THE MATHEMATICS OF MODELLING SUPERCRITICAL FLUID EXTRACTION OF ESSENTIAL OILS

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The goal of this study is to present the basic concepts of micro-scale mathematical model (MSMM) for describing the process of supercritical fluid extraction (SFE) of essential oils. The general equation of MSMM, which can be applied and valid for all the plant species, will be presented along with specific equations for the plant family, i.e. secretory structure. Four basic types of secretory structures have been identified so far and, accordingly, four different mechanisms, i.e. sets of equations, were used to describe the whole SFE process. Numerical solution of MSMM with specific constraints and initial conditions defines the concentration profiles along both the extraction vessel and secretory structure, consequently providing better understanding of the phenomenology of the SFE process. It is shown that the SFE is highly dependable on the secretory structure, i.e. its shape and location within the plant material.

INTRODUCTION

Mathematical modelling of the SFE of essential oils is being studied as long as the process itself. During the last two decades, three approaches, speaking in general terms, have been made to this subject: empirical modelling, modelling based on analogy with the process of heat transfer and modelling based on integration of differential mass balance [1]. Nowadays, the first two approaches are practically 'abandoned', and the third one is being used widely in its many forms. Sovova has postulated the most widely used model based on the concept of broken and intact cells, according to which the essential oil is located in cells within the plant material [2]. A fraction of cells, during the pre-treatment of plant material, is being broken and the essential oil becomes easily accessible to supercritical fluid (supercritical carbon dioxide – SC CO_2 is mostly used in SFE processes). The extraction of essential oil from intact cells is being carried out slowly throughout the plant material. Our group, in the last few years, tried to bring something new in the field of mathematical modelling of SFE processes [3-5]. The new mathematical model found its basis in the secretory structure of the plant material, i.e. the location of essential oil within the plant material. Four different secretory structures have been identified: glandular trichomes, secretory ducts, secretory cavities and secretory cells, and for each of them the phenomenology of the SFE process has been described previously [6]. In this work we present the mathematical tool used for solving equations that are describing the SFE process from above mentioned secretory structures.

MATERIALS AND METHODS

The general equation of the new mathematical model, i.e. the mass balance for the extractor vessel is:

$$\frac{\partial c^{sf}}{\partial t} = D_l \frac{\partial^2 c^{sf}}{\partial x^2} - u \frac{\partial c^{sf}}{\partial x} + ST \qquad (1)$$

where *ST* is the Source and Transfer term which describes essential oil transfer from specific secretory structure to supercritical fluid phase. In Table 1, Source and Transfer term is presented for each specific type of secretory structure.

The corresponding initial and boundary conditions are:

$$t = 0, \quad 0 \le x \le L, \quad c^{sf} = 0 \qquad (2)$$

$$t > 0, \quad x = 0, \quad c^{sf} = 0 \qquad (3)$$

$$t > 0, \quad x = L, \quad \partial c^{sf} / \partial x = 0 \qquad (4)$$

Table 1. Source and Transfer term for each type of secretory structure

Secretory structure	Source and Transfer term
Glandular trichomes (peltate glands)	$N\phi ak(c^* - c^{sf})$ for $t \le t_d$ (5) $N\phi ak(c^* - c^{sf}) + N(1-\phi)\varphi ak(c^* - c^{sf}) + N(1-\phi)(1-\varphi)a_{nd}\frac{3}{R_{nd}}D_m(c - c^{sf})$ for $t>t_d$ (6)
Secretory ducts	$a_w k(c^* - c^{sf})$ for $t \le t_w$ (7) $a_d k(c^e - c^{sf})$ for $t>t_w$ (8)
Secretory cavities and cells	$a_w k(c^* - c^{sf})$ for $t \le t_w$ (9) $Ma_c \frac{\bar{D_m}}{\delta}(c - c^{sf})$ for $t>t_w$ (10)

For each type of secretory structure another differential equation(s), describing the secretory structures behaviour during the process of SFE, needs do be solved along with equation (1). These equations, along with notation are listed below.

Glandular trichomes (peltate glands)	$-\frac{dR}{dt} = \frac{k}{c_{sat}}(c^* - c^{sf})$ for $t \le t_d$ (11) $-\frac{dc}{dt} = \frac{D_m}{4\pi R_{nd}^2}(c - c^{sf})$ for $t>t_d$ (12)
Secretory ducts	$-\frac{dR}{dt} = \frac{k}{c_{sat}}(c^* - c^{sf})$ for $t \le t_w$ (13) $-D_{12}\frac{dc^d}{dz} = k(c^e - c^{sf})$ for $t>t_w$ (14)
Secretory cavities and cells	$-\frac{dR}{dt} = \frac{k}{c_{sat}}(c^* - c^{sf})$ for $t \le t_w$ (15) $-\frac{dc}{dt} = \frac{3K\delta}{R^2}(c - c^{sf})$ for $t>t_w$ (16)

Notation

a specific surface of disrupted peltate gland referred to SC fluid volume, m^2/m^3

a_c specific surface of secretory structure referred to SC fluid volume, m^2/m^3

a_d specific surface of open duct ends available for mass transfer referred to SC fluid volume, m^2/m^3

a_{nd} specific surface of nondisrupted peltate gland containing essential oil saturated with CO_2 referred to SC fluid volume, m^2/m^3

a_R specific surface of the oil sphere reffered to SC fluid volume, m^2/m^3

a_w specific surface of wetted particles referred to SC fluid volume, m^2/m^3

c essential oil concentration in undisrupted secretory structure, $kmol/m^3$

c^e essential oil concentration in SC phase at the duct end, $kmol/m^3$

c^* concentration of the essential oil in SC CO_2 on SC phase-essential oil interface, $kmol/m^3$

c^{sf} essential oil concentration in supercritical phase, $kmol/m^3$

c_{sat} essential oil concentration in oil sphere of disrupted secretory structure saturated with carbon dioxide, $kmol/m^3$

c^d essential oil concentration in SC phase inside the duct, $kmol/m^3$

d_c secretory cell or cavity diameter, m

d_p plant particle diameter, m

$\overline{D}_m$ average diffusivity of the essential oil in plant material, m^2/s

D_l axial dispersion coefficient, m^2/s

D_m diffusivity of the essential oil in the nondisrupted stretched peltate gland membrane, m^2/s

D_{12} binary diffusivity of essential oil – SC CO_2 system, m^2/s

k mass transfer coefficient, m/s

K average value of mass transfer coefficient through the solid phase, m/s

M total number of secretory cavities or cells

N total number of peltate glands

R_d radius of the oil sphere from disrupted secretory structure (dependant on time and position), m

R_{nd} radius of the nondisrupted peltate gland, m

R radius of nondisrupted secretory structure in which the essential oil is saturated with CO2, m

t time, s

t_d time when peltate glands disruption caused by CO_2 dissolving occurs, s

t_w time when the oil that embedded the particles is extracted, s

u superficial SC fluid velocity, m/s

x axial coordinate along the extractor bed, m

Greek letters

δ difference between particle radius and secretory structure radius, m

ϕ fraction of peltate glands disrupted during the grinding pretreatment

φ fraction of peltate glands nondisrupted during grinding pretreatment which are disrupted by CO_2 dissolving

The above equations were solved numerically, using the explicit form of the finite difference method [7]:

$$\frac{\partial y}{\partial t} = \frac{y_{i,j+1} - y_{i,j}}{\Delta t} \quad (17),$$

$$\frac{\partial y}{\partial x} = \frac{y_{i+1,j} - y_{i-1,j}}{2\Delta x} \quad (18),$$

$$\frac{\partial^2 y}{\partial x^2} = \frac{y_{i+1,j} - y_{i,j} + y_{i-1,j}}{(\Delta x)^2} \quad (19).$$

where y is the dependable variable, i.e. c^{sf}, R, c and c^d.

Defining $\lambda=\Delta t/(\Delta x)^2$, the sufficient condition for convergence of the explicit method is $0<\lambda\leq 1/2$. Therefore, the condition for convergence can be met by appropriate choice of values of spatial and time increments.

The equations are solved in FORTRAN, dividing the extractor vessel into twenty and extraction time into ten thousand increments, solving the equations for each one of them. An algorithm is shown below for mathematics of SFE from secretory ducts.

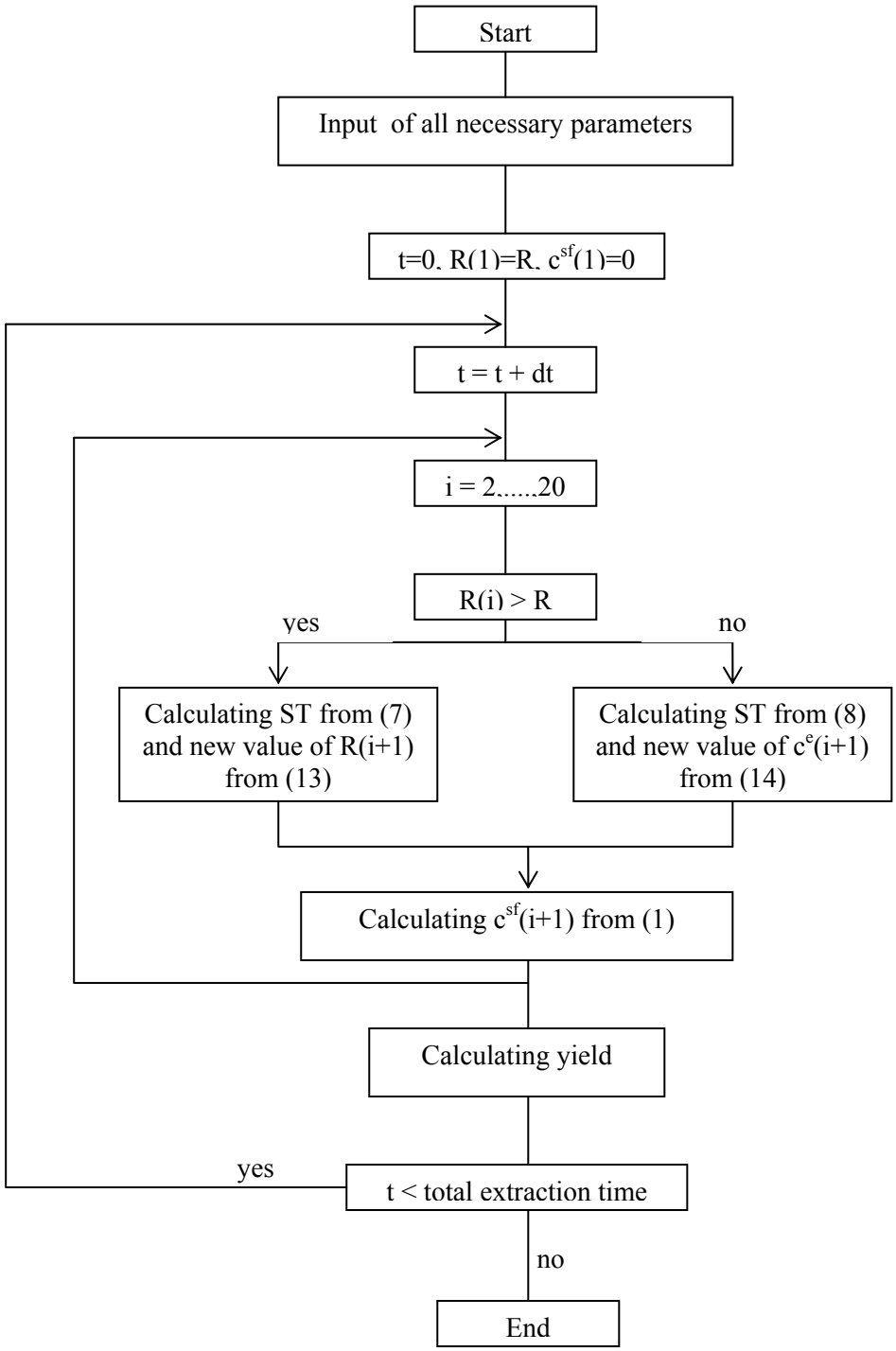

Figure 1. Algorithm for solving equations of the mathematical model for SFE from secretory ducts.

RESULTS AND DISCUSSION

The results of applying the described mathematical tools on experimental results of some SFE processes, involving all types of secretory structures, are shown in Figure 2 It is clear, in figures a, c and d, that the chosen processes of SFE are simulated with high accuracy, proving the validity of the new mathematical model and the tools used. Figure b shows concentration profiles along the extractor in different extraction times for SFE from rosemary leaves, pointing out the mechanism of the process. It is worthy noticing that, in comparison with previous models, additional parameters such as secretory structure dimensions are introduced in order to obtain better description of the phenomenology of the SFE process

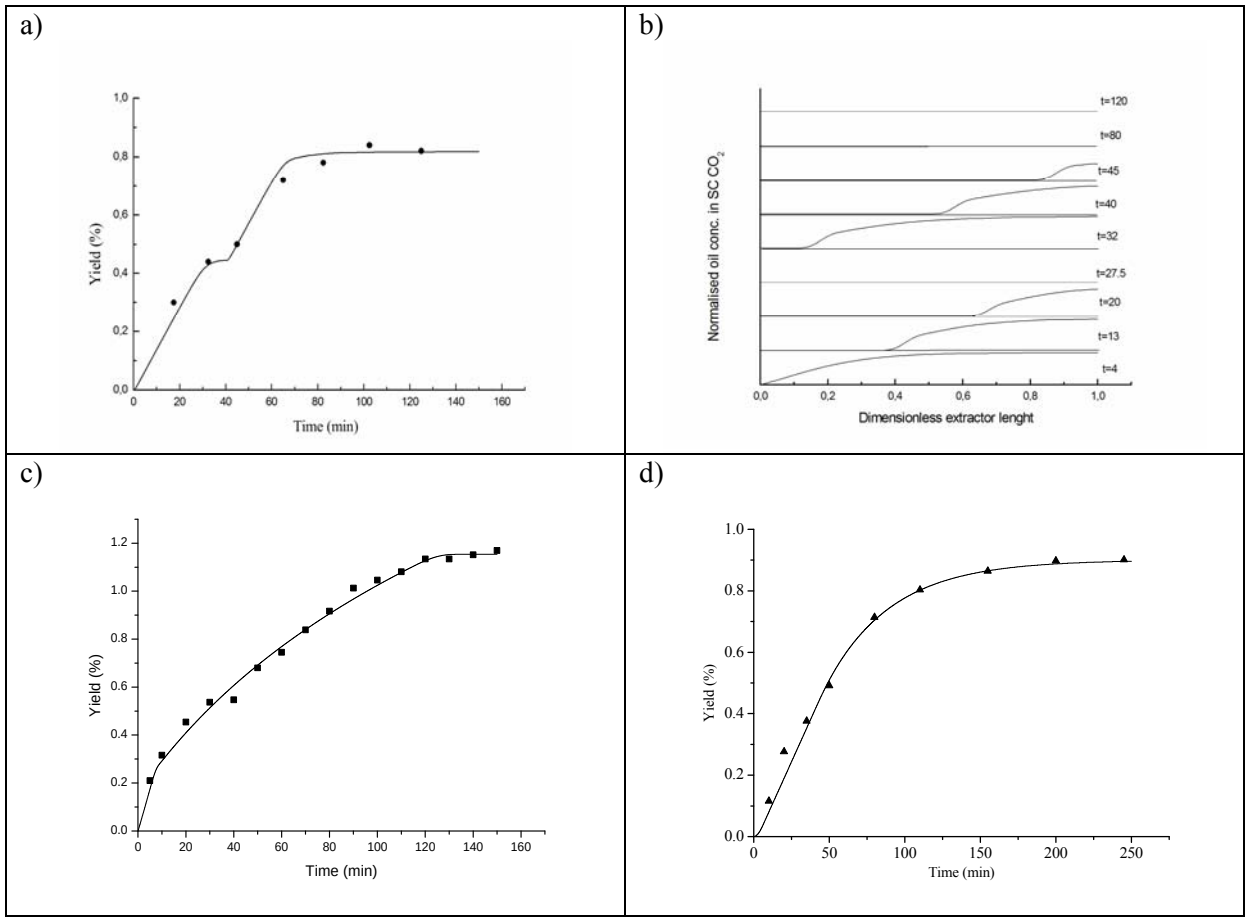

Figure 2. Examples of successful application of described mathematical tools: a) SFE from rosemary leaves (glandular trichomes, experimental results of Reverchon et al. [8]), b) Concentration profiles along the extractor in different extraction times for SFE from rosemary leaves, c) SFE from carrot seed (secretory ducts, experimental results [9]), d) SFE from valerian root (secretory cells, experimental results [10])

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