26.2

4. Conclusions

The experimental results show that the process parameters have important effect on the extraction efficiency. The optimum condition for the extraction of Hippophae Rhamnoides L 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 4~ 5h. The Hippophae Rhamnoides L seed oil extracted with SCF CO_2 has a high quality. The content of the saturated fatty acid is about 12.3% and unsaturated fatty acid is about 87.7%.

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