# SWELLING OF PLANT MATERIAL AND SFE PROCESS OPTIMIZATION

I. Zizovic[1,*], R. Eggers[2], H. Heinrich[2], P. Jaeger[3], M. Stamenić[1], J. Ivanović[1], and D. Skala[1,4]

[1] *Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia*
[2] *Hamburg University of Technology, Institute of Thermal Process Engnineering Heat and Mass Transfer D - 21071 Hamburg, Germany*
[3] *Eurotechnica GmbH, An den Stücken 55, D-22941 Bargteheide, Germany*
[4] *Texas A&M at Qatar, Education City, PO Box 23874, Doha, Qatar*
zizovic@tmf.bg.ac.yu, fax: +381 11 3370 473

The swelling behaviour of plant material was determined in two outermost cases: leaves of mint belonging to Lamiaceae family species and valerian root. Leaves of Lamiaceae family species are characterized by glandular trichomes as secretory structures which are placed on the very surface of the plant. On the other hand, root of valerian is characterized by small secretory cells placed within the plant tissue. Possibility to optimize process of supercritical extraction on the basis of obtained results was investigated as well. In the case of mint, hyssop and wild thyme leaves, it was proven that the exposure to supercritical carbon dioxide as a batch before the continuous extraction would lead to faster extraction. In the case of valerian root it was shown that pressure variation, as a pretreatment before continuous extraction, enabled much faster rate of extraction. The extraction processes were modeled by the models on the secretory structure scale.

## INTRODUCTION

In process of supercritical carbon dioxide extraction from plant material, compressed gas penetrates herbaceous material dissolving part of it, which may lead to changing tissue properties and finally the plant tissue may be subject to swelling. The extent to which changes occur depends on the specific structure of plant material as well as on the operational conditions (pressure and temperature). In this work, swelling behaviour of the plant material will be investigated in two outermost cases of plant tissue structures: leaves of mint belonging to Lamiaceae family species characterized by glandular trichomes as secretory structures which are placed on the very surface of plant and valerian root characterized by small secretory cells placed within the plant material.

## MATERIALS AND METHODS

Dry leaves of mint (*Mentha piperita*), hyssop (*Hyssopus officinalis*) and wild thyme (*Thymus serpulum*) as well as dry root of valerian (*V. officinalis* L - cultivar Arterner züctung) grown in northern Serbia, were used for experimental studies. The species were examined in the Institute for Medicinal Plant Research «Dr Josif Pančić» (Belgrade, Serbia). Commercial carbon dioxide (99% purity, Tehno-gas, Novi Sad, Serbia) was used for the extractions.

Swelling of plant tissues was detected optically inside a high-pressure view chamber [1]. Dry leaves of mint and dry valerian root were examined. A relative size change ($d/d_0$) of the plant material was determined. Swelling behavior of mint leaf was investigated at 40$^{o}$C and 10 MPa, while tests of valerian root were performed at 50 $^{o}$C and 15 MPa. Extractions with supercritical $CO_2$ were carried out in the Autoclave Engineers Screening System previously described [2]. SFE from Lamiaceae family species (mint, hyssop and wild thyme) were

carried out at  at 40°C and 10 MPa. Extractions from valerian root were carried out at 50°C and 15 MPa.

For the purpose of mathematical modeling, previously published mathematical models on the secretory structure scale were applied [3-5]. Material balance for the supercritical phase in the extractor vessel, for isothermal and isobaric system can be written as:

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

where $c^{sf}$ is the essential oil concentration in supercritical phase, $t$ is the extraction time, $x$ is the axial coordinate along the extractor, $D_l$ is axial dispersion coefficient, $u$ is superficial supercritical fluid velocity and $ST$ the is Source and Transfer term which describes essential oil transfer from specific secretory structure to supercritical fluid phase. The corresponding initial and boundary conditions are:

$$t = 0, \quad 0 \le x \le \mathrm{L}, \quad c^{sf} = 0 \qquad (1a)$$

$$t > 0, \quad x = 0, \quad c^{sf} = 0 \qquad (1b)$$

$$t > 0, \quad x = \mathrm{L}, \quad \frac{\partial c^{sf}}{\partial x} = 0\,. \qquad (1c)$$

where L is the extractor length.

According to the basic hypothesis of the models, mathematical equations describing the Source and Transfer terms ($ST$) for glandular trichomes (peltate glands) and secretory cells as secretory structures are presented in Table 1. The Eq. (1) was solved using the Finite Difference Method in Explicit form [6]. For this purpose the extractor was divided into twenty space increments.

Table 1. Source and Transfer term for SFE from peltate glands and secretorz cells

| Secretory structure | $ST$ |
|---|---|
| Glandular trichomes (peltate glands) | Previously published model [3] was applied for the SFE from peltate glands with pretreatment: $N\theta ak(c^* - c^{sf}) + N(1-\theta)a_{nd}\frac{3}{R_{nd}}D_m(c - c^{sf})$ and $\theta = \frac{\phi N + (1-\phi)\varphi N}{N}$ Improved model [4] was applied for SFE without pretreatment: $N\phi ak(c^* - c^{sf}) + N(1-\phi)\varphi ak(c^* - c^{sf}) +$ $N(1-\phi)(1-\varphi)a_{nd}\frac{3}{R_{nd}}D_m(c - c^{sf})$ Experimentaly determined function $\varphi$ [4] dependent on time was adopted for this study. |
| Secretory cavities and cells for $d_c \prec d_p$ | Previously published model [5] was applied for SFE from secretory cells with and without pretreatment: $a_R MPk(c^* - c^{sf}) + M(1-P)a_c K(c - c^{sf})$ |

RESULTS

The investigated leaves and root behaved in a different way with respect to swelling in supercritical carbon dioxide. The detected relative size change ($d/d_0$) of the plant material is presented in Fig. 1. While the mint leaves were swollen to almost 30% after 1 hour from the moment of pressurization, the valerian root nearly maintained its shape but showed considerable swelling during pressure release after six hours of exposure to supercritical carbon dioxide.

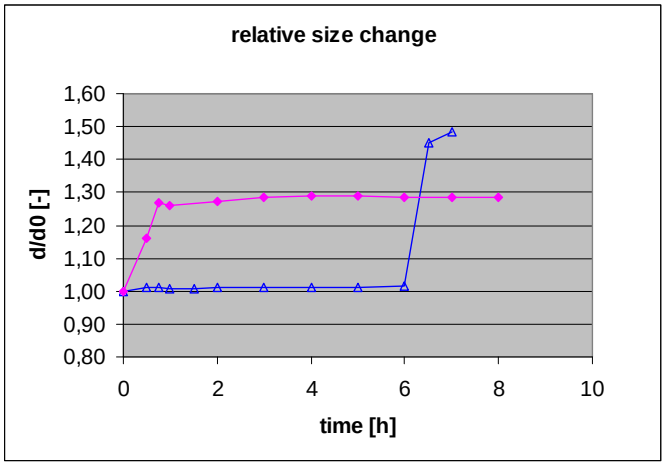


Fig. 1. Relative change in thickness of the mint leaf (◊) at 40°C and 10 MPa and valerian root (Δ) at 50°C and 15 MPa.

On the basis of the swelling behaviour, processes of supercritical extraction were optimized. In the case of SFE from Lamiaceae family species, it was assumed that exposure of plant material to supercritical fluid at extraction conditions as a batch before the continuous SFE would lead to swelling of plant material and faster extraction. This assumption was in accordance with previous investigation of glandular trichome behavior under supercritical conditions [3]. Total yields and modeling results of SFE from mint, hyssop and wild thyme, three members of Lamiace family, at 40°C and 10 MPa with and without optimal pretreatment are presented in Figs. 2, 3 and 4 respectively. Figures 2-4 also show results of calculation performed using corresponding mathematical models. The optimal pretreatment included exposure of milled plant material to supercritical fluid at the conditions of extraction for one hour before continuous SFE. In the case of SFE from valerian root it was assumed that pressure variation from 15 MPa to 6 MPa ($CO_2$ storage tank pressure), as a pretreatment before continuous extraction, will enable much faster rate of extraction. Total yields and modeling results of SFE from valerian root at 50°C and 15 MPa with and without optimal pretreatment are presented in Fig. 5. Optimal pretreatment, in this case, included exposure of milled plant material to supercritical fluid at extraction conditions (50°C and 15 MPa) and than decompression to the storage tank pressure (50°C and 6 MPa). Pressurization to working conditions commenced 10 minutes after decompression. Continuous SFE process followed. Results of mathematical modeling are presented in Tables 2 and 3.

Table 2. Parameters of the model [3, 4] for SFE from glandular trichomes (Lamiaceae)

| **Herb** | **Pretreatment** | **Fraction of disrupted** | $k \cdot 10^5$ **(m/s)** | $D_l \cdot 10^8$ **($m^2$/s)** | $c^* \cdot 10^3$ **(kmol/$m^3$)** | $D_m \cdot 10^{11}$ **($m^2$/s)** |
|---|---|---|---|---|---|---|

| | | glands* | | | | |
|---|---|---|---|---|---|---|
| Mint | no | $\varphi = 0.40$ | 2.97 | 2.13 | 15.0 | 0.95 |
| | yes | $\theta = 0.65$ | | | | |
| Hyssop | no | $\varphi = 0.40$ | 2.91 | 2.17 | 5.0 | 0.75 |
| | yes | $\theta = 0.65$ | | | | |
| Wild thyme | no | $\varphi = 0.40$ | 3.21 | 1.83 | 5.0 | 0.85 |
| | yes | $\theta = 0.65$ | | | | |

* Fraction of disrupted peltate glands at the beginning of the SFE ($\varphi$ or $\theta$)

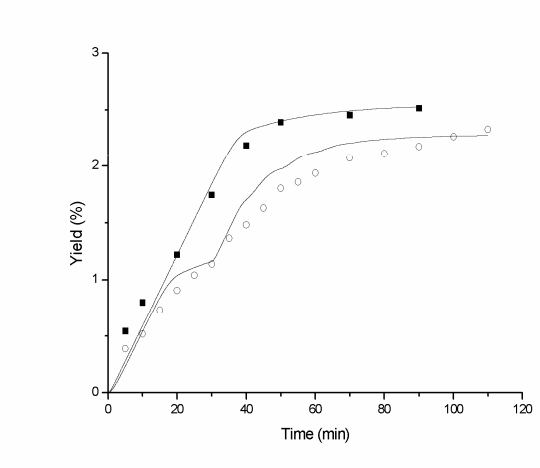


Fig. 2. SFE and modeling results for extraction from mint leaves at 10 MPa and 40°C K (○–without pretreatment, ■– with pretreatment).

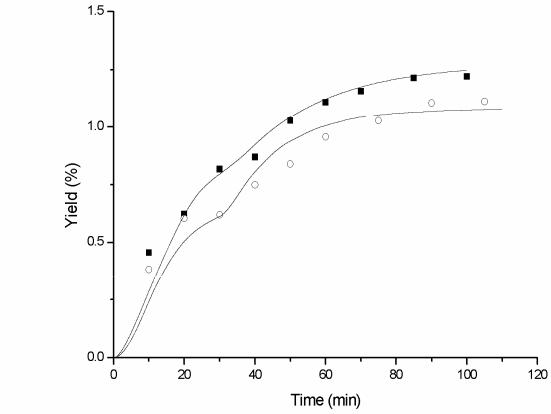


Fig.3. SFE and modeling results for extraction from hyssop leaves at 10 MPa and 40°C (○–without pretreatment, ■– with pretreatment).

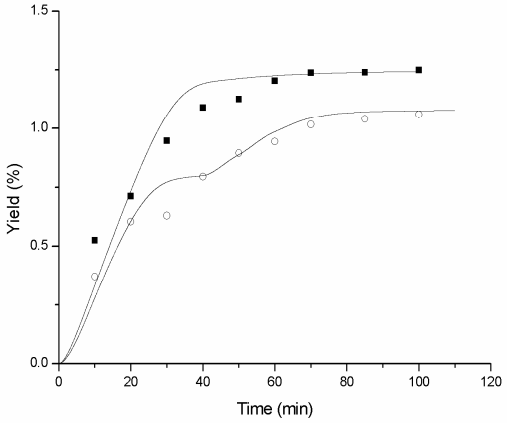


Fig. 4. SFE and modeling results for extraction from wild thyme leaves at 10 MPa and 40°C (○– without pretreatment, ■– with pretreatment).

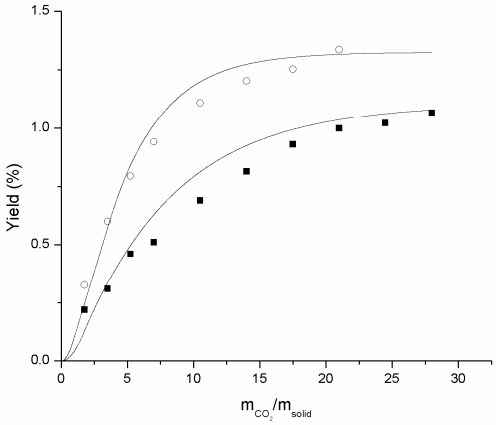


Fig. 5. Yield of total extract as a function of the specific amount of solvent $m_{CO_2}/m_{solid}$ (kg $CO_2$/ kg herbaceous material) for SFE from valerian root at 15 MPa and 50°C (■ –without pretreatment, ○ –with pretreatment).

Table 3. Parameters of the model [5] for the SFE from secretory cells (valerian root)

| **Pretreatment** | $k \cdot 10^5$, m/s | $D_l \cdot 10^7$, $m^2/s$ | $c^* \cdot 10^3$, $m^3/s$ | $K \cdot 10^{11}$, m/s | $P$ |
|---|---|---|---|---|---|
| no | 2.35 | 1.18 | 8.0 | 0.4 | 0.02 |
| yes | 2.35 | 1.18 | 8.0 | 0.7 | 0.02 |

CONCLUSION

According to the results of swelling tests, SFE results and mathematical modeling it can be concluded that in the case of Lamiaceae family leaves, exposure to supercritical carbon dioxide as a batch before the continuous extraction would lead to faster extraction. Due to the swelling of plant material, a fraction of peltate glands (which stayed untouched by grinding) was disrupted during pretreatment, leaving its oil content easy available for SFE. In the case of valerian root it was shown that pressure variation from 15 MPa to 6 MPa, as a pretreatment before continuous extraction, enabled much faster rate of extraction. Results of mathematical modeling (Table 3.) showed that the mean value of mass transfer coefficient through the solid phase (K) could be enlarged by 75% due to the swelling effect caused by the pressure variation before continuous SFE process.

ACKNOWLEDGMENTS

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**Notation**

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

$a_c$ specific surface of nondisrupted secretory cell 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 drom disrupted secretory cell to SC fluid volume, $m^2/m^3$

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

$c^*$ 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, $kmol/m^3$

$d_c$ secretory cell diameter, m

$d_p$ plant particle diameter, m

$D_l$ axial dispersion coefficient, $m^2/s$

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

$k$ mass transfer coefficient, m/s

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

$L$ length of the extractor bed, m

$M$ total number of secretory cavities

$N$ total number of peltate glands

$P$ fraction of cells disrupted by grinding

$R_{nd}$ radius of the nondisrupted peltate gland in which the essential oil is saturated

with $CO_2$, m

$t$ time, s

$u$ superficial SC fluid velocity, m/s

$x$ axial coordinate along the extractor bed, m

*Greek letters*

$\phi$ fraction of peltate glands disrupted during the grinding pretreatment

$\varphi$ fraction of peltate glands nondisrupted during grinding pretreatment which are disrupted by $CO_2$ dissolving

$\theta$ total fraction of disrupted peltate glands (due to grinding as well as due to $CO_2$ dissolving)

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