SUPERCRITICAL FLUID EXTRACTION OF OLEORESIN FROM CURCUMA XANTHORRHIZA : MODELING AND SIMULATION

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Supercritical Fluid Extraction have been used widely in the natural material industries ,because it produced excellent mass transfer properties, ease solubility control due to temperature and pressure. A mathematical model based on shrinking-core model of the extraction process and simulation were used. Previous worker's have used a model including axial dispersion. They give the effect of an inverse of dimensionless residence time and Peclet number parameters on the extracted concentration. The developed model include radial dispersion and simulation were used in this work. Mechanism of the extraction process involves dissolution of solute, diffusion to the surface of a solid particle in the porous region (intraparticle diffusion), and mass transfer across stagnant-film around the solid particle. Partial differential equation involves radial dispersion and simulation were used. Steady-state, with radial dispersion method was applied in this modeling's solution ; and Runge Kutta Method was used in this simulation' solution. These modeling and simulation results are compared to previous worker's and experimental data. CO_2 supercritical fluid extraction of curcuma xanthorrhiza performance in a high pressure extractor cell was used to get experimental data. The temperature in the range of 318 – 338 K and pressure of 10 – 20 MPa is used in this supercritical fluid extraction The curves of Peclet number, an inverse of dimensionless residence time, Biot number on the extracted concentrations are compared to study the effects of operating conditions. The mathematical model and simulation fitted well the experimental data.

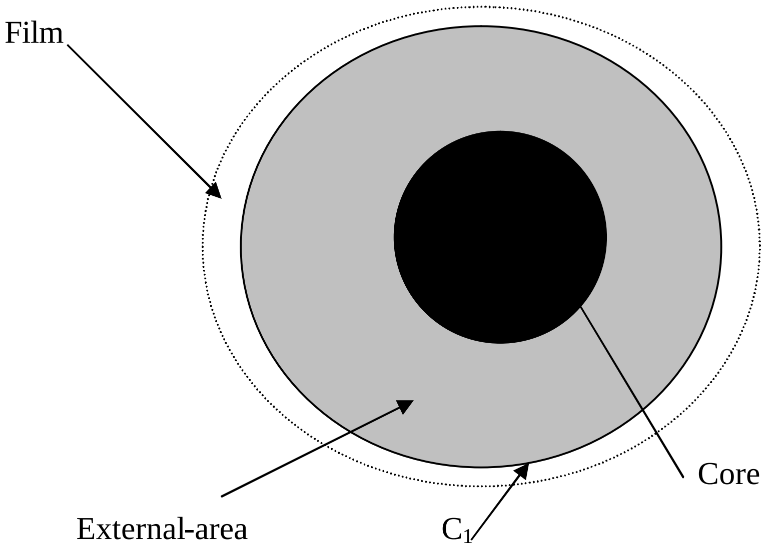
Introduction.

Supercritical Fluid Extraction in this work using supercritical CO_2 gas. Solubility of supercritical fluid is depend on temperature and pressure. At a lower pressure and near the critical point, only volatile components are extracted. Fatty acids, wax are extracted at a higher pressure, where fluids density is acted as a liquid. Mechanism of extraction from natural materials using supercritical fluids are assumed as follows : solubility of a solute into liquids and it diffused in the porous materials then moved across a film around the particle into bulk liquid. Assumption is made that Curcuma xanthorrhiza particle as a sphere. This sphere has a core in the middle and a external-area around the core. A film-stagnant in the outside of the sphere will separate between bulk-fluids and the particle. Partial differential equation is made in the bulk fluids, which is mass transfer in the axial convection, radial dispersion. Describing this model as follows, soluble's solute is diffused through external area to the surface particle, then across stagnant-film around the particle to the bulk-fluids The model is made according to the mass-transfer. The core will shrink according to the extraction time. This mass transfer is described as a shrinking-core model. Assumption is made to find a partial differential equation. Solvent flows into a extractor with v velocity to the axial direction through a packed-bed in a L cylindrical extractor height.

Previous workers are used a model according to the supercritical CO_2 extraction. Motonobu GOTO et all (1993) is searched peppermint oil extraction using semi-batch flows extraction. They used mathematical model based on local adsorption equilibrium, and they found an adsorption equilibrium constant by plotting theoretical extraction with experimental data, which is increasing with temperature and decreasing with pressure. Angel L et all (2000) are extracted Curcumins and essentials oil from Curcuma longa. Mathematical model is used to plot extraction curves. Motonobu et all (1996) are used supercritical fluids extraction with axial dispersion. An extraction mathematical model including axial convection and radial dispersion was used in this work.

Methods.

In this work the mechanism is described as follows



(Surface concentration)

Fig. 1 : The Shrinking Core Model.

According to Motonobu Goto theoretical extraction model :

1. External area

A mass balance for species A on a spherical shell of thickness ? r within external area :

$$\cancel{D_e 4\pi r^2(\partial C_A / \partial r)} - \cancel{[- D_e 4\pi r^2(\partial C_A / \partial r)} + \partial /\partial r\ [- D_e 4\pi r^2(\partial C_A / \partial r)\partial r] + R_A 4\pi r^2 \Delta r = 0 \qquad (1)$$

No reaction occur, equation (1) could be simplified :

$$(D_e/r^2)\ (\partial/\partial r)\ [\ r^2 \partial C_A / \partial r\ ]\ = 0 \qquad (2)$$

Where D_e is a constant

2. Diffusion flux at outer surface of a particle

$$D_e (\partial C_A / \partial r) \big|_{r=R} = k_f [C - C_A(R)] \qquad (3)$$

IC 1 At $t = 0 \longrightarrow r_c = R$

At initial condition no solute in bulk phase

IC 2 At $t = 0 \longrightarrow C = 0$

3. Average concentration of oil in a particle is equated to the right hand side of equation (3) which is mass transfer across film around the particle.

$$\left(\frac{(4/3)\,\pi R^3}{4\pi R^2}\right)\left(\frac{\partial q}{\partial t}\right) = k_f \left(C - C_A(R)\right) \qquad (4)$$

:

$$\frac{\partial q}{\partial t} = (3\,k_f / R)\,[\,C - C_A(R)] \qquad (5)$$

Motonobu Goto method is used in this work with developing radial dispersion as follows :

$$\underset{(a)}{\partial c/\partial t} + \underset{(b)}{v(\partial c/\partial z)} = \underset{(c)}{D_L(\partial^2 c/\partial z^2)} + \underset{(d)}{(D_L/r)\partial/\partial r(r\,\partial c/\partial r)} - \underset{(e)}{[(1-\varepsilon)/\varepsilon\,]\,3k_f /R[c - c_i(R)]} \qquad (6)$$

(a)accumulation rate ; (b) axial convection ; (c) axial dispersion; (d) radial dispersion; (e) mass-transfer across the film-stagnant around the particle.

Several dimensionless groups are defined

$X = C/C_{sat}$; $X_i = C_i/C_{sat}$;$\xi = r/R$; $Z = z/L$; $a = vR^2/D_eL$; $\theta = (D_e/R^2)t$; $b = C_{sat}/q_o$; $P_e = Lv/D_L$;$B_i = k_fR/D_e$ $G = D_L/D_e$; $y = q/q_o$.; $\gamma = r/ Rec$

and substituted into equation (1), we have

$$\partial X/\partial\theta + a(\partial X/\partial Z) = (a/P_e)(\partial^2 X/\partial Z^2) + (G/\gamma)(\partial/\partial\gamma)(\gamma\partial X/\partial\gamma) - [(1-\varepsilon)/\varepsilon]3B_I[X - X_i(1)] \qquad (7)$$

-

Boundary and initial conditions are :

X – (1/P$_e$)(?x/?Z) = 0 at Z = 0

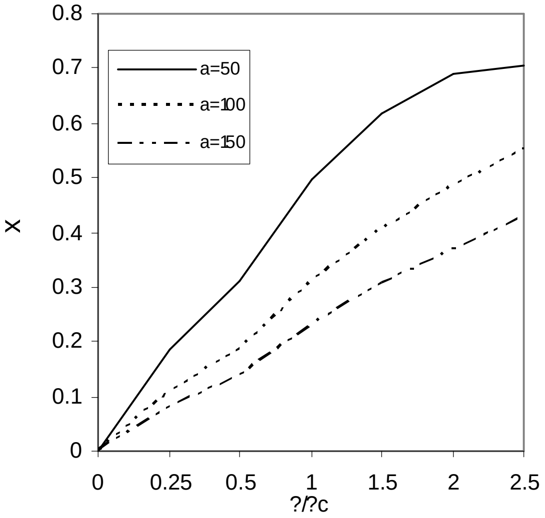
?x/?Z = 0 at Z = 1

X = 0 at ? = 0

?x/?r = 0 at ? = 0 (symmetry)

Equation (7) with boundary conditions and initial condition were solved numerically by Finite Different and Runge Kute methods.

Result and Discussion.



Fif 2 Effect of parameter a on the extracted concentration

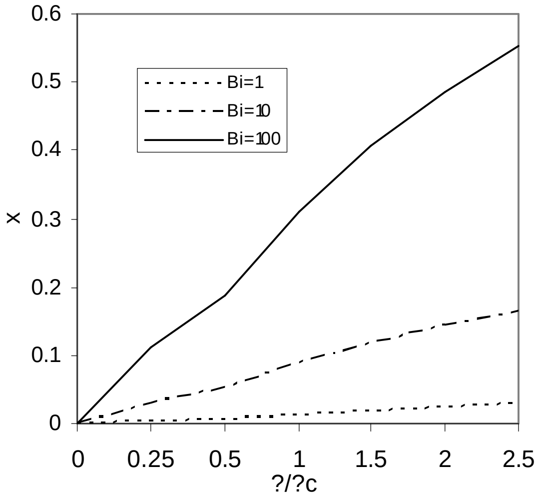


Fig 3 Effect of parameter Bi on the extracted concentration

Figure 2 shows extracted concentration x at the end of the extractor and dimensionless time at various parameter a, a = $(vR^2) / (LD_e)$, where parameter a is inverse of residence time. It is showed that parameter a increase with decreasing extracted concentration x, which is increased particle sizes. Figure 3 is a plot of concentration x at the exit of the extractor and dimensionless time at various parameter Bi, where Bi = $k_f R / D_e$. It is showed that parameter B_i increased with increasing extracted concentration x. For large B_i external mass-transfer controls the extraction process.

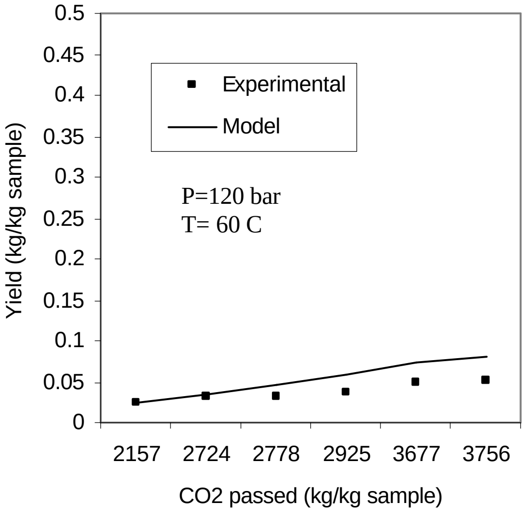


Fig 4 Effect of CO2 passed on the extraction yield

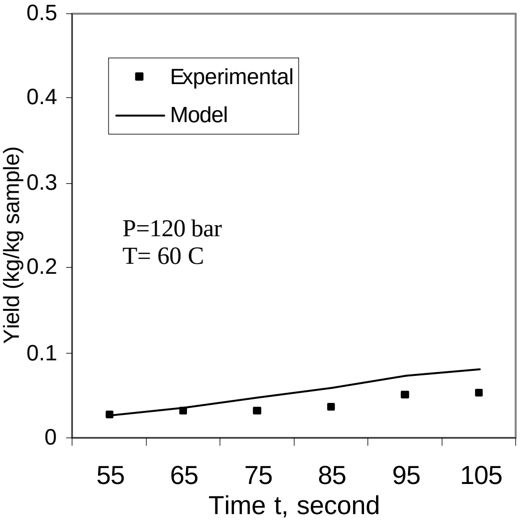


Fig 5 Effect of time on the extracted yield

Fig 4 is a plot of yield and cumulative CO_2 (kg/kg sample) passed through the extractor. Yield is defined as a weight extracted divided by the weight of the sample. Fig 5 shows yield and time. In Fig 4 the raised of the yield is smaller then cumulative CO_2 passed, it could be diffusion in the porous particle is dominant factor in this extraction

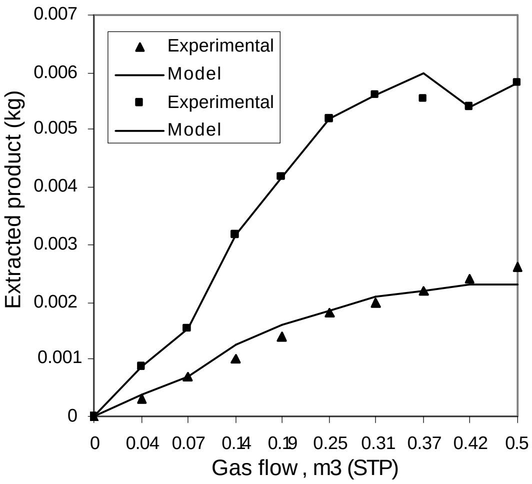


Fig 6 Comperison of experimental data and model calculation of extracted product and gas flow

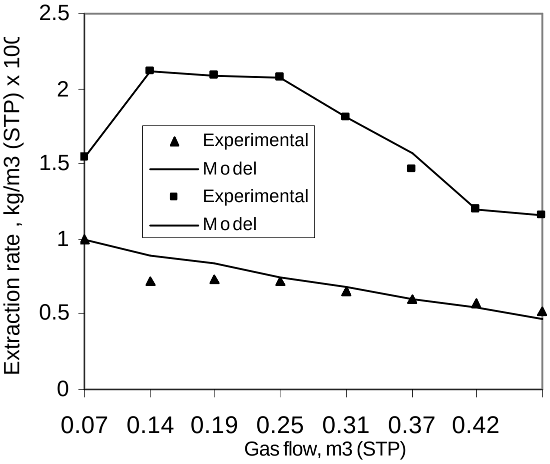


Fig 7 Comparison of experimental data and model calculation of extraction rate and gas flow

Fig 6 is a plot of extract versus gas flow which is comparison of experimental extraction of oil from rape seeds with carbon dioxide and model calculation. Experimental extraction data is measured by Brunner in 1984 at different conditions, 35 MPa, 316 K and 20.5 MPa, 324.7 K It is showed that pressure increase with increasing extracted products. Also it is showed that model calculation fitted well the experimental data. Fig 7 shows extraction rate versus gas flow. Parameters of model calculation were obtained from literature [3].One of the model calculation conditions are a = 4,9 ; b = 0.059 ; $D_e = 0.75 \times 10^{-10}$ m^2/s ; $P_e = 50$. And the other parameters are : a = 47.1 ; b = 0.014 ; $D_e = 1.5 \times 10^{-10}$ m^2/s ; $P_e = 50$; From these calculations it were found that $B_i = 23.5287$ for first calculation and $B_i = 47.0573$ for second calculation. It was concluded that first condition is better than second condition.

Conclusion.

A mathematical model based on shrinking-core model of the supercritical extraction process were used in this work and calculation of the model were applied to measure the effect of particle size, length of extractor, effective intraparticle diffusivity. Concentration x could be increased by decreasing parameter a, which is needed small particle and large L for supercritical fluid extraction. It was concluded that increasing extraction rate with decreasing parameter B_i, which is effective intraparticle diffusivity significantly effect to this supercritical fluid extraction.

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Nomenclature

B_i	biot number
C	concentration of solute in the bulk fluid-phase , mol/m^3
C_{sat}	saturation concentration of solute , mol/m^3
D_c	effective intraparticle diffusivity , m^2/s.
k_f	coefficient of external-film mass transfer, m/s
L	length of extractor ,m.
q	concentration of solid-phase, mol/m^3
R	radius of solid particle, m.
R_{ec}	radius of column extractor, m.
r	radial coordinate
r_c	radius of unleach core, m
X	dimensionless concentration in the bulk fluid-phase , C/C_{sat}.
Y	dimensionless solid-phase concentration, q/q_o
θ	dimensionless time, (De/R2)t
ξ	dimensionless radial coordinate, r/R.
ξ_c	dimensionless radius of unleached core, r_c/R.

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