Mass Transfer Modeling of Rosemary Oil Extraction with Supercritical Carbon Dioxide

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Abstracts

A simple mathematical model is presented for predicting the rate of extraction of rosemary from leaves. The model has two parameters including the film mass transfer and intraparticle diffusion coefficients; the last one was used as the model fitting parameter.

Experiments were carried out at two pressures (150 and 180 bar) at a fixed temperature (40°C), particle size (0.436mm) and CO_2 flow (5g/min). A good agreement between experimental and the theoretical results was obtained.

Keywords: supercritical extraction, mathematical model, rosemary

INTRODUCTION

The supercritical extraction of essential oil has been modelled by many authors. Modelling the process is fundamental for optimizing the process variables and predicting the course of the extraction. Several models [1-5] have been proposed for the prediction of extraction yields from plants. Generally, these models are based on differential mass balance equations in fluid and solid phases and reflect in their assumptions different extraction mechanisms involving different resistances to mass transfer: internal resistance, external resistance, axial dispersion in the bed, but also, localization of solute in the plant.

However, when resistance in the bed is not significant, writing the mass balance in a single particle by introducing a condition on the surface of the particle, to take account of external transfer, is sufficient to adequately describe the extraction process.

Based on this assumption, we propose in this work to modelling the extraction of rosemary oil from leaves. The performance of the proposed model will be was tested with our results published in a previous work [6].

MATHEMATICAL MODEL

According to above hypothesis, the mass balance for the spherical particle is given by the second Fick's law that for constant density and diffusivity and assuming unidirectional radial transport gives:

$$\frac{\delta C_s}{\delta t} = D_e \frac{\delta^2 C_s}{\delta r^2} \tag{1}$$

If the sphere is initially at uniform concentration C_{s_0}, and there is a surface condition:

$$D_e \frac{\delta C_S}{\delta r} = k_f (C_{S_S} - C^*) \tag{2}$$

where C_{S_S} is the actual concentration just within the sphere, and C^* is the concentration required to maintain equilibrium with the surrounding supercritical fluid. From equation (1) and the boundary condition (2), the following general solution is obtained [7]:

$$\frac{C_s - C^*}{C_{s0} - C^*} = \frac{2LR_P}{r} \sum_{n=1}^{\infty} \frac{e^{-D_e \beta_n^2 t R_P^2}}{\beta_n^2 + L(l-1)} \frac{\sin \beta_n r / R_P}{\sin \beta_n} \tag{3}$$

with β_n the eigenvalue for the transcendental equation:

$$\beta_n \cot \beta_n + L - 1 = 0 \tag{4}$$

and:

$$L = \frac{k_f R_P}{D_e} \tag{5}$$

with k_f the film mass transfer coefficient, R_P the particle size and D_e the solute diffusivity inside solid particles.

The term β_n depend on the boundary conditions as given by equation (4). Relationship (3), coupled to the particular solution obtained from equation (4), enables the degree of solute extraction from a single particle to be calculated as function of extraction time. The total amount of diffusing substance leaving the sphere can be written in the dimensionless form:

$$y(t) = \frac{m_t}{m_0} = 1 - \sum_{n=1}^{\infty} \frac{6L^2 e^{-\beta_n^2 Dt / R_P^2}}{\beta_n^2 \, \beta_n^2 + L(l-1)} \cdot \tag{6}$$

The initial mass of the oil available in the solid (m_0) is supposed to be equal to the asymptotical value of the mass of oil extracted,($m_{e\infty}$). Said y_∞ the asymptotic yield, then it is:

$$m_0 = \frac{m_{e\infty}}{m_0 \quad m_{e\infty}} = \frac{y_\infty}{1 \quad y_\infty} \tag{7}$$

The parameter k_f was estimated from Tan et al correlation [8]:

$$Sh = 0.38 Re^{0.83} Sc^{1/3} \tag{8}$$

where Re, Sc an Sh are the dimensionless Reynolds, Schmidt and Sherwood respectively.

The parameter D_e was adjusted and determined by minimizing the errors between experimental data and calculated yield values. The errors were quantified by defining average absolute deviation (AAD) as,

$$AAD \, (\%) = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{y_i - y_{mod,i}}{y_i} \right| 100 \tag{9}$$

Where n is the number of experimental points, Y_i is the yield determined by experimental point i, and Y_{mod},i is the yield obtained by the model in point i.

RESULTS

Before the mass transfer coefficient k_f can be calculated the diffusion coefficient of the solute in the carbon dioxide for the given temperature and pressure must first be know. In praxis, the solute consists of many components and multi component diffusion is required. In this study, an approximation to this multi component parameter is made by calculating the binary diffusion coefficient D_{12} for the diffusion of the components present in largest amount into the carbon dioxide. These are α-pinene, limonene, camphor, 1,8-cineole and borneol. The binary diffusivities were estimated using a Catchpole and King correlation [9]:

$$D_{AB} = 2{,}543.10^{-7} T_r \left(\rho_r^{2/3} - 0.4511 \right) \left(\frac{R}{X} \right)$$

$$X = \frac{\left(1 + \left(V_{C,Solute} / V_{C,Solvent} \right)^{1/3} \right)^2}{1 + \left(M_{Solvaet} / M_{Solute} \right)}$$

$$R = 0{,}664 X^{0,17} \quad 2 < X < 10$$

where T_r is the reduced temperature and ρ_r reduced density. The critical volume V_C used for the determination of D_{AB} was calculated by Lydersen's method [10].

The principal components in the plant have very similar diffusivities in carbon dioxide, being approximately 1.05×10^{-9} m^2/s at 150 bar and 0.99×10^{-9} m^2/s at 180 bar. The resemblance between the diffusivities solutes arises because of their similar structure.

The experimental results obtained at two pressures were fitted using only one adjustable parameter, intraparticle diffusion coefficient (D_e). The best fit values are summarized in table1 and there was a fairly good agreement between the model curves and the experimental data as shown in Figures 1 and 2.

Table 1: Parameters fitted

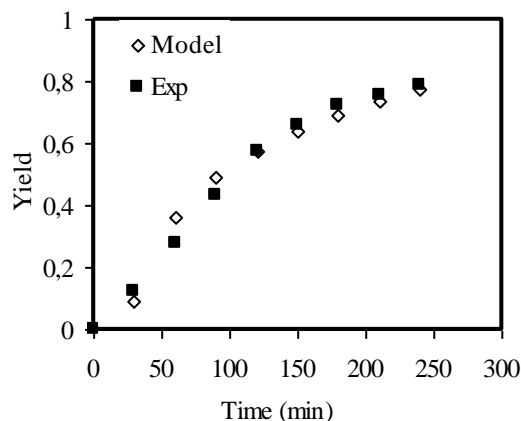| P (bar)	$k_f \times 10^5$ (m/s)	$D_e \times 10^{13}$ (m^2/s)	AAD (%)
150	2.94	5.6	5.1
180	3.26	3.8	2.8

Figure 1: Experimental and model extraction yields for rosemary essential oil extracted at 150 bar and 40°C.
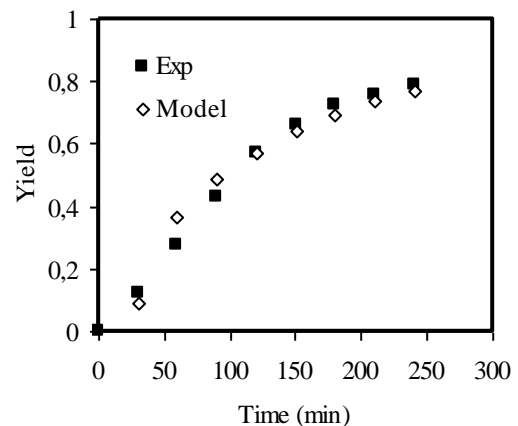

Figure 2: Experimental and model extraction yields for rosemary essential oil extracted at 180 bar and 40°C.

The comparison of diffusivities calculated, with the values given by literature [11], shows that our values are similar. The model represented the OEC curves adequately, mainly in the decreasing extraction rate, when the internal diffusion controls the mass transfer process.

CONCLUSION

The extraction of the essential oil of rosemary can be described in an adequate way by the suggested model. The model allows a good adjustment of the experimental data. Further refinements of the model are possible.

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