MODELING OF THE EXTRACTION OF SEMEN BIOTAE OIL USING SUPERCRITICAL CARBON DIOXIDE

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This study measured the extraction rate of the oil from the dried seeds of Semen Biotae using supercritical CO_2. Several effects of the operation pressure, temperature and CO_2 flow rate on the extraction results are investigated. It is shown that a lower temperature gives a higher extraction rate at 20.7 MPa, while a higher temperature favors the extraction at pressures greater than 34.5 MPa. The extraction was independent of the CO_2 flow rate that reveals phase equilibrium is the controlling step of the extraction. The extraction curves were modeled using the modified Lack's plug flow and the local adsorption equilibrium models. Optimally fitted parameters are reported and the correlation results are satisfactory.

INTRODUCTION

Semen Biotae is the dry and mature seed of *Biota orientalis (L.) Endl*. Used as the Chinese herb for a long time, Semen Biotae can improve the digest system, constipation, insomnia and diuretic problems. It can also treat cough and asthma as well as the inflammation. Many fatty acid oils and some essential oils such as borneol ($C_{10}H_{17}OH$) and saponin ($C_{32}H_{54}O_{18}$) exist in Semen Biotae.

Supercritical fluid extraction of seed oils has been investigated on many systems [1]. Effects of pressure, temperature, CO_2 flow rate and the operation time have been considered. Several mathematical models have been presented for the extraction curves. For example, Goto et al. [2] proposed a local adsorption model to analyze the extraction of essential oil from peppermint leaves. A modified Lack's plug flow model was employed to correlate the extraction curves of vegetable oil [3].

The objective of this study is to investigate the effects of pressure, temperature and solvent flow rate on the extraction of Semen Biotae. The modified Lack's plug flow and the local adsorption equilibrium models were used to correlate the extraction results. Optimally fitted parameters are reported that describe the mass transfer mechanism of the extraction process.

I. EXPERIMENTAL

The dried Semen Biotae produced in China was obtained from a chinese pharmacy in Taiwan. The seeds were stored in the refrigerator before the experiment. Carbon dioxide was purchase from San Fu Chemicals (Taiwan) with purity better than 99.5%. The experimental

apparatus was the ISCO extractor (ISCO SFX 2-10). Carbon dioxide was stored in the steel tank and was compressed to the operating pressure by two syringe pumps (ISCO 100 DX) alternatively. The experimental pressure, temperature and solvent flow rate were controlled at the desired values. The extracted solute was collected in an empty tube maintained at $0^{o}C$ and the solvent was then expanded to ambient pressure. In each experiment, 6 g of seed were loaded into the extractor of 10 ml in volume. The continuous extraction process started after the operating temperature (313.2, 323.2 and 333.2 K) and pressure (20.7, 27.6, 34.5 and 41.4 MPa) were reached. The supercritical CO_2 was set in static equilibrium with the solid for 40 minutes. The solvent then flowed downward continuously through the extractor and the total extraction time was 400 minutes. The extracts were collected when every 150 ml CO_2 was flowing through the extractor and the amount of extracted oil was determined gravimetrically. Each data point is the average value of two or three repeated experiments. The experimental accuracy is estimated to be within 5%.

II. EVALUATION OF THE EXTRACTION CURVES

Two mathematical models were employed for correlating the experimental data:

(1). The modified Lack's plug flow model [3]

This model describes an axial solvent flow with a superficial velocity through a cylindrical extractor. It discusses the mass transfer coefficients in both the solvent film and the sold phase. This model leads to three periods in the extraction process. In the first period, the solvent film resistance determines a constant extraction rate and most of the accessible solute were firstly extracted. In the second transition period, the rest of the accessible solute was extracted at a slower rate. Finally, the deeply seated solute was extracted at the slowest rate in the third period. The amounts of the yield e in these three periods are:

$$e = \begin{cases} qy_r[1-\exp(-Z)] & q < q_m \\ y_r[q-q_m\exp(z_w-Z)] & q_m \leq q < q_n \\ x_0-(y_r/W)\ln\{1+[\exp(Wx_0/y_r)-1]\exp[W(q_m-q)x_k/x_0\} & q \geq q_n \end{cases} \tag{1}$$

where x_0 is the initial concentration of oil inside the seed. When the oil concentration decreases to x_k, mass transfer becomes diffusion controlled in the solid phase. Parameters of the solvent amounts q_m and q_n define the boundaries of three transition regions. The dimensionless axial coordinate z_w indicates the plane of the extractor bed where the oil concentration equals x_k. According to the modified Lack's plug flow model [3], we have:

$$q_m = (x_0 - x_k)/y_r Z \tag{2}$$
$$q_n = q_m + (1/W)\ln\{[x_k + (x_0 - x_k)\exp(Wx_0/y_r)]/x_0\} \tag{3}$$
$$z_w/Z = (y_r/Wx_0)\ln\{[x_0\exp[W(q-q_m)]-x_k]/(x_0-x_k)\} \tag{4}$$

The values of Z and W are proportional to the external and internal mass transfer coefficients, respectively. Parameter y_r is the apparent solubility of the solute that is

estimated as a function of the temperature and density of supercritical CO_2 [4]. In this study, four parameters of $Z\dot{q}$, $W\dot{q}$, x_0 and x_k were regressed from the experimental extraction curves where $\dot{q}$ is the value of q per unit time. The corresponding values of q_m and q_n were evaluated and the agreement with experimental data were examined.

(2). The local adsorption equilibrium model [2]

This model is based on the local adsorption equilibrium of solute between the solid and fluid phase in the solid matrix. The solute was first desorbed from the solid matrix and dissolved into the supercritical fluid. The solute then diffused through the pores of solid to the external fluid film and was taken away by the bulk flow.

Goto et al. [2] considered a differential bed containing particles with slab geometry. The cumulative fraction, defined as the yield at a specific extraction time divided by that at an infinite time, was given by:

$$F(\boldsymbol{q}) = [A/(1-\boldsymbol{e})]\{[\exp(a_1\boldsymbol{q})-1]/a_1 - [\exp(a_2\boldsymbol{q})-1]/a_2\} \tag{5}$$

$$A = [(1-\boldsymbol{e})\boldsymbol{f}]/\{[\boldsymbol{b}+(1-\boldsymbol{b})K]\boldsymbol{e}(a_1-a_2)\} \tag{6}$$

$$a_1 = 0.5[-b+\sqrt{b^2-4d}] \quad \text{and} \quad a_2 = 0.5[-b-\sqrt{b^2-4d}] \tag{7}$$

$$b = \boldsymbol{f}/[\boldsymbol{b}+(1-\boldsymbol{b})K]+1/\boldsymbol{e}+\boldsymbol{f}(1-\boldsymbol{e})/\boldsymbol{e} \tag{8}$$

$$d = \boldsymbol{f}/\{[\boldsymbol{b}+(1-\boldsymbol{b})K]\boldsymbol{e}\} \tag{9}$$

where $\boldsymbol{q}$ and $\boldsymbol{f}$ are dimensionless variables, $\boldsymbol{q} = t/\boldsymbol{t}$ and $\boldsymbol{f} = k_p a_p \boldsymbol{t}$. Specific area a_p is the inverse of the half thickness of the seed, $\boldsymbol{e}$ and $\boldsymbol{b}$ are the porosities of the extraction bed and the seed, respectively. Residence time $\boldsymbol{t}$ is defined as the total bed volume divided by the volumetric flow rate of the supercritical fluid. The overall mass transfer coefficient k_p and the adsorption equilibrium constant K are two parameters obtained from regressing the experimental data.

III.   RESULTS AND DISCUSSION

The extracted material was a yellow oily liquid and the yield was about 20 wt% on the dry weight basis. Fig. 1 shows the effect of the operating pressure at 323.2 K. At constant temperature, the extractability increases with increase in pressure owing to lager solvent density. The effect of temperature is shown in Fig. 2 at 20.7 MPa pressure. At this fixed pressure, the yield increases with decreasing temperature where the solvent density is a dominant effect. At a higher pressure of 34.5 MPa, a crossover phenomenon was observed where the yield is higher at a higher temperature. This result is shown in Fig. 3 where the vapor pressure of solute becomes a more important factor than solvent density. We estimate the crossover pressure for this system is about 30 MPa. The effect of solvent flow rate on the extraction curve was investigated at 34.5 MPa and 333.2 K. Fig. 4 shows a plot of the yield against the accumulated solvent at three flow rates. All extraction curves are overlapping that indicates the exit solute concentration from the extractor was independent of the solvent flow rate. Therefore, an equilibrium condition existed between the solute in the fluid and solid phases. Our results are similar to those of Goto et al. [2] and Reverchon and Marrone [5].
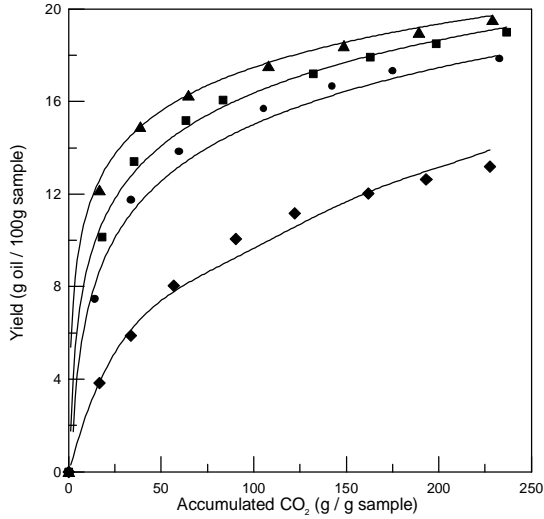
Fig.1. Effect of pressure on the extraction yield of Semen Biotae at 323.2 K and 3.5 ml/min. (？ 20.7 MPa ; ？ 27.6 MPa ; ¦ 34.5 MPa ; ？ 41.4 MPa; —, calculated results from the modified
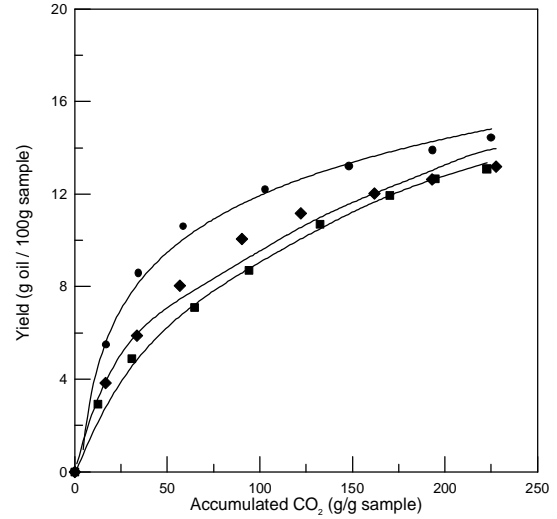
Fig.2. Effect of temperature on the extraction yield of Semen Biotae at 20.7 MPa and 3.5 ml/min. (？ 313.2 K ; ？ 323.2 K ; ¦ 333.2 K ; — calculated results from the modified

The density of supercritical CO_2 was calculated by the method proposed by Adachi and Sugie [6]. The physical properties of Semen Biotae were also estimated. The solid density, apparent density and specific area were 1289 kg/m^3, 989 kg/m^3 and 1000 1/m, respectively. Using these density data, porosity of the seed was calculated. The extractor bed void fraction was estimated as 0.393.

The modified Lack's plug flow model was employed in correlating the experimental results. The model parameters were evaluated where the following mean deviation is minimized:

$$MD(\%) = \frac{100}{N} \Sigma (\frac{e^{\exp} - e^{cal}}{e^{\exp}}) \tag{10}$$

The best-fitted four parameters of the modified Lack's plug flow model and the corresponding mean deviations are shown in Table 1. The grand deviation is less than 4% and this model gives reasonable correlation. The calculated results using these model parameters are also shown in Figs. 1-4, respectively.

The optimally fitted value of x_0 is 0.23 ± 0.03 for all operation conditions. The physical meaning of this parameter is the initial oil content of the solute-free solid that is expected as a constant in all extraction conditions. In our experiments, the weight of original sample is 6 g and the average yield is 0.2 g oil/g sample. From these data, the initial oil content is estimated as 0.25 g/g of solute free solid that is in good agreement with the model correlated value. The best-fitted x_k value is 0.14 ± 0.04 for all conditions. This value corresponds to the solute content in the deep pore site of particles. The difference between x_0 and x_k gives the solute content in the broken cells and the outer surface of the seed, which is

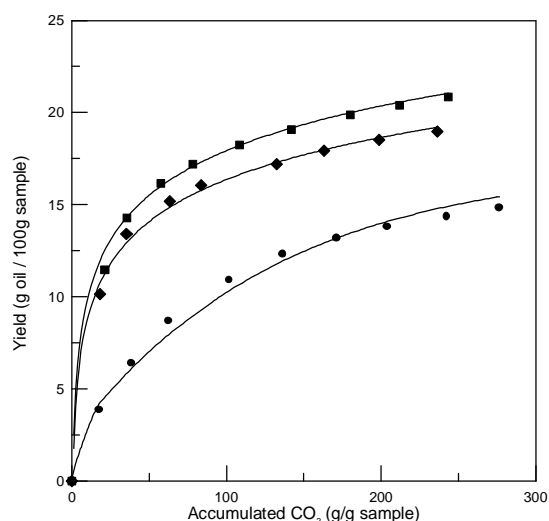the most accessible part in the supercritical extraction process.

Fig.3. Effect of temperature on the extraction yield at 34.5 MPa and 3.5 ml/min. (? 313.2 K ; ? 323.2 K ; ¦ 333.2 K ; — calculated results from the modified Lack's plug flow model)
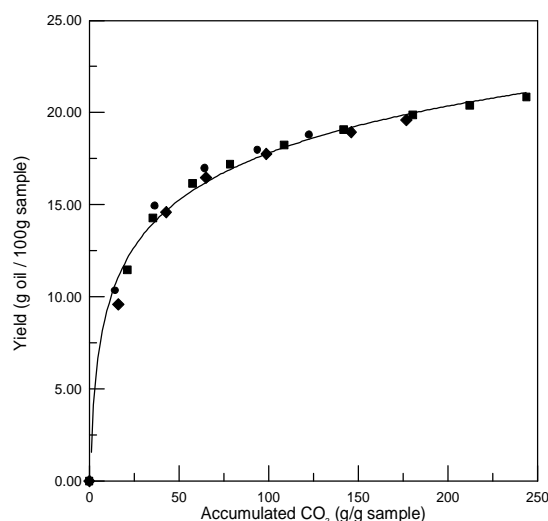
Fig.4. Effect of CO_2 flow rate on the extraction yield at 34.5 MPa and 333.2 K. (¦ 3.5 ml/min ; ? 2.7 ml/min ; ? 1.5 ml/min; —modified Lack's plug flow

The optimally fitted values of $Z\dot{q}$ and $W\dot{q}$ are proportional to the external and intra-particle mass transfer coefficients, respectively. Since $Z\dot{q}$ is about 50 to 100 times larger than $W\dot{q}$, intra-particle resistance owing to the molecular size and diffusivity is the major factor affecting the supercritical extraction. It is also observed in Table 1 that $W\dot{q}$ values increase with increasing temperature at 41.4 and 34.5 MPa, but decreases with temperature at 20.7 MPa. This result reveals the same tendency as the crossover effect on the extraction curves.

Table 1. Optimally fitted parameters of the modified Lack's plug flow model

Experimental conditions	x_0 (g solute/g solute free solid)	x_k (g solute/g solute free solid)	$Z\dot{q}\times10^2$ (1/s)	$W\dot{q}\times10^5$ (1/s)	MD(%)
P = 20.7 MPa					
313.2 K	0.237	0.138	2.02	4.40	2.90
323.2 K	0.235	0.162	1.30	4.18	5.54
333.2 K	0.256	0.185	1.02	3.08	4.72
P = 34.5 MPa					
313.2 K	0.215	0.179	1.13	7.21	4.06
323.2 K	0.209	0.173	1.24	20.31	1.92
333.2 K	0.250	0.142	1.33	22.53	2.72
P = 41.4 MPa					
313.2 K	0.206	0.105	1.42	8.51	2.25
323.2 K	0.238	0.106	1.86	23.66	2.94
333.2 K	0.264	0.111	1.99	24.10	3.13

The optimally fitted k_p and K parameters and the calculated deviations in the local adsorption equilibrium model are shown in Table 2. Satisfactory results are also obtained from this simple analytical model. Value of k_p is small and insensitive hence the mass transfer between the particle and the external film is fast. Parameter K is much more important that indicates desorption of solute from solid into the supercritical fluid is the controlling step for extraction. The variation of K with temperature at a given pressure again demonstrates the crossover effect.

Table 2. Optimally fitted parameters of the local adsorption equilibrium model

Experimental conditions	k_p (m/s)	K	MD(%)
P = 20.7 MPa			
313.2 K	0.0002	80	8.76
323.2 K	0.0030	83	4.38
333.2 K	0.0035	99	8.29
P = 34.5 MPa			
313.2 K	0.0081	76	5.84
323.2 K	0.0064	52	4.71
333.2 K	0.0048	43	5.05
P = 41.4 MPa			
313.2 K	0.0090	44	7.49
323.2 K	0.0085	37	6.63
333.2 K	0.0052	30	7.09

CONCLUSION

Extractions of seed oil from Semen Biotae using supercritical CO_2 under various conditions are investigated. The crossover phenomenon is observed around 30 MPa and the average maximum yield is 0.2 g oil/g of sample. Both the modified Lack's plug flow and local adsorption equilibrium models are employed in correlating the experimental data. Optimally fitted model parameters are reported and satisfactory calculation results are demonstrated. The model parameters reasonably explain the mass transfer mechanism in the extraction process.

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