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VESNA NAĐALIN<sup>1</sup>  
 ŽIKA LEPOJEVIĆ<sup>2</sup>  
 MIHAILO RISTIĆ<sup>3</sup>  
 JELENA VLADIĆ<sup>2</sup>  
 BRANISLAVA NIKOLOVSKI<sup>2</sup>  
 DUŠAN ADAMOVIĆ<sup>4</sup>

<sup>1</sup>Technical College of Applied Sciences in Zrenjanin, Zrenjanin, Serbia

<sup>2</sup>University of Novi Sad, Faculty of Technology, Novi Sad, Serbia

<sup>3</sup>Institute for Medicinal Plant Research "Dr Josif Pančić", Belgrade, Serbia

<sup>4</sup>Institute of Field and Vegetable Crops, Novi Sad, Serbia

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## INVESTIGATION OF CULTIVATED LAVENDER (*Lavandula officinalis* L.) EXTRACTION AND ITS EXTRACTS

### Article Highlights

- Physicochemical properties of lavender essential oil were determined
- Lavender flower was extracted with supercritical CO<sub>2</sub> under isothermal and isobaric conditions
- Modeling the extraction system lavender flower-supercritical CO<sub>2</sub> was performed
- Essential oil and CO<sub>2</sub> extracts of lavender flower analysis was done by GC/MS and GC/FID

### Abstract

*In this study essential oil content was determined in lavender flowers and leaves by hydrodistillation. Physical and chemical characteristics of the isolated oils were determined. By using CO<sub>2</sub> in supercritical state, the extraction of lavender flowers was performed with a selected solvent flow under isothermal and isobaric conditions. Qualitative and quantitative analysis of the obtained essential oil and supercritical extracts (SFE) was carried out using gas chromatography in combination with mass spectrometry (GC/MS) and gas chromatography with flame ionisation detector (GC/FID). Also, the analysis of individual SFE extracts obtained during different extraction times was performed. The main components of the analysed samples were linalool, linalool acetate, lavandulol, caryophyllene oxide, lavandulyl acetate, terpinen-4-ol and others. Two proposed models were used for modelling the extraction system lavender flower - supercritical CO<sub>2</sub> on the basis of the experimental results obtained by examining the extraction kinetics of this system. The applied models fitted well with the experimental results.*

*Keywords: lavender, extraction, extracts, modelling, supercritical CO<sub>2</sub>.*

Lavender (*Lavandula officinalis* L.) is a member of the Lamiaceae family and is a plant species that predominantly contains lipophilic components (essential oil) that are responsible for the anti-inflammatory, antiseptic, sedative and spasmolytic activity [1,2]. In addition, lavender contains hydrophilic components (phenolic compounds, flavonoids - mainly flavone glycosides, anthocyanins, tannins, etc.).

The complex chemical composition of this plant species represents the basis for its medicinal properties. Essential oil content in lavender flowers, obtained by steam distillation, ranges from 1-3%, and oil quality significantly depends on the total amount of

esters, which is around 35-55% recalculated on linalyl acetate [3]. In the essential oil of lavender more than 100 components have been isolated, of which the following were identified esters: linalyl acetate (17.6-53%), lavandulyl acetate (15.95%) and genaryl acetate (5.0%); alcohols: linalool (26-49%),  $\alpha$ -terpineol (6.7%) and terpinen-4-ol (0.03-6.4%); sesquiterpenes:  $\beta$ -caryophyllene (2.6-7.6%); monoterpenes: cis- $\beta$ -ocimene (1.3-10.9%); oxides: 1.8-cineole (0.5-2.5%). It was confirmed that lavender possesses 12% of tannins, while the content of camphor, ketones is less than 1%, which is much lower than other types of Lavandulaceae [4]. For this reason lavender found its application in the cosmetics and perfume industry, in contrast to Lavandulaceae with high camphor content, which are used as insecticides, rubefacients and for other purposes [5].

Correspondence: V. Nadalin, Technical College of Applied Sciences in Zrenjanin, Đorđa Stratimirovića 23, Zrenjanin, Serbia.

E-mail: vesna.nina@gmail.com

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It was established that the pharmacological activity of lavender derives from linalool [6]. Due to presence of linalool, linalyl acetate, and the mentioned esters and alcohols, the essential oil of lavender exerts anti-inflammatory, antifungal, antiseptic and sedative effects [7]. Higher concentrations of alcohols, aldehydes, esters, ketones and sesquiterpenes induce spasmolytic effects on smooth musculature [8,9].

It is particularly important to note that, with confirmed antibacterial and antifungal activity, lavender oil operates *in-vitro* on methicillin resistant strain of *Staphylococcus aureus* and vancomycin resistant strain *Enterococcus faecium* in concentrations less than 1% (v/v) [2,10].

The antioxidant property of lavender is associated with the presence of polyphenolic compounds. A qualitative analysis of these polyphenolic compounds in lavender extracts showed that rosmarinic acid is the most abundant phenolic constituent, which is known for its antiviral, antibacterial, antioxidant, anti-inflammatory and immune stimulating effect [11].

In studies carried out with ethanol extracts of lavender it was found that polyphenol content varies, not only in different parts of the plant (stem, flower and leaf), but also among *Lavandula* species. In the leaf extracts the concentrations of phenolic acids, flavonoids, procyanidins, total tannins and polyphenols are higher compared to extract of flowers and stems. Phenolic acids are the most abundant in the extract of lavender ranging from 2.41 to 5.32% in the leaves, followed by the flowers and then the stems. The content of total polyphenols in the extracts of leaves is 9.20%, flowers 8.46% and stems 4.54%. In the extracts of flowers and leaves the flavonoid content varies from 0.09-0.26%. The total tannin content in the leaves is 3.18%, flowers 2.77% and stems 1.38% [12].

Compared to conventional extraction procedures, the extraction of plant materials by gases under pressure, most notably carbon dioxide, has an important role for a number of reasons [13-15]. A supercritical fluid has a wide range of possibilities for selective extraction, fractionation and purification of natural materials [16]. Changing the pressure and/or temperature above the critical value for CO<sub>2</sub> ( $T_c = 31.1$  °C;  $p_c = 7.38$  MPa;  $d_c = 0.469$  g/ml) leads to changes in density and dielectric constant of CO<sub>2</sub>, which makes it possible to control the yield and composition of the obtained extracts [14]. The extraction procedure is performed at moderate temperatures and relatively low pressures, so it can be used for isolating thermolabile compounds [16,17]. In pro-

cedures of supercritical fluid extraction, carbon dioxide represents the most suitable solvent, due to its non-toxicity, chemical inertness, physiological inactivity, nonflammability and spontaneous release from the extract at atmospheric conditions [18,19].

### Mathematical modeling

Supercritical carbon dioxide extraction kinetic data of lavender flowers were modelled using two mathematical models that assume the extraction rate to be controlled by internal diffusion. The first model was a modified model [20] of Reverchon and Sesti Osseo [21], which had been successfully applied to supercritical fluid extraction of lavender flowers [22]. This model had two adjustable parameters. The second model was a simplified model suggested by Sovová [23] with three adjustable parameters. This model contains, in addition, an equation for the initial extraction from the surface of the plant. Sovová [23] used this model for mathematical modelling of some previously published experimental results of supercritical fluid extraction of lavender oil [24]; however, for a narrower range of the extraction pressures compared to this work. For modelling lavender oil extraction the shrinking-core model could also be used [24], as well as the model developed by Žižović *et al.* [25].

#### *Modified model [20] of Reverchon and Sesti Osseo model [21]*

Reverchon and Sesti Osseo proposed a model for supercritical extraction of basil oil by carbon dioxide [21]. This model has been expressed by the following equation:

$$Y = 100 \left( 1 - e^{-\frac{t}{\tau}} \right) \quad (1)$$

where  $Y$  is the normalized yield of extract:

$$Y = (y_e / y_{\max}) 100$$

$t$  is the extraction time,  $\tau$  is the internal diffusion time,  $y_e$  is the experimental value and  $y_{\max}$  is the yield maximum value. In order to avoid the use of  $\tau$  in Eq. (1), it was assumed that for a certain extraction system  $\tau$  could be considered approximately as constant, so the following expression has been derived:

$$Z = at + b \quad (2)$$

where  $Z$  is the modified  $Y$  defined as:

$$Z = \ln(1 - Y/100), \quad a = -1/\tau,$$

and  $b$  is a correction term.

Equation (2) has been applied on our data of lavender flower extraction by supercritical carbon dioxide. The modification of Eq. (1) is then [20]:

$$Y_m = 100(1 - e^{-(at+b)}) \quad (3)$$

where  $Y_m$  normalized yield obtained from modelling:

$$Y_m = \frac{y_m}{y_{\max}} 100$$

#### Sovová model [23]

Sovová [23] proposed a series of simplified models that can be successfully used for preliminary modelling of the extraction of various plant materials, which are based on combining the characteristic time for individual periods/phases that can be observed during the entire extraction process, such as external mass transfer, internal mass transfer, the hypothetical equilibrium extraction excluding the resistance of mass transfer, *i.e.*, combining the characteristic time of mass transfer in the fluid phase,  $t_f$ , characteristic time of internal mass transfer,  $t_i$ , characteristic time of extraction equilibrium,  $t_{eq}$ , and the mean residence time of the solvent in the extractor,  $t_r$  [23].

Taking into account that lavender belongs to the Lamiaceae family, Sovová suggested the model for a preliminary simulation of the extraction of lavender oil, which includes a plug flow of the solvent through the extractor [23] as:

$$y_e = Gx_u \frac{t}{t_1} \text{ for } t \leq t_1 = \frac{G}{K_m \dot{q} \left(1 - e^{-\frac{1}{\Theta_f}}\right)} \quad (4)$$

$$y_e = x_u - (1-G)x_u e^{-\left(\frac{t-t_1}{t_{\text{comb},i}}\right)} \text{ for } t > t_1$$

Three adjustable parameters of the model are  $K_m$ ,  $G$  and  $t_1$ .

The mass-related partition coefficient,  $K_m$ , is the ratio of the equilibrium mass concentrations on the particle surface: the initial concentrations of solute in the fluid,  $y_0$ , and solid phase,  $x_0$ , and it is of the utmost importance when there is a solute-matrix interaction, as is the case with the extraction of lavender oil [23].

The value of  $G$  is closely associated with the degree of fragmentation of particles. Namely, assuming that the content of extractable substances in the plant at the time when the material is fed into the extractor is  $x_u$ , the initial concentration of easily accessible oil in the broken (open) cells of the material is  $(x_u - x_k)$ , and the initial concentration of oil within the whole (intact) particles is  $x_k$ , and the share of oil in broken cells marked with  $G$  ( $G < 1$ ), the fraction of oil

that is trapped in the intact cells,  $1-G$ , is extracted much slower than those in open cells.

Characteristic time of internal mass transfer,  $t_i$ , can be used for calculation of the intraparticle diffusivity (effective diffusivity),  $D_e$ :

$$D_e = \frac{R^2 (1-G)^{2/3}}{15t_i} \quad (5)$$

The dimensionless mass transfer resistance in the fluid phase,  $\Theta_f$ , represents the ratio of the characteristic time of mass transfer in the fluid phase,  $t_f$ , and the fluid residence time in the extractor,  $t_r$  [23]:

$$\Theta_f = \frac{t_f}{t_r} \quad (6)$$

The characteristic time of mass transfer in the fluid phase,  $t_f$ , was calculated based on the coefficient of mass transfer in the phase of supercritical CO<sub>2</sub>:

$$t_f = \frac{\varepsilon}{k_f a_0} \quad (7)$$

The coefficient of mass transfer in the supercritical fluid,  $k_f$ , depends on the fluid speed and it is usually estimated based on the correlations between dimensionless numbers (Sherwood number,  $Sh$ , Reynolds number,  $Re$ , Schmidt number,  $Sc$  and Grashof number,  $Gr$ ), such as proposed by King *et al.* (1997) [26]:

$$\frac{Sh}{\sqrt[3]{Sc}} [1 + 1.5(1 - \varepsilon)] = 0.2548 Re^{1/2} \quad (8)$$

where the values of the Sherwood number,  $Sh$ , Reynolds number,  $Re$ , and Schmidt number,  $Sc$ , are given by the following equations:

$$Sh = \frac{k_f d}{D_{12}} \quad (9)$$

$$Re = \frac{ud\rho}{\mu} \quad (10)$$

$$Sc = \frac{\mu}{\rho D_{12}} \quad (11)$$

Due to the good transportation properties of supercritical carbon dioxide the characteristic time of mass transfer in the fluid phase,  $t_f$ , is much lower than the characteristic time of internal mass transfer,  $t_i$ . Still for small values of distribution coefficient  $K_m$ , the characteristic time of mass transfer during extraction depends on  $t_f$  and  $t_i$ ; it is obtained as a combination of these two times, *i.e.*, the combined characteristic time

which replaces the time  $t_i$ , can be calculated from the following equation:

$$t_{\text{comb},i} = t_i + \frac{t_i}{t_r} \frac{1}{\dot{q}K_m} \quad (12)$$

For sufficiently low values of  $\Theta_t$ ,  $t_{\text{comb},i} = t_i$ . Also, this simplification could be assumed if the dissolution of extract does not affect the internal diffusion rate [23]. Thus, the expression in the denominator of  $t_i$ , in Eq. (4), becomes:

$$1 - e^{-\frac{1}{\Theta_t}} = 1 \quad (13)$$

Taking into account that:

$$Y = (y_e/x_u)100$$

for a sufficiently low  $\Theta_t$ , the extraction yield according to the second model is:

$$Y = 100 G \frac{t}{t_1} \text{ for } t \leq t_1 = \frac{G}{K_m \dot{q}} \quad (14)$$

$$Y = 100 \left( 1 - (1-G)e^{-\left(\frac{t-t_1}{t_r}\right)} \right) \text{ for } t > t_1$$

To evaluate the model adjustable parameters ( $K_m$ ,  $G$  and  $t_1$ ), the model equation was fitted to various sets of experimental data by minimizing the discrepancies through the minimum sum of squares criterion.

## EXPERIMENTAL

### Plant material

Lavender was collected in full flowering in July 2011 from cultivated plants at the Institute of Field and Vegetable Crops Novi Sad, Department of Organic Production and Biodiversity-Bački Petrovac. Plant material was air-dried and the leaves, flowers and stems were separated and then milled. The milled and separated leaves, flowers and stems of lavender were used in this work.

### Chemicals

Commercial carbon dioxide (Messer, Novi Sad, Serbia) was employed as the extracting agent. All other chemicals were of analytical reagent grade.

### Determination of essential oil content

Essential oil content in the drug (flower and leaf) was determined by hydrodistillation according to procedure described in the literature [27], using a dis-

tillation apparatus defined in the German Pharmacopoeia DAB-8 [28].

### Determination of basic physicochemical properties of lavender essential oil

Relative density ( $d_{20}^{20}$ ) was determined by a pycnometer (5.0 ml), as suggested by the European Pharmacopoeia [27], while for determination of refractive indices ( $n_D^{20}$ ), an Atago RX-1000 digital refractometer was used. Determination of optical rotation of essential oil samples was done on a Polamat A device. The specific rotation was calculated using the following equation:

$$[\alpha]_D^t = \frac{\alpha(\text{read value})}{1.17543} \frac{V}{ml} \quad (15)$$

where  $\alpha$  is the read value of the measured optical rotation,  $V$  is the volume of the sample ( $\text{cm}^3$ ),  $l$  is the length of the cuvette (dm) and  $m$  is the mass of the sample (g).

### Drug extraction by supercritical carbon dioxide

The supercritical fluid extraction (SFE) with carbon dioxide was performed using a laboratory-scale high-pressure extraction plant - HPEP (Nova-Swiss, Effretikon, Switzerland). The main part and characteristics (manufacturer specification) of the plant were as follows: diaphragm-type compressor (up to 1000 bar), extractor with an internal volume of 200 ml ( $p_{\text{max}} = 700$  bar), separator with internal volume of 200 ml ( $p_{\text{max}} = 250$  bar) and maximum  $\text{CO}_2$  mass flow rate of approximately 5.7 kg/h.

Lavender flower (30 g) with an average particle diameter,  $d_s$  ( $d_s = 0.58$  mm), was extracted. The cumulative extraction yield was determined by measuring the mass of isolated extract after 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 h. Extraction was carried out under isothermal conditions at  $T = 313$  K and at pressures of 10, 15, 20, 25 and 30 MPa, as well as at temperatures,  $T$ , of 323 and 333 K and pressures of 10, 20 and 30 MPa, while the flow of extractant was 0.194 kg/h in all cases.

According to the previously described procedure the extraction of lavender flower was performed at a pressure  $p = 10$  MPa and temperature  $T = 313$  K, with the exception that during the time intervals of the extraction process (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 h) appropriate  $\text{CO}_2$  extracts were taken (SFE-1, SFE-2, SFE-3, SFE-4, SFE-5 and SFE-6). These  $\text{CO}_2$  extracts were subjected to quantitative and qualitative analysis.

The dependence of lavender flower extraction yield from the on the solvent flow rate,  $w$  ( $w_1 = 0.095$

kg/h;  $w_2 = 0.194$  kg/h;  $w_3 = 0.277$  kg/h) at a pressure of 10 MPa and temperature 313 K was also examined. Isolation of CO<sub>2</sub> extract, in all cases, was performed at a pressure of 1.5 MPa and temperature 298 K.

#### Analytical gas chromatography (GC/FID)

Using GC/MS and GC/FID, the qualitative and quantitative composition of essential oil obtained by hydrodistillation of lavender flower and leaves was determined, and the samples were labelled as La-ec and La-el. In addition, the analysis of CO<sub>2</sub> extracts obtained by extracting lavender flower at pressures of 10, 20 and 30 MPa and temperature 313 K was performed, while the samples were labelled as SFE-I, SFE-II and SFE-III. Samples of CO<sub>2</sub> extracts obtained at 10 MPa and 323 and 333 K were labelled as SFE-IV and SFE-V.

#### Sample preparation

Samples of essential oil and CO<sub>2</sub> extracts were prepared by dissolving them in methylene chloride-methanol mixture (9:1, v/v), with an approximate concentration of 20 mg/ml.

GC/FID analysis of the samples was carried out on an Agilent Technologies 7890A gas chromatograph equipped with split-splitless injector and automatic liquid sampler (ALS), attached to HP-5 column (30 m×0.32 mm, 0.25 μm film thickness) and fitted to a flame ionisation detector (FID). Carrier gas flow rate (H<sub>2</sub>) was 1 ml/min, injector temperature was 250 °C, detector temperature 300 °C, while column temperature was linearly programmed from 40–260 °C (at a rate of 4 °C/min), and held isothermally at 260 °C for the following 20 min. Solutions of lavender isolates were consecutively injected by ALS (1 μl, splitless mode). Area percent reports, obtained as result of standard processing of chromatograms, were used as the base for the quantification purposes.

#### Gas chromatography/mass spectrometry (GC/MS)

The same analytical conditions as those mentioned for GC/FID were employed for GC/MS analysis, along with column HP-5MS (30 m×0.25 mm, 0.25 μm film thickness), using an HP G1800C Series II GCD system (Hewlett-Packard, Palo Alto, CA, USA). Instead of hydrogen, helium was used as carrier gas. The transfer line was heated at 260 °C. Mass spectra were acquired in EI mode (70 eV), in *m/z* range 40–450. Sample solutions were injected by ALS (1 μl, splitless mode).

The constituents were identified by comparison of their mass spectra to those from Wiley275 and NIST/NBS libraries, using different search engines. The experimental values for retention indices were

determined by the use of calibrated Automated Mass Spectral Deconvolution and Identification System software [29], compared to those from available literature [30], and used as an additional tool to confirm MS findings.

## RESULTS AND DISCUSSION

The essential oil content was determined by hydrodistillation of lavender flowers and leaves, and found to be 2.39±0.015 and 0.52±0.011 ml/100 g drug, respectively. From the results, it can be seen that the essential oil content in the lavender flower is nearly 4.6 times higher than in the leaf. The essential oil of the flower has been isolated and its refractive index turned out to be  $n_D^{20} = 1.462 \pm 0.0042$ , its relative density  $d_{20}^{20} = 0.890 \pm 0.0044$  and specific rotation  $[\alpha]_D^{20} = -7.0 \pm 0.065$  (the values of physicochemical parameters represent an average value of three measurements ± standard deviation).

#### Supercritical CO<sub>2</sub> extraction of lavender flower

##### *Effect of solvent flow on the extraction yield*

Further testing was carried out by using an extraction procedure with supercritical CO<sub>2</sub> as an extractant in order to obtain lavender flower extracts and investigate the extraction kinetics. Firstly, the influence of supercritical CO<sub>2</sub> flow on extraction yield was examined. The following extractant flows were used:  $w_1 = 0.095$  kg/h,  $w_2 = 0.195$  kg/h and  $w_3 = 0.277$  kg/h, while the other extraction conditions were:  $p = 10$  MPa;  $T = 313$  K and  $t = 3$  h. The results are shown in Figure 1.

From the extraction kinetics results, it can be seen that the flow of the solvent has a notable influence on the extraction yield for the specific consumption of CO<sub>2</sub>, with  $q$  values up to 10 kg CO<sub>2</sub>/kg plant material. The highest yield for an extraction time of 3 h was achieved at the flow  $w_3$  (5.56 g/100 g drug), and the lowest at the flow  $w_1$  (4.62 g/100 g drug). However, for that time, the solvent's specific consumption values at flows  $w_3$  and  $w_1$  were about 28 and 10 kg CO<sub>2</sub>/kg plant material, respectively. At the solvent flow  $w_2$  the extraction yield for the extraction time of 3 h was 5.16 g/100 g drug, and  $q$  value was about 20 kg CO<sub>2</sub>/kg plant material, so this flow of supercritical CO<sub>2</sub> was used in further tests.

##### *Effect of pressure on the extraction yield*

The extraction of lavender flowers was performed by supercritical CO<sub>2</sub> to investigate the extraction yield at different working pressures but under constant temperature (isothermal conditions,  $T = 313$  K) during a 3 h extraction. Experimentally determined

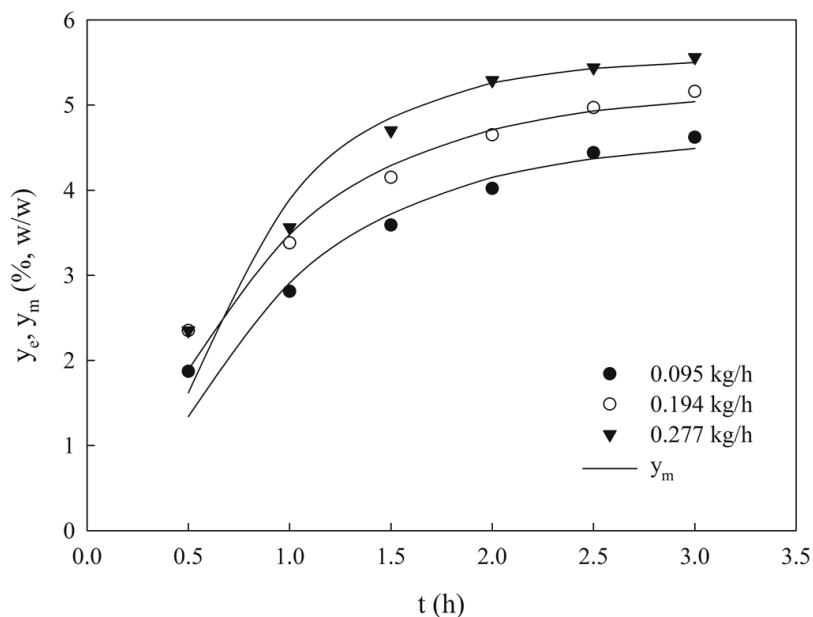


Figure 1. Results of modelling the lavender flower extraction yield in dependence of the solvent flow rate ( $p = 10$  MPa;  $T = 313$  K). Symbols - experimental results ( $y_e$ ); lines - modelled values ( $y_m$ ) by the modified model [20].

values of the lavender extract yield *versus* extraction time, obtained at pressures 10, 15, 20, 25 and 30 MPa are presented in Figure 2.

With the increase of pressure from 10 to 30 MPa, at constant temperature (313 K), the extraction yield increased from 5.16 to 7.08 g/100 g drug, which is understandable, because with the increase of pressure the density of the extractant also increases and thus the polarity of the solvent or the dielectric constant, *i.e.*, the dissolving power of the extractant.

#### Effect of temperature on extraction yield

The influence of temperature (313, 323 and 333 K) at pressures of 10, 20 and 30 MPa was investigated. The effect of temperature on the extraction yield of lavender extract at a flow rate of 0.194 kg/h of  $\text{CO}_2$  and at pressures of 10, 20 and 30 MPa *versus* extraction time is shown in Figures 3a-c, respectively.

From the results shown in Figure 3 it can be seen that at the pressure of 10 MPa the extraction yield decreased with the increase of temperature, due

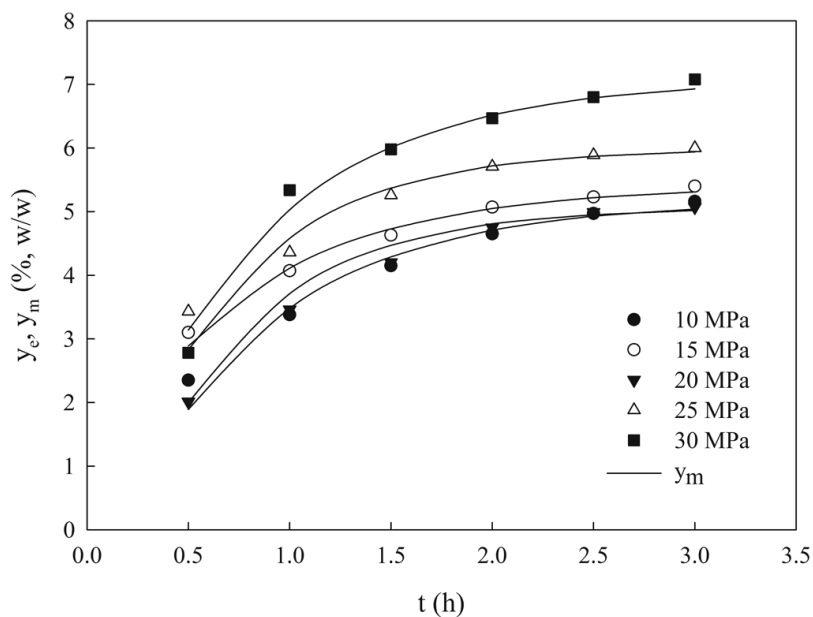


Figure 2. The influence of pressure on extraction yield with supercritical  $\text{CO}_2$  at 313 K. Symbols - experimental results ( $y_e$ ); lines - modelled values ( $y_m$ ) by the modified model [20].

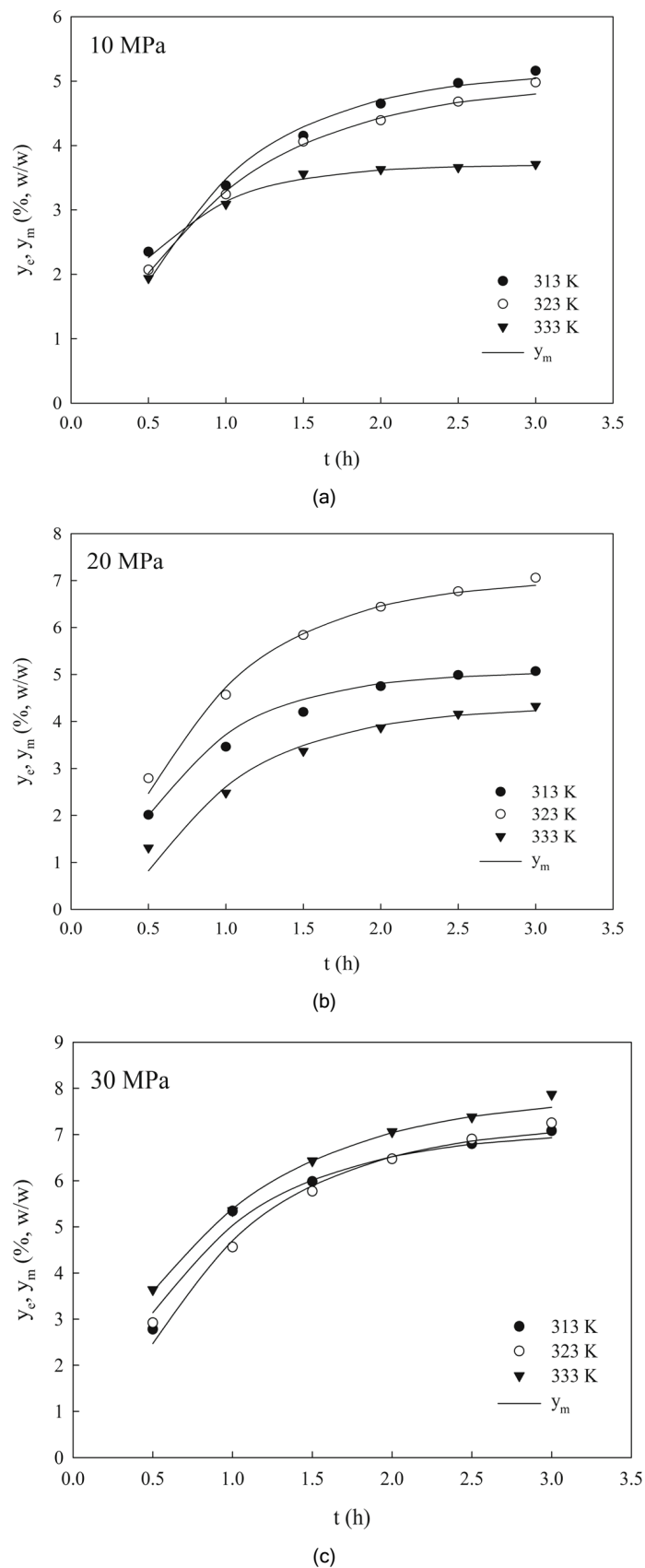


Figure 3. The influence of temperature on extraction yield at different pressures: a) 10, b) 20 and c) 30 MPa. Symbols - experimental results; lines - modelled values ( $y_m$ ) by the modified model [20].

to the fact that mostly essential oils are being extracted at the examined pressure, so the vapour pressures of the diluted components have an insignificant effect on the extraction yield. However, at higher pressures (Figure 3) and especially the results shown in Figure 3c indicated that with the increase of pressure the solvent density also increased. This led to the extraction of other components (wax and resin), besides the essential oil, whose vapour pressures significantly affect the extraction yield based on the applied temperature. This temperature effect is particularly expressed at the results shown in Figure 3c. At the pressure of 30 MPa and temperatures of 313, 323 and 333 K, it can be seen that the extraction yield was the highest at 333 K, and the lowest at 313 K because with the temperature increase the vapour pressure of diluted components increased, so the solubility depended on the equilibrium between the solvent density and changes of vapour pressure of the diluted components.

#### Kinetic modelling of the extraction system lavender flower-supercritical CO<sub>2</sub>

Based on the results of examining the kinetics of lavender flower extraction by supercritical CO<sub>2</sub> at 10, 15, 20, 25 and 30 MPa and at 313 K, the extraction system lavender flower - supercritical CO<sub>2</sub> was modelled by applying the modified model [20]. The modelling results are shown in Figure 2.

Since the modified model equation includes the value  $Z$  ( $Z = \ln(1-Y/100)$ ), *i.e.*,  $Z = at + b$ , Figure 4 shows the dependence between  $Z$  and  $t$ , from which parameters  $a$  and  $b$  were calculated (Table 1).

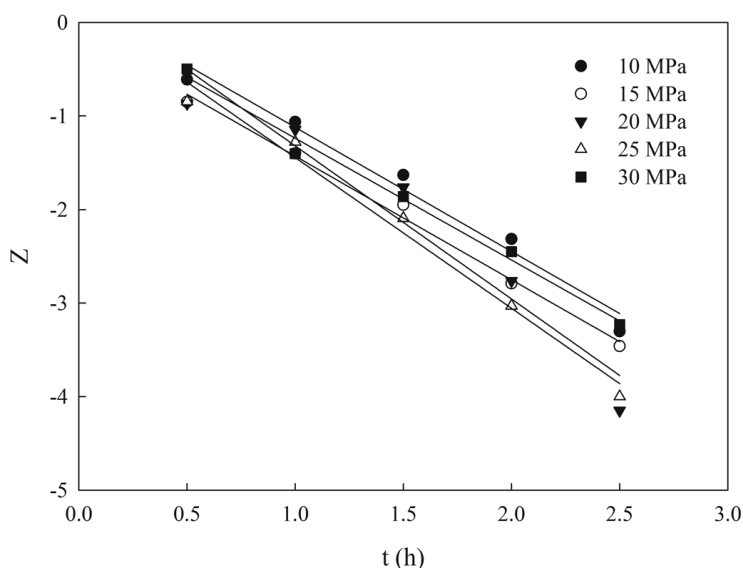


Figure 4. Dependence of  $Z$  ( $Z = \ln(1-Y/100)$ ) on time.

Table 1. Parameters in Eq. (2) and correlation coefficient,  $r$

Pressure, MPa	Parameters in Eq. (2)		
	$a$	$b$	$ r $
10	-1.327	0.2061	0.988
15	-1.322	-0.107	0.996
20	-1.636	0.3162	0.966
25	-1.611	0.1665	0.991
30	-1.302	0.0649	0.992

High values of the correlation coefficient,  $r$  (from 0.966 to 0.992) show that there is a strong correlation between  $Z$  and  $t$ .

The effect of temperature on the extraction yield and the modelling results is shown in Figure 3. By applying the same procedure as in the previous case the necessary parameters for obtaining the value of  $y_m$  were calculated. Based on the values of the influence of pressure on extraction yield under isothermal conditions, as well as the influence of temperature on extraction yield, the values of mean relative deviation ( $MRD$ ) were between 0.97 and 8.42 %, so it can be concluded that the applied modified model fits the experimental results of the extraction system lavender flower - supercritical CO<sub>2</sub> relatively well.

The results of investigating the kinetics of lavender flower - supercritical CO<sub>2</sub> extraction system were also modelled by applying the model proposed by Sovová [23] to the extraction experimental results, *i.e.*, the extraction yield as a function of time at pressures of 10, 15, 20, 25 and 30 MPa, temperature of 313 K and solvent flow rate 0.194 kg/h.

The physical parameters of supercritical CO<sub>2</sub> under experimental conditions are given in Table 2.



Table 2. Physical parameters of supercritical CO<sub>2</sub> at various experimental conditions. Mass flow rate of CO<sub>2</sub>: 0.194 kg h<sup>-1</sup>

<i>T</i> / K	$\rho$ / MPa	$u \times 10^4$ / m·s <sup>-1</sup>	$\rho$ / kg·m <sup>-3</sup>	$\nu \times 10^8$ / m <sup>2</sup> ·s <sup>-1</sup>	<i>Re</i>	$D_{12} \times 10^8$ / m <sup>2</sup> ·s <sup>-1</sup>	$k_f \times 10^6$ / m·s <sup>-1</sup>
313	10	0.68	630	7.66	0.51	2.3	5.6
	15	0.55	781	8.81	0.36	1.6	3.8
	20	0.51	841	9.47	0.31	1.4	3.4
	25	0.49	880	9.99	0.28	1.3	3.1
	30	0.47	911	10.4	0.26	1.2	2.9
323	10	1.11	385	7.41	0.87	4.4	11.1
	20	0.54	785	8.87	0.36	1.6	3.8
	30	0.49	871	9.87	0.29	1.3	3.1
333	10	1.48	290	8.34	1.03	6.0	15.4
	20	0.59	724	8.36	0.41	2.0	4.7
	30	0.52	830	9.38	0.32	1.5	3.5

The residence time of the solvent in the extractor was calculated based on the value of the specific flow rate, porosity of the layer and density of both phases. The density of the solid phase was taken from literature data [24]. For the values of supercritical fluid density and coefficient of dynamic viscosity corresponding values for CO<sub>2</sub> were taken. The density of CO<sub>2</sub> was estimated based on the Dohrn-Prausnitz equation, using PE2000 software [31], and the coefficient of dynamic viscosity on the basis of Jossi, Stiel and Thodos method [32]. The dimensionless resistance to mass transfer in the supercritical fluid,  $\theta_t$ , was calculated on the basis of the coefficient of mass transfer in the phase of supercritical CO<sub>2</sub>. Binary diffusion coefficient of lavender oil in the carbon dioxide,  $D_{12}$ , was estimated as an average value based on the binary diffusion coefficient values for the most abundant components of lavender oil (camphor, fenchone, eucalyptol, campholenal, fenchol, camphene, thymol, myrtenol, furfuryl alcohol, linalyl acetate) and for the calculation the method proposed by Catchpole and King [33] was used. The self-diffusion coefficient of carbon dioxide is  $4.944 \times 10^{-8}$  m<sup>2</sup> s<sup>-1</sup> [32], while the critical molar volume of the solute was determined by a method proposed by Joback [32]. The values of mass transfer coefficient in the phase of supercritical CO<sub>2</sub> were estimated based on the Sherwood number values calculated from a correlation proposed by King *et al.* [26]. The characteristic dimension is the particle diameter.

During supercritical fluid extraction of any essential oil from its plant material, the essential oils and cuticular waxes are co-extracted at all experimental conditions; but if the extraction pressure is increased the contribution of the waxes in the extract will be more relevant, meaning that solubility of waxes will be increased and consequently its' extraction kinetics will be changed compared to some other ope-

rating conditions. Nonetheless, to selectively extract the essential oil, for example, in order to investigate its extraction kinetics, extraction step must be followed by fractional separation. The essential oil content in the plant material at the time when the material is fed into the extractor,  $x_u$ , can be easily determined by hydrodistillation. Moreover,  $x_u$  equals the essential oil yield maximum value,  $y_{max}$ . Therefore, the essential oil extraction curves have the same asymptote for  $t$  approaching infinity regardless of different operating conditions.

In this work, the obtained lavender extracts were not additionally separated and contained, besides the lavender essential oil, a larger or smaller amount of co-extracted substances, depending on extraction pressure, temperature and extraction time. Following the previously adopted procedure for assessment of the essential oil yield maximum value, the yield maximum value,  $y_{max}$ , could be determined as the asymptote of extraction curves for  $t$  approaching infinity. Thus,  $y_{max}$  becomes in fact an additional adjustable parameter of the model for extraction that depends on the extraction pressure and temperature; the value determined by this way is more reliable for experiments that last longer.

Due to consistency, the same way of calculation of the asymptotic yield was also applied in the Sovová model [23], in order to obtain the content of extractable substances in the plant,  $x_u$ , to be pressure and temperature dependent parameter. The model adjustable parameters ( $K_m$ ,  $G$  and  $t_f$ ) and  $x_u$  were determined by fitting the model in Eq. (4) to various sets of experimental data by minimizing the discrepancies through the minimum sum of squares criterion.

The results of modelling of the extraction of lavender flowers at 313 K and pressures 10, 15, 20, 25 and 30 MPa by the Sovová model [23] are presented in Table 3. The comparison between the expe-

Table 3. The results of modelling the extraction of lavender at 313 K, 0.194 kg h<sup>-1</sup> CO<sub>2</sub> flow rate and different pressures. Model: Sovová [23]

Parameter	$p$ / MPa				
	10	15	20	25	30
$x_u \times 10^3$ / kg ext. (kg matter) <sup>-1</sup>	57.8	57.5	59.3	64.0	84.6
$\Theta$	0.013	0.015	0.016	0.017	0.017
$G$	0.40	0.50	0.50	0.54	0.62
$K_m$	0.12	0.18	0.14	0.15	0.09
$t_i$ / min	28	23	30	30	57
$t_{\text{comb},i}$ / min	77	62	101	62	145
$t_j$ / min	76	62	100	61	144
AARD <sup>a</sup> / %	1.42	1.10	6.30	3.93	1.49
MRD <sup>b</sup> / %	0.47	0.37	2.10	1.31	0.50
SD <sup>c</sup> / %	0.05	0.06	0.28	0.21	0.09

$${}^a \text{AARD} = \frac{100}{N - NP} \sum_j \left| \frac{y_{e,j} - y_{m,j}}{y_{e,j}} \right| ; {}^b \text{MRD} = \frac{100}{N} \sum_j \left| \frac{y_{e,j} - y_{m,j}}{y_{e,j}} \right| ; {}^c \text{SD} = \sqrt{\frac{\sum_j (y_{e,j} - y_{m,j})^2}{N - 1 - NP}}$$

rimental extraction curves of the lavender extract at 313 K and pressures 10, 15, 20, 25 and 30 MPa and those obtained by the Sovová model [23] is shown in Figure 5. The average value of the effective internal diffusivity was calculated as  $D_e = 4.4 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  (standard deviation of  $1.57 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ) by using Eq. (5), and based on the characteristic time of internal mass transfer,  $t_i$ , given in Table 3.

In literature [23], it could be found that the characteristic time of internal diffusion, the diffusion of the lavender oil through the wall of intact trichomes, was pressure and temperature dependent and varied between 123 min at (10 MPa, 308 K) and 500 min at (8 MPa, 323 K). In our work, this effect was not noticeable, mainly because the fact that the extract comprised not only the oil but co-extractable substances too, as well as due to the way of  $x_u$  determination. The

characteristic time of mass transfer during extraction depends only on the characteristic time of internal mass transfer ( $t_{\text{comb},i} \approx t_i$ ) and therefore instead of Eq. (4), Eq. (14) can be used for mathematical modelling.

The results of modelling of the extraction of lavender flowers at 323 and 333 K and pressures 10, 15, 20, 25 and 30 MPa by the Sovová model [23] are presented in Table 4. Comparison between the experimental extraction curves of the lavender extract at 313 K and pressures 10, 15, 20, 25 and 30 MPa and those obtained by the Sovová model [23] is shown in Figure 5.

Values of the partition coefficient  $K_m$  (Tables 3 and 4) varied between 0.08 at 20 MPa, 333 K and 0.18 at 15 MPa, 313 K. The literature values of the partition coefficient  $K_m$  varied between 0.085 at 8 MPa, 323 K and 0.29 at 14 MPa, 323 K [25]. Accord-

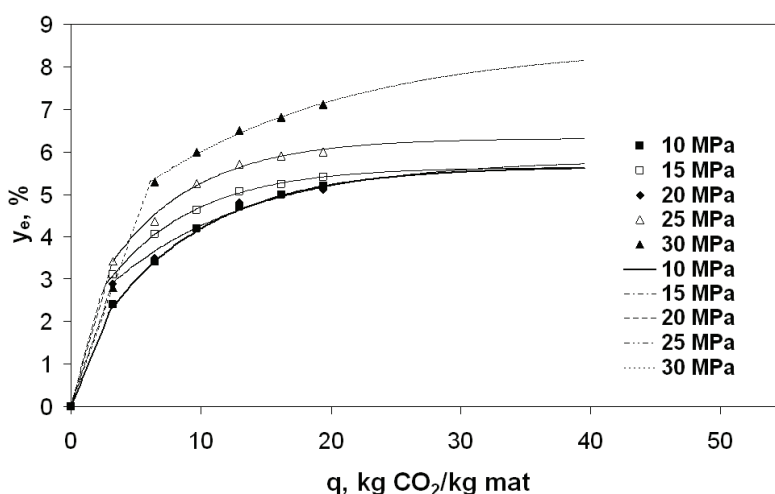


Figure 5. Comparison between the experimental extraction curves of the lavender extract at 313 K and pressures 10, 15, 20, 25 and 30 MPa and those obtained by the Sovová model [23]. Symbols - experimental results; lines - calculated values by Eq. (4).

Table 4. The results of modelling the extraction of lavender at 323 and 333 K, 0.194 kg h<sup>-1</sup> CO<sub>2</sub> flow rate and pressures 10, 20 and 30 MPa. Model: Sovová [23]

Parameter	$p$ / MPa					
	10		20		30	
$T$ / K	323	333	323	333	323	333
$x_{i0} \times 10^3$ / kg ext. (kg matter) <sup>-1</sup>	53.7	38.7	74.7	45.5	79.9	84.2
$\Theta_f$	0.011	0.010	0.015	0.013	0.017	0.016
$G$	0.40	0.39	0.49	0.49	0.50	0.50
$K_m$	0.11	0.14	0.11	0.08	0.10	0.12
$t_1$ / min	30	23	40	52	42	35
$t_{\text{comb},i}$ / min	65	27	61	46	84	78
$t_f$ / min	64	27	60	45	82	77
AARD / %	3.03	1.24	3.64	5.44	4.48	2.27
MRD / %	1.01	0.62	1.21	0.80	1.49	0.76
SD / %	0.14	0.05	0.19	0.13	0.25	0.16

ing to Sovová [23], as the glandular trichomes ruptured not only during the pre-treatment of the plant but also when exposed to dense CO<sub>2</sub>, where the effect depends on the extraction conditions, the adjusted parameter  $G$  varied between 0.35 at 10 MPa, 308 K and 0.69 at 14 MPa, 323 K. In the present work,  $G$  varies from 0.39 (10 MPa, 333K) to 0.62 (30 MPa, 313 K). Therefore, the results of this preliminary evaluation with the simplified model indicate that the model of essential oil extraction on micro-scale describing the rupture of glandular trichomes in detail [25] would be appropriate to simulate these data.

Based on the AARD values (from 1.10 to 6.30%) it can be concluded that the Sovová model [23] fits the experimental results of the extraction system lavender flower-supercritical CO<sub>2</sub> fairly well.

### Isolation of CO<sub>2</sub> extracts (SFE)

In order to isolate CO<sub>2</sub> extracts during different time intervals of extraction, tests were carried out with lavender flower at 10 MPa and 313 K. SFE extracts were obtained at different time intervals during extraction (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 h).

The highest yield of SFE extract was achieved in the first 0.5 h (2.39%). The yield of other SFE extracts is much lower and ranges between 0.09 and 0.57%. The first two extracts (SFE-1 and SFE-2) make up more than 75% of the total extract obtained during the 3 h extraction.

### Qualitative and quantitative analysis of essential oil and SFE extracts by gas chromatography

Qualitative and quantitative analysis of essential oil and SFE extract samples were carried out using gas chromatography. The results are given in Table 5.

Table 5. GC analysis of essential oils and CO<sub>2</sub> extracts of lavender flower; KIE = Kovats (retention) index experimentally determined [29] - uncorrected value; KIL = Kovats (retention) index - literature data [30]; n.i. = not identified; n/a = not available; tr. = traces (< 0.01%); La-el = leaf essential oil; La-ec = flower essential oil; SFE-I ( $p = 10$  MPa;  $T = 313$  K;  $\tau = 0.0-0.5$  h); SFE-II ( $p = 10$  MPa;  $T = 313$  K;  $\tau = 3$  h); SFE-III ( $p = 20$  MPa;  $T = 313$  K;  $\tau = 3$  h); SFE-IV ( $p = 30$  MPa;  $T = 313$  K;  $\tau = 3$  h); SFE-V ( $p = 10$  MPa;  $T = 333$  K;  $\tau = 3$  h)

Component	Component content, mass%								KIE	KIL
	Essential oil <sup>a</sup>		Supercritical fluid extracts (SFE) <sup>b</sup>							
			Sample label							
	La-el	La-ec	SFE-I	SFE-II	SFE-III	SFE-IV	SFE-V			
$\alpha$ -Pinene	0.08	0.06	tr.	0.04	0.07	0.07	0.04	0.04	924.0	932
Camphene	0.12	0.05	0.04	0.06	0.08	0.10	0.06	0.05	937.8	946
$\beta$ -Pinene	0.41	0.43	0.31	0.24	0.26	0.31	0.24	0.24	966.0	974
3-Octanone	0.08	0.16	0.12	0.11	0.10	0.12	0.08	0.08	981.6	979
Myrcene	0.38	0.58	0.29	0.12	0.17	0.29	0.14	0.13	984.0	988
Butyl butanoate	0.05	0.09	0.03	0.08	0.05	0.04	0.06	0.06	991.4	993
Dehydroxy-cis-linalool oxide	0.08	0.24	0.07	0.16	0.09	0.07	0.11	0.11	1001.4	1006

Table 5. Continued

Component	Component content, mass%								KIE	KIL
	Essential Oil <sup>a</sup>		Supercritical fluid extracts (SFE) <sup>b</sup>							
	Sample label									
	La-el	La-ec	SFE-1	SFE-I	SFE-II	SFE-III	SFE-IV	SFE-V		
Hexyl acetate	0.48	0.04	0.02	tr.	tr.	0.04	0.01	0.01	1009.6	1007
<i>p</i> -Cymene	1.11	0.19	0.08	0.06	0.07	0.07	0.05	0.04	1016.7	1020
Limonene	0.69	0.35	0.17	0.13	0.10	0.14	0.11	0.10	1019.8	1024
1.8-Cineole	1.04	0.36	0.17	0.15	0.14	0.15	0.13	0.12	1021.7	1026
<i>cis</i> - $\beta$ -Ocimene	0.25	0.55	0.82	0.65	0.36	0.54	0.48	0.55	1031.3	1032
<i>trans</i> - $\beta$ -Ocimene	0.24	0.43	0.20	0.10	0.08	0.14	0.11	0.11	1041.4	1044
$\gamma$ -Terpinene	0.06	0.06	0.02	0.02	tr.	0.03	0.03	0.01	1050.4	1054
<i>cis</i> -Sabinene hydrate	0.08	0.05	0.17	0.12	0.05	0.06	0.09	0.15	1061.0	1065
<i>cis</i> -Linalool oxide (furanoid)	0.66	1.58	1.22	1.11	1.15	1.24	1.15	1.10	1065.3	1067
Terpinolene	0.15	0.02	tr.	0.02	tr.	tr.	0.02	0.01	1079.6	1086
<i>trans</i> -Linalool oxide (furanoid)	0.60	1.23	1.09	1.00	1.10	1.24	1.02	1.00	1081.3	1084
Linalool	25.75	48.44	31.48	28.25	25.24	25.64	29.55	29.76	1099.1	1095
1-Octen-3-yl acetate	0.48	0.54	0.44	0.47	0.34	0.34	0.48	0.43	1107.7	1110
<i>cis</i> - <i>p</i> -Menth-2-en-1-ol	0.35	0.10	0.07	0.09	0.18	0.16	0.10	0.09	1116.5	1118
Octan-3-ol acetate	0.05	0.03	0.05	0.05	0.06	0.08	0.04	0.04	1119.5	1120
<i>trans</i> -Pinocarveol	0.26	0.12	0.05	0.03	tr.	0.03	tr.	0.03	1132.4	1135
Camphor	2.35	0.43	0.25	0.25	0.22	0.24	0.29	0.24	1135.4	1141
Borneol	0.08	0.05	0.09	0.14	0.15	0.16	0.16	0.16	1160.0	1165
Lavandulol	11.11	4.85	4.97	2.91	3.13	3.76	3.30	3.35	1163.8	1165
Terpinen-4-ol	2.31	3.39	2.70	2.45	2.26	2.36	2.64	2.53	1170.5	1174
Cryptone	1.21	0.11	0.07	0.08	tr.	0.13	0.09	0.04	1179.7	1183
$\alpha$ -Terpineol	3.27	1.40	0.66	0.99	tr.	0.70	0.97	0.82	1186.0	1186
(3 <i>Z</i> )-Hexenyl butanoate	1.66	2.89	1.08	1.00	2.70	2.02	1.21	1.10	1189.6	1187
Verbenone	1.07	0.29	0.14	tr.	0.13	0.16	0.14	0.14	1202.5	1204
<i>cis</i> -Sabinene hydrate acetate	0.05	0.14	0.07	0.06	0.19	0.18	0.07	0.06	1218.8	1219
Nerol	0.91	0.74	0.09	0.17	0.15	0.17	0.16	0.09	1225.3	1227
Hexyl 2-methyl butanoate	0.23	0.10	0.02	0.04	0.08	0.08	0.01	0.01	1230.1	1233
Cumin aldehyde	1.23	0.35	0.15	0.15	0.16	0.13	0.09	0.09	1235.7	1238
Carvone	0.54	0.13	0.09	0.08	0.11	0.06	tr.	tr.	1239.4	1239
Linalool acetate	12.59	11.85	27.57	25.60	22.95	22.83	26.94	27.11	1252.3	1254
Dihydrolinalool acetate	tr.	tr.	0.08	0.04	0.06	0.10	0.04	0.05	1268.4	1272
Bornyl acetate	0.62	0.14	0.35	0.32	0.67	0.80	0.41	0.36	1277.2	1287
Lavandulyl acetate	4.49	5.34	2.53	4.68	3.89	3.20	4.91	4.75	1285.0	1288
<i>p</i> -Cymen-7-ol	0.41	0.14	0.11	0.15	0.22	0.21	0.15	0.17	1291.9	1289
Carvacrol	0.07	tr.	0.09	0.10	0.18	0.17	0.13	0.03	1306.0	1298
<i>p</i> -Vinylguaiaicol	0.12	tr.	0.34	0.41	1.36	1.07	0.46	0.46	1311.3	1309
Hexyl tiglate	0.04	0.06	0.12	0.09	0.07	0.07	0.10	0.10	1324.9	1330
3-Oxo- <i>p</i> -menth-1-en-7-al	0.31	0.09	1.32	0.99	1.26	1.41	1.25	1.17	1330.1	1330
n.i.	tr.	0.03	0.08	0.13	0.22	0.21	0.15	0.12	1341.3	
n.i.	0.07	0.13	0.59	0.40	0.19	0.26	0.27	0.64	1345.9	
n.i.	0.04	0.07	0.56	0.33	tr.	0.17	0.18	0.60	1349.1	
Neryl acetate	0.03	tr.	0.09	0.24	0.27	0.12	0.20	0.23	1358.1	1359
$\alpha$ -Copaene	0.49	0.76	0.07	0.10	0.20	0.19	0.12	0.12	1364.9	1374
Geranyl acetate	1.11	1.45	0.35	0.24	0.24	0.42	0.40	0.44	1377.4	1379
n.i.	0.16	0.03	0.02	0.03	2.79	2.77	0.14	0.06	1393.1	
n.i.	0.05	tr.	0.13	0.15	0.23	0.26	0.18	0.16		

Table 5. Continued

Component	Component content, mass%								KIE	KIL
	Essential Oil <sup>a</sup>		Supercritical fluid extracts (SFE) <sup>b</sup>							
	Sample label									
	La-el	La-ec	SFE-1	SFE-I	SFE-II	SFE-III	SFE-IV	SFE-V		
n.i.	0.03	tr.	0.16	0.14	0.18	0.20	0.16	0.15		
n.i.	0.04	0.02	0.12	0.11	0.13	0.13	0.13	0.13		
<i>trans</i> -Caryophyllene	4.33	2.20	5.86	5.72	5.08	5.06	6.22	6.22	1408.5	1417
<i>trans</i> - $\alpha$ -Bergamotene	0.15	0.02	0.12	0.11	0.17	0.17	0.17	0.10	1425.3	1432
<i>cis</i> - $\beta$ -Farnesene	0.13	tr.	0.21	0.19	0.28	0.40	0.33	0.21	1434.8	1440
$\alpha$ -Humulene	0.57	0.30	1.37	1.31	1.20	1.22	1.46	1.45	1441.9	1452
<i>trans</i> - $\beta$ -Farnesene	0.14	0.10	0.29	0.23	0.33	0.40	0.26	0.27	1448.3	1454
Linalool isovalerate	tr.	0.01	0.14	0.11	0.37	0.43	0.11	0.12	1457.9	1466
$\gamma$ -Murolene	0.34	0.16	0.53	0.70	0.99	0.94	0.75	0.73	1469.7	1478
<i>trans.trans</i> - $\alpha$ -Farnesene <sup>b</sup>	tr.	tr.	0.27	0.57	0.95	0.67	0.66	0.47	1498.1	1498
$\gamma$ -Cadinene	0.18	0.02	0.29	0.56	0.93	0.71	0.61	0.46	1502.7	1513
Photosantalol	1.27	0.09	0.13	0.05	0.12	0.14	0.05	0.06	1510.9	1511
Elemol	0.19	0.01	0.06	0.09	0.31	tr.	0.12	0.08	1535.1	1548
n.i.	0.04	tr.	0.09	0.18	0.39	0.38	0.21	0.14		
n.i.	0.53	0.26	0.24	0.24	0.37	0.35	0.28	0.23	1541.3	
n.i.	0.03	tr.	0.13	0.17	0.20	0.19	0.19	0.18		
Caryophyllene oxide	8.56	4.04	4.15	3.74	3.66	3.95	4.27	4.16	1572.7	1582
Humulene epoxide II	0.34	0.08	0.13	0.12	0.15	0.14	0.18	0.08	1597.7	1608
epi- $\alpha$ -Cadinol ( $\tau$ -cadinol)	0.72	0.11	0.06	0.06	0.06	0.05	0.13	0.07	1631.7	1638
14-Hydroxy-(Z)-caryophyllene	0.58	0.17	0.07	0.03	0.05	0.04	0.13	0.03	1649.7	1666
Cadalene	0.82	0.41	0.32	0.31	0.33	0.38	0.38	0.35	1664.2	1675
Mustakone	0.21	0.03	0.03	tr.	tr.	0.04	0.03	0.01	1669.1	1676
n.i.	0.15	0.10	0.33	0.28	0.33	0.38	0.36	0.31	1672.4	
n.i.	0.25	0.03	0.05	0.13	0.16	0.11	0.14	0.13		
n.i.	0.02	0.01	0.06	0.10	0.11	0.07	0.10	0.10		
n.i.	0.04	0.01	0.13	0.10	0.05	0.10	0.09	0.14	1754.6	

<sup>a</sup>Essential oil obtained by hydrodistillation; <sup>b</sup>extracts obtained by supercritical CO<sub>2</sub>; <sup>c</sup>tentative identification

From the results shown in Table 5 it can be seen that essential oil and CO<sub>2</sub> extracts obtained from the extraction of lavender flower at different pressures and temperatures have complex chemical compositions. Components that are present in the highest percentage are: linalool (from 25.24 to 48.4%); linalool acetate (from 11.85 to 27.11%); lavandulol (from 2.91 to 11.11%); caryophyllene oxide (from 3.66 to 8.56%); lavandulyl acetate (from 3.20 to 4.91%); terpinen-4-ol (from 2.26 to 3.39%).

The essential oil of the flower contains a much higher percentage of linalool (48.44%) than the essential oil of leaf (25.75%), while its content in the extracts ranges between 25.24 and 29.76%. The linalool acetate content in essential oils is nearly the same (about 12%) and significantly higher in the extracts (from 22.83 to 27.11%). Esters are probably hydrolysed in the process of obtaining essential oil

from the drug by hydrodistillation, which has been reported in the literature [15, 24].

Furthermore, it can be seen that CO<sub>2</sub> extracts contain a higher number of compounds than essential oils, especially the components with higher retention times, which are mainly present in waxes.

The analysis of SFE extracts (from SFE-1 to SFE-6) was performed. The content of dominant components in the extract SFE-1 is shown in Table 5 while the complete chemical composition other isolated extracts (from SFE-2 to SFE-6) is not shown in this work. On the other hand, from the change of dominant component content in the isolated extracts (Figure 6), it can be seen that their chemical composition is similar to the extracts obtained at different pressured and temperatures.

The results shown in Figure 6 represent the extraction of lavender flower at different times of extraction (0.0-0.5; 0.5-1.0; 1.0-1.5; 1.5-2.0; 2.0-2.5;

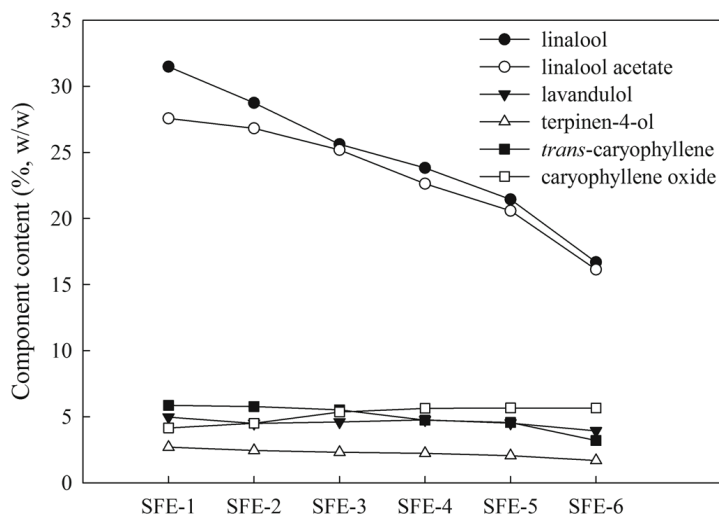


Figure 6. The change of dominant component content in CO<sub>2</sub> extracts obtained by extracting lavender flower with supercritical carbon dioxide ( $p = 10$  MPa;  $T = 313$  K).

2.5–3.0 h), where their qualitative and quantitative analysis was carried out by GC/MS and GC/FID. For example, for the extraction period 0.0–0.5 h the extract labelled SFE-1 was obtained, for the period 0.5–1.0 h extract SFE-2 and so on. Extract SFE-1 represents 60% of the total mass of all obtained extracts and extract SFE-2 about 14%, which means that over 70% of the extraction is completed in the first hour of the extraction process.

From the results shown in Figure 6 it can be seen that the content of linalool and linalool acetate in the first two CO<sub>2</sub> extracts is relatively high, in contrast to their content in other extracts. Since the first two extracts represent, as noted earlier, about 75% of the total extract yield, it can be concluded that for an extraction time of one hour a high yield of CO<sub>2</sub> extract is obtained with a relatively high content of dominant components (linalool and linalool acetate).

The content of other components in the extracts was practically the same.

Based on the results of extracts analysis by gas chromatography, it can be particularly concluded that the contents of components such as hydrocarbons (heptacosane, 2-methyloctacosane, nonacosane, untri-acontane) and hexadecanoic acid in the extracts constantly increase from SFE-1 to SFE-6.

## CONCLUSION

Using the hydrodistillation procedure, the content of essential oil in lavender flower was determined to be 2.39 ml/100 g drug, in contrast to the essential oil content in the leaf (0.52 ml/100 g drug).

By using GC/MS and GC/FID it was found that the examined samples (essential oils and SFE

extracts) contain high quantities of linalool (25.24–48.44%), linalool acetate (11.85–27.57%), lavandulol (2.91–11.11%), caryophyllene oxide (3.66–8.56%) and others as main components.

Under isothermal conditions ( $T = 313$  K), the extraction yield increases with the increase of pressure, which is in accordance with the increase of the dissolution power of the extractant. The highest yield was obtained with CO<sub>2</sub> at a pressure of 30 MPa (7.08 mass%). At higher pressures, especially at 30 MPa, the extraction yield was the highest at 333 K and the lowest at 313 K, because vapour pressure increased with the increase of temperature; thus, the solubility was determined by the equilibrium between the solvent density and the changes of vapour pressure of diluted components.

Based on the results of the extraction of lavender flower and obtained individual extracts for different periods of extraction, it was concluded that after 1 h of extraction, an extract was obtained with a high yield (about 75%) and with almost the same qualitative and quantitative composition compared to the yield after 3 h of extraction. These results are of interest in practice.

Based on the *MRD* (%) values (from 0.37 to 2.10 and from 0.97 to 8.42) for the Sovová model and the modified model respectively, it can be concluded that the applied models fit the experimental results of the extraction system lavender flower-supercritical CO<sub>2</sub> well.

## Acknowledgement

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**Nomenclature**

$a_0$	specific surface area, $\text{m}^2 \text{m}^{-3}$
$a$	the adjustable parameter of Eq. (2), $\text{s}^{-1}$
$b$	the adjustable parameter of Eq. (2)
$d_p$	average particle diameter, m
$d_s$	average particle diameter, mm
$D_{12}$	binary diffusion coefficient of lavender oil in the carbon dioxide, $\text{m}^2 \text{s}^{-1}$
$D_e$	effective intraparticle diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
$G$	initial fraction of extract in open cells, the adjustable parameter of Eq. (4),
$k_f$	mass transfer coefficient in fluid phase (external coefficient), $\text{m}^2 \text{s}^{-1}$
$K_m$	mass-related partition coefficient, the adjustable parameter of Eq. (4), $\text{kg plant} (\text{kg solvent})^{-1}$
$MRD$	mean relative deviation
$N$	number of experimental points at one extraction curve
$NP$	number of adjustable parameters in a model
$\dot{q}$	specific flow rate, $\text{kg} \cdot (\text{kg plant})^{-1} \cdot \text{s}^{-1}$
$R$	spherical particle radius, m
$r$	correlation coefficient
$t$	extraction time, s
$t_1$	time of the end of the first extraction period, s
$t_{\text{comb},i}$	combined characteristic time of mass transfer - substitute for $t_i$ , s
$t_{\text{eq}}$	characteristic time of equilibrium extraction, s
$t_f$	characteristic time of the fluid phase mass transfer, s
$t_i$	characteristic time of the solid phase mass transfer (internal diffusion), s
$t_r$	residence time, s
$U$	superficial velocity, $\text{m s}^{-1}$
$W$	solvent mass flow rate, $\text{kg s}^{-1}$
$x_0$	initial solid phase concentration, $\text{kg} \cdot (\text{kg plant})^{-1}$
$x_k$	the initial concentration of solute within the whole (intact) particles, $\text{kg} \cdot (\text{kg plant})^{-1}$
$x_t$	transition concentration, $\text{kg} \cdot (\text{kg plant})^{-1}$
$x_u$	concentration of extract in the plant before extraction, $\text{kg} \cdot (\text{kg plant})^{-1}$
$Y$	( $=y_e/y_{\text{max}}$ ) 100 normalized yield of extract
$Y_m$	normalized yield obtained from modelling, Eq. (3)
$y_e$	extraction yield, $\text{kg} \cdot (\text{kg plant})^{-1}$
$y_{\text{max}}$	the maximum yield, $\text{kg} \cdot (\text{kg plant})^{-1}$
$y_m$	( $= y_{\text{max}} Y_m / 100$ ) extraction yield obtained from the $Y_m$
$y_0$	initial fluid phase concentration, $\text{kg} \cdot (\text{kg solvent})^{-1}$
$y_{\text{sat}}$	solubility, $\text{kg} \cdot (\text{kg solvent})^{-1}$
$Z$	( $= \ln(1 - Y/100)$ ) variable (transformed normalized yield of extract)
$\epsilon$	free void

$\Theta_f$	( $= t/t_r$ ) dimensionless external mass transfer resistance
$\rho$	solvent density, $\text{kg m}^{-3}$
$\mu$	solvent viscosity, Pa s
$A$	cross sectional area ( $\text{m}^2$ )
$D$	diameter of column (m)
$D_R$	inner diameter of riser (m)
$D_D$	inner diameter of downcomer (m)
$k_L a$	volumetric mass transfer coefficient ( $1/\text{s}$ )
$L$	distance between the conductivity sensors (m)
$H$	height (m)
$N_G$	gas power output (W)
$\Delta p$	pressure drop (bar)
$t_c$	liquid circulation time (s)
$t_m$	mixing time (s)
$t$	time (s)
$U_G$	superficial gas velocity, column based (m/s)
$W_{LD}$	downcomer interstitial liquid velocity (m/s)

**Abbreviations**

ALR	airlift reactor
BC	bubble column
DT-ALR	draft tube airlift reactor
EL-ALR	external loop airlift reactor
rps	rotations per second

**Greek letters**

$\epsilon_G$	gas holdup
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**Subscripts**

C	circulation
D	downcomer
DT	draft tube
G	gas phase
L	liquid phase
R	riser
S	separation zone

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VESNA NAĐALIN<sup>1</sup>  
 ŽIKA LEPOJEVIĆ<sup>2</sup>  
 MIHAILO RISTIĆ<sup>3</sup>  
 JELENA VLADIĆ<sup>2</sup>  
 BRANISLAVA NIKOLOVSKI<sup>2</sup>  
 DUŠAN ADAMOVIĆ<sup>4</sup>

<sup>1</sup>Visoka tehnička škola strukovnih studija u Zrenjaninu, Zrenjanin, Srbija

<sup>2</sup>Univerzitet u Novom Sadu, Tehnološki Fakultet, Novi Sad, Srbija

<sup>3</sup>Institut za proučavanje lekovitog bilja "Dr Josif Pančić", Beograd, Srbija

<sup>4</sup>Institut za ratarstvo i povrtarstvo, Novi Sad, Srbija

NAUČNI RAD

## ISPITIVANJE EKSTRAKCIJE I EKSTRAKATA GAJENE LAVANDE (*Lavandula officinalis* L.)

*U radu je postupkom hidrodestilacije izvršeno određivanje sadržaja etarskog ulja u cvetu i listu lavande. Izolovanom etarskom ulju određene su fizičko-hemijske karakteristike. Korišćenjem CO<sub>2</sub> u superkričnom stanju izvršena je ekstrakcija cveta lavande odabranim protokom rastvarača, primenom izoternog i izobarnog postupka. Primenom gasne hromatografije sa masenom spektrometrijom (GC/MS) i gasne hromatografije sa plameno jonizujućim detektorom (GC/FID), izvršena je kvantitativna i kvalitativna analiza etarskog ulja i superkričnih ekstrakata (SFE). Takođe je izvršena i analiza pojedinačnih SFE ekstrakata dobijenih tokom različitih perioda ekstrakcije. Nađeno je da su glavne komponente analiziranih uzoraka: linalool, linalool-acetat, lavandulol, kariofilen-oksidi, lavandulil-acetat, terpinen-4-ol i dr. Korišćenjem odabranih modela izvršeno je modelovanje ekstrakcije sistema cvet lavande - superkrični CO<sub>2</sub> na osnovu eksperimentalnih rezultata ispitivanja kinetike ekstrakcije. Odabrani modeli dobro fituju eksperimentalne rezultate.*

*Ključne reči: lavanda, ekstrakcija, ekstrakti, modelovanje, superkrični CO<sub>2</sub>.*