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RESEARCH ARTICLE

Microwave-assisted Hydrodistillation for Extraction of Essential Oil from Patchouli (*Pogostemon cablin*) Leaves

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Abstract

Conventional hydrodistillation (HD) and microwave-assisted hydrodistillation (MAHD) methods has been compared and evaluated for their effectiveness in the isolation of essential oils (EOs) from patchouli (Pogostemon cablin) leaves. The MAHD method offers important advantages over HD, viz. shorter extraction time (126 min vs. 417 min for HD); better yields (2.7227 % v/w vs. 2.6132 % v/w for HD); environmental impact (energy cost is appreciably higher for performing HD than that required for rapid MAHD extraction); and provides a more valuable EO (with high amounts of oxygenated compounds). It also offers the possibility for better reproduction of the natural aroma of the EO from patchouli leaves than that obtained using HD. The extraction of patchouli consisted of an initial, fast oil distillation followed by a slow oil distillation. Based on the experimental kinetic results, a semi-empirical model was fitted. The experimental investigation shows also that the operation time for MAHD in opposite to classical HD, for the same product quantity, was shorter. Higher yield results from higher extraction rates by microwave and could be due to a synergy of two transfer phenomena: mass and heat acting in the same way.

Keywords

Pogostemon cablin, essential oil, extraction, hydrodistillation, microwave-assisted hydrodistillation

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1 Introduction

Patchouli oil is obtained from the leaves of *Pogostemon cablin* (patchouli), a plant of the Lamiaceae family, originating from Malaysia and India [1]. It is an important essential oil (EO) in the perfume industry, used to give a base and lasting character to a fragrance [2, 3, 4]. The EO is very appreciated for its characteristic pleasant and long lasting woody, earthy, and camphoraceous odor, as well as for its fixative properties, being suitable for use in soaps and cosmetic products [5,6]. It is also on the FDA's (Food and Drug Administration) list of substances approved for human consumption, in section 172.510, as a natural additive for food flavoring [7]. Moreover, the plant (*Pogostemon cablin*) is widely used in traditional Chinese medicine as it offers various types of pharmacological activity according to the composition of the oil [1, 8].

Since there is no synthetic replacement for patchouli oil, the demand is very high in the international markets. The world demand of patchouli oil is currently stood at 587 tons per annum. The demand of patchouli has never stopped increasing. It is anticipated that the price of patchouli will remain high in the future because of high demand of patchouli worldwide and introduction of new application of patchouli oil. In view of the importance of patchouli oil to many sectors of industries, it would be benefitial to improve the production of patchouli oil. As a result of this, prospects for discovering method of inducing patchouli production are very promising. It is expected that through understanding of the mechanism of patchouli extraction, there will be sufficient supply to meet market demands. Therefore, there is strong incentive to optimize the patchouli oil extraction yield.

With increasing energy consumption and the drive to improve efficiency, industries and research institutions are challenged to find ways which can simplify operation procedure, meet low cost requirements and achieve good quality. Moreover, in order to reduce the extraction time and possibly improve the extraction yield, to enhance the quality of the extracts and also to reduce the operation costs, new approaches such as microwave-assisted extraction (MAE) have also been sought.

Nowadays microwave-assisted hydrodistillation (MAHD) became a widely used method for obtaining of EOs from different medicinal plants, do to its advantages (e.g. more effective heating, shortened extraction time) in comparison with the classical hydrodistillation (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 [9, 10].

Instead to the HD process, during the MAHD 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 [10].

In order to make adequate use of microwave to enhance extraction efficiency, researchers try to find the kinetic law of the effective composition diffusion in the microwave-assisted hydrodistillation. So far, the researches on the kinetic law of the effective composition diffusion mainly established some kinetic models such as the Garce-Ayuso et al. (1999) [11] established MAE mathematics model by data regression and Li He et al. (2004) [12] established kinetic models for MAE of the resveratrol in giant knotweed on the basis of the Fick's diffusion law. Huang Ruihua et al. (2005) [13] established the heat and mass co-transfer mathematics model for MAE of the icariin in epimedii leave on basis of the Fick and Fourier's law. Yang Junhong et al. (2006) [14] established kinetic models for MAE of the rutin in hawthron on basis of the microwave-pretreatment reflux technology. The established kinetics models can provide important theory guidance for microwave-assisted hydrodistillation, whereas the kinetics models were established under special extraction conditions, which had not universal adaptability.

Thus, the objectives of this work was to use the MAHD techniques for the extraction of EOs from dried *Pogostemon cablin* leaves commonly used in the food, pharmaceutical and cosmetic industries. Another attempt was to compare extraction time, extraction yield/efficiency, chemical composition, energy consumption and environmental considerations with those of the conventional HD method. Furthermore, the kinetics model on basis of MAHD and HD experiment results, will be numerically simulated and the kinetic model can contribute to the fundamental understanding of the process.

2 Materials and methods

2.1 Material and chemicals

Dried leaves of *P. cablin* was collected from Tulungagung, East Java, Indonesia. The leaves then were chop to a size around 5-10 mm using a commercial grade blender (Arte Blender, BL-001) and stored at room temperature until required. Distilled water and anhydrous sodium sulphate used in the experimental work were all of analytical grade.

2.2 Microwave-assisted hydrodistillation

In employing MAHD, we used a domestic microwave oven (EMM-2007X, Electrolux, 20 l, maximum delivered power of 800 W) with wave frequency of 2450 MHz. The dimensions of the PTFE-coated cavity of the microwave oven were 46.1 cm x 28.0 cm x 37.3 cm. The microwave oven was modified by drilling a hole at the top. A round bottom flask with a capacity of 1000 ml was placed inside the oven and was connected to the three-way adapter and liebig condenser through the hole. Then, the hole was closed with PTFE to prevent any loss of the heat inside.

Twenty grams of dried *P. cablin* leaves and 400 ml of distilled water (leaves-to-water ratio of 1:20) were placed in the reaction flask and heated by microwave irradiation with 600 W (75 % power) for 126 min [15]. The different densities and their immiscibility required that the water and EO be separated from each other by separating funnel and the excess water be refluxed to the extraction vessel in order to provide uniform conditions of solid-to-liquid ratios for extraction. During the first 30 min, the collected EOs were decanted from the condensate in 10 min intervals. Decantation of the EOs was then continued with 15 min intervals. The EO was collected in amber vials, dried under anhydrous sodium sulfate and stored at 4 °C. The extraction yield of EO was calculated according to the equation given:

$$\text{Extraction yield}(\%, \text{v/ w}) = \frac{\text{Volume of extracted essential oil}}{\text{Mass of dried material}} \times 100$$

2.3 Hydrodistillation

Hydrodistillation was employed more or less like MAHD, but a laboratory hot plate (CORNING PC-600, 1043 W, 50 Hz) was used instead of the microwave oven. Twenty grams of dried *P. cablin* leaves and 400 ml of distilled water (leaves-to-water ratio of 1:20) were placed into the HD with a liebig condenser, and EOs were extracted for 417 min, in 30 min intervals [15]. The EO was collected in amber vials, dried under anhydrous sodium sulfate and stored at 4 °C.

2.4 Chemical analysis of essential oil constituents

Essential oils composition was determined by gas chromatography coupled to mass spectrometry (GC–MS) analysis on a Hewlett–Packard 6890 gas chromatograph coupled to a 5973A mass spectrometer, using two fused-silica-capillary columns with different stationary phases. The non-polar column was HP5MS™ (30 m length, 0.25 diameter and 0.25 μm film thickness) and the polar one was a Stabilwax ™ consisting of Carbowax™-PEG (60 m length, 0.25 mm diameter and 0.25 μm film thickness). GC–MS spectra were obtained using the

following conditions: carrier gas He; flow rate 1.0 ml min^{-1}; split 1:50; injection volume 1.0 μL; injection temperature 300 °C; oven temperature progress from 100 to 250 °C at 10 °C min^{-1}; the ionisation mode used was electronic impact at 70 eV. Most constituents were tentatively identified by comparison of their GC Kovats retention indices (RI), determined with reference to an homologous series of C_5–C_{28} *n*-alkanes and with those of authentic standards available in the authors' laboratory. Identification was confirmed by comparison of their mass spectral fragmentation patterns with those stored in the MS database (National Institute of Standards and Technology and Wiley libraries) and with mass spectra literature data [16, 17]. For each compound on the chromatogram, the percentage of peak area relative to the total peak areas from all compounds was determined and reported as relative amount of that compound.

2.5 CO_2 emission

The measurements of CO_2 emitted were carried out based on the procedures mentioned in the previous studies: to obtain 1 kWh of energy from coal or fossil fuels, 800 g of CO_2 will be released into the atmosphere during their combustion [18].

3 Kinetic model

A semi-empirical model for hydrodistillation was described by Milojević (2008) [19]. It assumes that, at particle level, the volatile compounds follow an unsteadystate diffusion transport. So, inside of particle, the field of one volatile species is given by Fick's second law (Eq. (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:

$$\frac{\partial q_p}{\partial t} = D_{eff} \frac{\partial^2 q_p}{\partial x^2} \tag{1}$$

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

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

A distorted model, of above shortly presented model, has, respect to particle extraction yield, an integral solution given by Eq. (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.).

$$\frac{q_0 - q}{q_0} = A \cdot e^{-kt}. \tag{2}$$

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 MAHD 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 EO evaporation from particle surface at $t = 0$.

$$t = 0;\ q = q_w \tag{3}$$

$$\frac{q}{q_0} = \frac{q_w}{q_0} = b \tag{4}$$

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:

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

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

(a) the pressure and temperature are constant in the extraction device;
(b) there are no heat loss and vapors condense only in the condenser;
(c) the suspension in the extraction flask is perfectly mixed;
(d) 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:

$$\frac{dm}{m_{pm}} = \frac{HR \cdot y}{m_{pm}} dt = dq \tag{6}$$

$$\frac{m}{m_{pm}} = q \tag{7}$$

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, t_d, depending on the hydrodistillation rate (*HR*).

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

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

4 Results and discussion

4.1 Temperature profile

Figure 1 shows the temperature profile during extractions by HD and MAHD from EOs of *P. cablin* leaves. In all extraction methods, the initial temperature of samples was 25 °C. The extraction temperature was equal to the boiling point of water (100 °C) at atmospheric pressure as regards HD and MAHD. It accordance with Raner et al. [20] reported that variation of microwave power from 500 to 1,000 W had no significant effect on the extraction yield. The decrease in extraction yield was found at temperatures higher than 110 °C because of instability of compounds and consequent thermal degradation [21].

The first EO droplets were observed after 57.0 min in HD and 6.0 min in MAHD. The most important reason for this difference is that MAHD apply three ways of heat transfer within the samples, namely irradiation, conduction, and convection. On the other hand, heat transfer in HD takes place through conduction and convection only [15, 22]. The rapid temperature rise in MAHD is the reason behind the time reduction accordingly.

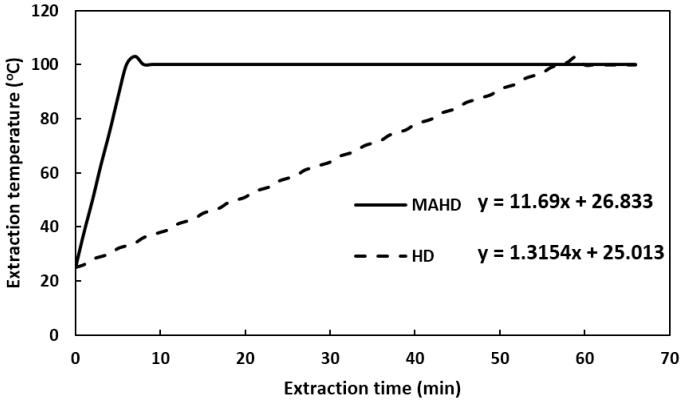

Fig. 1 Time-temperature profile of *Pogostemon cablin* leaves essential oil extraction with hydrodistillation (HD) and microwave-assisted hydrodistillation (MAHD) methods

The rate of temperature rise was measured by determining the slope of the linear part of the temperature profile (Fig. 1). The details in Table 1 show that the rates of temperature elevations in the MAHD method was 8.9 times greater than that of the HD method. This phenomenon can also be attributed to the high dielectric constant of water which absorbs the irradiation from the microwaves and causes a more rapid rise in temperature, compared to the case of HD [23]. These results are in good agreement with the findings of Mazidi et al. (2012) [24]. They found that in comparison to the conventional HD, the MAHD method can accelerate the rate of extraction by increasing the temperature rapidly and by causing the quicker rupturing of EO glands in Black Zira.

4.2 Comparison of extraction kinetics of the extraction method

Table 1 shows the effect of different extraction methods on total extraction time, extraction duration (i.e., the difference between the total extraction time and the time when the first droplets of EOs begin to appear), yield and rate of EO accumulation. MAHD was clearly quicker than the conventional HD. Full recovery of EOs was achieved within the first 126 min of operation in MAHD, respectively, whereas it took at least 417 min for the HD to fulfill the extraction operation. Farhat et al. (2011) [25] found that less time was needed for EOs to be extracted thoroughly from orange peels via microwave extraction (12 min) than via the HD (40 min). Also, Bousbia et al. (2009) [26] presented similar findings in their study on EOs extracted from lime wherein it took 15 min for the microwave hydrodiffusion and gravity method to accomplish the extraction process, in comparison with HD which took 180 min.

Table 1 The effect of hydrodistillation (HD) and microwave-assisted hydrodistillation (MAHD) of *Pogostemon cablin* essential oil (EO) on the extraction kinetics

Extraction parameter	HD	MAHD
Rate of temperature increase (°C/min)	1.3154	11.69
Starting time of EO accumulation (min)	57	6
Total extraction time (min)	417	126
Extraction duration (min)	360	120
Yield (%, v/w)	2.61	2.72
Rate of EO accumulation (ml/min)	0.0013	0.0043

As is shown in Table 1, there were slightly differences in the final yields obtained by HD (2.61% v/w) after 417 min and MAHD (2.72% v/w) after 126 min. Since the EO quantity of the samples was constant and since we had no EO loss caused by evaporation, the final yields in all the two extraction methods (HD and MAHD) were slightly equal. Golmakani and Rezaei (2008a) [15] investigated the effect of different extraction methods on EO yields of *Zataria multiflora* Boiss. They found that the final yields in HD and MAHD were 3.44 and 3.66 %, respectively, and that there were no significant differences among the yields obtained through HD and MAHD.

The rates of EO accumulation observed in HD and MAHD are shown in Table 1. This index was obtained by dividing the amount of extracted EOs (ml) by the corresponding total extraction time (min), which equaled the average rates of EO

accumulation (ml/min). The results show that the average rates of EO accumulation by MAHD was 3.3 times greater than that of HD. Additionally, the findings revealed that the shorter extraction time in MAHD was not only caused by their earlier onset of extraction, but also by their higher extraction rates which is mainly due to the more efficient heat transfer conducted by the microwave [19].

According to Fig. 2, the extraction yields by MAHD was 1.75% v/w, after 16 min. These yields were slightly similar to the amount of yield obtained by the conventional HD after 117 min. Therefore, the extraction time in HD was at least 7.3 times lengthier than that of the MAHD. Microwave extraction offers a rapid delivery of energy to a total volume of water and also to the *P. cablin* leaves matrix with a subsequent heating of the water and the *P. cablin* leaves matrix. This delivery of energy via the microwave occurs efficiently and homogeneously. Since the water within the *P. cablin* leaves matrix absorbs microwave energy, cells are ruptured by internal superheating which facilitates diffusion of chemicals from the matrix, thus improving the recovery of EOs.

As it is shown in Fig. 2, the extraction patterns for the two methods were similar, and two phases were observed in the process of extraction kinetics. The first part (I and I') was presented by an ascending line, which denotes the rapid increase in the yield and which represents approximately 89.45 and 95.81 % of the total yield in HD and MAHD, respectively. In the second part, II and II' correspond to a horizontal line which marks the end of the extraction process. The rapid increase in the yield during the first step suggested that the EOs was easily accessible by the steam. Indeed, the microwave irradiations distended the *P. cablin* leaves and lead to the rupture of the glands. However, one of the most striking differences observed between the MAHD and HD methods is the ability of the MAHD process to raise the extraction yield of the sample quickly and notably, within a short time. This higher rate of yield is a result of the higher extraction potential of microwaves and could be due to a synergy combination of the two transfer phenomena – mass and heat – acting in the same way [27]. This could be explained by the fact that the mass transfer occurs from the inside to outside in the HD and MAHD methods (Fig. 3 E–F). The rate of heat transfer differed among the MAHD and the HD. In the case of the HD, heat transfer occurred from the outside to the inside, exclusively because of conduction and convection happening through the water surrounding the *P. cablin* leaves (Fig. 3 C). However, we can suggest that the extraction mechanism of EO obtained by MAHD is partly due to internal heating of in situ water under microwaves irradiation from the inside to the outside of *P. cablin* leaves, and also mostly due to heat transfer from the outside to inside, similar to the case of HD (Fig. 3 D). In MAHD, heat transfer partly occurred from the inside to the outside and mostly from the outside to the inside of the *P. cablin* leaves, which facilitates oil diffusion from the inside of the leaves via steam by an increase in the extraction yield due to the synergy combination of the two transfer phenomena – mass and heat – acting in the same direction (i.e., from the inside to the outside).

4.3 Composition of essential oil

The essential oil from the leaf of *Pogostemon cablin*, grown in Indonesia was extracted by the conventional HD and MAHD and analyzed by gas chromatography-mass spectrometry (GC-MS). A total of 26 compounds were identified in patchouli EOs using two techniques (Table 1). Using MAHD, 19 compounds were detected, while 14 compounds were detected in HD. MAHD and HD enabled the detection of the most volatile active compounds in patchouli EO, such as patchoulol, δ-guaiene, α-guaiene and β-caryophyllene, but their proportions depend strongly on the extraction technique. Four new

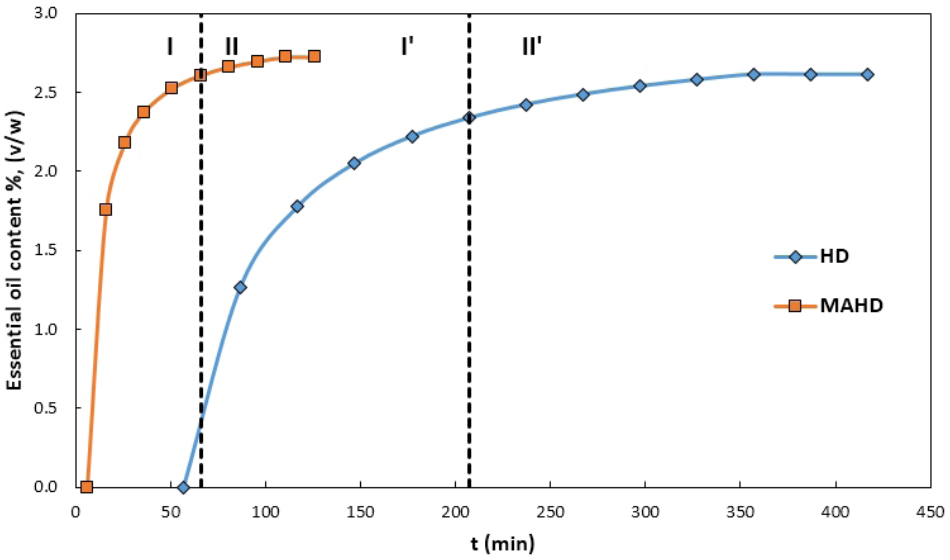

Fig. 2 Extraction yield as a function of time for the hydrodistillation (HD) and microwave-assisted hydrodistillation (MAHD) of essential oils from *Pogostemon cablin* leaves

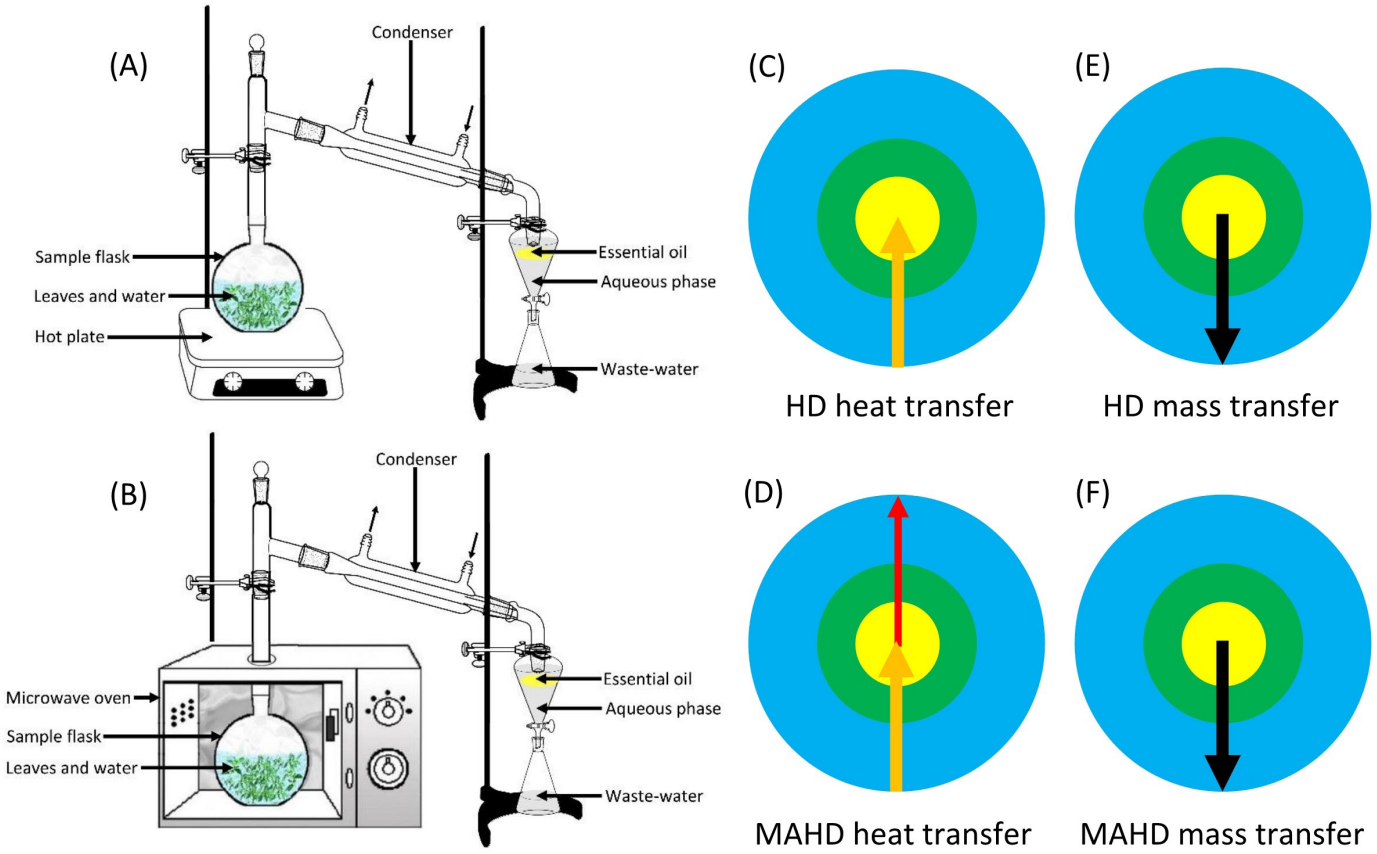

Fig. 3 A schematic display of heat and mass transfer during hydrodistillation (HD) and microwave-assisted hydrodistillation (MAHD) of essential oil from *Pogostemon cablin* leaves

compounds were characterized from patchouli EO extracted by the MAHD; namely, 2(1H)-naphthalenone, octahydro-1-methyl-1-(2-propenyl)-, (1a,4ab,8aa)-; iso-.aplha.-cedren-15-al; 7-oxabicyclo[4.1.0]heptane, 1,3,3-trimethyl-2-(3-methyl-1,3-butadienyl)-, [1a,2b(Z),6a]- and hexahydrothunbergol.

Substantially higher amounts of sesquiterpenes and lower amounts of oxygenated compounds were present in the EOs of the *Pogostemon cablin* extracted by MAHD in comparison with HD. The sesquiterpenes (δ-guaiene, etc.) were present in larger amounts in the HD EOs than in the MAHD EO, but the extract obtained by MAHD was more concentrated in oxygenated compounds. The EOs of patchouli leaves isolated by either MAHD or HD contained the same dominant components. Patchoulol was the main oxygenated component in the EO extracted from patchouli leaves, but the relative amounts differed for the two isolation methods; it was the most abundant oxygenated component of the MAHD extract (26.32 %), whereas the HD extracts contained 27.78 %. Taking into account the comparison studies of extraction method between MAHD and HD by other researchers on different plants, it seems the constituents and their concentrations obtained by both of method were almost similar [15,28,29]. All these results have proved that microwave greatly accelerated the extraction process, but without causing significant affect in the EO composition.

Sesquiterpenes are less valuable than oxygenated compounds in terms of their contribution to the fragrance of the EO. Conversely, the oxygenated compounds are highly odoriferous and, hence, the most valuable. The greater proportion of the detected compounds and the proportion of oxygenated compounds in MAHD EOs were probably due to the diminution of thermal and hydrolytic effects compared with with HD, which is time- and energy-consuming. Water is a polar solvent, which accelerates many reactions, especially reactions via carbocation as intermediates. Slight differences between the compositions for these extraction methods can be noted for the extraction of EO from patchouli leaves, as shown in Table 2.

The MAHD method offers the possibility for better reproduction of the natural aroma of the patchouli EO than that obtained using HD. MAHD could be a good alternative for the isolation of EOs from patchouli leaves.

4.4 Extraction kinetics and modelling

Kinetics of EO extraction from patchouli leaves using MAHD has been compared with that of HD on Fig. 2. Extraction with MAHD started at much earlier time than that with HD (6 min vs. 57 min, respectively). This is due to the more efficient heat flow involved with microwaves. Unlike the classical conductive heating methods, microwaves can heat the entire sample

Table 2 Chemical compositions of essential oils (EO) obtained from *Pogostemon cablin* leaves by HD and MAHD using GC-MS

No.	Compounds[1]	CAS Number[2]	Molecular Formula	Molecular Weight (g/mol)	RT[3] (min)	Area [%]	
						HD	MAHD
Sesquiterpenes							
1	δ-Elemene	20307-84-0	$C_{15}H_{24}$	204.35	7.82	nd	0.25
2	β-Patchoulene	514-51-2	$C_{15}H_{24}$	204.35	8.52	2.34	2.87
3	β-Elemene	515-13-9	$C_{15}H_{24}$	204.35	8.56	1.17	nd
4	Valencene	4630-07-3	$C_{15}H_{24}$	204.35	8.61	nd	1.86
5	β-caryophellene	87-44-5	$C_{15}H_{24}$	204.35	9.06	4.94	4.63
6	α-Guaiene	3691-12-1	$C_{15}H_{24}$	204.35	9.25	15.91	12.18
7	Seychellene	20085-93-2	$C_{15}H_{24}$	204.35	9.47	6.95	8.42
8	α-Humulene	6753-98-6	$C_{15}H_{24}$	204.35	9.59	0.69	nd
9	α-Gurjunene	489-40-7	$C_{15}H_{24}$	204.35	9.63	1.47	11.13
10	α-Patchoulene	1405-16-9	$C_{15}H_{24}$	204.35	9.70	5.47	nd
11	β-Selinene	17066-67-0	$C_{15}H_{24}$	204.35	9.88	0.49	nd
12	β-Maaliene	489-29-2	$C_{15}H_{24}$	204.35	9.93	nd	0.73
13	Aromadendren	109119-91-7	$C_{15}H_{24}$	204.35	10.06	0.62	nd
14	β-Chamigrene	18431-82-8	$C_{15}H_{24}$	204.35	10.07	3.73	nd
15	δ-Guaiene	3691-11-0	$C_{15}H_{24}$	204.35	10.17	23.07	14.69
16	Selina-3,7(11)-diene	6813-21-4	$C_{15}H_{24}$	204.35	10.35	nd	0.90
17	Aromandendrene	489-39-4	$C_{15}H_{24}$	204.35	10.81	nd	0.25
18	Valencene	4630-07-3	$C_{15}H_{24}$	204.35	12.65	nd	1.91
Oxygenated terpenes							
19	2,6,6-Trimethyl-cyclohex-2-en-1-yl		$C_{14}H_{24}O$		9.01	0.55	nd
20	2(1H)-Naphthalenone, octahydro-1-methyl-1-(2-propenyl)-, (1a,4ab,8aa)-	97571-39-6	$C_{14}H_{22}O$	206.32	11.02	nd	2.64
21	Aromadendrene oxide	1000156-12-8	$C_{15}H_{24}O$	220.35	11.19	nd	2.68
22	Viridiflorol	552-02-3	$C_{15}H_{26}O$	222.37	11.74	nd	5.93
23	Patchoulol	5986-55-0	$C_{15}H_{26}O$	222.37	12.30	27.78	26.32
24	7-Oxabicyclo[4.1.0]heptane, 1,3,3-trimethyl-2-(3-methyl-1,3-butadienyl)-, [1a,2b(Z),6a]-	97550-03-3	$C_{14}H_{22}O$	206.32	13.40	nd	0.12
25	Iso-.aplha.-cedren-15-al	69993-59-5	$C_{15}H_{22}O$	218.33	13.54	nd	0.35
26	Hexahydrothunbergol	20489-83-2	$C_{20}H_{40}O$	296.53	16.54	nd	0.11
Extraction time (min)						417	126
Total non-oxygenated compounds (%)						66.85	59.82
Total oxygenated compounds (%)						28.33	38.15
Total identified (%)						96.18	97.97

MAHD, Microwave-assisted hydrodistillation; GC-MS, Gas chromatography-mass spectrometry; nd, not detected.

[1]Essential oil compounds sorted by chemical families. [2]Abstract Service number. [3]Retention time.

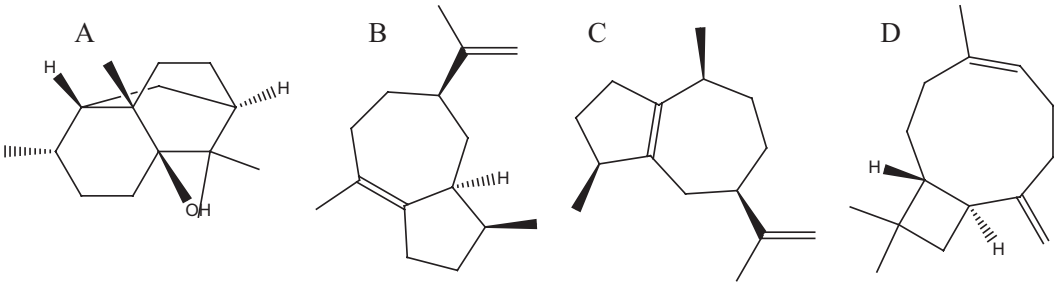

Fig. 4 Major compounds in patchouli EO (A. patchoulol; B. δ-guaiene; C. α-guaiene; D. β-caryophyllene)

almost simultaneously and at a higher rate [30]. Full recovery of EOs was achieved within the first 126 min of operation with MAHD. In the case of HD, a time period of at least 417 min was necessary for such purpose.

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

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

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

The proposed model, defined by Eq. (9), is a two-parameter one, where one parameter, b, characterizes the fast oil distillation stage (the so called fast distillation coefficient), and the other, k, characterizes the slow oil distillation stage (the so called slow distillation coefficient). The parameters k and b becomes as slope (Eq. (10)) and intercept (Eq. (11)) of linear dependence predicted by Eq. (9).

$$n = \ln(1-b) \tag{10}$$

$$b = 1 - e^{n} \tag{11}$$

The parameters of the kinetic model, b and k, were calculated from the experimental data by means of the linear regression method using Eq. (9); the obtained values are presented in Table 3. Generally, both kinetic parameters on MAHD were greater than on HD. The fast distillation coefficient and slow distillation coefficient in MAHD was 1.48 and 3.53 times greater than that of the HD, respectively. These results imply that the extraction yield during the first step suggested that the EOs was easily accessible by the steam and a similar extraction yield was achieved at significantly shorter extraction time when using MAHD instead of HD.

Table 3 Values of the kinetic parameters of Eq. (9)

Type of process	Leaves-to-water ratio (w/w)	k (min^{-1})	b (l)
Hydrodistillation (HD)	1:20	0.0111	0.2978
Microwave-assisted hydrodistillation (MAHD)	1:20	0.0392	0.4418

The experimental and calculated extractions kinetic curves for HD and MAHD processes are presented in Fig. 5. Value of correlation coefficients of the linearized kinetic models ($r^2_{HD} = 0.9797$ and $r^2_{MAHD} = 0.9720$) shows a good fitting of the model with experimental data. The kinetics for both processes is presented bellow:

$$V_{HD} = 0.5332 \cdot \left(1 - 0.7022 \cdot e^{-0.0111\tau}\right) \ (\text{ml/g leaves}) \tag{12}$$

$$V_{MAHD} = 0.5487 \cdot \left(1 - 0.5582 \cdot e^{-0.0392\tau}\right) \ (\text{ml/g leaves}) \tag{13}$$

Relations Eq. (12) and (13) confirm that in HD and MAHD the extraction occurs after the same law. In relations Eq. (12) and (13) τ is the reduced time (the difference between current time and the initial time - the moment when the first oil drop is obtained).

4.5 Cost, cleanliness and scale-up considerations

The reduced extraction time is clearly advantageous for the proposed MAHD method in terms of cost and energy. The energy requirement needed to perform the extraction methods, based on the power consumptions of the hot plate (in HD) and the microwave oven (in MAHD), considering the total periods of full extractions, was 7.2489 kWh for HD and 1.2600 kWh for MAHD (Fig. 6). Relative electric consumption for the production of 1 ml EO in HD and MAHD was 13.8670 and 2.3134 kWh/ml EO, respectively (Fig. 6). This indicates a substantial saving in the extraction cost when using MAHD instead of HD.

Regarding the environmental impact of pollution, the calculated quantity of CO_2 emitted in the atmosphere was higher in the case of HD (5.7991 kg CO_2) than those of MAHD (1.0080 kg O_2) (Fig. 6). Golmakani and Rezaei (2008) [19] found that the amount of CO_2 which was released into the atmosphere was higher in HD (1600 g CO_2) than that in MAHD (990 g CO_2). Relative amounts of CO_2 emissions that result from the production of 1 ml EO were higher in HD (11.0936 kg CO_2/g EO) than that in MAHD (1.8507 kg CO_2/g EO) (Fig. 6). This finding further indicated that there was a significant difference between MAHD and HD in terms of the amount of CO_2 released into the atmosphere for the production of 1 ml EO. Therefore, MAHD can be suggested as an "environmentally friendly" extraction method, which avoids the use of organic

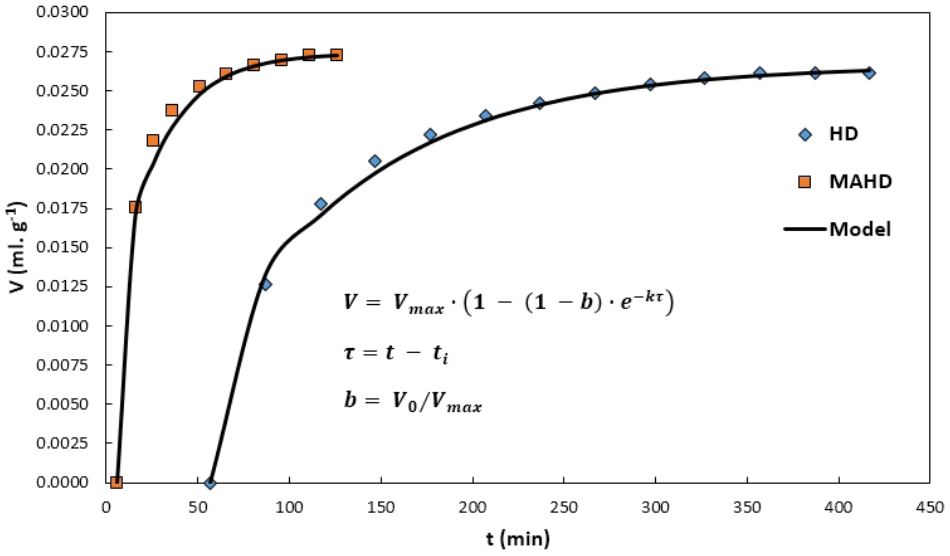

Fig. 5 Comparison of the kinetic for the hydrodistillation (HD) and microwave-assisted hydrodistillation (MAHD) of essential oils from patchouli leaves

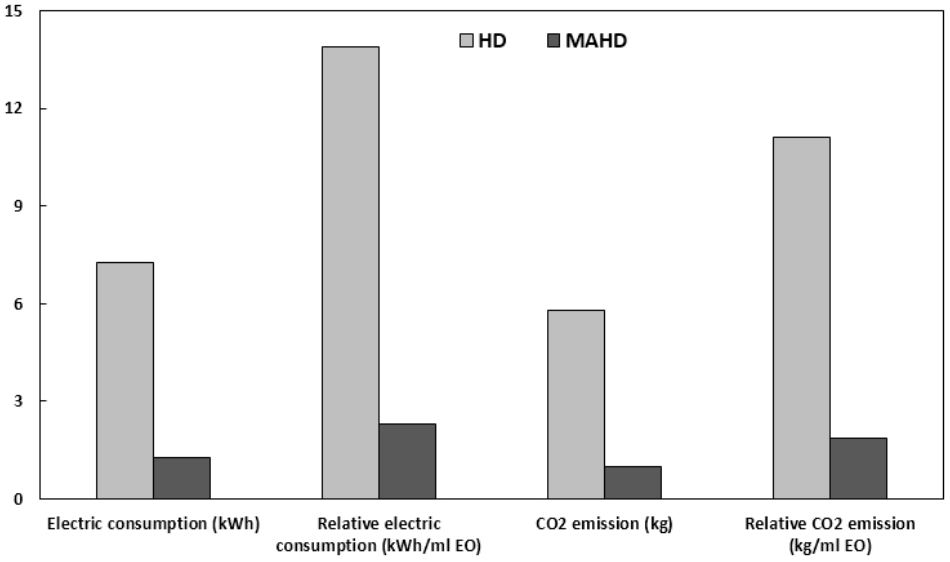

Fig. 6 Electric consumption of hydrodistillation (HD) and microwave-assisted hydrodistillation (MAHD) of essential oil (EO) from *Pogostemon cablin* leaves

solvents typical to Soxhlet and ultrasound-assisted extractions as well as accelerated solvent extraction. MAHD can also be offered for the production of larger quantities of EOs by applying the existing large-scale microwave extractors instead of the conventional hydrodistillation extractors.

5 Conclusions

Microwave-assisted hydrodistillation (MAHD) of essential oil (EO) using patchouli leaves offered important advantages over conventional hydrodistillation (HD): shorter isolation times (126 min vs. 417 min for HD); better yields (with MAHD the obtainable EO quantity is higher with 4.0389 % than in case of HD); it is environmentally friendly (the amount of CO_2 emission – a result of the EO extraction process – was dramatically higher in HD than that of MAHD); has reduced cost; is less energy consuming; and has the possibility of better reproduction of the natural aroma of the patchouli EO compared to HD. The general goal of this work was to confirm the efficiency of MAHD method and to explain how MAHD speed up the extraction process, without causing considerable changes in the EO composition. Therefore, a semi-empirical model was used to describe the kinetics of EO extracted by HD and MAHD. Based on this model, the fast distillation coefficient (about 1.48 times) and slow distillation coefficient (about 3.53 times) is much higher for the MAHD. Based on our results, MAHD can be termed as "green" extraction methods (from an energy consumption point of view). In addition to that, MAHD can also be proposed to be utilized for large-scale productions of EOs by commercializing the equipment instead of the conventional HD apparatus.

Nomenclature

A	constant, Eq. (2), l
b	fast distillation coefficient ($=q_w/q_0$), l
D_{eff}	effective diffusion coefficient (m^2/s)
HR	hydrodistillation rate (ml/min)
k	slow distillation coefficient (min^{-1})
m	mass of patchouli oil collected in the separator (g)
m_{pm}	mass of plant materials in a batch (g)
q	essential oil yield at any moment of hydrodistillation (g/g)
q_0	essential oil content initially present in the leaves (initial average concentration of essential oil in the plant particles) (g/g)
q_p	average concentration of essential oil in the plant particles at any moment of hydrodistillation ($=q_0 - q$) (g/g)
$q_{p,s}$	concentration of essential oil at the free surface of the plant particles at any moment of hydrodistillation (g/g)
q_w	essential oil concentration at $t = 0$ (g/g)
t	time (min)
t_d	time delay (min)
x	distance along the direction of diffusion (m)
y	volume fraction of patchouli oil in the vapour phase near the free surface of the boiling suspension, l

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