Modeling of Optimized Supercritical Carbon Dioxyde Extraction of Essential Oils from Hyssop (*Hyssop officinalis*), Thyme (*Thymus serpullum*) and Valerian (*Valeriana officinalis*)

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ABSTRACT

The aim of this work was to model the process of carbon dioxide supercritical fluid extraction (SFE) of essential oils from different plant material. Two models were applied on experimental results: the widely used model of Sovová which is universal and describes the SFE process regardless of the plant material; and the model based on the secretory structure of the plant material which is strongly dependant on the type of oil storage within the plants. These models were used to describe two types of SFE processes: the classical SFE, in which grounded plant material is loaded into the extractor vessel, and after reaching operational conditions, supercritical extraction takes place immediately; and the optimized SFE, in which the plant material is subjected to pretreatment which includes exposing the grounded plant material to supercritical fluid at operational conditions for chosen amount of time (batch operation) prior to the continuous process of SFE. The pretreatments were found to be optimal for selected plants regarding their secretory structure.

Both models showed good agreement with experimental results, and values of the model parameters showed the influence of supercritical carbon dioxide on plant material during the pretreatment period.

INTRODUCTION

Exposure of herbaceous matrix to supercritical fluid leads to partial dissolving of plant material in compressed gas, which may cause changing of tissue properties and finally the plant tissue might 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). Swelling of plant material leads to increased diffusion coefficient that causes faster mass transfer through the particle of plant material in the SFE process. Hence, if the continuous SFE process started from already swollen plant material, some amount of supercritical fluid could be saved.

According to previous investigation [1], two characteristic types of plant material swelling behavior were recognized. The first type of behavior is characteristic for Lamiaceae family species (mint, rosemary, sage, hyssop, thyme, etc.) which undergo considerable swelling during exposure to supercritical carbon dioxide. The optimal pre-treatment, which will enable extraction from already swollen herbaceous matrix includes, exposure of milled plant material to supercritical fluid before continuous SFE. The second type of behavior is characteristic for valerian root which maintained its shape during the exposure to supercritical carbon dioxide, but showed considerable swelling during pressure release. The optimal pre-treatment in this case includes pressure variation before continuous SFE which enables extraction from already swollen plant material.

The aim of this study is to model the optimized SFE process and to show, by values of process parameters, the benefits of optimized over classical SFE process.

MATERIALS AND METHODS

Dry leaves of Hyssop (*Hyssop officinalis*), Thyme (*Thymus serpullum*), as well as dry root of valerian (*V. officinalis* L) were used in experimental studies. Commercial carbon dioxide (99% purity, Tehno-gas, Novi Sad, Serbia) was used for the extractions. The plant material was milled to the particle size 0.7 mm for hyssop and thyme, and 0.4 mm for valerian.

Extractions with SC CO_2 were carried out in an Autoclave Engineers Screening System shown in Figure 1 as described previously [2]. Experiments with hyssop and thyme were carried out at 10 MPa and 313 K, while those with valerian were carried out at 15 MPa and 323K. The pretreatment of hyssop and thyme consisted of keeping the plant material at extraction conditions for 1 hour (batch) prior to continuous extraction. In the case of valerian, the plant material was kept on extraction conditions for 15 minutes, then decompressed to 60 MPa, and after 10 minutes pressurized to the working conditions again. Then the continuous SFE process commenced.

On both classical and optimized SFE process two mathematical models were applied: the widely used Sovova's model [3], and the model on the micro-scale [4]. Sovova's model is based on the concept of broken and intact cells and is applicable on any extraction from plant material. The model on the micro-scale is strongly based on the secretory structure of the plant material.

RESULTS

Experimental results of the SFE processes, as well as the results of mathematical modelling, are shown in figures 1-3. In all three cases, the influence of pretreatment is evident as the overall yield increases. It is obvious the yields are higher from the beginning of SFE processes, which means that some amount of essential oil is liberated from its storage during the pretreatment. It will also be shown, through the values of model parameters that the pretreatment influences the plant material as well, making the extraction runs faster.

Figure 1. Yield of essential oil as a function of specific amount of solvent and simulations for SFE from hyssop (● –without pre-treatment, ○ – with pre-treatment)

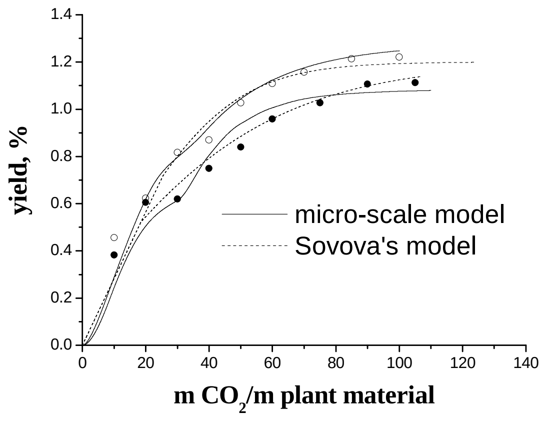


Figure 2. Yield of essential oil as a function of specific amount of solvent and simulations for SFE from thyme

(● –without pre-treatment, ○ – with pre-treatment)

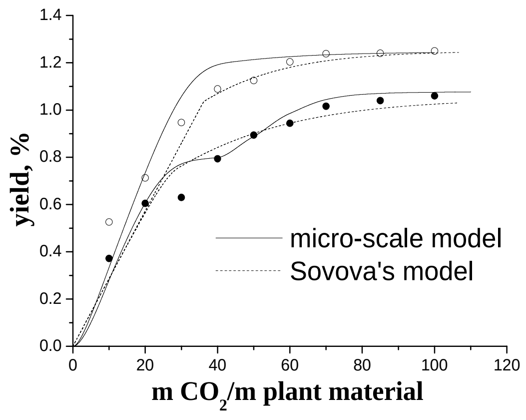
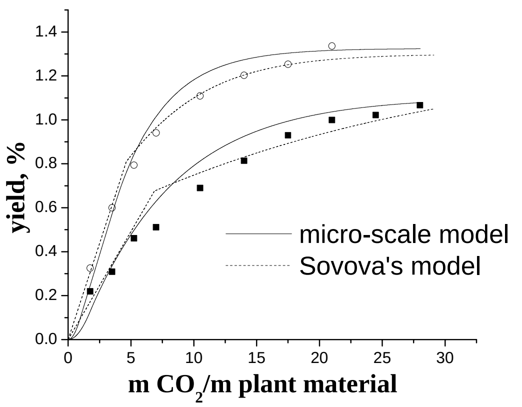


Figure 6. Yield of essential oil as a function of specific amount of solvent and simulations for SFE from valerian
(● –without pre-treatment, ○ – with pre-treatment)



All experiments confirmed the well known assumption of two fractions of essential oil within the plant material. One is easy accessible fraction which is extracted rapidly at the beginning of the process, and the other is the fraction which is extracted slowly in the later stage of the SFE process.

Both mathematical models simulate experimental results with good accuracy. However, some differences are obvious, especially regarding the SFE from hyssop and thyme. These plants are members of the family *Lamiaceae*, which have secretory trichomes as essential oil reservoirs. These glands are located on the surface of the plant material (leaves in this case), and are known to crack under the influence of the SC CO_2 [5]. That is why there is a sudden increase in the slope of the curve in the case of the micro-scale model, which indicates the cracking of some fraction of glands, thus liberating the oil from within them. This increase is much smaller, or there isn't any, in the case of SFE with pretreatment, because most of the glands crack under the influence of SC CO_2 during the pretratment, before the continuous process starts [5]. Other differences originate from different views on SFE process. While Sovova's model assumes that the essential oil is spread throughout the particles of plant material, in the micro-scale model essential oil is located within secretory structures inside (in this case valerian) or on the surface (in this case hyssop and thyme) of the plant material.

The influence of SC CO_2 on the dynamics of SFE process can also be seen through the values of model parameters, namely those which describe the diffusion through the plant material. These values for valerian are shown in Table 1.

Table 1. Values of diffusion coefficients for SFE from valerian in Sovova's and in the micro-scale model.

	Pretreatment	$k_s \cdot 10^8$, m/s (Sovova's model)	$K \cdot 10^{10}$, m/s (micro-scale model)
Valerian	yes	1.55	7.0
	no	0.35	4.0

It is evident that the diffusion coefficients are larger when there is a pretreatment of plant material. The probable reason for this is that the pretreatment itself, the decompression step in the case of valerian, influences the particle of plant material in the way that it is swollen, making the path for essential oil easier. The difference in the order of magnitude (10^{-8} for Sovova's and 10^{-10} for micro-scale model) is due to the different approach in establishing the model itself, namely the location of essential oil within the plant material.

CONCLUSION

The pretreatment of plant material shows evident influence on the SFE process, by increasing the overall yield. It also influences the plant material itself which is evident from the values of diffusion coefficients. These results are very interesting for possible optimization of the SFE process, and should be further investigated.

Both models simulated experimental results with good accuracy.

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REFERENCES :

[1] ZIZOVIC, I., EGGERS, R., HEINRICH, H., JAEGER, P.,STAMENIĆ, M., SKALA, D. 11th European Meeting on Supercritical Fluids, **2008**, Full text available in electronic form.
[2] ZIZOVIC, I., STAMENIĆ, M., ORLOVIĆ, A., SKALA, D., J. Supercrit. Fluids, Vol. 39, **2007**, p. 338
[3] SOVOVA, H., Chem. Eng. Sci., Vol. 49, **1994**, p. 409.
[4] STAMENIĆ, M., ZIZOVIC, I., ORLOVIĆ, A., SKALA, D., J. Supercrit. Fluids, Vol 46, **2008**, p. 285
[5] ZIZOVIC I., STAMENIC M., A. ORLOVIC, SKALA D. Skala. Chem. Eng. Sci. Vol. 60, 2005, p. 6747.