

초임계 이산화탄소를 이용한 유채꽃씨유 추출

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Supercritical Extraction of Rape seed oil using Carbon dioxide

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1. Introduction

Rape seed oil has been used for a long time as a crop for many applications, such as oil in lamps and cooking oil. Recently, the rape seed oil has become very widespread, including margarine, biodiesel fuel, lubricants and meal for livestock. The trait considered of rape seed oil is the erucic acid content in the oil. Erucic acid is a 22-carbon fatty acid desired in high concentration for the industrial uses and desired in very low concentrations for edible canola oils and meal for livestock.

Supercritical fluid extraction (SFE), particularly concerning the recovery of essential oil, is an attractive alternative to the traditional separation methods, such as organic solvent extraction, since thermal degradation and solvent contamination of the extract are avoided. The most frequently employed supercritical fluid is CO₂ due to its low toxicity, good safety and low critical temperature [1]. There were many literatures about the natural material extraction with SFE such as soy bean, wheat germ, sunflower, cotton seed, grape seed, and so on [2].

2. Experimental method

2.1 Materials

Liquid carbon dioxide with a purity of 99.0% was supplied by a local company Hyup-Sin (Korea). Rape seed producing in Jeju, Korea was used. It was milled before used. Extraction was carried out in the supercritical extraction apparatus (as shown Fig.1.).

2.2 SFE method

The exact weighted amount of rape seed was filled in extractor. Liquid carbon dioxide from the cylinder pumped with a high pressure pump (Model P-50, Thartech., USA). The pressure was maintained and controlled with a back pressure regulator (Model NO. 26-1761-24, Tescom, USA). The extractor containing the raw material was controlled thermostatically by air bath at 50 ± 1 °C. The temperature inside extractor was measured by a K-type thermocouple. The pressure was measured using a pressure gauge (Model CM, HEISE, USA). After leaving the extractor, the stream of carbon dioxide loaded extract flowed through back pressure regulator. Then, the pressure was reduced down to 60bar and the seed oil was separated from the stream in the separator. Gaseous carbon dioxide leaving separator passed the activated carbon filter. Then it was condensed and recycled.

2.3 Organic solvent extraction method

Organic solvent extraction was performed by the Soxhlet apparatus. Chloroform and n-hexane was used as a solvent. The extraction process was run continuously for 6 hours. After extraction, the solution was cooled and the solvent was removed by a rotary evaporator.

2.4 Correlation by Catchpole Model [3]

Model equations for the fluid phase concentration, C , and particle phase concentration, q , are presented below, subject to boundary condition (3). The assumptions are no axial or radial dispersion, uniform initial concentration of oil in the solids, and constant interstitial solvent velocity

The nomenclature used is given list of symbols at the end of paper.

$$0 = \frac{\partial C}{\partial t} + U \frac{\partial C}{\partial Z} + \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial q_{av}}{\partial t} \quad (1) \quad D_e \frac{\partial q}{\partial r} = k_f (C - C_{ps}) \quad (3)$$

$$\frac{\partial q}{\partial t} = \frac{D_e}{r^2} \frac{\partial \left(r^2 \frac{\partial q}{\partial r} \right)}{\partial r} \quad (2)$$

Equation (1) means total balance of oil released from particles and dissolved in solvent in extractor. Equation (2) means assumption that particle is a sphere. Coefficient γ is used to compensate error. $D_e = D_{12}/\gamma$. Equation (3) is model equation by film theory. Because particle pore size is enough large and the density of solvent is relatively high, Fick's diffusion is used. In the general case, there will be an equilibrium condition at the fluid/particle interface of the form $q_r = KC_{ps}$. For seed oils, there appears to be no equilibrium constraint to extraction from the solid phase. Glueckauf's linear driving force approximation is proposed for the change in average particle phase concentration.

$$\frac{\partial q_{av}}{\partial t} = \frac{15 D_e}{R^2} (C_{ps} - C^*) \quad (4)$$

and as the extraction reaches completion, $\partial q_{av}/\partial t = 0$. q_{av} is given by equation (5):

$$q_{av} = \int_0^R q r^2 dr \quad (5)$$

Differentiation of equation (5) with respect to time gives a second expression for $\partial q_{av}/\partial t$:

$$\frac{\partial q_{av}}{\partial t} = \frac{3}{R^3} \int_0^R \frac{\partial q}{\partial t} r^2 dr \quad (6)$$

Inserting equation (2) into equation (6) gives a new expression for $\partial q_{av}/\partial t$:

$$\frac{\partial q_{av}}{\partial t} = \frac{3 D_e}{R} \left(\frac{\partial q}{\partial r} \right)_{r=R} \quad (7)$$

Equation (3), (4) and (7) can be combined to eliminate the unknowns C_{ps} and $\partial q_{av}/\partial t$. The solution can be inserted into equation (1) to give an equation for C in terms of Z and t only:

$$\frac{\partial C}{\partial t} = -U \frac{\partial C}{\partial Z} - \frac{k_p a_p}{\varepsilon} (C - C^*) \quad (8)$$

To obtain the final working equation, it was assumed that the solid concentration profile with bed height Z could be approximated by a step change, with $q_{av} = 0$ prior to step, and $q_{av} = q_0$ following the step. Solving (8) according to this assumption gives:

$$C_L = C^* \{1 - \exp[-B(Z - Z_e)]\} \quad (9) \quad Z_e = L - \frac{1}{B} \ln[\exp(BL) + \exp(GBt) - 1] + G \quad (10)$$

$$F(t) = 100 Z_e / L \quad (11)$$

The model parameter D_{12} , k_f , C^* were estimated as follows:

$$D_{12} = 2.543 \times 10^{-7} T_r \left(\rho_r^{-\frac{2}{3}} - 0.451 \right) \left(1 + \frac{4401}{M} \right)^{0.5} \left(1 + \left(\frac{V_c}{939} \right)^{\frac{1}{3}} \right)^2 \quad C^* = (\rho/1000)^{0.724} \exp \left(40.361 - \frac{18708}{T} + \frac{2186840}{T^2} \right)$$

$$k_f = 0.82 (D_{12} / d) \text{Re}^{0.66} \text{Sc}^{\frac{1}{3}}$$

The equilibrium solubility C^* was also determined by comparing the cumulative mass of oil collected versus carbon dioxide usage during the initial stage of an extraction trial. The fluid phase concentration tends towards saturation for a sufficient bed height and low degree of extraction.

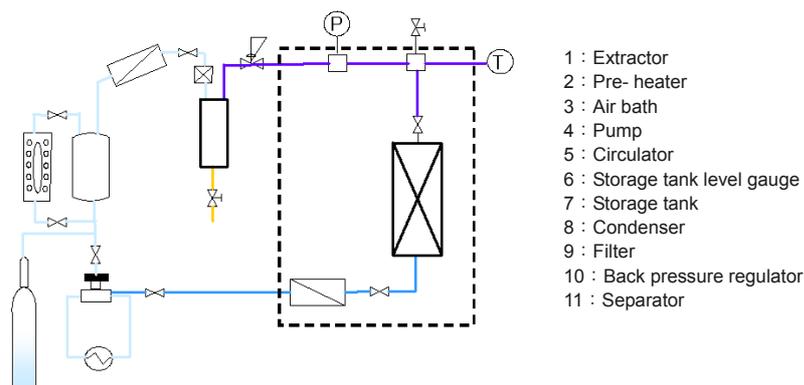


Fig. 1. Schematic diagram of extractor.

2.5 The fatty acid composition in oil analysis

The oils obtained were analyzed using a Hewlett Packard GC 4890D gas chromatograph equipped with a flame ionization detector and a capillary (HP-5M) column (30m × 0.32mm i.d., film thickness 0.25 μm). The carrier gas was helium (1ml/min). The detector temperature was set to 230°C, while the injection temperature was 250°C. The oven temperature was held at 50°C for the first time. Then it was raised with a rate of 10°C/min to 100°C, where it was held for 5min. And again it was raised with a rate of 10°C/min to 250°C, where it was held for 10min. Finally, it was raised with a rate of 10°C/min to the final temperature, 280°C.

3. Results and discussion

As shown in Fig. 2, the extraction rate increased with increasing solvent flow rate. Mass transfer coefficients in the fluid and overall mass transfer coefficient calculated by modeling, k_f and k_p , increases as the solvent flow rate increased. This is attributed to the enhancement of mass transfer rate in the fluid phase by convection as the flow rate increased.

Fig. 3 shows the effect of pressure on extraction. The extraction rate increased with increasing pressure. The solubility of oil in scCO₂ was enhanced with increasing pressure due to the increase of the density of solvent. Increase in the solubility of oil in scCO₂ increases the driving force in the fluid phase and consequently extraction rate increases. The overall mass transfer coefficient, k_p , increased with increasing pressure. On the other hand, mass transfer coefficient in fluid phase, k_f , decreased with increasing pressure. This is reason that the diffusivity of oil in scCO₂ decrease as the pressure increase. Therefore, mass transfer resistance increase and the extraction rate decrease. However, increase in the driving force by the solubility affects the extraction rate more than increase in mass transfer resistance.

The table 2 shows the fatty acid composition (area %) of oils from the SFE and the organic solvent extraction. The composition of the saturated fatty acid and unsaturated fatty acid was about 4.97% and 84.96% for SFE, about 4.90% and 85.18% for organic solvent extraction. The composition of oils obtained by SFE and organic solvent were similar.

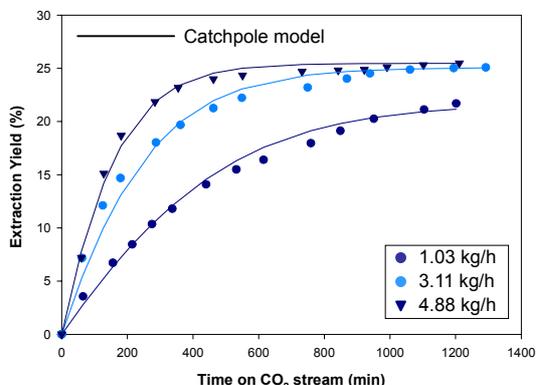


Fig. 2. Effect of flow rate at 50°C and 300bar.

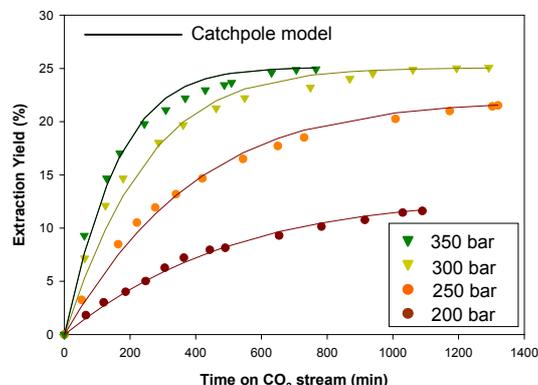


Fig. 3. Effect of pressure at 50°C and 3.11kg/h.

Table 1
Estimated mass transfer and diffusion coefficients

	Pressure (bar)	Temperature (°C)	Flow rate (kg/h)	$k_p(\text{m/s}) \times 10^7$	$k_f(\text{m/s}) \times 10^5$	AARD (%)
A	200	50	3.11	3.64	8.38	3.29
B	250	50	3.11	4.34	7.24	3.54
C	300	50	1.03	2.58	3.12	3.33
D	300	50	3.11	5.20	6.44	4.37
E	300	50	4.88	7.86	8.67	2.55
F	350	50	3.11	5.43	6.02	3.24

Table 2
Compounds identified and their composition (peak area %) in oils

	Component (fatty acid)	Area (%)							
		A	B	C	D	E	F	n-hexane	chloroform
1	Palmitic	2.67	2.62	2.53	3.71	3.44	2.71	3.28	3.15
2	Oleic, Linolic, Linolenic	36.92	35.33	35.80	35.48	35.55	36.13	35.69	35.60
3	Stearic	0.93	0.91	0.89	1.08	1.18	0.91	1.17	1.09
4	Erucic	49.44	50.98	50.75	49.48	48.60	50.15	49.58	50.12
5	The others	10.04	10.16	10.03	10.26	10.73	10.10	10.27	10.04

4. Conclusion

The effect of process parameter, flow rate and pressure, on the supercritical extraction of rape seed oil was studied. The extraction rate was enhanced as pressure and flow rate increased. The extraction data were correlated using mathematical model developed by O.J. Catchpole. In general, the fit of model was good. Mass transfer coefficients in the fluid overall mass transfer coefficient calculated by modeling, k_f and k_p , increased as the solvent flow rate was increased. As the pressure was increased, k_f decreased and k_p was increased.

The composition of the saturated fatty acid and unsaturated fatty acid by GC analysis was about 4.97% and 84.96% for SFE, about 4.90% and 85.18% for organic solvent extraction. The fatty acid composition of oils obtained by SFE and organic solvent were similar

5. References

1. M. A. McHugh and V. J. Krukons, "Supercritical Fluid Extraction, Butterworths," Boston, **1986**
2. E. Stahl, K.-W. Quirin and D. Gerard, "Dense Gases for Extraction and Refining", Springer-Verlag, Berlin, **1986**
3. O. J. Catchpole, E. W. Andrews, G. N. Toikka and G. T. Wilkinson, *Proceedings of the 3rd Int. Symp. On Supercritical Fluids, Ed. Perrut, 1994*, 47