# EXTRACTION OF HO-SHO (*CINNAMOMUM CAMPHORA NEES & EBERM VAR. LINALOOLIFERA FUJITA*) ESSENTIAL OIL BY SUPERCRITICAL $CO_2$: EXPERIMENTS AND MODELING

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## SUMMARY

The supercritical extraction of comminuted leaves of a variety of Camphor Tree known as Ho-Sho (*Cinnamomum camphora Nees & Eberm var. linaloolifera Fujita*) with $CO_2$ was studied. Experiments were carried out within the following ranges: $CO_2$ flow rate between 1 and 4 mL/min; pressure between 80 and 100 bar; temperature between 40 and 60 °C and particle size between 0.37 and 1.0 mm. The equipment used was a HP 8670 T supercritical fluid extractor module with an extraction cell of 7 mL volume. Two mathematical models for the process were proposed. The model 1 was a modified version of the traditional *shrinking core model* with the effective diffusivity and the external mass transfer coefficient as fitting parameters. The model 2 considered a radial concentration gradient in the solid phase and an additional kinetic parameter based on an Arrhenius like expression. Both models considered axial dispersion and took into account the cell pressurization step. The best fit between the extraction model curves and the experimental data has been obtained using the model 2. Among the experiments executed, the largest essential oil yield was obtained at the following conditions: $CO_2$ flow rate of 2.5 mL/min, pressure of 90 bar, temperature of 60 °C and particle size of 0.37 mm.

Keywords: supercritical extraction, essential oil, ho-sho, mathematical modeling, *shrinking core model*

## INTRODUCTION

Linalool is an important intermediary in the manufacturing of vitamin E and constitutes, like geranial, raw material for the production of vitamin A (Bauer and Garbe, 1985). Linalool can be synthesized by different chemical routes from α-pinene or from isoprene. The world consumption of linalool in 1988 was estimated in six million metric tons (Clark, 1988) and is growing year after year, because it is not only used for the production of vitamins, but also in the fragrance industry. An alternative for the production of linalool from a natural source is the essential oil obtained from a plant known as ho-sho (*Cinnamomum camphora Nees & Eberm var. linaloolifera Fujita*) which is a tree native from China, Formosa and Japan. The main component of ho-sho essential oil is linalool (80-90%). Natural sources of linalool appear to be interesting, mainly for the fragrance industry, because the smell of plant materials is usually the result of the complex interactions occurring among the components of the mixture (REVERCHON, 1997). In this work we have studied the extraction of ho-sho essential oil using supercritical $CO_2$ as solvent, for being a process that

produces excellent quality oils and also to the fact that we are dealing with a clean technology.

## MATERIALS AND METHODS

Ho-sho leaves from plant exemplars existing in the Biotechnology Institute of the University of Caxias do Sul have been picked and submitted to drying in controlled conditions (temperature 20-22 °C and related air humidity 50-60%) during a period of seven days. After the drying period the leaves were submitted to the grinding process, using a Tecnal TE-650 mill (Tecnal, Brazil). Tyler sieves have been used to classify particles in desired size fractions (average diameter of 0.37 mm, 0.50 mm and 1.0 mm). Then, the particles were introduced into the extraction cell, which internal volume was about 7 mL.

The experimental extraction runs with supercritical $CO_2$ were carried out in the Hewlett-Packard 7680 T extraction module, and followed a 3x3 graeco-latin square design type, according to the experimental matrix presented on Table 1:

Table 1: Experimental matrix

| Run | Flow Rate (mL/min) | Pressure (bar) | Temperature (°C) | Particle Size (mm) |
|-----|--------------------|----------------|------------------|--------------------|
| 1 | 1,0 | 80 | 40 | 0,37 |
| 2 | 1,0 | 90 | 50 | 0,50 |
| 3 | 1,0 | 100 | 60 | 1,00 |
| 4 | 2,5 | 80 | 50 | 1,00 |
| 5 | 2,5 | 90 | 60 | 0,37 |
| 6 | 2,5 | 100 | 40 | 0,50 |
| 7 | 4,0 | 80 | 60 | 0,50 |
| 8 | 4,0 | 90 | 40 | 1,00 |
| 9 | 4,0 | 100 | 50 | 0,37 |

For each run, the oil obtained in pre-defined time intervals was collected in separate flasks, allowing the construction of extraction curves.

The gas chromatography using an internal standard was the method used in the quantification of the extracted essential oil. This method consists in adding a known amount of a substance (which is called the standard) to the extract before the chromatographic analysis. This substance must have a response factor similar to the main components of the extract. Considering this criterion, the 3-octanol (Aldrich, USA, 97% purity) was chosen as internal standard for having a molal mass close to the linalool, the main component in the extracted essential oil. It has also been considered that the other oil components had the same response factor. Thus, the total extracted essential oil amount was calculated using the results of the chromatographic analysis and the extract yield was determined. All the analysis were carried out in a gas chromatograph HP GC 6890 Series, equipped with a data acquisition software (HP Chemstation), detector FID (Flame Ionization Detector), fused silica capillary column HP-Innowax (30 m x 320 µm), 0.50 µm film thickness (Hewlett-Packard, USA) with the following temperature program: from 40 °C (8 minutes) to 180 °C at 3 °C/min, 180-230°C at 20 °C/min, 230 °C (20 minutes); injector temperature, 250 °C; split ratio, 1:50; carrier gas: $H_2$; column head pressure 34 kPa; injected sample volume, 1.0 µL.

# MATHEMATICAL MODELING

The proposal presented in this work includes the mathematical modeling of the extractor pressurization stage, besides the extraction stage itself. Thus, the initial conditions for the extraction stage will be the ones obtained by the end of the pressurization stage.

In the pressurization stage, the fluid phase is modeled as an infinite bath. The fluid properties are considered dependent only on time. To each experiment, the pressure variation with time was measured and then fitted by an algebraic expression. $CO_2$ density was estimated using the Peng-Robinson equation of state. Therefore, the equation for the fluid phase in the pressurization stage can be written as:

$$\frac{dC_1(t)}{dt} = -\frac{C_1(t)}{\rho_1(t)} \cdot \frac{d\rho_1(t)}{dt} - \frac{(1-\varepsilon)}{\varepsilon} \frac{3k_f}{R} \left( C_1(t) - C_{p1}(r,t)\big|_{r=R} \right) \tag{1}$$

Initial condition: $\qquad\qquad C_1(0) = 0$. $\qquad\qquad\qquad\qquad\qquad\qquad$ (2)

For the extraction stage, the fluid phase equation is obtained considering the axial dispersion term and the process occurring in isothermal and isobaric conditions. The resulting equation is:

$$\frac{\partial C(z,t)}{\partial t} = D_L \frac{\partial^2 C(z,t)}{\partial z^2} - v \frac{\partial C(z,t)}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon} \frac{3k_f}{R} \left( C(z,t) - C_p(z,r,t)\big|_{r=R} \right) \tag{3}$$

Initial condition: $\qquad C(z,0) = C_1(t = pressurization\ time)$ $\qquad\qquad$ (4)

Boundary conditions:

$$z = 0, \qquad vC(z,t) - D_L \frac{\partial C(z,t)}{\partial z} = 0 \qquad (\forall\, t) \tag{5}$$

$$z = L, \qquad \frac{\partial C(z,t)}{\partial z} = 0 \qquad (\forall\, t) \tag{6}$$

For mass balance in the solid phase, two distinct models are proposed, based on differentiated kinetics. Model 1 is based on the shrinking core model, traditionally used in the chemical reactor area, where it is known as "non-reacted core model", initially adapted by Roy et al. (1996) and improved by Spricigo(1998). The model assumes the existence of a solute core inside a spherical particle that will decrease continuously during extraction. The equation that governs mass transfer inside the particle pores considers an effective diffusivity for the oil in the $CO_2$. The solute diffuses inside the pores in the region between core surface ($r = r_c$) and particle surface ($r = R$). It is assumed that, on the core surface, the solvent is always saturated. The solubility of the essential oil was calculated from the results of Chang and Chen (1999), considering the oil as pure linalool. When the core is extinguished, the boundary condition for the pore oil concentration becomes a symmetry condition. Thus, the model obtained for the solid phase can be written as:

Pressurization stage:

$$\frac{\partial C_{p1}(r,t)}{\partial t} = \frac{D_{ef}}{\varepsilon_p}\left(\frac{\partial^2 C_{p1}(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C_{p1}(r,t)}{\partial r}\right) - \frac{C_{p1}(r,t)}{\rho_1(t)}\frac{d\rho_1(t)}{dt} \tag{7}$$

Initial condition: $\quad C_{p1}(r,0) = 0 \quad (\forall r)$. $\hspace{3cm}$ (8)

Boundary conditions:

$r = r_{c1};\qquad C_{p1}(r,t) = C_{sat1}(t) \qquad\qquad$ if $\quad r_{c1} \neq 0;$ $\hspace{2cm}$ (9)

$r = r_{c1};\qquad \dfrac{\partial C_{p1}(r,t)}{\partial r} = 0$ (symmetry) $\quad$ if $\quad r_{c1} = 0.$ $\hspace{1.5cm}$ (10)

$r = R;\ D_{ef}\left.\dfrac{\partial C_{p1}(r,t)}{\partial r}\right|_{r=R} = k_f\left(C_1(t) - C_{p1}(r,t)\big|_{r=R}\right) \qquad (\forall t).$ $\hspace{1cm}$ (11)

Extraction stage:

$$\frac{\partial C_p(z,r,t)}{\partial t} = \frac{D_{ef}}{\varepsilon_p}\left(\frac{\partial^2 C_p(z,r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C_p(z,r,t)}{\partial r}\right) \tag{12}$$

Initial condition: $\quad C_p(z,r,0) = C_{p1}(r, t = pressurization\ time) \qquad (\forall z)$ $\hspace{1cm}$ (13)

Boundary conditions:

$r = r_c;\qquad C_p(z,r,t) = C_{sat} \qquad\qquad$ if $\ r_c \neq 0;$ $\hspace{2cm}$ (14)

$r = r_c;\qquad \dfrac{\partial C_p(z,r,t)}{\partial r} = 0$ (symmetry) $\qquad$ if $\ r_c = 0;$ $\hspace{1.5cm}$ (15)

$r = R;\qquad D_{ef}\left.\dfrac{\partial C_p(z,r,t)}{\partial r}\right|_{r=R} = k_f\left(C(z,t) - C_p(z,r,t)\big|_{r=R}\right) \qquad (\forall t)$ $\hspace{0.5cm}$ (16)

The present proposal for the calculation of the shrinkage of the core differs from that of Spricigo (1998). In this work it is considered that the variation of the oil mass in the core is equal to the oil mass flow rate at the surface of core multiplied by the surface area of the core. After the algebraic manipulation the equations obtained for both stages of the process become:

Pressurization stage:

$$\frac{dr_{c1}(t)}{dt} = \frac{D_{ef}}{C_N}\cdot\frac{\rho_1(t)}{\rho_s}\cdot\left.\frac{\partial C_{p1}(r,t)}{\partial r}\right|_{r=r_{c1}} \tag{17}$$

Initial condition: $\quad r_{c1}(0) = R$ $\hspace{6cm}$ (18)

Extraction stage:

$$\frac{\partial r_c(z,t)}{\partial t} = \frac{D_{ef}}{C_N} \cdot \frac{\rho}{\rho_s} \cdot \frac{\partial C_p(z,r,t)}{\partial r}\bigg|_{r=r_c} \tag{19}$$

Initial condition:   $r_c(z,0) = r_{c1}(t = \text{pressurization time})$   $(\forall z)$. $\tag{20}$

Model 2 makes use of a differential equation for diffusion inside the pores that is applied to the whole particle domain (different from model 1 where diffusion takes place outside the core region) and an equation for mass transfer from solid to fluid based on oil solid concentration and the distance from the saturation condition in the fluid phase. It has also been considered a radial gradient of solid oil concentration, instead of considering an average concentration value, as it is usual in literature works. Therefore, the equations for solid phase for model 2 are:

Pressurization stage:

$$\frac{\partial C_{p1}(r,t)}{\partial t} = \frac{D_{ef}}{\varepsilon_p}\left(\frac{\partial^2 C_{p1}(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C_{p1}(r,t)}{\partial r}\right) - \frac{C_{p1}(r,t)}{\rho_1(t)}\frac{d\rho_1(t)}{dt} - \frac{\rho_s}{\varepsilon_p \rho_1(t)}\frac{\partial q_1(r,t)}{\partial t} \tag{21}$$

$$\frac{\partial q_1(r,t)}{\partial t} = -K(T)\,\rho_1(t)\,q_1(r,t)\left(C_{sat1}(t) - C_{p1}(r,t)\right) \tag{22}$$

Initial conditions:

$$C_{p1}(r,0) = 0 \qquad (\forall r) \tag{23}$$
$$q_1(r,0) = C_N \qquad (\forall r) \tag{24}$$

Extraction stage:

$$\frac{\partial C_p(z,r,t)}{\partial t} = \frac{D_{ef}}{\varepsilon_p}\left(\frac{\partial^2 C_p(z,r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C_p(z,r,t)}{\partial r}\right) - \frac{\rho_s}{\varepsilon_p \rho}\frac{\partial q(z,r,t)}{\partial t} \tag{25}$$

$$\frac{\partial q(z,r,t)}{\partial t} = -K(T)\,\rho\,\,q(z,r,t)\left(C_{sat} - C_p(z,r,t)\right) \tag{26}$$

Initial conditions:

$$C_p(z,r,0) = C_{p1}(r,t = \text{pressurization time}) \qquad (\forall z); \tag{27}$$
$$q(z,r,0) = q_1(r,t = \text{pressurization time}) \qquad (\forall z). \tag{28}$$

Boundary conditions:

$$r = 0; \qquad \frac{\partial C_p(z,r,t)}{\partial r} = 0 \ \text{(symmetry)} \tag{29}$$

$$r = R; \qquad D_{ef} \frac{\partial C_p(z,r,t)}{\partial r}\bigg|_{r=R} = k_f \left( C(z,t) - C_p(z,r,t)\big|_{r=R} \right) \qquad (\forall t) \tag{30}$$

The axial dispersion coefficient was estimated by a correlation proposed by Tan and Liou (1989). The models were solved by the method of lines, through spatial discretization using finite differences followed by an integration in time using Euler's method.

## RESULTS AND DISCUSSIONS

In the simulations performed, the external film mass transfer coefficient ($k_f$), the effective diffusivity ($D_{ef}$) and, in case of model 2, the kinetic coefficient (K), were considered the fitting parameters. The initial estimates for the external film mass transfer coefficient were obtained by Wakao and Kaguei (1982) correlation. For the effective diffusivity the starting value was obtained by the equation proposed by Pinto (1994). The initial estimates for the kinetic parameter (K) were obtained as a temperature function, using an Arrhenius like expression.

The optimization of the parameters was made without using a specific algorithm, that is, by a trial and error procedure, and considered the minimization of an objective function (F), define by:

$$F = \sum_{i}^{n} (M_{calc,i} - M_{exp,i})^2 \tag{31}$$

where:

$n =$      number of experimental points for each run;

$M_{calc,i} =$      accumulated extracted oil mass until time corresponding to point $i$, obtained in simulation;

$M_{exp,i} =$      accumulated extracted oil mass until time corresponding to point $i$, experimental.

During the optimization process, in both models a low sensitivity to the external film mass transfer coefficient was verified, indicating that extraction is controlled by intraparticle mass transfer. Thus, the option was keeping the values of these parameters obtained directly by Wakao and Kaguei (1982) correlation. Related to the effective diffusivity parameter, the final values obtained for each experiment were from one to two orders of magnitude smaller than the initial estimates. The difficulty faced in this parameter prediction is associated to the fact that different vegetal structure types present different mass transfer resistances, that makes more difficult correlate the effective diffusivity with the oil-$CO_2$ binary diffusivity, as reported by Gaspar et al. (2003).

The initial guess for the kinetic parameter (K), obtained by an Arrhenius like equation, using a value for the frequency factor of $1.0 \times 10^{13}$ $m^3 kg^{-1} s^{-1}$ and an activation energy of $1.0 \times 10^5$ J/mol, resulted in values from one to two orders of magnitude smaller than the values

obtained at the end of optimization. As the value for the frequency factor was somewhat arbitrary, a correction in this factor could be incorporated, allowing better initial estimates. The results obtained in the optimization are reported in Table 2:

Table 2: Optimized parameter model values

| Run | $k_f$ x $10^4$ (m/s) | $D_{ef}$ (m²/s) Model 1 | $D_{ef}$ (m²/s) Model 2 | $K$ (m³kg⁻¹s⁻¹) |
|-----|----------------------|-------------------------|-------------------------|-----------------|
| 1 | 3,351 | $4,105 \times 10^{-12}$ | $2,085 \times 10^{-11}$ | $2,047 \times 10^{-4}$ |
| 2 | 2,525 | $8,537 \times 10^{-12}$ | $3,309 \times 10^{-11}$ | $2,489 \times 10^{-4}$ |
| 3 | 1,513 | $7,834 \times 10^{-11}$ | $7,700 \times 10^{-11}$ | $1,340 \times 10^{-1}$ |
| 4 | 2,316 | $4,631 \times 10^{-11}$ | $4,308 \times 10^{-11}$ | $6,728 \times 10^{-3}$ |
| 5 | 4,895 | $4,024 \times 10^{-11}$ | $6,163 \times 10^{-11}$ | $2,058 \times 10^{-2}$ |
| 6 | 2,302 | $7,146 \times 10^{-12}$ | $5,287 \times 10^{-12}$ | $6,141 \times 10^{-3}$ |
| 7 | 4,991 | $9,717 \times 10^{-11}$ | $1,580 \times 10^{-10}$ | $3,087 \times 10^{-2}$ |
| 8 | 2,182 | $2,127 \times 10^{-11}$ | $1,634 \times 10^{-11}$ | $1,433 \times 10^{-2}$ |
| 9 | 5,406 | $2,269 \times 10^{-11}$ | $1,771 \times 10^{-11}$ | $3,700 \times 10^{-2}$ |

## CONCLUSIONS

In this work, two mathematical models were proposed to represent the essential oil supercritical extraction process from leaves of a plant known as ho-sho, using $CO_2$ as solvent. Both models contemplated the extractor pressurization initial stage, which is a differential in this work related to previous ones, found in literature. The model that best reproduced the extraction curves was model 2, which used a non-conventional kinetic parameter based on an Arrhenius like equation. It was found that extraction is controlled by intraparticle mass transfer. Additional work has to be done for correlate the effective diffusivity with the oil-$CO_2$ binary diffusivity. For the set of performed experiments, the largest essential oil yield obtained (4.31% w/w dry weight basis) occurred under the following conditions: pressure of 90 bar; temperature of 60°C; $CO_2$ flow rate of 2.5 mL/min and particle size of 0.37 mm.

## LIST OF SYMBOLS

$C_1(t) =$      solute concentration in $CO_2$ in the bed void volume, in the extractor pressurization stage (kg oil/kg $CO_2$);

$C(z,t) =$      solute concentration in $CO_2$ in the bed void volume, in the extraction stage (kg óleo/kg $CO_2$);

$C_N =$      initial solid phase concentration (kg oil/kg solid);

$C_{p1}(r,t) =$      solute concentration in the pore volume of solid in the extractor pressurization stage(kg oil/kg $CO_2$);

$C_p(z,r,t) =$      solute concentration in the pore volume of solid in the extraction stage (kg oil/kg $CO_2$);

$C_{sat1}(t) =$      saturation concentration of solute in fluid phase in the extractor pressurization stage (kg oil/kg $CO_2$).

| | |
|---|---|
| $C_{sat} =$ | saturation concentration of solute in fluid phase (kg oil/kg $CO_2$); |
| $D_{ef} =$ | effective diffusivity ($m^2/s$); |
| $D_L =$ | axial dispersion coefficient ($m^2/s$); |
| $k_f =$ | external film mass transfer coefficient (m/s); |
| $K =$ | kinetic parameter ($m^3 \, kg^{-1} s^{-1}$); |
| $L =$ | bed lenght (m); |
| $q_1(r,t) =$ | solute concentration in solid phase in the extractor pressurization stage (kg oil/kg solid); |
| $q(z,r,t) =$ | solute concentration in solid phase in the extraction stage (kg oil/kg solid); |
| $r =$ | radial coordinate in the particle (m); |
| $r_{c1}(t) =$ | core radius in the extractor pressurization stage (m); |
| $r_c(z,t) =$ | core radius in the extraction stage (m); |
| $R =$ | particle radius (m); |
| $t =$ | time (s); |
| $T =$ | temperature (K); |
| $v =$ | interstitial velocity of solvent in bed (m/s); |
| $z =$ | axial coordinate (m); |
| $\varepsilon =$ | voidage of the extraction bed (-); |
| $\varepsilon_p =$ | porosity of the solid (-); |
| $\rho_1(t) =$ | density of $CO_2$ in the extractor pressurization stage ($kg/m^3$); |
| $\rho =$ | density of $CO_2$ in the extraction stage ($kg/m^3$); |
| $\rho_s =$ | density of the porous solid matrix ($kg/m^3$); |

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