ABSTRACT

Being interested in the sizing and optimization of supercritical fluid extraction plants for solid substrates, we are developing a computational tool to estimate changes in residual solute content in a solid substrate within one of the extraction vessels in a multi-vessel plant with a simulated counter-current contact between the solid substrate and continuously flowing supercritical CO₂. In this contribution we are illustrating the use of our computational tool to assess the productivity of vegetable oil of plants with six cubic meters of total extraction volume and having three or four vessels with an inner diameter of 68.3 cm using 5 mm-diameter pre-pressed rapeseed pellets (equivalent diameter = 6.67 mm, bulk density = 500 kg/m³) as the substrate, and 2400-to-6000 kg/h of CO₂ at 40 °C and 30 MPa as the solvent. For the purpose of assessing the annual productivity we assumed the plant operated continuously (24 h/day) during 300 day/year using 60 °C and 8 MPa as the separation conditions. As expected, the productivity of the plant increased as the number of the extraction vessels or as the mass flow rate of CO₂ increased. However, this increased productivity should be associated with increased investment and operational costs which were not estimated as part of our work. Thus, our main result at present is a map of vegetable oil productivity as a function of plant configuration that we plan to use for the economic optimization of the process.

INTRODUCTION

Solid substrates have been commercially processed in supercritical fluid extraction (SCFE) plants for more than two decades [1]. There are large-scale applications of the process in the European Community, the United States, and other developed countries, including the decaffeination of coffee beans (extractors ≥20 m³) and extraction of hops (extractors ≈5 m³) [1] using supercritical carbon dioxide (SC-CO₂) as the solvent. Smaller scale applications carried out worldwide include the extraction of essential oils, specialty lipids, oleoresins, and other high-value compounds from plant materials and other natural products [2].

The industrial application of the SCFE technology contrasts with a limited information in open literature about the sizing of SCFE plants for solid substrates [3]. We believe this is not due to lack of knowledge as much as protection of their expertise by plant manufactures, who share it on condition that potential customers purchase their processing plants. The literature on optimization and scaling-up of SCFE processes is limited to mathematical expressions for a preliminary estimation of both capital (investment) and operating (production) costs based on limited information about similar processes [4,5], or so-called Level 1 estimates having errors of up to 50% [6]. On the other hand, to the best of our knowledge, there is no Level 2 cost estimates (having errors below 30% [6]), which should be based on the sizing of the main components of the SCFE plants.
Commercial SCFE plants are composed of several vessels and operate by contacting the packed solid substrate with continuously flowing SC-CO$_2$ in a simulated counter-current contact mode. In our opinion, a very important tool for sizing such plants would probably be a computer-based simulation algorithm that can predict changes in residual solute content in a solid substrate within a packed bed as it is being extracted with SC-CO$_2$ having a variable solute concentration. Indeed the concentration of solute in SC-CO$_2$ changes as the solvent moves from one extraction vessel to other and exchanges solute with substrates having progressively more solute. This solute concentration also suffers transient changes when extraction vessels with exhausted substrate are taken out and extraction vessels with fresh substrate are placed into the solvent cycle.

The objective of this work is to simulate an industrial-scale SC-CO$_2$ extraction process for vegetable substrates (pretreated oilseeds), and to study the effect on the productivity of oil of the number of extraction vessels ($n$), the length-to-diameter ($L/D$) ratio of the vessels, and the superficial velocity of the CO$_2$ ($U$). We selected the extraction of vegetable oils because there is validated information in literature about the SC-CO$_2$ extraction process [7], including the physical properties of oil+CO$_2$ mixtures, the solubility of the oil in SC-CO$_2$ as a function of system temperature and pressure [8], and the effective diffusivity of the oil in pre-pressed and flaked substrates [9].

**MATERIALS AND METHODS**

**Simulation model**

We adapted a mathematical model based on the Shrinking Core (SC) hypothesis [10], which is adequate to describe the extraction of oil from pre-pressed oilseeds [9]. Specifically, the model assumes an spherically-shaped porous matrix with evenly distributed vegetable oil, and describes the movement of the boundary between an inner core with condensed oil and an outside region where the oil moves by diffusion, where the core moves towards the center of the particle as the extraction progresses.

Germain et al. [11] programmed the differential mass balance and kinetic equations of the SC model proposed by Goto et al. [10] in MATLAB software. In the program, the spatial derivatives of the model are estimated using second-order finite differences, and the resulting time-dependent differential equations are solved numerically using the modified formula of order 2 of Rosenbrock [11].

We adapted the program of Germain et al. [11] to our specific needs. Our aim was to simulate the steady-state conditions in a single extraction vessel during a whole cycle (duration = $t_c$ hours) that considered $n$ stages; $(n-1)$ extraction stages of counter-current like extraction, and the remaining stage destined to decompressing / unloading / loading / recompressing operations. This whole cycle is representative of the $N_c$ (=300×24×$n/t_c$) annual cycles of the $n$-vessel extraction plant (continuous 24 h/day production during 300 day/year, for a grand total of 7200 h/year of continuous production). During the first stage of the cycle, the extraction vessel with fresh substrate is fed with the partially saturated SC-CO$_2$ current leaving an extraction vessel during the $(n-1)$ stage. During the second stage the extraction vessel with partially exhausted substrate is fed with a less concentrated SC-CO$_2$ current leaving an extraction vessel during the $(n-2)$ stage, and so on up to the $(n-1)$ stage where the extraction vessel with nearly exhausted substrate is contacted with the regenerated CO$_2$ coming from the separation vessel for the oil. The challenge was to achieve coincidence between the simulated temporal oil concentration profiles in the SC-CO$_2$ current leaving the extraction vessel during the last $(n-2)$ stages with those fed during the first $(n-2)$ stages. This was done by successive
approximations up to reaching a practical coincidence criterium (≤1% discrepancies; ≤10 loops). The temporal oil concentration profiles were stored in history vectors.

**Experimental Design**

We applied our computational tool to plants having three ($L/D = 8$) or four ($L/D = 6$) vessels with an inner diameter of $D = 0.683$ m and variable length $L$. This kept the total plant volume constant ($n \ V = 6$ m$^3$). We also kept constant the extraction conditions (40 ºC and 30 MPa), the oil separation conditions (60 ºC and 8 MPa), the annual plant occupancy factor (continuous 24 h/day during 300 day/year), and the geometry and packing of the substrate. We assumed pre-pressed pellets of 5-mm diameter and 20-mm length, having an equivalent diameter (the diameter of the sphere having the same ratio of external surface-to-volume as the pellets) of $d_{SV} = 6.67$ mm, a bulk density of $\rho_b = 500$ kg/m$^3$, and a bed porosity $\epsilon_b = 0.6$. On the other hand we used mass flow rates ($Q$) in the 2400-to-6000 kg/h of CO$_2$ range, which resulted in superficial solvent velocities in the recommended interval of $2 \leq U \leq 5$ mm/s [12]. Table 1 summarizes the independent variables of the problem.

The simulation program was run using cycle times that dependent on the number of the extraction vessels and the mass flow rate of CO$_2$ so as to achieve all yields of $\geq$95% of oil.

**Table 1.** Dimensions of extraction vessels in the SCFE plants as a function of vessel number.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$L/D$ (-)</th>
<th>$L$ (m)</th>
<th>$V$ (m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>8</td>
<td>5.5</td>
<td>2.0</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>4.1</td>
<td>1.5</td>
</tr>
</tbody>
</table>

**Model parameters**

Based on the work of del Valle et al. [9] we assumed that the vegetable substrate (pre-pressed rapeseed) contained $C_o = 200$ g oil/kg substrate. For the estimation of the physical properties of the loaded SC-CO$_2$ phase, we neglected the effect of the dissolved lipids on the density ($\rho$) and viscosity ($\mu$) of the SC-CO$_2$ at process temperature and pressure conditions (40 ºC and 30 MPa), which we estimated using NIST Standard Database v5.0 [13] for CO$_2$ ($\rho = 910$ kg/m$^3$ and $\mu = 9.38 \times 10^{-5}$ Pa•s). On the other hand, we estimated the effective diffusivity of the oil in the solid matrix ($D_e = D_{12} F$) using the microstructural correction factor ($F = 0.172$) reported by del Valle et al. [9] and the binary diffusion coefficient $D_{12}$ of the oil (component 2) in CO$_2$ (component 1) at process conditions. $D_{12}$, in turn, was estimated as a function of the reduced temperature ($T_r = 1.029$) and reduced density ($\rho_r = 1.943$) of the SC-CO$_2$ and the molecular weight ($MW_2 = 885$ Da) and critical volume ($V_{c2} = 3234$ cm$^3$/mol) of a typical triacyl glycerol (triolein) in vegetable oils using the equation of Catchpole and King [14] ($D_{12} = 3 \times 10^{-9}$ m$^2$/s at 40 ºC and 30 MPa). The estimated value of the effective diffusivity was $D_e = 5.16 \times 10^{-10}$ m$^2$/s. We estimated the external mass coefficient ($k_f$) using the dimensionless correlation of King and Catchpole [15] for the dimensionless Sherwood number ($Sh = k_f \ d_{SV} D_{12}^{-1}$) as a function of the dimensionless Reynolds number ($Re = \rho \ U \ d_{SV} \ \mu^{-1}$) and dimensionless Schmidt number ($Sc = \mu \ \rho^{-1} D_{12}^{-1}$). The estimated values of $k_f$ are informed in Table 2 as a function of the mass flow rate of CO$_2$. Finally, we estimated oil solubility of the oil in SC-CO$_2$ under extraction and separation conditions using the correlation of del Valle et al. [11]. This provided us with the maximal concentration of oil in the loaded SC-CO$_2$ leaving the extraction vessel in the last stage of the process ($C_{sat} = 7.92$ g oil/kg CO$_2$) and minimal concentration of the regenerated SC-CO$_2$ being recycled from the separation vessel ($C_{sep} = 0.164$ g oil/kg CO$_2$).
Table 2. Calculated external mass transfer coefficients as a function of the CO\(_2\) flow rates.

<table>
<thead>
<tr>
<th>(Q) (kg CO(_2)/h)</th>
<th>(U) (m/s × 10(^3))</th>
<th>(k_f) (m/s × 10(^5))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2400</td>
<td>2.00</td>
<td>3.05</td>
</tr>
<tr>
<td>3600</td>
<td>3.00</td>
<td>3.98</td>
</tr>
<tr>
<td>4800</td>
<td>4.00</td>
<td>4.81</td>
</tr>
<tr>
<td>6000</td>
<td>5.00</td>
<td>5.58</td>
</tr>
</tbody>
</table>

Output variables

The outputs of the simulation were the yield of oil (\(Y\), g oil/kg substrate) and the total extraction time (or cycle time \(t_c\), h) that allowed the recovery of \(\geq 95\%\) of the oil in the pre-pressed substrate. With this information we determined the number of cycles per year (\(N_c\)), Eqn. 1, the annual production of oil (\(P\), ton oil), Eqn. 2, and the annual consumption of CO\(_2\) (\(M_{\text{CO}_2}\), ton CO\(_2\)), Eqn. 3. For the purpose of estimating \(M_{\text{CO}_2}\) we assumed that 50% of the CO\(_2\) which can be contained in the void volume of an extraction vessel was lost in each cycle, which would happen if the new vessel coming into the process were pressurized by expanding the fluid phase of the exhausted vessel leaving the process, prior to the decompressing / unloading / loading / recompressing stage. Considering that \(\rho_b = 500\) kg/m\(^3\), \(\rho = 910\) kg/m\(^3\), \(y\) \(\varepsilon_b = 0.6\), Eqs. 1-3 were as follows:

\[
N_c = \frac{7200 \times n}{t_c} \tag{1}
\]

\[
P = N_c \times V \times \rho_b \times Y = 3.6 \times n \times V \times Y \times t_c \tag{2}
\]

\[
M_{\text{CO}_2} = \frac{N_c \times V \times \varepsilon_b \times \rho}{2} = 983 \times n \times V \times \frac{t_c}{t_c} \tag{3}
\]

RESULTS AND DISCUSSION

Tables 3 summarizes the results for the SCFE plant having three extraction vessels \((n = 3)\), each with a capacity of two cubic meters \((V = 2\) m\(^3\)). In the table, \(t_{95\%}\) represents the time required to recover 95% of the oil \((190\) g oil/kg substrate) when using as the solvent a CO\(_2\) stream containing \(C_{\text{sep}} = 0.164\) g/kg of oil. This level of residual oil is the expected for the recycled CO\(_2\) stream coming from a separator operating at 60 °C and 8 MPa. Thus, \(t_{95\%}\) represents the shortest possible cycle time that would allow recovering 95% of the oil in pre-pressed rapeseeds when using an SCFE plant having one or two extraction vessels. Such types of plants, however, cannot take advantage of the simulated counter-current contacting mode between the solid substrate and the continuously flowing SC-CO\(_2\) stream that can be achieved in commercial-scale multi-vessel SCFE plants having three or more extraction vessels. The actual cycle time \(t_c\) was about 50% longer than \(t_{95\%}\) and this is due to the fact that during half of the extraction period the substrate is extracted with a CO\(_2\) stream containing \(\geq 0.164\) g/kg of oil, because it picked some oil when passing though a vessel containing a more exhausted substrate. The annual oil productivity of the three-vessel plant increased from 160 to 184 ton (an increment of about 15%) when the mass flow rate of CO\(_2\) increased from 2400 to 6000 kg/h due partially a reduction in the external mass transfer coefficient (cf. Table 2). Most benefits of an improved external mass transfer occur in the initial stages of the extraction
Table 3. Annual oil productivity and CO₂ consumption of three-vessel SCFE plants as a function of mass flow rate of CO₂.

<table>
<thead>
<tr>
<th>Q (kg CO₂/h)</th>
<th>t₉₅% (h)</th>
<th>tₑ (h)</th>
<th>Nₑ (-)</th>
<th>P (ton oil)</th>
<th>M₃CO₂ (ton CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2400</td>
<td>9.0</td>
<td>13.5</td>
<td>1600</td>
<td>160</td>
<td>874</td>
</tr>
<tr>
<td>3600</td>
<td>7.0</td>
<td>10.5</td>
<td>2057</td>
<td>165</td>
<td>1124</td>
</tr>
<tr>
<td>4800</td>
<td>5.5</td>
<td>8.3</td>
<td>2618</td>
<td>183</td>
<td>1430</td>
</tr>
<tr>
<td>6000</td>
<td>4.7</td>
<td>7.1</td>
<td>3064</td>
<td>199</td>
<td>1673</td>
</tr>
</tbody>
</table>

process, and there is virtually no benefit when the rate is controlled internally in the final stages of the extraction process. Moreover, the increment in oil productivity is associated with an increase in the capital and operational cost because of the larger solvent recycling capability. This was not accounted for in this work. Not only did the productivity of oil increase but also the consumption of CO₂, with an associated increment in the operational costs, when the mass flow rate increased. Indeed, there was not a proportional increment in CO₂ consumption, which increased from 5.4 to 8.4 ton/ton oil (an increment of about 54%) when the mass flow rate of CO₂ increased from 2400 to 6000 kg/h.

Tables 4, on the other hand, summarizes the results for the SCFE plant having four extraction vessels (n = 4), each with a capacity of one and a half cubic meters (V = 1.5 m³). Observations derived from the analysis of Table 4 for a four-vessel plant are similar of those made about Table 3 for a three-vessel plant. In this particular case, the actual cycle time tₑ was about 32-34% longer than t₉₅%, and the improvement compared to previous case is due to a contacting between the solid substrate and the continuously flowing SC-CO₂ stream more closely resembling a true counter-current contact, as expected for an increase in the number of extraction vessels. The productivity of oil of the four-vessel SCFE plant increased from 334 to 401 ton (an increment of about 20%) but the consumption of CO₂ increased from 4.9 to 7.9 ton/ton oil (an increment of about 64%) when the mass flow rate of CO₂ increased from 2400 to 6000 kg/h. This suggests a more positive effect of the CO₂ flow rate as the number of extraction vessels in the SCFE plant increases, probably because when the contacting mode is more nearly counter-current, it is possible to take advantage of the improved extraction rates during the externally-controlled period to a greater extent. Overall, a switch from three to four extraction vessels in the SCFE plant increased oil productivity about 100-110% when keeping constant the mass flow rate of CO₂. It is interesting to compare a SCFE plant for n = 3 and Q = 6000 kg/h of CO₂ (least external resistance to mass transfer) with the one for n = 4 and Q = 2400 kg/h of CO₂ (more nearly counter-current contacting between the solid substrate and the SC-CO₂) because of a similar consumption of CO₂ in the two cases. It can be observed that the productivity of oil in is about 100% larger in the four- than the three-vessel plant, which should have smaller operational and capital costs for the solvent recycling part of the plant, at the expense of a larger capital cost for the extraction part of the plant.

We are currently extending the use of our computational tool to five- and six-vessel SCFE plants, which will allow us to reviews the length-to-diameter ratio of the vessels up to the lowest recommended value L/D = 4 [12]. In parallel, we are computing the energy requirements of the process, and collecting information for sizing and costing the various components of the plants. This will allow us drawing maps of productivity of oil and consumption of CO₂ and other consumables (electrical power, steam, cooling water) as a function of plant configuration. We envision using this information for the optimization of the
Table 4. Annual oil productivity and CO₂ consumption of four-vessel SCFE plants as a function of mass flow rate of CO₂.

<table>
<thead>
<tr>
<th>Q (kg CO₂/h)</th>
<th>t₉₅% (h)</th>
<th>tᶜ (h)</th>
<th>Nᶜ (-)</th>
<th>P (ton oil)</th>
<th>M₃₀₂ (ton CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2400</td>
<td>5.5</td>
<td>7.3</td>
<td>3927</td>
<td>334</td>
<td>1608</td>
</tr>
<tr>
<td>3600</td>
<td>4.3</td>
<td>5.7</td>
<td>5023</td>
<td>352</td>
<td>2057</td>
</tr>
<tr>
<td>4800</td>
<td>3.5</td>
<td>4.7</td>
<td>6171</td>
<td>370</td>
<td>2527</td>
</tr>
<tr>
<td>6000</td>
<td>2.8</td>
<td>3.7</td>
<td>7714</td>
<td>401</td>
<td>3159</td>
</tr>
</tbody>
</table>

process from and economical standpoint. Indeed, the information contained in such maps could be used to assess the total (investment plus 15 year-processing) cost of the different SCFE plants, to compare the alternatives, and to determine what plant configuration is the best.

Acknowledgements. This work was funded by Fondecyt (project 108-0211) from Chile.

REFERENCES