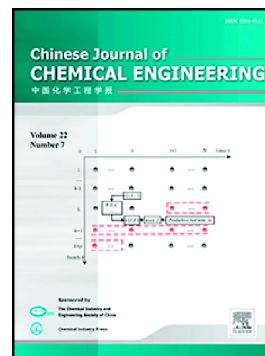


## Accepted Manuscript

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## Chemical Engineering Thermodynamics

A new kinetic model for the common juniper essential oil extraction by microwave hydrodistillation

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**Abstract**

The main objective of the present study was to model the kinetics of essential oil extraction from swelled ground juniper berries by classic hydrodistillation (HD) and microwave-assisted hydrodistillation (MAHD). A new phenomenological kinetic model was developed on the basis of the juniper essential oil extraction mechanism that assumed three mass transfer processes occurring simultaneously: washing, unhindered diffusion and hindered diffusion. The new model was compared to the existing kinetic models. Among the tested models, the new model had the smallest mean relative percentage deviation and the highest corrected Akaike information criterion value. In addition, that, the new model was verified for HD and MAHD of essential oils from some other plant materials. On the basis of the above-mentioned facts, the new model can be recommended for modeling the kinetics of essential oil extraction by both HD and MAHD.

**Keywords:** *Juniperus communis* L.; essential oil; kinetics; microwave-assisted hydrodistillation; modeling.

## Introduction

*Juniperus communis* L. (common juniper) is an evergreen, very resistant, dense and irregularly branched bush 1-3 m high, or tree 8-12 m high [1]. Of all conifers, common juniper has greatest distribution and can be found in North America, Europe and Asia. In Europe, it can be found from northern Scandinavia to southern Spain [2]. Essential oil is the most important bioactive ingredient of fruit berries [3]. Due to its strong antibacterial, antifungal, antiviral, antioxidant and anti-inflammatory properties, juniper essential oil (JEO) is used in modern pharmacy, medicine, veterinary medicine, food and cosmetics industry [3-6]. The most frequently used technique for JEO extraction is hydrodistillation (HD); nowadays, microwave-assisted hydrodistillation (MAHD) is often used as well [7, 8]. The extraction of JEO can also be performed by supercritical carbon dioxide extraction [9-12], extraction with organic solvents [10], simultaneous distillation and extraction [13], as well as simultaneous hydrodistillation and rectification [14].

Although a large number of papers dealing with the influence of the operating factors on yield and composition of the essential oils from different plants have been published [15], only a few papers are related to the kinetics of JEO extraction by HD [7,8, 16, 17] or MAHD [7, 8]. The existing models describing the kinetics of HD and MAHD assume two simultaneous processes [7, 15, 16]: (a) rapid distillation of the essential oil from external surfaces of the plant particles (so called washing) and (b) slow diffusion of the essential oil through the plant particles.

The present paper deals with the kinetics of essential oil extraction from juniper berries by HD and MAHD. A new phenomenological kinetic model was developed, which assumed that JEO distillation by HD and MAHD occurs *via* three simultaneous processes: washing, unhindered diffusion and hindered diffusion. So far, the two diffusions occurring within plant particles have been considered as a united mass transfer (diffusion) process. The unhindered diffusion involves the essential oil mass transfer from ruptured organs without any limitation while the hindered diffusion is the essential oil mass transfer through membranes of intact plant organs. This novel kinetic model was compared with several existing models like the phenomenological model involving simultaneous washing and diffusion [7,18], the model involving instantaneous washing and diffusion [16], the exponential model involving only diffusion [19] and the second-order model [20].

## 2. Material and methods

### 2.1. Juniper berries

Ripe juniper berries were collected from the southern hillsides of the Kopaonik mountain (1000 m above the sea level), Kosovo and Metohija, in September 2014. The juniper berries were dried in the shade and packed in the multilayer paper bags.

### 2.2. Preparation of juniper berries for JEO distillation

Before JEO distillation, dried juniper berries were swelled by the optimal procedure described elsewhere[15]. Berries (300 g) were immersed in distilled water (1000 ml) and kept 24 h for swelling. Then, the swelled berries were separated from the soaking water and divided into three approximately equal parts for being ground. The swelled berries and the soaking water (100 ml) were added to a Bosh disintegrator (500 W; medium intensity) and ground for 1 min with pauses after 20 s and 40 s when additional batches of the soaking water (50 ml) were added. Finally, 200 ml of distilled water was added to the joint suspension (300 g of berries + 1000 ml of soaking water) to achieve the juniper berries-to-water mass ratio (hydromodul) of 1:4.

### 2.3. JEO distillation: equipment and procedure

For both HD and MAHD, the Clevenger apparatus was employed, as in the previous study [7]. For HD, the distillation 2 L round-bottom flask was placed in an electric heater. For MAHD, the Clevenger apparatus was placed in a laboratory microwave oven (maximum power: 900 W; frequency: 50 Hz). The intensity of heating in both processes (700 W) ensured the floral water flow rate of  $(8.5 \pm 0.5)$  ml/min. The applied apparatuses are schematically shown in Fig. 1.

The prepared berries suspension was added to the distillation flask and then heated. The appearance of the first drop of the JEO designated the beginning of the distillation process. From that moment, the time and the volume of the JEO collected in the graduated tube were recorded during 4 h of distillation. The collected JEO was dried over anhydrous sodium sulfate, stored in glass bottles and held in a refrigerator at 4 °C until analysis.

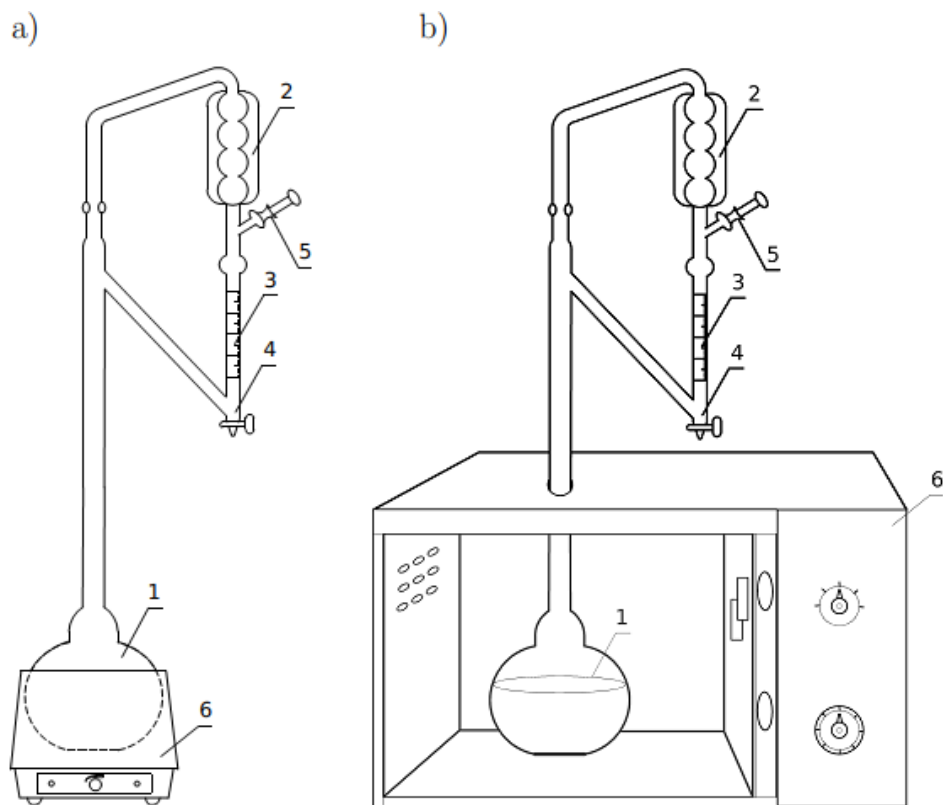


Figure. 1. Apparatuses for conventional HD(a) and MAHD (b): 1) distillation flask, 2) condenser, 3) graduated oil separatory tube, 4) tap with an extension, 5) side tube with ground stopper, and 6) heating mantle

#### 2.4. Kinetic modeling of JEO extraction by HD and MAHD

The kinetic model was derived for a batch distillation vessel, where the plant material was immersed in water. The suspension was heated by either a conventional electric heater or microwave irradiation; water vapor was produced and carried essential oil vapor from the distillation vessel into a condenser. Then, the resulting condensate was gravitationally separated into the essential oil and the floral water.

It was assumed that the extraction of JEO occurred through three simultaneous processes. The main part of available JEO was located at the external surfaces of the plant particles while the rest of it was distributed within the plant particles. JEO from the external surfaces was extracted during the fast initial stage of distillation process, the so-called “washing”. The remaining JEO, i.e. the JEO from ruptured and unruptured organs, was extracted during the “unhindered” and “hindered” diffusion, respectively. These diffusional processes became

significant in the latter stage of the hydrodistillation and both were much slower than the washing. Of the two diffusional processes, unhindered diffusion was considered faster. The kinetics of all three processes obeyed the first order law with respect to the essential oil in the plant particles:

$$-\frac{dq_p}{dt} = k \cdot q_p \quad (1)$$

where  $q_p$  was the average content of essential oil in the plant particles (g/100 g) at time  $t$ , and  $k$  was the process rate constant.

To develop the mathematical model of this process, several assumptions were made, which have already been used for modeling the kinetics of HD [15, 16] and MAHD [7]:

- i) Plant particles were isotropic and equal in size, shape and initial essential oil content;
- ii) The essential oil was considered to be a pseudo-single component;
- iii) The amount of the essential oil that could be extracted corresponded to the amount of the essential oil distilled off until the system reached equilibrium when no further distillation of JEO occurred;
- iv) The fractions of the essential oil extracted via washing, unhindered diffusion and hindered diffusion ( $f_w$ ,  $f_{d1}$  and  $f_{d2}$ , respectively) were assumed to be constant;
- v) The rate constants for washing ( $k_w$ ), unhindered diffusion ( $k_{d1}$ ) and hindered diffusion ( $k_{d2}$ ) were constant;
- vi) There was no resistance to the mass transfer of essential oil from the external surfaces of the plant particles;
- vii) The water phase and the essential oil were completely immiscible;
- viii) The amount of the essential oil available for hydrodistillation corresponded to the amount of the essential oil that distilled off until reaching the equilibrium, i.e.  $t = 0$ ,  $q_p = q_\infty$ ;

ix) The amount of essential oil collected in the separator, divided by the amount of the plant material, was equal to the essential oil yield from the plant material in the distillation vessel with a time delay.

For  $t = 0$ ,  $q_p = q_\infty$ , so integration of Eq. (1) gave the following expressions for washing, unhindered diffusion and hindered diffusion, respectively:

$$\frac{q_{p,w}}{q_\infty} = e^{-k_w \cdot t} \quad (2a)$$

$$\frac{q_{p,d1}}{q_\infty} = e^{-k_{d1} \cdot t} \quad (2b)$$

and

$$\frac{q_{p,d2}}{q_\infty} = e^{-k_{d2} \cdot t} \quad (2c)$$

Taking into account the assumption iv), the amount of essential oil that remained in the plant particles until time  $t$  was

$$\frac{q_p}{q_\infty} = f_w \cdot e^{-k_w \cdot t} + f_{d1} \cdot e^{-k_{d1} \cdot t} + f_{d2} \cdot e^{-k_{d2} \cdot t} \quad (3)$$

where  $f_w = q_{p,w}/q_\infty$ ,  $f_{d1} = q_{p,d1}/q_\infty$  and  $f_{d2} = q_{p,d2}/q_\infty$ . It was obvious that

$$f_w + f_{d1} + f_{d2} = 1 \quad (4)$$

Hence, the amount of essential oil extracted until time  $t$ ,  $q$  ( $= q_\infty - q_p$ ), was as follows

$$\frac{q}{q_\infty} = 1 - f_w \cdot e^{-k_w \cdot t} - f_{d1} \cdot e^{-k_{d1} \cdot t} - f_{d2} \cdot e^{-k_{d2} \cdot t} \quad (5a)$$

or

$$q = q_\infty \left( 1 - f_w \cdot e^{-k_w \cdot t} - f_{d1} \cdot e^{-k_{d1} \cdot t} - f_{d2} \cdot e^{-k_{d2} \cdot t} \right) \quad (5b)$$

Eq. (5b) described the variation of the essential oil yield from the plant material with the progress of distillation (here called Model I).



If hindered diffusion was negligible ( $f_{d2} = 0$ ), then Eq. (5a) was simplified to the following expression (named Model II):

$$\frac{q}{q_{\infty}} = 1 - f_w \cdot e^{-k_w t} - (1 - f_w) \cdot e^{-k_{d1} t} \quad (6a)$$

or

$$q = q_{\infty} \left[ 1 - f_w \cdot e^{-k_w t} - (1 - f_w) \cdot e^{-k_{d1} t} \right] \quad (6b)$$

Some authors developed the same model for conventional HD [15]. Also, Sovová and Aleksovski [18] derived the same kinetic expression from a phenomenological model for HD of essential oil from the seeds. This model was verified for the MAHD of essential oil from juniper berries [7].

Two simpler kinetic models, called Model III and Model IV, were derived from Eq. (6) by assuming instantaneous washing followed by diffusion ( $k_w \rightarrow \infty$ ) and diffusion with no washing ( $k_w \rightarrow \infty$  and  $f_w = 0$ ):

$$\frac{q}{q_{\infty}} = 1 - (1 - f_w) \cdot e^{-k_{d1} t} \quad (7a)$$

or

$$q = q_{\infty} \left[ 1 - (1 - f_w) \cdot e^{-k_{d1} t} \right] \quad (7b)$$

and

$$\frac{q}{q_{\infty}} = 1 - e^{-k_{d1} t} \quad (8a)$$

or

$$q = q_{\infty} \left( 1 - e^{-k_{d1} t} \right) \quad (8b)$$

Eqs. (7) were the same as the kinetic expression developed by Milojević et al. [16] for conventional HD, where  $f_w$  was the washing coefficient, corresponding to the washable part of

the essential oil that can be extracted, and  $k_{d1}$  was the coefficient of slow essential oil distillation. The model has been verified for the extraction of the essential oil by HD [16, 21, 22] and MAHD [23,24].Eqs. (8) were based on the assumption of the pseudo first-order kinetics with respect to the essential oil remaining in the plant material. This model was verified for the kinetics of HD [19]and MAHD [23].

Besides the above-mentioned kinetic models, the second-order rate of essential oil extraction from plant particles has sometimes been used for describing the process kinetics (Model V):

$$\frac{dq}{dt} = k_2(q_\infty - q)^2 \quad (9)$$

where  $k_2$  was the second-order rate constant. This model means that the essential oil extraction occurs in two simultaneous processes: a rapid extraction at the beginning and a slow extraction in the latter stage until the end of extraction process[25]. After integration and transformation, the following expression was derived:

$$q = q_\infty \frac{t}{\frac{1}{q_\infty k_2} + t} \quad (10)$$

where  $1/q_\infty k_2$  corresponded to the time when  $q = q_\infty/2$ . This is a hyperbole meaning that when  $t \rightarrow \infty$ , then  $q \rightarrow q_\infty$ . This model was verified for the kinetics of MAHD [25,26,27].

The parameters of the used kinetic models were calculated by the non-linear least square method on the basis of the experimental JEO yields using Curve Fitting Toolbox from MATLAB 2011b. The mean relative percentage deviation,  $MRPD$ , and the coefficient of determination,  $R^2$ , were used to assess the goodness of fit of the used kinetic models on the basis of the experimental and model values of JEO yield,  $q_i$  and  $q_{m,i}$ , respectively:

$$MRPD = \frac{100}{n} \sum_{i=1}^n \frac{|q_i - q_{m,i}|}{q_{\text{exp}}} \quad (11)$$

$$R^2 = 1 - \frac{\sum_{i=1}^n (q_i - q_{m,i})^2}{\sum_{i=1}^n (q_i - \bar{q})^2} \quad (12)$$

where  $\bar{q}$  was the mean of the analyzed set of experimental values.

The corrected Akaike Information Criterion (*AICc*) was used for selecting the best model among the five tested models with different number of parameters, which were developed on the basis of the same datasets:

$$AICc = AIC + \frac{2K(K+1)}{n-K-1} \quad (13)$$

where  $AIC = -2 \cdot \log(L) + 2K$  was the Akaike information criterion,  $L$  was the maximum value of the likelihood function,  $n$  was the data sample size and  $K$  was the number of parameters. It provided information about the relative quality of the compared models (not in an absolute terms). If  $n$  was large with respect to  $K$ , the *AIC* correction term was negligible. In cases where there were relatively few data per estimated parameter, *AICc* should be used rather than *AIC*. According to a rule of thumb, this correction was needed if  $n/K < 40$  [28]. The preferred model with respect to relative quality was the model with the minimum *AICc* value.

### 3. Results and discussion

#### 3.1. Kinetic modeling of JEO distillation

The kinetics of JEO distillation by HD and MAHD was described by five models (Tab. 1). Values of the models parameters and the statistical criteria used for assessing the goodness of fit (*MRPD* and  $R^2$ ) are presented in Tab. 1. On the basis of the high coefficient of determination ( $R^2 > 0.90$ ) and the acceptable *MRPD* ( $< \pm 15\% - 25\%$ ), all five models could be used for modeling the kinetics of HD and MAHD. Among these five models, the Model I, Eq. (5), which included simultaneous washing, unhindered diffusion and hindered diffusion, appeared to be the best one for both HD and MAHD of JEO as it had the largest coefficient of determination ( $R^2 > 0.97$ ) and the lowest *MRPD* ( $\pm 1\%$  for HD and  $\pm 10.4\%$  for MAHD). The second best model, with almost the same  $R^2$ - and *MRPD*-values as the Model I, was found to be the model of

simultaneous washing and diffusion (Model II). The worst in this group of models was the second-order model (Model V) while the simplest exponential model (Model IV) was as good as the other two-parameter model (Model III). A good agreement between the experiment and the tested models is illustrated by Fig. 2-6. Validity of the Models II and III has already been reported for JEO extraction by HD [15] and MAHD [7]. Fig. 7, where  $AIC_c$ -values of the five developed kinetic models are compared, clearly shows that Model I is the best for HD while, all models are approximately equally efficient for MAHD, the Model II and Model IV being a little better than others.

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Table 1. Values of the kinetic models' parameters.<sup>a</sup>

Model	Parameter	Distillation method	
		HD	MAHD
Model I: $q = q_{\infty} (1 - f_w \cdot e^{-k_w t} - f_{d1} \cdot e^{-k_{d1} t} - f_{d2} \cdot e^{-k_{d2} t})$ $f_w + f_{d1} + f_{d2} = 1$	$k_w / \text{min}^{-1}$	0.2194	0.0895
	$k_{d1} / \text{min}^{-1}$	0.0469	0.0772
	$k_{d2} / \text{min}^{-1}$	0.0065	0.0030
	$f_w$	0.462	0.536
	$f_{d1}$	0.304	0.250
	$q_{\infty} / \text{g}/100 \text{ g}$	2.309	2.452
	$R^2$	0.999	0.972
	$MRPD/\%$	$\pm 1.0$	$\pm 10.4$
Model II: $q = q_{\infty} [1 - f_w \cdot e^{-k_w t} - (1 - f_w) \cdot e^{-k_{d1} t}]$ $f_{d1} = 1 - f_w$	$k_w / \text{min}^{-1}$	0.1753	0.0873
	$k_{d1} / \text{min}^{-1}$	0.0173	0.0085
	$f_w$	0.619	0.860
	$q_{\infty} / \text{g}/100 \text{ g}$	2.185	2.200
	$R^2$	0.999	0.972
	$MRPD/\%$	$\pm 1.2$	$\pm 10.7$
Model III: $q = q_{\infty} [1 - (1 - f_w) \cdot e^{-k_{d1} t}]$	$k_{d1} / \text{min}^{-1}$	0.0746	0.0753
	$f_w$	0.0676	0 <sup>c</sup>
	$q_{\infty} / \text{g}/100 \text{ g}$	2.004	2.076
	$R^2$	0.960	0.967
	$MRPD/\%$	$\pm 6.2$	$\pm 11.5$
Model IV: $q = q_{\infty} (1 - e^{-k_{d1} t})$	$k_{d1} / \text{min}^{-1}$	0.0833	0.0753
	$q_{\infty} / \text{g}/100 \text{ g}$	1.988	2.076
	$R^2$	0.956	0.967
	$MRPD/\%$	$\pm 7.0$	$\pm 11.5$
Model V: $q = q_{\infty} \frac{t}{\frac{1}{q_{\infty} k_2} + t}$	$k_2 / \text{L g}^{-1} \text{ min}^{-1}$	0.0556	0.0433
	$q_{\infty} / \text{g}/100 \text{ g}$	2.195	2.324
	$R^2$	0.995	0.954
	$MRPD/\%$	$\pm 2.0$	$\pm 13.5$

<sup>a</sup> Pretreatment conditions: one-minute grinding and 24 h swelling. Hydromodul: 1:4. Distillation rate: about(8.5 $\pm$ 0.5) ml/min.

<sup>c</sup>Very small value, practically equal to zero.

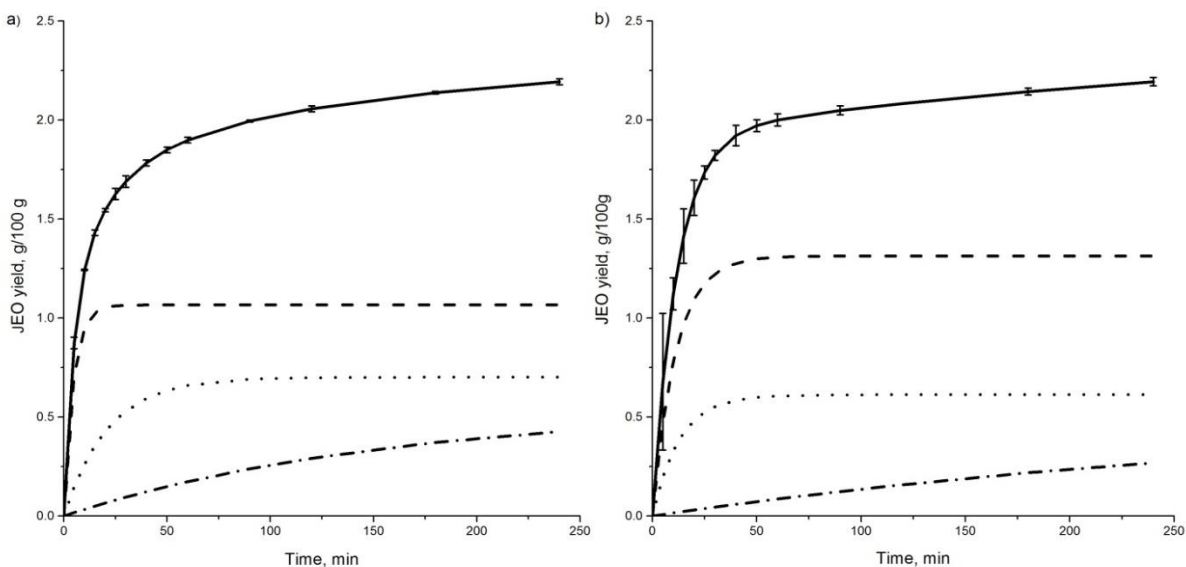


Figure 2. Model I: Contributions of three mass transfer processes occurring simultaneously with the progress of the JEO HD (a) and MAHD (b) (washing stage –dashed lines, unhindered diffusion – dotted lines, hindered diffusion – dash dotted lines and total – solid line) (hydromodul: 1:4 and distillation rate: about  $8.5 \pm 0.5$  ml/min).

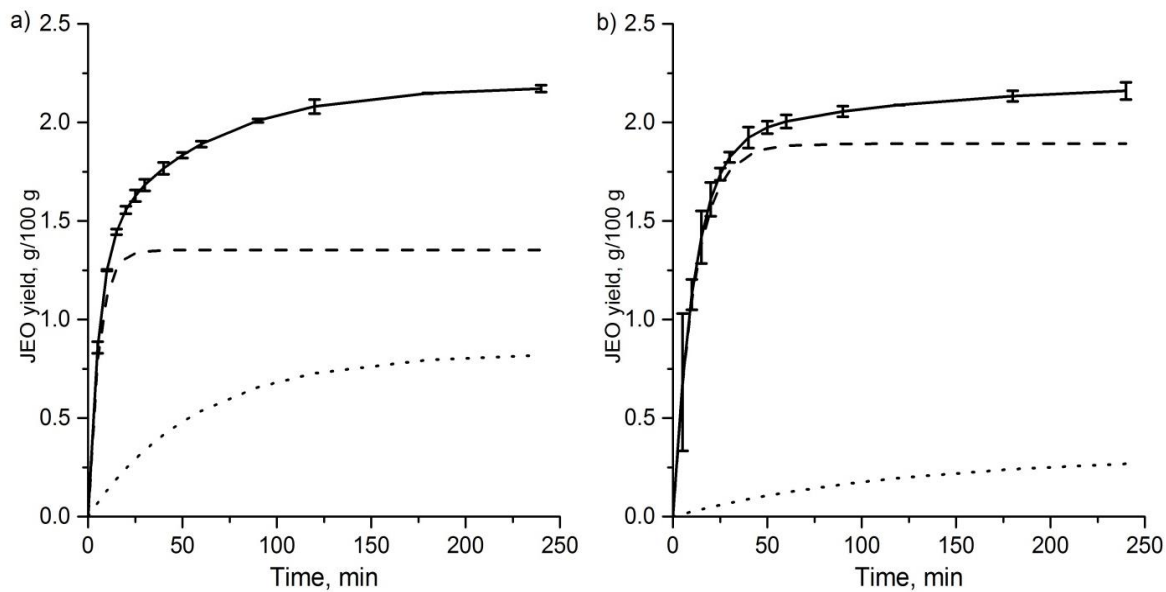


Figure 3. Model II: Contributions of two mass transfer processes occurring simultaneously with the progress of the JEO HD (a) and MAHD (b) (washing stage –dashed lines, unhindered diffusion – dotted lines and total – solid line) (hydromodul: 1:4 and distillation rate: about  $8.5 \pm 0.5$  ml/min).

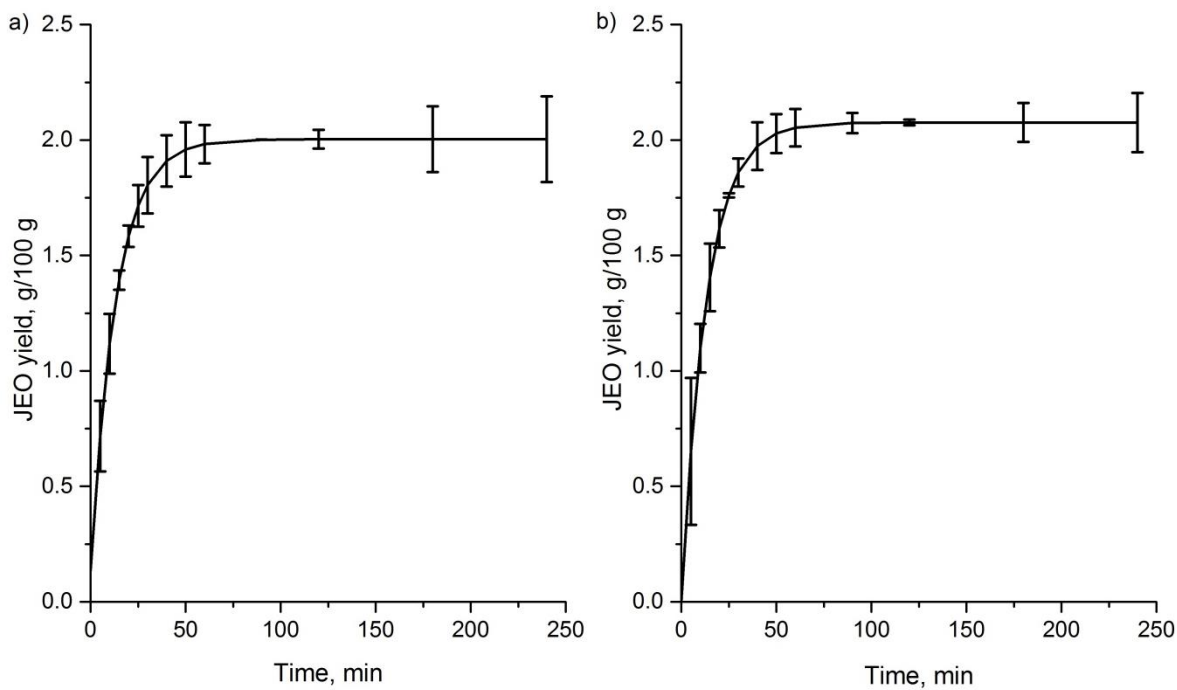


Figure 4. Comparison of the Model III (line) with the experimental data for HD (a) and MAHD (b) (juniper berries-to-water ratio: 1:4 g/ml and distillation rate: about  $8.5 \pm 0.5$  ml/min).

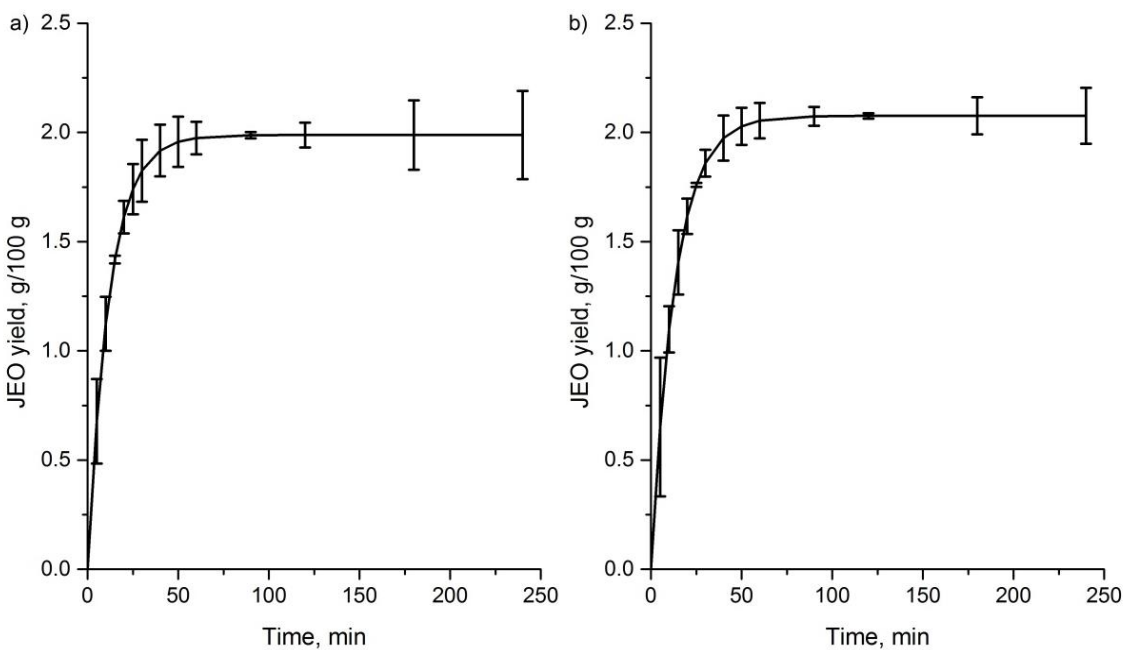


Figure 5. Comparison of the Model IV (line) with the experimental data for HD (a) and MAHD (b) (juniper berries-to-water ratio: 1:4 g/ml and distillation rate: about  $8.5 \pm 0.5$  ml/min).

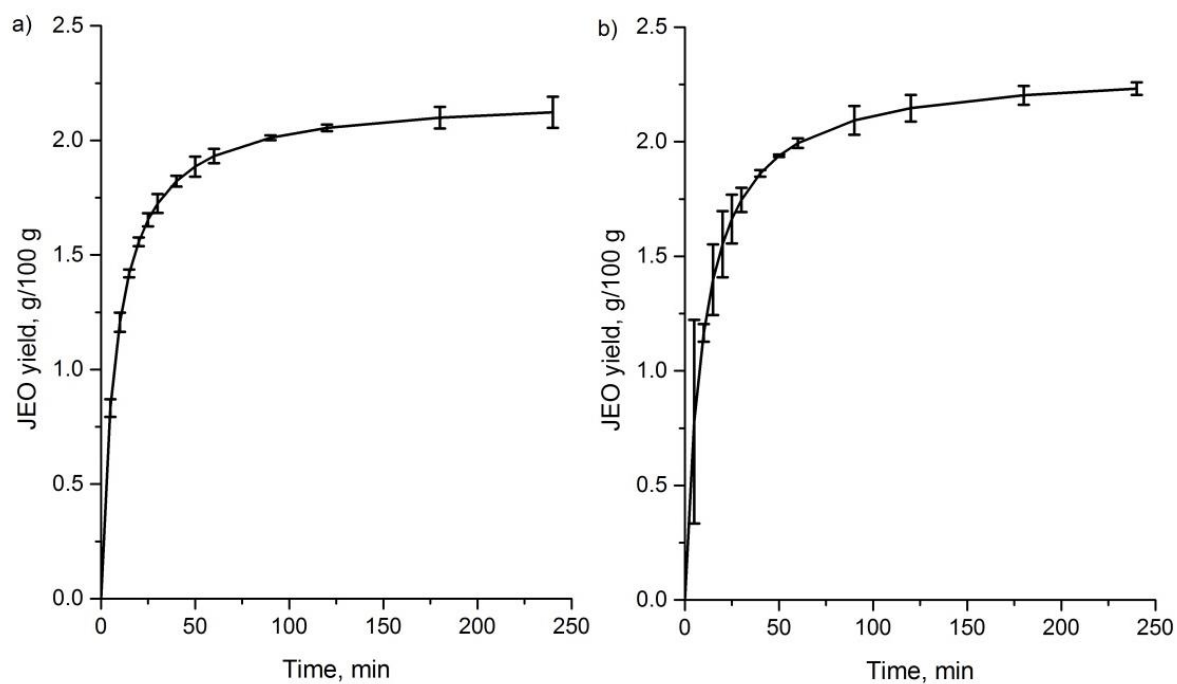


Figure 6. Comparison of the Model V (line) with the experimental data for HD (a) and MAHD (b) (juniper berries-to-water ratio: 1:4 g/ml and distillation rate: about  $8.5 \pm 0.5$  ml/min).

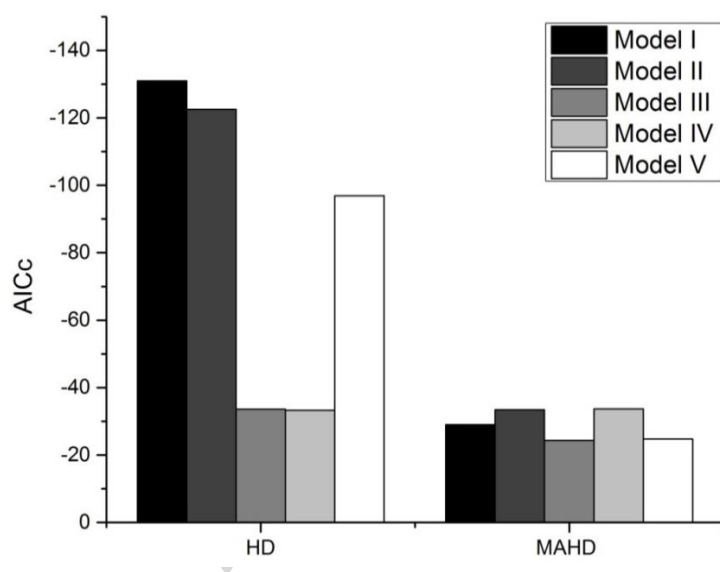


Figure 7. AICc-values of various kinetic models for the JEO distillation by HD and MAHD



### 3.2. Influence of the heating method on kinetic parameters

The influence of the heating method on Model I kinetic parameters was not clear for all parameters, such as for  $k_{d2}$ ,  $f_w$  and  $f_{d1}$ . The washing rate constant,  $k_w$ , was larger for HD while the unhindered diffusion rate constant,  $k_{d1}$ , was larger for MAHD (Tab. 1). The JEO fraction due to hindered diffusion,  $f_{d2}$ , was not influenced by heating method.

In the case of Model II, both the washing and diffusion rate constants,  $k_w$  and  $k_{d1}$ , respectively, were larger for HD than for MAHD. The JEO fraction due to washing,  $f_w$ , was larger for MAHD than for HD. Logically, the JEO fraction due to diffusion,  $f_{d1}$ , was larger for HD. The values of these three parameters were smaller than those previously reported by Pavićević et al.[7] for MAHD of dry-ground juniper berries at similar distillation rates. This could be attributed to the different origin of the juniper berries and the hydromodul applied in the present (1:4) and previous (1:3) study.

The equilibrium JEO yield calculated by all five models agreed quite well with the experimentally determined values (*MRPD* less than about  $\pm 8\%$ ); the best agreement was observed for Models II and V ( $\pm 1.4\%$  and  $\pm 3.9\%$ , respectively).

### 3.3. Verification of Model I

As can be seen in Tab. 2, the kinetics of HD and MAHD of essential oils from not only juniper berries [7] but also fennel seeds [23], aerial parts of summer and winter savory [29] and dried aerial parts of thyme [30] was successfully described by Model I, as indicated by a high  $R^2$ -values (close to 1) and acceptable *MRPD*-values. Therefore, the proposed mechanism of essential oil distillation might be considered as general for HD and MAHD for any plant material. However, for various plant materials, the values of the kinetic parameters differed probably due to specificity of their organs containing essential oil, different pretreatment method, distillation conditions, etc. Hence, it was not possible to observe a general behavior of the kinetic parameters. Also, the values of Model I's parameters for MAHD of dry-ground juniper berries based on the data of Pavićević et al.[7] (Tab. 2) differed from those obtained in the present study

(Tab. 1) at approximately the same distillation rate, which was probably due to the different origin of juniper berries and the hydromodul applied in the two studies present. Tab. 2 illustrates the effects of microwave irradiation energy dissipation and distillation rate on the kinetic parameters of Model I. For MAHD, the two diffusion rate constants increased with increasing microwave irradiation energy dissipation while the washing rate constant increased with the increasing of the distillation rate. For both MAHD and HD, the diffusion rate constants generally did not depend on the distillation rate.

Table 2. Verification of Model I, Eq. (5b), which includes simultaneous washing, unhindered diffusion and hindered diffusion, for the essential oil distillation by HD and MAHD from various plant materials.

Plant	Simultaneous washing, unhindered diffusion and hindered diffusion								Reference
	$f_w$	$f_{d1}$	$f_{d2}$	$k_w \times 10^3 / \text{min}^{-1}$	$k_{d1} \times 10^3 / \text{min}^{-1}$	$k_{d2} \times 10^3 / \text{min}^{-1}$	$MRPD / \%$	$R^2$	
Sumer savory, dried aerial parts									[29]
HD	0.522	0.146	0.332	283.4	126.1	12.5	0.9	0.999	
MAHD									
220 W <sup>a</sup>	0.353	0.338	0.309	84.1	21.3	21.2	4.2	0.986	
440 W	0.506	0.296	0.198	92.3	24.6	24.5	2.4	0.994	
660 W	0.317	0.358	0.325	80.0	30.3	30.2	1.9	0.995	
Winter savory, dried aerial parts									
HD	0.509	0.118	0.373	250.2	122.1	13.0	0.9	0.999	
MAHD									
220 W	0.341	0.541	0.118	136.1	17.7	17.4	7.0	0.957	
440 W	0.377	0.481	0.142	183.0	26.7	26.1	4.4	0.924	
660 W	0.471	0.310	0.219	34.17	34.0	33.6	2.9	0.988	
Thyme, dried aerial parts									[30]
HD	0.464	0.224	0.312	102.5	26.57	19.2	0.4	0.999	
MAHD	0.433	0.473	0.094	98.4	47.0	39.1	2.5	1	
Fennel seeds, crushed									[23]
HD	0.500	0.270	0.230	167.6	141.3	141.7	20.4	0.990	
MAHD	0.615	0.169	0.216	171.1	169.3	170.9	15.1	0.993	
Juniper berries, ground									[7]
HD									
3 ml/min <sup>b</sup>	0.442	0.284	0.274	115.6	12.1	12.2	1.4	0.998	
6 ml/min	0.609	0.168	0.224	86.8	11.6	10.7	1.2	0.999	
MAHD									
3 ml/min	0.412	0.421	0.167	240.9	24.4	23.8	1.1	0.997	
6 ml/min	0.318	0.545	0.137	373.1	23.3	23.6	1.0	0.999	
9 ml/min	0.347	0.616	0.037	1611.0	46.2	21.5	0.8	0.999	
Juniper berries, ground and swelled; about 8.5 ml/min <sup>b</sup>									This work
HD	0.462	0.304	0.234	219.4	46.9	6.5	±1.0	0.999	
MAHD	0.536	0.250	0.214	89.5	77.2	3.0	±10.4	0.972	

<sup>a</sup> Microwave irradiation energy dissipation.<sup>b</sup> Distillation rate.

### 3.4 Mechanism of JEO distillation according to Model I

Change of the JEO yield with the progress of both HD and MAHD was the same as for any other plant material. Initially, JEO distillation was rapid due to extracting the JEO located at the external surfaces (washing) while it slowed down in the latter stage approaching the equilibrium (unhindered and hindered diffusional processes). The contributions of the three mass transfer mechanisms occurring simultaneously with the progress of the HD and MAHD were calculated on the basis of the developed kinetic model that includes simultaneous washing, unhindered diffusion and hindered diffusion (Model I) (Fig 2.). Regardless of the distillation technique (HD or MAHD), the washing of the essential oil located originally at the external surfaces of the plant particle contributes predominantly in the first 20 to 30 min of the distillation. On the basis of the  $f$ -parameters ( $f_w, f_{d1} + f_{d2}$ ), three conclusions can be withdrawn. First, washing is more important for MAHD than HD, which can be attributed to the increased availability of the JEO from the organs close to the external surface of the plant particles because of the favorable action of microwave irradiation. Second, the contribution of the unhindered and hindered diffusion was somewhat higher in HD than in the MAHD. Since the sum of three  $f$ -parameters is equal to 1 (i.e.  $f_w + f_{d1} + f_{d2} = 1$ ) and  $f_w$  is higher for MAHD, the sum  $f_{d1} + f_{d2}$  must be larger for HD. Finally, the contribution of the hindered diffusion was less compared to unhindered diffusion in both distillation techniques, which was probably because of much slower rate of hindered diffusion compared to that of unhindered diffusion.

## 4. Conclusions

A new phenomenological kinetic model involving simultaneous washing, unhindered diffusion and hindered diffusion (the so-called Model I) was developed for the JEO extraction by both HD and MAHD. This model was agreed very well with the experiments as indicated by the  $R^2$  - and MRPD-values. Compared to the well-known kinetic models, it had the smallest MRPD-value for both HD and MAHD and the smallest AICc-value for HD. Besides that, this model was verified for HD and MAHD of essential oils from some other plant materials. Therefore, this model can be recommended for modeling the kinetics of essential oil extraction from plant materials by both HD and MAHD.

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