Application of Serially-Interconnected Perfectly-Mixed Tanks Model to Dense-Gas Extraction of Plants

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Serially-Interconnected Perfectly-Mixed Tanks mathematical model is used in an attempt to explain the release mechanism of extractable compounds from plant matrices during supercritical-fluid extraction. Plant cells, taken as perfectly-mixed tanks, are assumed to contain most of the extractable solute in a free-liquid state, while the rest of the extractable solute is considered as adsorbed species on the cell walls. Through permitting partial bypass of the dense-gas solvent phase it is shown that the final yield of the extracted solute may be independent of the total mass of solvent used during extraction.

Introduction

Mathematical models have been suggested in literature to study the extraction of essential oils, valuable or hazardous components from solid-like natural matrices with Supercritical Fluids (SF), which has mostly been the subject of experimental investigations [1,2]. Most of these mathematical models consist of the equations used in modeling of the conventional adsorption, desorption, and extraction operations. However, straightforward extensions of such models for application to SF extraction (leaching) of natural matrices do not capture some important phenomena occurring in the distinct regions of an extractor filled with complex natural matrices; such as the interparticle or intraparticle zones. The Serially-Interconnected Perfectly-Mixed Tanks (SI-PMT) model [3], makes it possible to consider extractable components existing in a free-liquid state in cellular-structured natural bodies in addition to the commonly accepted adsorbed state on solid-like walls.

In the SI-PMT model, the release phenomenon arising during SF extraction from plant matrices is modeled as PMT, containing the extractable solute both in a free-liquid state and also as adsorbed species on the cell walls. The model permits partial bypass of the solvent (dense-gas) phase, thus allowing a combination of various stream types, hence permitting the model to be used for various extraction scenarios. Using this model it is possible to consider dense-gas solvent streams entering each individual cell as fresh feeds and as outputs of the previous cell, or to assume that some portion of a stream after exiting a PMT bypasses the succeeding cells.

This study aims to show that, by permitting the dense-gas solvent to bypass a portion of the plant cells, the SI-PMT model can simulate an experimental conclusion [4] that the final yield of the extracted solute may be independent of the total mass of solvent used during extraction.

Modeling

Fig.1 depicts a single PMT where solute(s) is accessible both in a free-liquid state in the cell and also in an adsorbed state on the walls of the plant cell. Initially, at the beginning of extraction, it is assumed that the solute loadings (adsorbed amount) on the cell walls in the liquid and gas phases are equal to their respective equilibrium (adsorption equilibrium) loadings corresponding to the liquid- and gas-phase solute concentrations. During extraction, the extractable components in an adsorbed state could be desorbed both in the dense-gas and liquid phases. On the other hand, solute, present as a free-liquid, can only be extracted in the liquid phase. These competing mass-transfer mechanisms; extraction from the liquid phase and desorption from the cell walls, determine the concentration of the compounds in the solvent phase leaving a PMT.

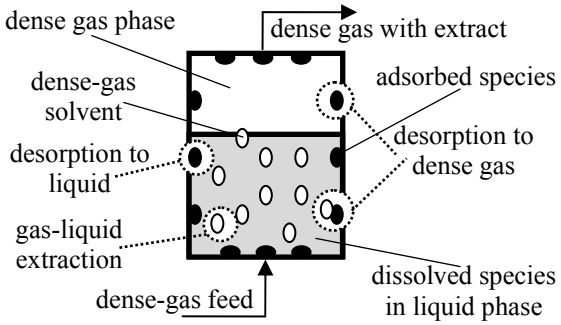


Figure 1. A single plant cell represented as a PMT.

The SI-PMT model could be represented as in Fig.2 for *n* stages, permitting combinations of various stream types entering and leaving the plant cells. It is evident from Fig.2 that means of transport between the PMTs is quite flexible and the solvent phase may enter each cell directly as fresh feed or as a product of the preceding cell. Once out of a PMT, the stream may leave the extracted body as is, or re-enter another PMT, possibly only partially.

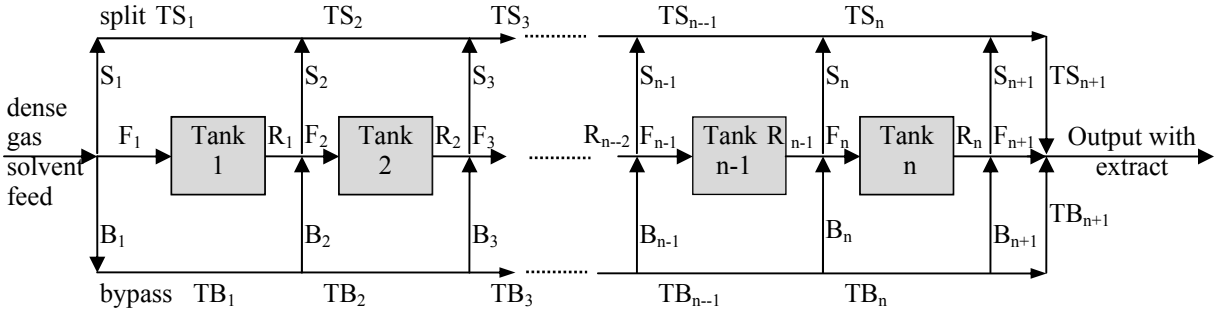


Figure 2. The Serially-Interconnected Perfectly-Mixed Tanks (SI-PMT) representation.

During the extraction and desorption process, the cell liquid volume may decrease due to depletion of the solute in the free-liquid state. This effect may be taken into consideration as:

$$V_{L(i)} = f\left(c_{L(i)}, c^{o}_{L(i)}, V^{o}_{L(i)}\right) \tag{1}$$

Fresh solvent entering a cell, B_i, and the split which leaves the cell, S_i, are a fraction of the main bypass stream, TB_i, and output of the previous PMT, R_{i-1}, respectively:

$$B_{i+1} = b\,TB_i \qquad S_{i+1} = s\,TS_i \tag{2}$$

The input stream of a PMT, F_i, is a combination of the output stream of the previous one, R_{i-1}, fresh solvent added to the system, B_i, and the split which leaves the system, S_i.

$$F_i = R_{i-1} + B_i - S_i \tag{3}$$

During the extraction and desorption process the main bypass stream, TB_i, decreases and the main split stream, TS_i, increases continuously.

$$TB_i = TB_{i-1} - B_i \qquad TS_i = TS_{i-1} + S_i \tag{4}$$

The model equations representing stage *i* in Fig.2 are given as:

Mass balance for the solute over the solvent phase:

$$\begin{aligned} V_{G(i)}\frac{dc_{G(i)}}{dt} &= F_i c^{i}_{G(i)} - R_i c_{G(i)} \\ &+ K_{OGL} a_{GL} V_T\left(c^{*}_{G(i)} - c_{G(i)}\right) \\ &- K^{P}_{SG} a_{SG} V_T\left(q^{*}_{G(i)} - \overline{q}_{G(i)}\right) \\ &+ c_{G(i)}\frac{dV_{L(i)}}{dc_{L(i)}}\frac{dc_{L(i)}}{dt} \end{aligned} \tag{5}$$

Mass balance for the solute over the stationary liquid phase:

$$\begin{aligned} \left(V_{L(i)} + c_{L(i)}\frac{dV_{L(i)}}{dc_{L(i)}}\right)\frac{dc_{L(i)}}{dt} = \\ - K_{OGL} a_{GL} V_T\left(c^{*}_{G(i)} - c_{G(i)}\right) \\ - K^{P}_{SL} a_{SL} V_T\left(q^{*}_{L(i)} - \overline{q}_{L(i)}\right) \end{aligned} \tag{6}$$

Mass balance for the solute over the cell walls in contact with the gas phase:

$$\begin{aligned} V_{G(i)}\frac{d\overline{q}_{G(i)}}{dt} &= K^{P}_{SG} a_{SG} V_T\left(q^{*}_{G(i)} - \overline{q}_{G(i)}\right) \\ &+ \overline{q}_{G(i)}\frac{dV_{L(i)}}{dc_{L(i)}}\frac{dc_{L(i)}}{dt} \end{aligned} \tag{7}$$

Mass balance for the solute over the cell walls in contact with the liquid phase:

$$\begin{aligned} V_{L(i)}\frac{d\overline{q}_{L(i)}}{dt} &= K^{P}_{SL} a_{SL} V_T\left(q^{*}_{L(i)} - \overline{q}_{L(i)}\right) \\ &- \overline{q}_{L(i)}\frac{dV_{L(i)}}{dc_{L(i)}}\frac{dc_{L(i)}}{dt} \end{aligned} \tag{8}$$

The gas-liquid phase equilibrium is defined as:

$$c^{*}_{G(i)} = \frac{\alpha_0 c_{L(i)}}{1 + \alpha_1 c_{L(i)}} \tag{9}$$

The gas- and liquid-phase adsorption equilibria are defined as:

$$q^{*}_{L(i)} = \frac{\beta_0 c_{L(i)}}{1 + \beta_1 c_{L(i)}} \qquad q^{*}_{G(i)} = \frac{\chi_0 c_{G(i)}}{1 + \chi_1 c_{G(i)}} \tag{10}$$

Comparison with Experimental Results

An earlier experimental work [4] was concerned with the supercritical-CO_2 extraction of spearmint oil *(Mentha Spicata)* from Turkish mint-plant leaves in a 600 cm^3 basket-type extractor. The amount of sample was 125 g and via water distillation in a Clevenger apparatus it was determined that the oil content was about 1.5 cm^3. Extraction experiments were carried out at 40 and 60^{o}C temperature levels, within the 8-11 MPa pressure range, and for 1, 2, and 4 h extraction times. One of the conclusions of the study was that rather than the *total mass of the solvent* (CO_2) used, the *extent of extraction* was the dominating variable on the relative (relative to water distillation) volumetric essential-oil yields observed. Fig.3 shows the relative oil yields against the total mass of CO_2 used at different extraction conditions. The figure reveals that, at fixed temperature and pressure, the relative yields at constant extraction times form clusters even though in

some *time clusters* the total mass of solvent used varies significantly.

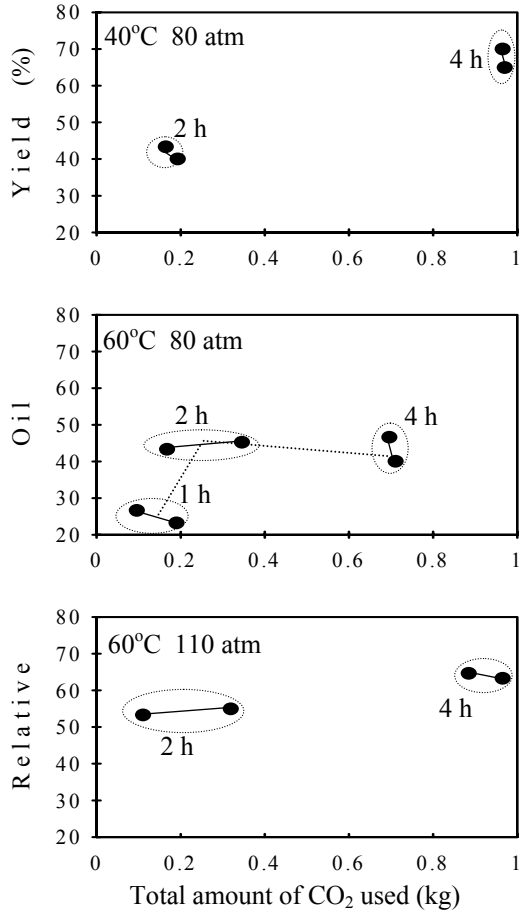


Figure 3. Relationship among relative essential-oil yield, extent of extraction, and total mass of solvent used in experiments [4].

Fig.4 shows the simulated relationship among the relative essential-oil yield, extent of extraction, and total mass of solvent used as obtained from the SI-PMT model, some parameters of which are listed in Table 1. The experimental (Fig.3) and the simulated (Fig.4) *relative-oil-yield* values are qualitatively analogous: In Fig.3, the yields represent the per cent of the accessible oil extracted via the SF solvent and were determined by comparing the volumes of the essential oil obtained in the Clevenger apparatus before and after the SF extraction. Similarly, in Fig.4, the yields represent the per cent of the oil (treated as a single solute) extracted and were determined by comparing the initial amount of the oil (solute) that was distributed equally over *n* stages and the total amount of the solute collected (integral sample) from the output of the cells (Fig.2) within the extraction times simulated.

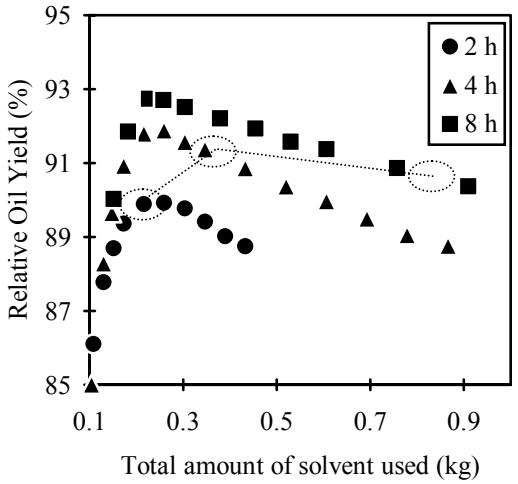


Figure 4. Relationship among relative essential-oil yield, extent of extraction, and total mass of solvent used according to the SI-PMT model (ℓ⌐◆ simulation results).

The time clusters in Fig.3, indicated by dotted ellipses, can be considered as attempts of extent-of-extraction replicates, in which some variations of solvent amount exist. In Fig.4, the time clusters indicated by dotted ellipses, analogous to those in Fig.3, can be similarly considered to embody uncertainties in adjustments or measurements of solvent amounts, or mismatch between the model and the experimental system. It is clear that the yield levels corresponding to time clusters in Fig.3, at the 60°C and 80 atm experimental conditions, and the yield levels in Fig.4 are in qualitative agreement. This agreement, that could be obtained by allowing some portion of the solvent to bypass the cells, shows that the SI-PMT model can predict the experimental behavior at the least qualitatively. Fig.4 clearly contains more detailed information which can be conveyed to Fig.3 by analogy to fill in the information gaps that are present in the experimental observations.

The maxima exist in Fig.4, in the yield values plotted against the total amount (flowrate) of solvent that was passed through the cells at constant extraction times, since as the flowrate of the solvent increases, the residence time and thus the gas-phase solute concentrations within each cell decrease away from equilibrium values. These maxima are not clear in limited experimental results (Fig.3) or can be misinterpreted as experimental error without the insight provided by the SI-PMT model.

Conclusions

The SI-PMT model helps to explain the release mechanism of solutes from plant matrices during SF extraction and its qualitative predictions can be utilized in pre- or evolutionary design of such extraction systems.

Table 1. Values of some key parameters used in the SI-PMT model simulations (Fig.4).

b	= 0	$K_{OGL}a_{GL}$	= 0.0195
$c^{o}_{L(i)}$	= 0.00336	$K^{P}_{SG}a_{SG}$	= 0.122
s	= 0.75	$K^{P}_{SL}a_{SL}$	= 0
$V^{o}_{L(i)}$	= 0.0113	β_0	= 2.919
V_T	= 0.0907	β_1	= 169.0
α_0	= 1.53	χ_0	= 2.919
α_1	= 2878.1	χ_1	= 169.0
n	= 10		

Nomenclature

a_{GL} gas/liquid interfacial area for extraction, cm^2-gas/cm^3-cell

a_{SG} gas/solid interfacial area for sorption, cm^2-gas/cm^3-cell

a_{SL} liquid/solid interfacial area for sorption, cm^2-liquid/cm^3-cell

b bypass coefficient

B_i bypass stream entering i^{th} cell, cm^3-gas/s

$c_{G(i)}$ gas-phase concentration of solute in i^{th} cell, g/cm^3-gas

$c_{L(i)}$ liquid-phase concentration of solute in i^{th} cell, g/cm^3-liquid

$c^{*}_{G(i)}$ gas-phase concentration of solute in equilibrium with liquid-phase concentration in i^{th} cell, g/cm^3-gas

$c_{Gin(i)}$ gas-phase concentration of solute in i-1^{th} cell, g/cm^3-gas

$c^{0}_{L(i)}$ initial liquid-phase concentration of solute in i^{th} cell, g/cm^3-liquid

F_i input stream of i^{th} cell, cm^3-gas/s

K_{OGL} overall gas/liquid mass-transfer coefficient, cm/s

K^{P}_{SG} solid/gas mass-transfer coefficient, cm/s

K^{P}_{SL} solid/liquid mass-transfer coefficient, cm/s

n number of cells (tanks)

$\bar{q}_{G(i)}$ average adsorbed-phase concentration from gas phase in i^{th} cell, g/cm^3-gas

$\bar{q}_{L(i)}$ average adsorbed-phase concentration from liquid phase in i^{th} cell, g/cm^3-liquid

$q^{*}_{G(i)}$ equilibrium loading from gas phase in i^{th} cell, g/cm^3-gas

$q^{*}_{L(i)}$ equilibrium loading from liquid phase in i^{th} cell, g/cm^3-liquid

R_i output stream of i^{th} cell, cm^3-gas/s

s split coefficient

S_i split stream leaving i-1^{th} cell, cm^3-gas/s

t time, s

TB_i main bypass stream, cm^3-gas/s

TS_i main split stream, cm^3-gas/s

$V_{G(i)}$ gas volume of i^{th} cell, cm^3-gas

$V_{L(i)}$ liquid volume of i^{th} cell, cm^3-liquid

$V^{0}_{L(i)}$ initial liquid volume of i^{th} cell, cm^3-liquid

V_T total volume of the cell, cm^3-cell

α_0 coefficient of gas/liquid phase equilibrium

α_1 coefficient of gas/liquid phase equilibrium

β_0 coefficient of gas/solid sorption equilibrium

β_1 coefficient of gas/solid sorption equilibrium

χ_0 coefficient of liquid/solid sorption equilibrium

χ_1 coefficient of liquid/solid sorption equilibrium

Acknowledgment

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