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THE KINETIC OF ESSENTIAL OIL SEPARATION FROM FENNEL BY MICROWAVE ASSISTED HYDRODISTILLATION (MWHD)

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Multe din noile direcţii de dezvoltare a separării uleiurilor volatile din materiale vegetale prin hidrodistilare sunt reprezentate de utilizarea unor variante de încălzire cu microunde. În lucrarea de faţă hidrodistilarea în câmp de microunde (MWHD) este utilizată pentru a caracteriza cinetica extracţiei uleiului esenţial de fenicul. Instalaţia experimentală pentru MWHD este reprezentată de un balon de hidrodistilare rotativ cuplat cu ajutorul unei extensii Clevenger modificate. La datele cinetice de extracţie ce au fost obţinute a fost cuplat un model semiempiric. Comparaţia între produsele obţinute este făcută prin analiza trans-anetolului a fenchonului şi respectiv a metil-cavicolului. A fost obţinut ca timpul de operare cu instalaţia MWHD, pentru cantităţi similar de produs sunt mai scurte ceia ce înseamnă o implicare în exprimarea consumului de energie a procesului.

More of the newest developments in volatile oils extraction from vegetal materials by hydro distillation (HD) are represented by the different variants with microwave heating of the samples. In this paper the microwave assisted hydrodistillation (MWHD) was compared with conventional technique, hydrodistillation (HD), in order to characterize the kinetic of fennel essential oil extraction. The laboratory pilot MWHD device is based on an original rotated apparatus, where the extraction flask is placed in a domestic microwave oven and the vapors tube-condenser system presents a modified Clevenger extension. Based

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on the experimental kinetic results, a semi-empirical model was fitted. The gas chromatograph oil analysis respect to trans-anethole, fenchon and methyl-chavicol reveals slowly difference between HD and MWHD operating procedures. The experimental investigation shows also that the operation time for MWHD in opposite to classical HD, for the same product quantity, was shorter. Consequently, the use of MWHD reduces the energy consumption of extraction process.

Keywords: microwave assisted hydro distillation, volatile oil, fennel extraction, kinetic model

1. Introduction

Chemical species produced by world's plants can be dominant resources for different industries, such as pharmaceuticals, food colorants, fragrances and flavors.

The essential oils separated from a wide range of vegetal species contain various compounds having biological activity. As a consequence, they are applied in medicine thanks to their antibacterial, antioxidant, anti-inflammatory, antiseptic or larvicidal properties. In obtaining of volatile compounds from vegetal materials, at pilot or industrial scale generally hydrodistillation (HD), also known as steam-distillation, or solvent extraction is used. These methods have some disadvantages like thermal decomposition of extracts, its contamination with solvent or solvent residues. The pollution of residual vegetal material with solvent can be also an important environmental problem. At present time new green techniques, such as supercritical fluid extraction, ultrasound and microwave assisted techniques, are potential solutions for energy consumption reduction [1-3], and/or for solving the environmental problems of residues [1].

Nowadays MWHD became a widely used method for obtaining of essential oils from different medicinal plants, do to its advantages (e.g. more effective heating, shortened extraction time) in comparison with the classical HD. The heating process is based on the molecular motions of the polar molecules and ions inside the solvent and vegetal matrix; it is strongly influenced by the dielectric constants of the solid-liquid-vapors system, developed by process evolution. This heating way realizes a more homogeneous temperature distribution at plant powder suspension level [4, 5].

Instead to the HD process, during the MWHD a pressure difference occurs between the inner and outer side of the plant cells, therefore the contained compounds are more easily released to the surrounding solution, resulting a higher effective mass transport coefficient. Practically, the extraction process improvement is a result of breaking the external cell wall [5].

Seeds of *Foeniculum vulgare* Miller (Fennel from *Apiaceae* class) are used for appetizing, as digestive aid, sedative and anticonvulsive and are added as spice in breads, fishes, salads and cheeses [2,5]. A lot of papers reported the essential oil composition of fennel [4, 7-10]. The mainly identified substances are *trans*-anethole (82.2-86.8%), methyl chavicol (4.0-4.9%) and limonene (2.2-4.9%). The bitter fennel (*F. vulgare* subsp. *vulgare* var. *vulgare*) contains *trans*-anethole (60%) and fenchon (15%). The sweet fennel (*F. vulgare* subsp. *vulgare* Miller) contains more (E)-anethole (80%) as the main component [4]. Methyl-chavichol possess carcinogenic effect, its LD_{50} is about to 150-600 $mg\cdot kg^{-1}$bw [11]. In practice as a result of heating isomerization of *trans*-anethole to methyl-chavichol can occur.

The aim of this study is to realize a comparison between MWHD and HD processes and characterize the kinetic of essential oil extraction from fennel seeds.

2. Experimental

Materials and methods

As vegetal material, fennel (*Foeniculum vulgare* var. *vulgare*) seeds have been selected, which was collected in 2007 and stored in a cool and dry location.
Microwave assisted and classic hydrodistillation devices: The original designed and build MWHD apparatus is presented in Fig. 1.

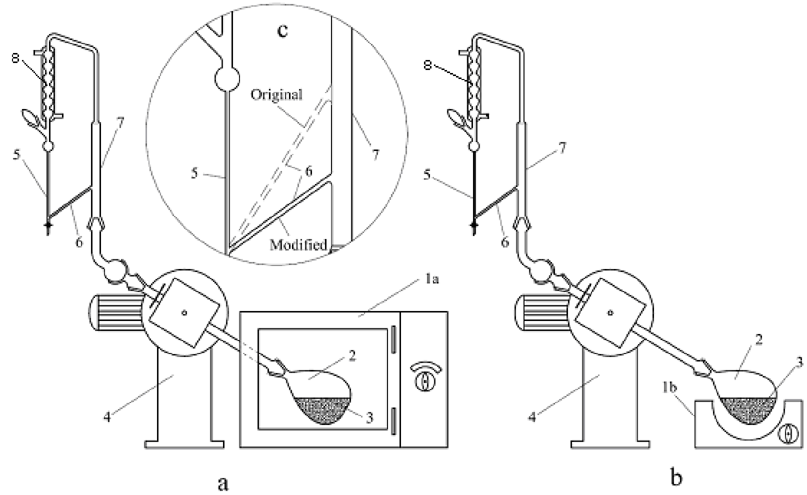

Fig. 1. Hydrodistillation apparatus with a modified Clevenger extension: (a) Microwave assisted hydrodistillation apparatus, (b) Hydrodistillation apparatus, (c) Structural differences of the original and the modified Clevenger extension:
1a-microwave oven; 1b-heating mantle with temperature regulation; 2-flask; 3-plant material; 4-rotation head; 5-phase separator tube; 6-reflux tube; 7-vapor tube and 8- cooler-condenser.

In all cases 25 g of dried fennel seeds powder were placed in the distillation flask of the apparatus. In case of microwave assisted hydrodistillation the volume of introduced water was 50 mL and for the classic method was 200 mL. The distillation flask's rotation speed was 50 rpm. The heating power of both processes was fixed at 300 W. The radiation frequency in microwave oven was 2.45 GHz. With the modified Clevenger extension (in contrast to classical apparatus) it is possible to measure the ejection velocity of condensed volatile oil production from the plant. The time evolution of extracted volatile oil volume was measured. At the end of extraction the obtained quantities of essential oil was stored over anhydrous sodium sulphate in glass vials, at 4 ºC, until analysis.

Qualitative analysis. The obtained essential oils were analyzed using Varian CP 3380 gas chromatography coupled to flame ionization detector, CP-Sil 88 (100 m x 0.25 mm) silica capillary column, operated at the following conditions: carrier gas H_2 (pressure 235 kPa); injected probe volume was 1 μL. The temperature program: injection 270 ºC; oven temperature program: from 50 to 210 ºC with 5 $^{o}C\cdot min^{-1}$ gradient, then constant temperature was applied; analysis time less than 40 min.

3. Results and discussion

Composition of the essential oil obtained by HD and MWHD

The GC analysis for main components of the products is presented in Fig. 3. The compositions of the HD and MWHD obtained oils show a slight dependence from the applied method. In case of MWHD the content of methyl-chavicol was higher with 5.5%, decreasing the amount of trans-anethole with the same proportion. The trans-anethol – methyl-chavicol isomerization (fig. 4) is possible during both hydrodistillation processes and this fact can explain the mentioned composition differences between HD and MWHD extracts.

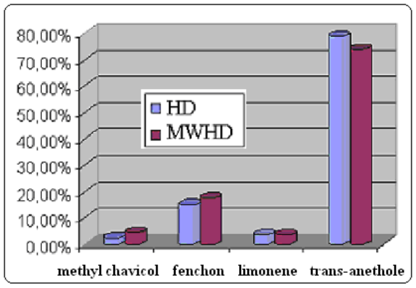

Fig. 3 Fennel volatile oil composition obtained by HD and MWHD

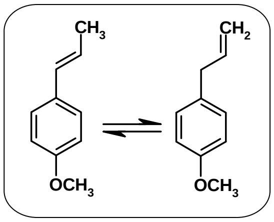

Fig. 4 Isomerization reaction

The mathematic model

A semi-empirical model for hydrodistillation was described by Milojević [3]. It assumes that, at particle level, the volatile compounds follow an unsteady-state diffusion transport. So, inside of particle, the field of one volatile species is given by Fick's second law (1) where D_{eff} is determined by nature of extraction solvent and of extracted species, by material structure (porosity and pore tortuosity) and, also, by local temperature: $\frac{\partial q_p}{\partial t} = D_{eff} \frac{\partial^2 q_p}{\partial x^2}$ (1)

To solve this model, for the MWHD process, several assumptions were made whereas:

(I) all solid particles of plant material are homogeneous related to oil concentration in matrix;
(II) the essential oil concentration at external surface of particle is near to zero do to the rapid dissolving process;
(III) the particle temperature remains unchanged, or it increases by a known law.

	Nomenclature
A	constant
b	fast distillation coefficient
D_{eff}	effective diffusion coefficient, $[\mathrm{m^2 \cdot s^{-1}}]$
HR	hydrodistillation rate, $[\mathrm{ml \cdot min^{-1}}]$
k	slow distillation coefficient, $[\mathrm{min^{-1}}]$
m	mass of oil collected in the separator, [g]
m_{pm}	mass of plant materials in the batch, [g]
q	oil yield at any moment of hydrodistillation, $[\mathrm{g \cdot g^{-1}}]$
q_o	initial oil content in the probe, $[\mathrm{g \cdot g^{-1}}]$
q_{p}	average concentration of oil in the plant particles at any moment of hydrodistillation, $[\mathrm{g \cdot g^{-1}}]$
$q_{\mathrm{p,s}}$	concentration of oil at the free surface of the plant particles at any moment of hydrodistillation, $[\mathrm{g \cdot g^{-1}}]$
q_w	surface essential oil concentration at t = 0 $[\mathrm{g \cdot g^{-1}}]$
t	time, [min]
td	time delay, [min]
x	distance along the direction of diffusion,
y	volume fraction of fennel oil in the vapor phase near the free surface of the boiling suspension

A distorted model, of above shortly presented model, has, respect to particle extraction yield, an integral solution given by equation (2). This distorted model accepts appropriate initial and boundary conditions of those characterizing the original model (initial constant species concentration in the particle, constant particle temperature, particles identity etc.).

$$\frac{q_0 - q}{q_0} = A \cdot e^{-kt} \qquad (2)$$

The described mathematical model of the HD process is based on a similar mechanism with the classical extraction, which have two important stages: the first is the diffusion of oil from the inner part of the solid particles to the outer surface and, the second stage is given by the dissolving of oils in extraction media at outer particle surface. Although the second process is the first to take place, mass transfer is achieved as described above. At the beginning of the MWHD process, due to the state of distillation process, the oil washing from particles surfaces is rapid and the surface oil concentration level is fixed at q_w value. Considering this observation, with the extension of distillation rate at the particle level, it can be written relation (3) and (4). Here *b* is a fast distillation coefficient, characterizing the essential oil evaporation from particle surface at $t = 0$.

$$t = 0: \; q = q_w \qquad (3) \qquad \frac{q}{q_0} = \frac{q_w}{q_0} = b \qquad (4)$$

At current time, the oil concentration in particle is controlled by diffusion and so its dynamic shows a slow exponential decrease (eq.2). Therefore, the basic kinetic equation for the distillation process will be obtained by combining eq. 2 and 4, resulting:

$$\frac{q_0 - q}{q_0} = (1 - b) \cdot e^{-kt} \qquad (5)$$

The established mathematical model, given by equation (5), is completed with solid phase mass balance. The following assumptions were made:

- the pressure and temperature are constant in the extraction device;
- there are no heat loss and vapors condense only in the condenser;
- the suspension in the extraction flask is perfectly mixed;
- plug flow is assumed for movement of vapor phase through the flask, connecting tube and condenser.

According to these assumptions, the differential and integral mass balance for solid phase is as follows:

$$\frac{dm}{m_{pm}} = \frac{HR \cdot y}{m_{pm}} dt = dq \qquad (6) \qquad ; \quad \frac{m}{m_{pm}} = q \qquad (7)$$

Equation (6) describe that the mass of evaporated oil in flask from the outer surface of particles during a period of time is equal to the mass of oil extracted from plant in the flask for the same period of time. In separator this mass will appear after a time delay, *dt*, depending on the hydrodistillation rate (*HR*).

When the time evolutions of the oil extraction yield ($\frac{q_0 - q}{q_0}$) is experimentally established, the logarithmic model state is used for computing b and k process parameters:

$$\ln\left(\frac{q_0 - q}{q_0}\right) = \ln(1 - b) - kt \qquad (8)$$

Kinetics of hydrodistillation processes

During HD and MWHD processes the variation of collected essential oil quantities was determined. In case of HD process the heating time to boiling temperature was 319 s. In MWHD the heating time was shorter, namely 200 s. min and during both procedure the initial process velocity of oil collection was about 0.1 mL˙min^{-1}. The obtained total volume of volatile oil from 25 g of fennel seeds by MWHD was 0.57 mL, higher with 0.04 mL than for HD. After 24 min operation the collected oil volume does not show further increase.

For model parameters k and b identification, in equation (8) $\frac{q_0 - q}{q_0}$ was replaced with $1 - \frac{V}{V_{\max}}$ as follows:

$$\ln\left(1 - \frac{V}{V_{\max}}\right) = \ln(1-b) - k\tau \qquad (9)$$

where V is time dependent collected essential oil volume and $V_{\max}$ represents the oil volume at the end of extraction.

The parameters k and b becomes as slope (eq. (10) and intercept (eq.(11)) of linear dependence predicted by eq.(9).

$$n = \ln(1-b) \qquad (10)$$

$$b = 1 - e^{n} \qquad (11)$$

The experimental and calculated extractions kinetic curves for HD and MWHD processes are presented in Fig. 2.

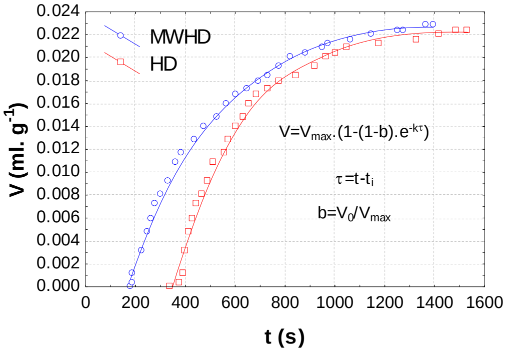

Fig. 2. Comparison of the kinetic of the two hydrodistillation method

Value of correlation coefficients of the linearized kinetic models ($r^2_{HD}=0.995$ and $r^2_{MWHD}=0.994$) shows a good fitting of the model with experimental data. The kinetics for both processes is presented bellow:

$$V_{HD} = 0.0212 \cdot (1 - 0.9165 \cdot e^{-0.0034\tau}) \text{ (ml/g fennel)} \qquad (13)$$

$$V_{MWHD} = 0.0228 \cdot (1 - 0.8993 \cdot e^{-0.0034\tau}) \text{ (ml /g fennel)} \qquad (14)$$

Relations (13) and 14) confirm that in HD and MWHD the extraction occurs after the same law. In relations (13) and (14) τ is the reduced time (the difference between current time and the initial time - the moment when the first oil drop is obtained).

4. Conclusions

The composition of the volatile oil obtained by HD and MWHD is very similar. With MWHD the obtainable essential oil quantity is higher with 7.5% than in case of HD. The modified Clevenger apparatus is appropriate to obtain kinetic data of hydrodistillation processes independent of heating method. The velocity of the two methods is quit the same, but the induction period is much shorter (about a third) for the MWHD. The used semiempirical model describes well both HD and MWHD processes. The quantitative and qualitative results for the obtained volatile oil are in concordance with literature data.

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