PROCEEDINGS OF THE
ELEVENTH ANNUAL

CONFERENCE
ON
APPLIED MATHEMATICS

University of Central Oklahoma
Edmond, Oklahoma
February 10-11, 1995
ON A MATHEMATICAL MODEL FOR OIL EXTRACTION USING HIGH PRESSURE SOLVENT FLOW

M. Mercedes Esquível*, Manuel L. Esquível† and M. G. Bernardo-Gil**

*Dep. de Engenharia Química, IST, Av. Rovisco Pais, 1096 Lisboa Codex, Portugal

†Dep. de Matemática, FCT-UNL, Quinta da Torre, 2825 Monte da Caparica, Portugal

Compressed carbon dioxide is used to extract oil from oily materials. In this work two partial differential equation models are developed to study the time evolution of the oil concentration in the carbon dioxide flow and to study the time evolution of the oil concentration in the residual materials.

These models are based on the models proposed by Bulley et al.¹ and Lee et al.², and are obtained by quantifying the mass transfer occurring inside a tubular extractor and making reasonable assumptions about the phenomena described. The Cauchy problems arising are then solved and the solutions obtained are discussed. As a particular solution, the model used by King et al.³ is found.

The models are validated by using experimental data on the extraction of oil from olive husk.

Keywords: Supercritical Solvent Extraction, Carbon Dioxide, Oil, Olive Husk Oil, Models
INTRODUCTION

The application of dense supercritical gases for the extraction of substances from solid materials is the aim of many research studies\textsuperscript{4-7}, namely in the extraction of oils\textsuperscript{3,8-12}.

In a previous publication\textsuperscript{13}, equipment and procedures for the extraction of olive husk oil with compressed carbon dioxide were described. Extraction curves at 12, 15 and 18 MPa and 308, 313 and 318 K were obtained. In this work two models are developed to study the time evolution of the oil concentration in the carbon dioxide flow and to study the time evolution of the oil concentration in the residual materials. The validation of theses models is made using those data.

The main part of the installation is an extractor of height \( h = H \), which is full of granulated olive husk. The solvent (compressed carbon dioxide) enters the extractor at height \( h = 0 \) and leaves it at the top (height \( h = H \)) charged with oil (Figure 1).

The granulated material inside the extractor allows the solvent to get an almost optimal area of contact with the free surface of the grains. The process involved causes the transfer of the oil contained in the grains towards the CO\(_2\) flow.

The main goal of this work will be to study the evolution in time (hereafter denoted by the variable \( t \)) of the oil concentration in the CO\(_2\) flow (the \( Y = Y(t,h) \) function), and the concentration of the remaining oil in the solid bed (the \( X = X(t,h) \) function). As indicated, both the \( X \) and the \( Y \) functions can be considered height dependent.

In the derivation of the model, the following assumptions are made:

- The extractor has horizontal sections of constant area \( A \).
- There is uniform distribution of the materials in the extractor, which lead to a constant porosity \( \varepsilon \).
- The axial dispersion is negligible.
- The overall mass transfer coefficient, \( K \), is not time or height dependent.
- The interfacial area, \( a \), is constant.
• The solvent density, $\rho$, is constant.

• The solvent superficial velocity, $U$, is constant.

• There is uniform density of grained materials in the extractor, $\rho_s$.

**MASS TRANSFER MODELS**

The mathematical model for the oil in the solvent phase

The mass exchange of oil in the CO$_2$ laying in an infinitesimal element of height $dl$ (see Fig 1) can be quantified in the following balance:

$$
\left( \frac{\partial}{\partial t} \right)_{Adl} \varepsilon \rho Y(t, l) = \left[ AU \rho Y(t, h) \right]_{h=1} - \left[ AU \rho Y(t, l) \right]_{h=1+dl} + Ka Adl (Y^* - Y(t, l))
$$

(1)

$Y^*$ being the concentration of the oil ($\varepsilon_{oil} / \varepsilon_{CO_2}$) in the solution in contact with the particles which have an oil concentration $X(t, h)$.

This equation states that the time variation of the mass of oil in an element $dl$ at height $h=l$, is equal to the difference between the entering mass at height $l$ and the leaving mass at height $l+dl$, summed with the mass that is being transferred from the materials to the CO$_2$.

Under some mild hypothesis on the regularity of the function $Y$, the equation 1 is equivalent to the following linear partial differential equation of the first order:

$$
\varepsilon \rho \frac{\partial Y}{\partial t} + U \rho \frac{\partial Y}{\partial h} = Ka (Y^* - Y)
$$

(2)

If we suppose that at time $t=0$ the solvent is arriving precisely to the top of the extractor, the initial condition must be:
\( \forall h \in [0, H] \; \; Y(0,h) = \phi(h) \) \hspace{1cm} (3)

where \( \phi \) is a given function.

The mathematical model for the remaining oil in the solid bed

In an similar way, the time variation of the mass of the remaining oil in the solid bed can be accounted on the following balance:

\[
\frac{\partial}{\partial t}((1 - \epsilon) A \, dl \, \rho_s \, X) = 0 - 0 - K_a (Y^* - Y) \tag{4}
\]

which is equivalent, under the right regularity assumptions, to the following equation:

\[
(1 - \epsilon) A \, \rho_s \, \frac{\partial X}{\partial t} = - K_a (Y^* - Y(t,t)) \tag{5}
\]

In order to formulate the initial condition in a coherent way with the model for the \( Y \) function, in which for \( t=0 \) the solvent had just crossed the extractor for the first time, we must have:

\( \forall h \in [0, H] \; \; X(0,h) = X_0(h) \) \hspace{1cm} (6)
SOLUTIONS FOR THE MATHEMATICAL MODELS

1. Solution for the model of the oil in the solvent flow

Case A: The particular case where \( Y^\ast \) is time independent

If \( Y^\ast \), the concentration of oil in solvent phase near the interface solid/liquid, is constant in time, PB1, the Cauchy problem which summarizes the first mathematical model:

\[
\text{PB1} = \begin{cases} 
\varepsilon \rho \frac{\partial Y}{\partial t} + U \rho \frac{\partial Y}{\partial h} = K a (Y^\ast - Y) \\
\forall h \in [0, H] \quad Y(0, h) = \phi(h), \quad \phi(0) = 0, \quad \phi(H) = Y_H
\end{cases}
\]

can be studied using the separation of variables technique and in doing so, one shall obtain some qualitative results about the general form of the function \( \phi \), which defines the initial condition of the problem, \( Y_H \) being in any case, a measurable result.

After performing the change of variable \( Z = Y^\ast - Y \), one is left with the Cauchy problem:

\[
\begin{cases} 
\varepsilon \rho \frac{\partial Z}{\partial t} + U \rho \frac{\partial Z}{\partial h} = -K a Z \\
\forall h \in [0, H] \quad Z(0, h) = Y^\ast - \phi(h), \quad \phi(0) = 0, \quad \phi(H) = Y_H
\end{cases}
\]

The very special form of the differential equation (i.e. \( dZ(\varepsilon \rho, U \rho) = -K a Z \)) suggest that one looks for a strictly positive, exponential type function, in separable variables:

\( Z(t, h) = f(t) \cdot g(h) \). Replacing this particular type of function in the partial differential equation, one gets:
\[ \forall t, \forall h \quad \frac{-\varepsilon \rho}{K a} f(t) = 1 + \frac{U \rho}{K a} g(h) \quad (7) \]

This equation is verified only if both terms are constant and equal, say, to \( \lambda \).

The partial differential equation for the function \( Z \) is now equivalent to a set of two ordinary differential equations of the first order, which are trivially solved to give:

\[ \forall t, h \quad Z(t, h) = c_r \exp \left( -\frac{\lambda}{\varepsilon \rho} K a t \right) c_g \exp \left( -\frac{(1 - \lambda) K a h}{U \rho} \right) \]

where \( c_r \) and \( c_g \) stand for the constants of integration of the differential equations for the functions \( f \) and \( g \). Using the initial conditions one can state that:

\[ Z(0, 0) = c_r c_g = Y^* \]

\[ Z(0, h) = Y^* \exp \left( -\frac{(1 - \lambda) K a h}{U \rho} \right) = Y^* - \phi(h) \]

This last equation shows that the general form for the function \( \phi \) is:

\[ \forall h, \phi(h) = Y^* (1 - \exp \left( -\frac{(1 - \lambda) K a h}{U \rho} \right)) \quad (8) \]

If one assumes that \( \phi(H) = Y_H \) is known, there is only one value of the parameter \( \lambda \) for which equation (7) is satisfied:

\[ \lambda_H = 1 + \frac{U \rho}{K a H} \ln \left( 1 - \frac{Y_H}{Y^*} \right) \quad (9) \]

Performing the substitutions and the calculations one get for \( Z \):
\[
\forall t, \forall h \ Z(t,h) = Y^* \exp\left(\frac{-K a t}{\varepsilon \rho}\right)(1 - \frac{Y H}{Y^*})\left(\frac{h}{H} - \frac{U t}{\varepsilon H}\right)
\]

The question naturally arises of knowing if the solution one has obtained under the hypothesis of \(Z\) being a function of separable variables, is in fact a solution for the Cauchy problem formulated without that hypothesis. The standard existence and unicity results for linear partial differential equations of the first order\(^{13}\) give to that question a positive answer. In fact as \(S\), the hypersurface in \(\mathbb{R}^2\) defined by \(S = \{(0, h) : h \in [0, H]\}\) is of class \(C^1\) and non-characteristic for the operator \(\zeta\) defined by:

\[
\zeta Z = \varepsilon \rho \frac{\partial Z}{\partial t} + U \rho \frac{\partial Z}{\partial h} + K a Z
\]

which means that the vector \((\varepsilon \rho, U \rho)\) is non-tangent to \(S\) at all points. So, there is an unique regular solution to the Cauchy problem posed.

Just performing the backward change of variables on the function \(Z\), one is able to state the solution of the mathematical model for the oil in the solvent, in the particular case where \(Y^*\) is time independent:

- The Cauchy problem PB1 has an unique solution given by:

\[
\forall (t, h) \in [0, +\infty] \times [0, H] \quad Y(t, h) = Y^* \left[1 - \exp\left(\frac{-K a t}{\varepsilon \rho}\right)(1 - \frac{Y H}{Y^*})\left(\frac{h}{H} - \frac{U t}{\varepsilon H}\right)\right]
\]

(10)
• If, in the model, one takes for \( t=0 \), the moment in which the CO₂ flow enters the extractor, then the function \( \phi \) defining the initial conditions must have constant value zero, that means \( \phi (H) = Y_H = 0 \) in the last equation and that amounts to:

\[
\forall (t, h) \in [0, +\infty) \times [0, H] \quad Y(t, h) = Y^* \left[ 1 - \exp \left( -\frac{K \alpha t}{\varepsilon \rho} \right) \right]
\]  \( (11) \)

This particular form for the function describing the time evolution for the concentration of the oil in the solvent flow has been used by King et al. ³

• Under the hypothesis \( Y^* \) be time independent, the function \( \phi \) describing the initial conditions is necessarily of the form represented in equation (8), and also of the form:

\[
\phi (h) = \begin{cases} 
0, & h \in \left[ -\infty, 0 \right], \\
Y^* \left( 1 - \left( 1 - \frac{Y_H}{Y^*} \right)^{\frac{h}{H}} \right), & h \in \left[ 0, H \right], \\
Y_H, & h \in \left[ H, +\infty \right]. 
\end{cases}
\]

obtained by making the substitution of the value of \( \lambda_H \), given by equation (9) and by incorporating the necessary extensions in order to have a continuous function everywhere defined.

Case B: The case where \( Y^* \) is a time dependent function, \( Y^* = v(t) \)

The Cauchy problems to be solved are given by PB2, where:
\[ PB2 = \left\{ \begin{array}{l}
\varepsilon \rho \frac{\partial Y}{\partial t} + U \rho \frac{\partial Y}{\partial h} = K a (v(t) - Y) \\
\forall h \in [0,H] \quad Y(0,h) = \phi(h), \quad \phi(0) = 0, \quad \phi(H) = Y_H
\end{array} \right. \]

and the general theory for this kind of problems\(^{13}\) shows that one must look for solutions of the system of ordinary differential equations with initial conditions, in the auxiliary variables \(x_1\) and \(x_2\), given by:

\[
\begin{bmatrix}
\frac{d x_1}{d t} = \frac{d x_2}{d t} = \frac{d Y}{d t} \\
\varepsilon \rho U \rho - K a (v(x_1) - Y)
\end{bmatrix}
\begin{bmatrix}
(x_1, x_2, Y)_{t=0} = (0, C, \phi(C))
\end{bmatrix}
\]

Solving the differential equation given by the first equality, in the first equation above and using the initial conditions, one obtains \(x_2\) as a function of \(x_1\), and the constant \(C\) as a relation between \(x_1\) and \(x_2\):

\[
x_2 = \frac{U}{\varepsilon} x_1 + C
\]

while the second equality is a non-homogeneous ordinary differential equation of the first order given together with the initial conditions by:

\[
\begin{bmatrix}
\frac{dY}{dx_1} = \frac{K a}{\varepsilon \rho} (v(x_1) - Y) \\
Y(x_1)_{x_1=0} = \phi(C)
\end{bmatrix}
\]

The solution of this problem is straightforward and one obtains \(Y\) as a function of \(x_1\):

\[
Y(x_1) = \left[ \frac{K a}{\varepsilon \rho} \int_0^{x_1} v(u) \exp \left( \frac{K a u}{\varepsilon \rho} \right) du + \phi(C) \right] \exp \left( \frac{K a x_1}{\varepsilon \rho} \right)
\]

(13)
Using the expression that gives $C$ as a relation between $x_1$ and $x_2$, returning to the original variables and replacing the function $\phi$ according to his extended definition given in case A, one obtains the final conclusion:

- The Cauchy problem PB2 admit the unique solution given for all $(t,h) \in [0, +\infty[ \times [0,H]$ by:

$$Y(t,h) = \left[ \frac{K a}{\varepsilon \rho} \int_0^t v(u) \exp \left( \frac{K a u}{\varepsilon \rho} \right) du + \phi(h - \frac{U t}{\varepsilon}) \right] \exp \left( -\frac{K a t}{\varepsilon \rho} \right) \quad (14)$$

- Replacing the function $v$ by a constant $Y^*$ and performing the calculations needed, one obtains again the solution for the particular case given in the equation (10). Also, it is easy to verify directly that the function $Y$ given by equation (14), is in fact, a solution for the Cauchy problem PB2.

2. Solution for the model of remaining oil in the solid bed

The evolution in time of the remaining oil in the solid bed was modeled by equations (4) and (5) which constitute a simple Cauchy problem given by:

$$\text{PB3 } = \begin{cases} 
(1 - \varepsilon) \rho s \frac{\partial X}{\partial t} = - K a (v(t) - Y) \\
\forall h \in [0,H] \quad X(0,h) = X_0(h)
\end{cases}$$

$X(h)$ being calculated from the balance: $X(h) M_b = M_i - \Phi(h) M_s$, and $M_i$ being the initial mass of oil in the bed, and $M_b$ and $M_s$ being the mass of solid in the bed and the mass of solvent, respectively.

By performing an integration in the variable $t$ and using the expression found for $Y$, one obtains the solution for PB3:
\[ X(0, h) = X_0(h) - \frac{K a}{(1 - \varepsilon) \rho_s} \int_0^1 (v(u) - Y(u, h)) \, du \]  

(15)

**VALIDATION OF THE MODELS**

In a previous work\textsuperscript{12} it was described the equipment, the materials and the experimental procedure on the extraction of oil from olive husks using supercritical carbon dioxide. The results were discussed in terms of the influence of pressure and temperature on the rate of extraction and on the acidity of the oil.

In figure 2 are presented the curves of the time evolution of \( Y^* \) at 313 K and 12 and 15 MPa.

When the curves for \( Y^* \) where obtained, the solvent at the appropriate temperature and pressure has passed continuously through the extractor that was filled up with ground olive husk, and a very low superficial velocity was used allowing a very long residence time of the solvent in the extractor approaching the equilibrium conditions. The average loading over each interval is calculated from the solvent gas passed in that interval and the product collected. The efficiency of extraction was assessed by mass balance between the olive husk oil collected and the weight loss (on a water-free basis) of the contents of the extractor.

Using mathematical software (MATHEMATICA (TM) and SYSTAT (TM)) it was found that one expression that statistically can be taken to represent these data, is of the following form:

\[ Y^* = v(t) = \alpha + \delta \exp(-\gamma t) + \beta \exp\left(-\frac{t^2}{\sigma}\right) \]  

(16)

The parameters calculated for this correlation are presented in table I, and the results are compared with the experimental ones at figure 3.
determined, it is possible to use equation (14) to simulate the extraction curves. The values of these variables used in this work are indicated in table II.

The unique variable which is unknown is the mass transfer coefficient $K$. The initial value is estimated by using empirical correlations $^{14}$, and the calculated value are indicated in table II.

In order to determine the mass transfer coefficient which gives the simulated curves best adapted to the experimental ones, it may be observed that the right member of equation (14) defines a function of two variables $w(t,K)$, which has continuous first order derivatives. It can also observe that the simulated curves present a peak of maximum value corresponding to a certain value of the time variable. As the same phenomena occurs in the experimental curves, we shall call "peak-time", the value of the time variable at which the curves (both simulated and experimental) present their maximum value.

Now, on the basis of the regularity of the function $w(t,K)$, we can say that for each value $t_1$ of the time variable, chosen close enough to the peak-time value, exists a value $K_1$ of the $K$ variable such that the curve $w(t_1,K_1)$ in the $t$ variable has a peak of maximum value exactly at time $t_1$. Accordingly the value of $K$ used to simulate the extraction curves presented was determined as the (numerical) solution of the equation in the $K$ variable

$$\left[ \frac{\partial w(t,K)}{\partial t} \right]_{t=t_p} = 0$$

where $t_p$ was chosen as the peak time for the experimental extraction curves

The agreement between experimental and calculated data is good if the equation (14) is multiplied by a factor $F_c$. In the conditions used, this factor has the value of 0.55 at both the pressures. In figures 3 and 4, extraction curves for various residence times ($\tau$) are compared with the curve obtained with the model.
The residence time is defined as the quotient between the volume of bed and the volumetric flow rate of compressed solvent.

CONCLUSIONS

A mass transfer model was developed to explain the time evolution of the concentration of olive husk oil in solvent phase for a fixed bed extractor. This model permits to predict the extraction curves for any pressure, temperature and superficial flow velocity of the compressed fluid since the curve $Y^* = v(t)$ is known. If this curve is constant the model is simplified, obtaining the equation used by Bernardo-Gil et al.\textsuperscript{16} for the extraction of rapeseed.

The exact determination of the peak time is very important for the prediction of the mass transfer coefficient, since this coefficient is calculated equalizing to zero the first derivative of the function that represents the curve at the point $t = t_p$.

At 12 MPa the predicted results are very similar to the experimental ones. However at 15 MPa, the results are not so good, mainly due to the uncertainty in the determination of $t_p$ that leaves to a value of $K$ with less precision.

ACKNOWLEDGMENTS

The authors are gratefully acknowledge the financial support from the Junta Nacional de Investigação Científica e Tecnológica, though the project JNICT - 87.195/BIO. We should like to thank the computational facilities offered by the Mathematics Department of F.C.T. - UNL.
REFERENCES

(12) Esquivel, M.; Bernardo-Gil, M. G.:J. of Supercritical Fluids, accepted.
FIGURE CAPTIONS

Figure 1 - Schematic diagram of the extractor

Figure 2 - Evolution of $Y^*$ with time at 313 K. * Experimental points at 12 MPa.
        _ v(t) at 12MPa. + Experimental points at 15 MPa. -- v(t) at 15 MPa.

Figure 3 - Extraction curves at 313 K and 12 MPa. * Experimental points at $\tau=124$ s.
        x Experimental points at $\tau=150$ s. + Experimental points at $\tau=190$ s.
        _ Calculated curve with the model

Figure 4 - Extraction curves at 313 K and 15 MPa. + Experimental points at $\tau=155$ s.
        x Experimental points at $\tau=213$ s. * Experimental points at $\tau=265$ s.
        _ Calculated curve with the model
Table I. Parameters for $Y^* = v(t)$

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$P = 12$ MPa</th>
<th>$P = 15$ MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0.68620</td>
<td>1.27856</td>
</tr>
<tr>
<td>$\delta$</td>
<td>1.98717</td>
<td>-1.30787</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.000082</td>
<td>0.000182</td>
</tr>
<tr>
<td>$\beta$</td>
<td>3.71762</td>
<td>4.23119</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>$4.0042 \times 10^8$</td>
<td>$3.6654 \times 10^8$</td>
</tr>
</tbody>
</table>
Table II. Values of some variables used in the extraction of olive husk oil.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>P = 12 MPa</th>
<th>P = 15 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U / \text{cm s}^{-1}$</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>$\rho_s / \text{g cm}^{-3}$</td>
<td>0.5164</td>
<td>0.5164</td>
</tr>
<tr>
<td>$\rho_o / \text{g cm}^{-3}$</td>
<td>0.66193</td>
<td>0.77957</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>0.603</td>
<td>0.603</td>
</tr>
<tr>
<td>$a / \text{cm}^2 \text{cm}^{-3}$</td>
<td>61.87</td>
<td>61.87</td>
</tr>
<tr>
<td>$K / \text{cm s}^{-1}$</td>
<td>$2.2 \times 10^{-5}$</td>
<td>$5.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>$T / \text{K}$</td>
<td>313</td>
<td>313</td>
</tr>
</tbody>
</table>
\[ h = H \]
\[ h = 0 \]
\[ h = l + dl \]
\[ h = l \]

\[ \text{CO}_2 \]