Process Enhancement of Supercritical Fluid Extraction Assisted by Ultrasonic Fields

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Abstract:

In order to improve the operation conditions to the supercritical fluid extraction for natural plants, biomaterials, and vegetable seeds processing, the ultrasonic fields were assisted into the supercritical fluid extraction. The supercritical fluid extraction apparatus with ultrasonic field was specially designed and installed. For the Hippophe Rhamnoides L. seed, soybean seed, and liquorice roots extraction, the pressure was 25-30MPa, temperature was 40-50□, and fluid flow rate is 0.2-0.5m^3/h. The frequency of the ultrasonic field was 20-35kHz, and the power was 150W. The product yield can be averagely increased about 16.9-33.2% by adding USFE into SCFE. Comparison the supercritical carbon dioxide extraction results with and without ultrasonic field, it can be found out that the operation pressure can be reduced into 20% or the extraction time can be decreased to 30% when the other parameters were constant with ultrasonic fields. It seams indicate that the ultrasonic field may improve the supercritical fluid extraction process.

Keywords: Supercritical fluid extraction, ultrasonic field, process enhancement, natural plants.

Introduction:

In the recent 20 years, the supercritical fluid technology (SCFT) has been paid more and more attention to scientists [1]. As an important part of SCFT, supercritical fluid extraction (SCFE) was always used to processing the natural plants, biomaterials, vegetable seeds, and pharmaceutics etc [2-5]. Carbon dioxide is the most widely used supercritical fluid solvent due to the following properties such as mildness critical conditions (about 7.38MPa, 31□), nontoxic, nonflammable, and low cost and so on. Usually, the SCFE processes have to operate under a high pressure (10-30MPa), so the fabricating cost of the equipments is very high. Therefore, how to reduce the operation pressure or increase the extraction rate becomes an interesting work. For instance, we can use entrainer, co-solvent, and assisted physical filed (electronic field, magnetic field, ultrasonic field etc), so as to enhancement method for SCFE. There are two reasons that make us add an entrainer or co-solvent into the SCFE process as an assistant method: 1) in order to reduce the operation pressure or extraction time; 2) for polarity components extraction. As we known, usually the adapted entrainers or co-solvents are the organic solution. These have been researched much more [6-8]. Ultrasonic field extraction (USFE) is also a kind of method for material separation [9].

But it is not reported in literatures about SCFE assisted USFE. So, the aim of this work was focused to that add USFE to SCFE and try to improve the extraction conditions for the seed oil processing.

Experiments:

Hippophae Rhamnoides L seed (HRLS) (produced in eastern area of Inner Mongolia, China) was milled and sieved to appropriate particle size (0.2-0.4mm) before use. They contain 5.23wt% oil and 11.60wt% water. The soybean seed was in flake with about 4mm diameter and 0.2mm thickness. The oil content is about 18.50wt% and water 13.10wt%. The liquorice root was milled and sieved into 0.3-0.4mm particles. The purity of carbon dioxide supplied by Guangming Gas Plant was better than 99.9%. The original and operation conditions were listed in Table 1.

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 (V_1) was first filtered (F) and passes through a cold bath (E_1, about –10□) and then is pumped with a two-pistons high pressure pump, model 2JX-40/8 (B, Hangzhou, P.R.China), and heated by a tubular heat exchanger (E_2) to the extraction temperatures. The carbon dioxide was transported into the extractor (T_1) and contacted with the materials.

The extractor (60mm inter diameter and 300mm long) was specially designed with an ultrasonic field emission head (UE) installed in the end of the extractor. The ultrasonic field power is 150W and the frequency is 20-30kHz. The extractor containing the raw material was in a thermostatically controlled by an electrical heating tape, the temperature inside the extractor being controlled by a digital controller (Yuyao, Zhejiang, P.R.China, model number TDA-8002) within ±0.1□. The pressure at the exit of the extractor was measured using a pressure gauge within ± 0.01MPa. After leaving the extractor, the stream of carbon dioxide loaded with extract flowed through sequence of needle valves (Y_{1-3}, 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 use of a Wet Test Meter (L_1, Changchun Meter Company, Jilin, P.R.China, model number LML-2) within ± 0.001L.

Results and discussion:

1) Enhancement effects

For the HRLS extraction, the operation conditions were as follows: pressure was 30MPa, temperature was 40□, particles size was 0.2-0.4mm, and carbon dioxide flow rate was 0.2m^3/h (STP). For every operation condition, the run was performed by means of SCFE under both with and without USFE in order to make a comparison. Fig.2 shows that the extraction yield changes with the extraction time. From this figure, we can find out that these two curves have same trends with the extraction time increasing. But, the yield is quite different between two curves. For SCFE+USFE process, at any time, the yield (Y_2) is greater than that one (Y_1) of only SCFE process. The maximum yield increment is about 31.3wt% (□$Y=Y_2-Y_1$). If we define the AARD% is as equation (1),

$$AARD\% = \frac{1}{N}\sum_{n=1}^{N}\frac{Y_2 - Y_1}{Y_1}\times 100\% \tag{1}$$

Then, from Fig. 2, we can obtain the AARD is about 16.9%. It means that the extraction process can be significantly enhanced over the same time intervals in the presence of USFE. So, this may give us a method to improve our practical SCFE process for the natural materials processing by a really “green chemistry” approach. Because the SCFE+USFE process is simpler than that of SCFE added organic entrainer or co-solvent regarding to the phase separation and solvent treatment after extraction operation, the total economic properties of SCFE+USFE process maybe better than that of SCFE added entrainer.

After that, in order to further verify the effect of this method to other materials, we also selected the soybean seed and liquorice root as objectives. For soybean seed extraction, the pressure was 25MPa, temperature was 50□, the seed was in a form of flake with about 4mm diameter and 0.4mm thickness, and carbon dioxide flow rate was 0.35m^3/h (STP). The comparison curves are shown in Fig. 3. The maximum yield increment is about 54.6wt%. The AARD is about 33.2%. It indicated that SCFE+USFE method also has an excellent enhancement effect for the soybean seed extraction.

For the liquorice root extraction, the operation condition were as follows: pressure was 30MPa, temperature was 40□, particles size was 0.2-0.4mm, and carbon dioxide flow rate was 0.5m^3/h (STP). The comparison curves are shown in Fig. 4. The maximum yield increment is about 38.1wt%. The AARD is about 21.4%. It indicated that SCFE+USFE method also has an obvious enhancement effect for the liquorice root extraction.

Further analysis for Figs.2-4, we can calculate that the operation pressure can be reduced about 20% or the extraction time can be decreased to 30% when the other parameters were constant with ultrasonic fields.

2) Enhancement mechanisms

The contribution of ultrasonic fields to the SCFE process maybe include the following ways: 1) The destroy of the resort film layer on the interface of the fluid and the solid phase, this makes the transfer was enhanced. 2) The SCF was forced stirring and vibration by ultrasonic fields, it makes the fluid concentration degree was increased between the near and remote of the interface of the fluid as well as the solid phase. 3) Natural materials may be regarded as a porous matrix containing solute components, when a part of the walls has been broken open by ultrasonic fields, so that a part of the solute is directly exposed to the SCF solvent. In the fact, the affect mechanism of ultrasonic fields to the SCFE process is very complex according to different cell organization structures of the solid materials.

Conclusions:

Under the conditions of this work, it seams indicate that the ultrasonic field may improve the supercritical fluid extraction process. The product yield can be averagely increased about 16.9-33.2% by adding USFE into SCFE. Comparison the supercritical carbon dioxide extraction results with and without ultrasonic field, it can be found out that the operation pressure can be reduced into 20% or the extraction time can be decreased to 30% when the other parameters were constant with ultrasonic fields.

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Table 1 The original information of materials and operating conditions

Material Species	P(MPa)	T(☐)	Size (mm)	Method	Water contents (wt%)
HRL seeds	30	40	0.2-0.4	SCFE+USFE	11.60
Soybean seeds	25	40	φ4×0.2	SCFE+USFE	13.10
Liquorice roots	25	40	0.3-0.4	SCFE+USFE	8.20

HRL: Hippophane Rhamnoides L.

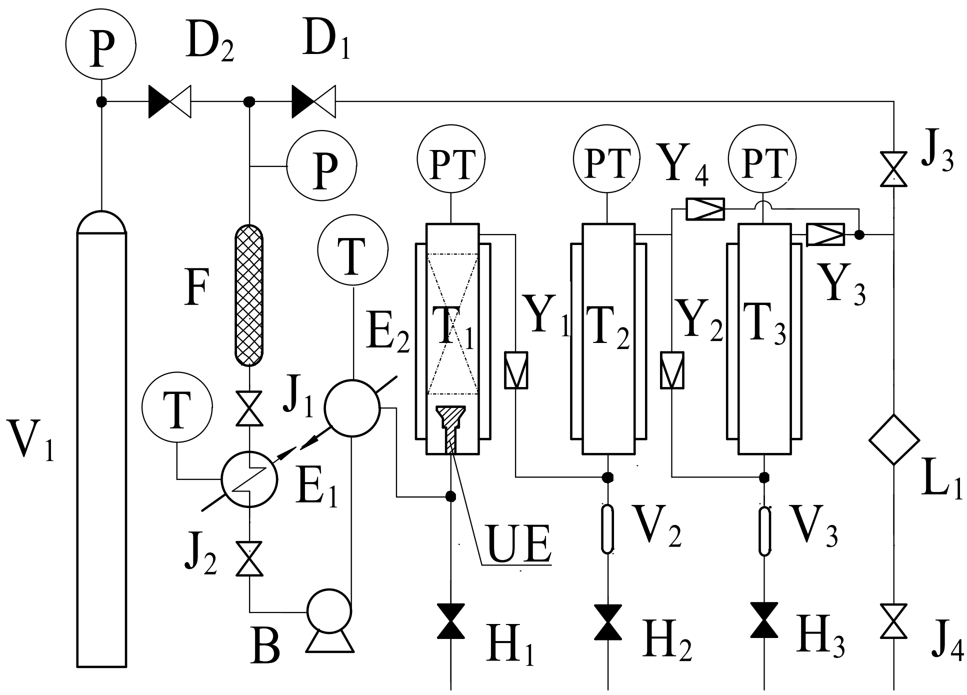

Figure 1 The diagram of the SCFE apparatus with an USFE system

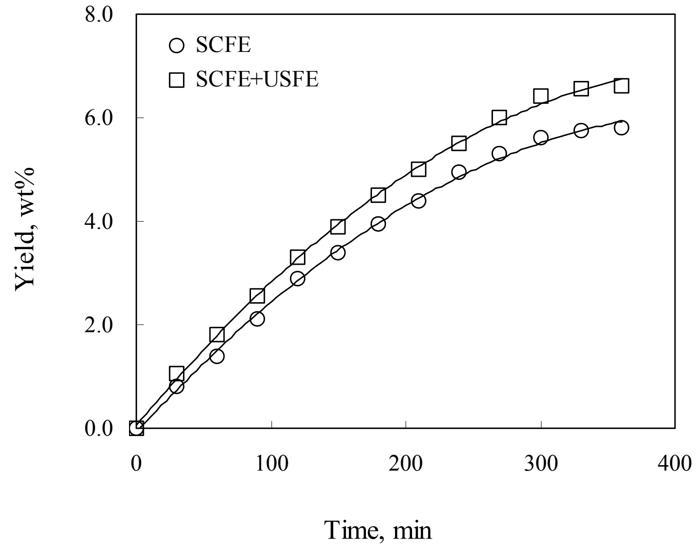

Figure 2 The extraction yield and time curves for HRLS. Pressure, 30MPa; Temperature, 40□; Flow rate, $0.20 m^3/h$; AARD%=15.7%.

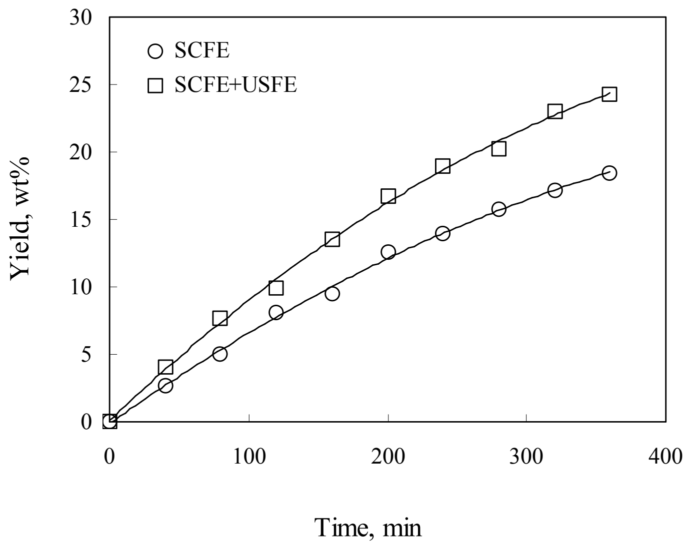

Figure 3 The extraction yield and time curves for soybean seed. Pressure, 25MPa; Temperature, 50℃; Flow rate, 0.35m^3/h; AARD%=33.2%.

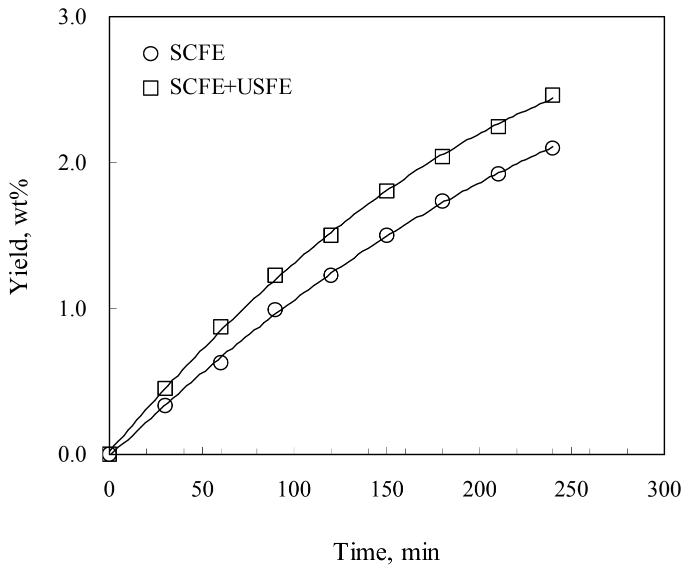

Figure 4 The extraction yield and time curves for liquorice root. Pressure, 30MPa; Temperature, 40℃; Flow rate, 0.50m^3/h; AARD%=21.36%.