SUPERCRITICAL EXTRACTION OF SOLID MATRICES. MODEL FORMULATION AND EXPERIMENTS

L. RUETSCH[†] , J. DAGHERO[†] and M. MATTEA[‡]

[†] Facultad de Ingeniería, Univ. Nac. de Río Cuarto, 5800 Río Cuarto, Argentina
{lruetsch, jdaghero} @ ing.unrc.edu.ar
[‡] Facultad de Ingeniería, Univ. Nac. de Río Cuarto-CONICET, 5800 Río Cuarto, Argentina
mmattea @ ing.unrc.edu.ar

Abstract— **Nowadays, supercritical extraction of solid matrices is used frequently to obtain valuable substances especially by food and pharmaceutical industries. Most often, solid particles are arranged in a fixed bed configuration and the supercritical fluid flows through the bed extracting the desired solute. In this study, a mathematical model is set to simulate this process. The influence on the extraction yield of processing variables such as temperature, pressure and flow velocity as well as some process parameters like particle size, void fraction and bed height are predicted by the model. This model was used to simulate the extraction of essential oil from clove buds with supercritical CO_2. Experiments were carried out at different pressures (90-120 bar) at a fixed temperature and CO_2 flow. A good agreement between experimental and theoretical results was obtained.**

Keywords— **Supercritical Extraction, Mathematical Modeling, Solid Matrix.**

I. INTRODUCTION

Supercritical CO_2 extraction of vegetable oils and essential oils from plant materials is an alternative process to solvent extraction and steam distillation. Supercritical fluids have advantages over conventional solvents, such as: a)low viscosity and large diffusivity ensuing excellent mass transfer characteristics, b)variable dissolving power, b)very low surface tension allowing it to penetrate easily into the porous structure of a solid matrix to extract the solute and c)low latent heat of evaporation and high volatility favoring its removal from extracted products by simple expansion.

Process temperature and pressure affect significantly the dissolving power of supercritical fluids. At lower pressure (near the critical point) volatile components, such as essential oils are selectively extracted, while other components present in the vegetable matter such as waxes, resins and dyes have low solubility in these conditions. However, coextraction of waxes is common since they are located on the surface and they are extracted with a very limited mass transfer resistance (Reverchon, 1997).

Supercritical extraction has been applied to a large number of solid matrices to obtain valuable substances, mostly in food and pharmaceutical industries (King & Bott, 1993; Palmer & Ting, 1995). Most often, raw materials prepared to enhance solvent extraction are arranged in a fixed bed configuration and the supercritical fluid flows continuously through the bed extracting the desired solute. After the extractor, one or more separation stages are used to precipitate the solute from the supercritical solution.

The analysis of products and the assessment of their composition as a function of the extraction pressure and temperature have been reported for several vegetable matter (Stahl *et al.*, 1988). However, some other process parameters like particle size, milling conditions, fluid velocity and extraction time are not conveniently incorporated into these studies. Such parameters influence the extraction process to an extent that they can not be neglected in the analysis

Reliable mathematical models for supercritical extraction process can be developed that include all these parameters. Mathematical models can be used to generalize the experimental results to new process conditions and extracted materials. Even more, they are useful to develop scale-up procedures from laboratory to pilot and to industrial scale. Different approaches have been proposed to obtain mathematical models that simulate supercritical fluid extraction from solid particles (Brunner, 1994; Reverchon, 1997; Goto *et al.*, 1998). In this work, differential mass balances are used to elaborate a model that takes into account the following mechanisms: *i*)the dissolution of solid or liquid component into supercritical fluid filling the particle pores, *ii*)diffusion through porous cellular material and *iii*)external mass transfer around the solid particle to the main fluid stream. The resulting equations are solved using numerical techniques. Results obtained during the extraction of essential oil from clove buds with supercritical CO_2 are used to check the model.

II. METHODS

A. Model development

In order to obtain the mathematical model, the following simplifying assumptions were made: a) The extractor is well represented by a packed bed made of spherical, isotropic microporous particles arranged in a cylindrical geometry; b)Solutes are considered as single chemical compounds; c)Variables involved in the analysis do not change over the extractor cross section; d) Pressure drop and temperature gradient through the bed are low enough to consider that fluid density remains constant along it; e) A solute back flow develops in the bulk supercritical fluid phase due to a concentration gradient along the bed (axial dispersion); f) Inside particles, the supercritical fluid fills the micropores and forms a stationary phase; a solute concentration gradient along the particle radius is established and the solute diffuses out towards the bulk fluid phase; g) Initially, the solute is uniformly distributed throughout the solid that constitutes particles; h) The solute concentration in supercritical fluid that fills the particle micropores, C_p, is in local equilibrium with the solute concentration in solid phase, C_s, and i) Particle porosity (ε_p), particle size (R_p), void fraction in the bed (ε_b), solute diffusivity inside solid particles (D_{eff}) and dispersion coefficient (D_{ax}) are constant and uniform along the bed. Figure 1 depicts a view of the bed and a solid particle; the expected concentration profiles are also shown.

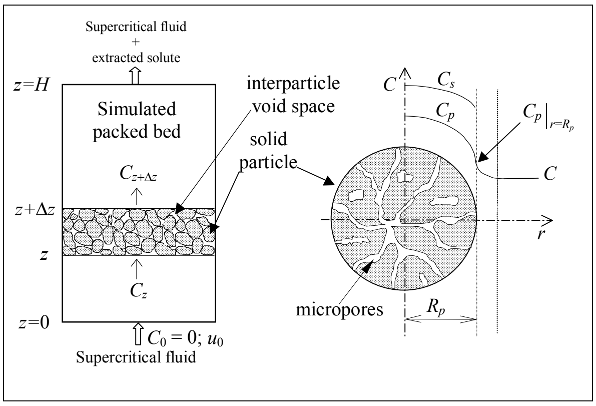

Figure 1. Schematic representation of extracting bed and enlarged view of solid particles

Under these assumptions, the material balances for the solute in bulk fluid phase and fluid phase inside particles, lead to:

i) Bulk fluid phase:

$$\frac{\partial C}{\partial t}+\frac{u_o}{\varepsilon_b}\frac{\partial C}{\partial z}=D_{ax}\frac{\partial^2 C}{\partial z^2}+\frac{(1-\varepsilon_b)}{\varepsilon_b}a_f k_f\left(C_p\Big|_{R_p}-C\right) \qquad (1)$$

ii) Fluid phase in micropores:

$$\frac{\partial C_p}{\partial t}+\frac{(1-\varepsilon_p)}{\varepsilon_p}\frac{\partial C_s}{\partial t}=\frac{D_{eff}}{\varepsilon_p r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_p}{\partial r}\right) \qquad (2)$$

In Eq. (1), C is the solute concentration in the bulk fluid phase, u_0 is the superficial fluid velocity, a_f is the effective solid-liquid contact area for mass transfer ($a_f = 3/R_p$) and k_f is the mass transfer coefficient for the solute transport through the external fluid film around solid particles. D_{ax}, D_{eff} and k_f are evaluated from existing correlations (King and Bott, 1993) as follows:

$$k_f=\left(\frac{\mathrm{D}_{12}}{2R_p}\right)\left(0.82\,\mathbf{Re}^{0.66}\mathbf{Sc}^{1/3}\right) \qquad (3)$$

$$D_{ax}=\left(\frac{\mathrm{D}_{12}}{\varepsilon_b}\right)\left(20+0.5\,\mathbf{Re}\ \mathbf{Sc}\right) \qquad (4)$$

$$D_{eff}=\varepsilon_b^2\,\mathrm{D}_{12} \qquad (5)$$

In these equations, D_{12} is the binary diffusion for the solute-CO_2 system, $\mathbf{Re}=(u_0 R_p\rho/\mu)$ is the Reynolds number and $\mathbf{Sc}=(\mu/\rho \mathrm{D}_{12})$ is the Schmidt number. Here it is assumed that at the surface of pores within a particle, the solute dissolves into the fluid phase at a rate large enough to reach the equilibrium value instantaneously. The following BET type equilibrium equation is used to relate C_s and C_p :

$$C_s=\frac{C_m\,k\,\overline{C}_p}{(1-\overline{C}_p)[1+(k-1)\overline{C}_p]} \qquad (6)$$

In Eqn. (6) $\overline{C}_p=(C_p/C^*)$ is the dimensionless solute concentration in micropores, C_m represents the monolayer capacity and k is a constant related to the net heat of adsorption (Adamson, 1982). Equations (1), (2) and (6) are solved subjected to the following initial and boundary conditions:

$$t=0;\ 0\le z\le H:\ C=0 \qquad (7)$$

$$t=0;\ 0\le z\le H;\ 0\le r\le R_p:\ C_p=C_{p,0} \qquad (8)$$

$$t=0;\ 0\le z\le H;\ 0\le r\le R_p:\ C_s=C_{s,0} \qquad (8.a)$$

$$z=H;\ t>0:\ \frac{\partial C}{\partial z}=0 \qquad (9)$$

$$z=0;\ t>0:\ D_{ax}\frac{\partial C}{\partial z}=u_0(C-C_0) \qquad (10)$$

$$r=R_p;\ 0\le z\le H;\ t>0:\ -D_{eff}\frac{\partial C_p}{\partial r}=k_f(C_p-C) \qquad (11)$$

$$r=0;\ 0\le z\le H;\ t>0:\ \frac{\partial C_s}{\partial r}=\frac{\partial C_p}{\partial r}=0 \qquad (12)$$

Equation (6) is assumed to be valid at t=0 and so, the total solute concentration existing in solid particles at the beginning of the extraction process, $C_{T,0}$, is computed as:

$$C_{T,0} = \varepsilon_p\, C_{p,0} + (1-\varepsilon_p)\, C_{s,0} \qquad (13)$$

The degree of extraction at different times, Y, defined as the mass of solute extracted related to the initial mass of solute, is evaluated as:

$$\mathrm{Y} = \frac{q}{\rho M_0} \int_0^t C(t)\Big|_{z=H} dt \qquad (14)$$

being ρ the CO_2 density at the extraction conditions, M_0 the initial mass of solute and q the CO_2 mass flow rate.

Equations (1) and (2) are solved simultaneously. The spatial derivatives are discretized using a finite difference scheme and the resulting system of ordinary differential equations is integrated by a Runge-Kutta method with adaptive length step. To begin with the solution procedure, Eqn. (6) and Eqn. (13) are used to compute the initial conditions, $C_{p,0}$ and $C_{s,0}$. After C is calculated, Eqn. (14) is integrated by a numerical method to compute the degree of extraction.

B. Experimental Procedure

The extraction trials were carried out on a pilot plant system (extractor volume: 1.5 L) with a single stage separation and solvent recycle capabilities as it is shown in Fig. 2.

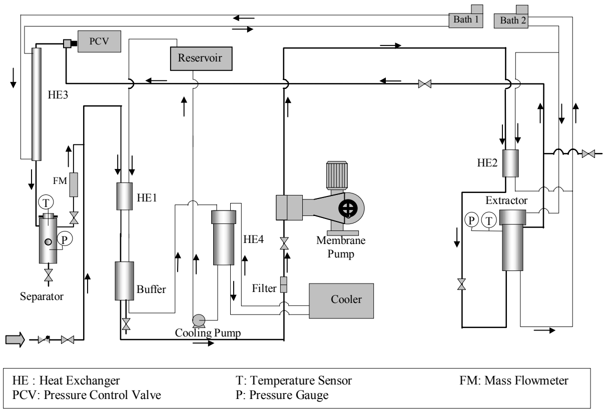

Figure 2. Schematic layout of the experimental set-up (supercritical extraction plant)

Liquid CO_2 (food grade) from PRAXAIR (Córdoba, Argentina) was used as solvent. The CO_2 coming from a cylinder with a siphon attachment is passed through a heat exchanger (HE1) and stored in a thermostatic buffer. The subcooled CO_2 is then compressed up to the operating pressure by a membrane pump (Lewa, Germany). The compressed CO_2 is then passed through a heat exchanger (HE2) where it reaches the extraction temperature. At this point the CO_2 is in the supercritical condition and goes into the extractor. A thermostatic jacket allows to control the extraction temperature between 20ºC and 80°C.

The supercritical CO_2 with dissolved compounds goes out of the extractor getting the pressure control valve (PCV) where the pressure is reduced. At this point the CO_2 becomes gaseous and the solute precipitates. After the control valve a heat exchanger (HE3) supplies the required energy to compensate cooling produced by Joule-Thompson effect. The solutes are collected in the bottom of the separator and the solvent returns to the buffer passing through the mass flowmeter (FM) (Rheonik, Germany).

Two extraction conditions (P_e=90 bar, T_e=50°C and P_e=120bar, T_e=50°C) using the same mass flow rate (q=5 Kg CO_2/h) were tested. In both cases the separator was operated at P_s=60bar and T_s=50°C. This condition was selected in order to minimize the residual solubility in the gaseous CO_2 (Stahl *et al.*, 1988). Clove buds were used as a model solid. Solid moisture content at extraction conditions, measured according to AOCS Ca 2a-45 (Firestone, 1989), was 9%. In each experiment, about 0.8 kg of clove buds were used. Samples were milled in a knife mill (Retsch SM100) before they were put into the extractor. The arithmetic mean particle size (Rice, 1995) was evaluated from a sieve analysis of the whole sample as R_p=0.395x10^{-3} m.

The solid sample was introduced into the extractor, it was closed and the whole system heated up to the extraction temperature. At this point, the compressed CO_2 at the same temperature was admitted into the extractor with the PCV valve totally closed. After a short time (usually in the order of 1 to 2 min.) the pressure reached the extraction pressure and the whole system started to work in a closed-loop scheme as described above.

C. Results and Discussion

Figure 3 shows the degree of extraction predicted by the model and the experimental values resulting from the trials described above. C_m in Eqn. (6) was set equal to initial solid concentration, $C_{s,0}$ and C^* were computed from the experimental outputs using the initial slope in a Y-m_{CO2} plot (Maxwell, 1996). The resulting C^* values were 0.034 Kg solute/Kg CO_2 and 0.0025 Kg solute/Kg CO_2 for P_e=120bar-T_e=50°C and P_e=90bar-T_e=50°C respectively. The equilibrium parameter k was adjusted to the experimental results at P_e=90bar-T_e=50°C by means of a least-square method (Rice, 1995). Then, assuming that this parameter is not a strong function of the extraction pressure, the k value so obtained was used to predict the Y values at P_e=120bar-T_e=50°C. As it can be seen in Fig. 3, there is a very good agreement between the predicted and experimental results. It is observed that at 90bar and 50ºC the clove oil is extracted at a steady state for as long as 400min showing that oil solubility in CO_2 plays a major role in the extraction process. However, at 120bar and 50ºC, the extraction rate starts declining when the extracted oil reaches about 50% (Y=0.5). This may be due to different reasons, namely *i*)either the intraparticle diffusional resistance or the external fluid film resistance is controlling the extraction rate and/or *ii*)the solute is retained by the solid matrix which makes it unavailable to the solvent.

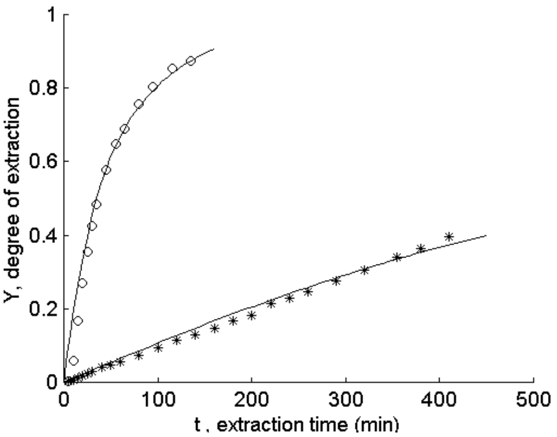

Figure 3. Extraction of essential oil from clove bud. Experimental results and model output. *: P_e=90bar-T_e=50°C ; o: P_e=120bar-T_e=50°C; — : model output. Model parameter: k =15.

The predicted solute concentration profiles in both, the bulk fluid phase and the fluid phase inside particles for the case P_e=120bar-T_e=50°C, are shown in Fig. 4 and Fig. 5 respectively. Axial dispersion effects on C at small time values can be observed in Fig. 4.

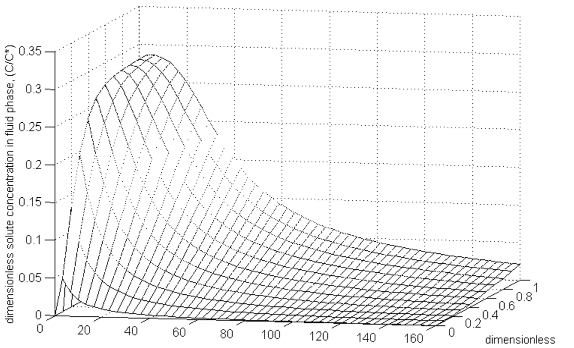

Figure 4. Dimensionless solute concentration profiles in bulk fluid phase, (C/C^*).

Inside solid particles, a solute distribution is established during the extraction process. At a given position along the bed, such a distribution flattens with time as it is shown in Fig. 5. The internal profiles are quite independent from radial position and the C_p values at r=R_p are close to the C values at the corresponding z position (see Fig. 4), suggesting that solute-solid affinity, quantified by Eqn. 6, is the reason for the decline of the extraction rate under the conditions of this experience.

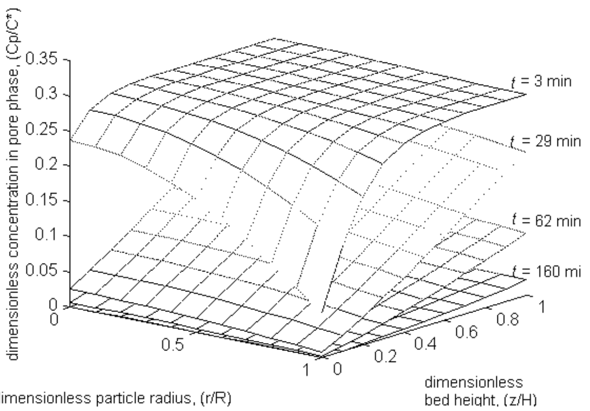

Figure 5. Dimensionless solute concentration profiles in micropores, (C_p/C^*).

III. CONCLUSIONS

The mathematical model presented in this work behaves very well to represent the extraction of essential oil from clove buds. The model, developed from differential mass balances allows considering the main transport mechanisms involved in the extraction process. The full set of resulting equations is solved by numerical techniques to obtain the degree of extraction and concentration profiles in a packed bed extractor

Aknowledgements

The authors wish to thank the Volkswagen Foundation, the Technische Universität Hamburg-Harburg and the National University of Río Cuarto for their financial assistance to this work

REFERENCES

Adamson, A.W. *Physical Chemistry of Surfaces.* (4th Ed.) John Wiley & Sons. NY (1982).

Brunner, G. *Gas Extraction. Springer Verlag*, Berlin (1994).

Firestone D., Official methods and recommended practices of the American Oil and Chemists' Society, American Oil Chemist's Society, Champaign, IL (1989)

Goto M., B. Roy, A. Kodama and T. Hirose, Modeling Supercritical Fluid Extraction Process Involving Solute-Solid Interaction. *J. Chem. Eng. Japan* **31**, 171-177 (1998).

King, M.B. and T.R. Bott, *Extraction of Natural Products Using Near-Critical Solvents*. Chapman & Hall (1993).

Maxwell R., Solubility Measurements of Lipid Constituents in Supercritical Fluids. Ch. 2 in *Supercritical Fluid Technology in Oil and Lipid Chemistry*. W. King & R. List Eds. AOCS Press (1996).

Palmer, M.V. and S.T. Ting, Applications for Supercritical Fluid Technology in Food Processing. *Food Chemistry* **52**, 345-348 (1995).

Reverchon E., Supercritical Fluid Extraction of Essential Oils and Related Materials. J. Supercritical Fluids, **10**: 1-37 (1997).

Rice J.A., *Mathematical Statistics and Data Analysis* (2nd Ed). *Duxbury Press*. USA (1995).

Stahl, E., W. Quirin and D. Gerard, *Dense Gases for Extraction and Refining*. *Springer Verlag.* Berlin (1988).

Received: September 16, 2001.
Accepted for publication: November 11, 2002.
Recommended by Guest Editors J. Cerdá, S. Díaz and A. Bandoni.