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Research article

Effect of process variables on heating profiles and extraction mechanisms during hydrodistillation of eucalyptus essential oil

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ABSTRACT

The effect of different process variables, such as solid/liquid ratio (1: 1, 1: 3, or 1: 5 g/ml) and stirring speeds (0, 200, or 400 rpm), was studied on the extraction mechanisms of eucalyptus essential oil obtained by hydrodistillation (HD). Different performance parameters such as obtained yield, energy requirements, and environmental impact were compared to those obtained by steam distillation (SD). Two different mathematical models were used to describe the process behavior. The obtained results indicate that the system with a solid/liquid ratio of 1:5 g/ml using a stirring speed of 400 rpm yielded maximum for HD (1.19% ± 0.01%). The environmental impact expressed as Ecopoints (EI99) ranged between 50.87 ± 13.18 and 78.17 ± 13.82 mPT/g essential oil (EO) for systems with steam injection, whereas for HD took values between 16.9 ± 0.3 and 19.24 ± 1.4 mPT/g EO at optimal operating conditions. The model parameters allowed us to identify that large amounts of steam at lower heating velocities induce a high accumulation of EO in the aqueous layer (vapor-liquid equilibrium at the interface), favoring the extraction process.

1. Introduction

The growing consumer preference for natural products has led to new essential oils (EO) applications in cosmetics, personal care products, pharmaceuticals, and the food industries. Grand View Research Inc. estimated that the global essential oil market was worth approximately US$ 3.4 billion in 2015, and the United States essential oil market is expected to grow from ~US$4.8b in 2019 to ~US$7.3b in 2024 (Grand View Research Inc, 2021).

Essential oils are complex mixtures of low molecular weight compounds such as hydrocarbons, terpenes, alcohols, compounds carbonyl, aromatic aldehydes, and phenols found in leaves, roots, stems, or seeds of some plants. Although there exist different extraction methods to obtain EO, the most popular procedures in the industry are the so-called traditional methods as steam distillation (SD), hydrodistillation (HD), and steam water distillation (Božović et al., 2017). In recent years, emergent technologies for EOs extraction as supercritical fluid extraction, ohmic heating assisted hydrodistillation, ultrasound-assisted extraction, and microwave-assisted extraction have been explored. These emergent methods are expected to reduce extraction times, improve obtained yields, reduce or eliminate the use of solvents or water, minimize environmental impacts, and increase the quality of extracted oils (Badwaik et al., 2015; Sereshti et al., 2012; Navarrete et al., 2012; Périno-Issartier et al., 2013; Hashemi-Moghaddam et al., 2015).

For instance, Farhat et al. (2017) evaluated the extraction of rosemary EO by four different methods, namely Steam Distillation (SD), Hydrodistillation (HD), Microwave Assisted Hydrodistillation (MAHD), and Solvent-Free Microwave Extraction (SFME). Their results showed a reduction in processing times from 180 min (HD) to 35 min (SFME). Similar results are presented in Karakaya et al. (2014) for rosemary EO extraction with HD and MAHD, reporting that extraction time was reduced by 65% when using MAHD. Golmakani and Moayyedi (2015) compared the process performance of HD, MAHD, and SFME during the extraction of lemon EO. They described a clear advantage of emergent technologies in energy consumption and, therefore, in environmental impact, measured as carbon footprint (203 g CO_2/g EO for MAHD and 176 g CO_2/g EO for SFME) compared to conventional HD (437 g CO_2/g EO). Hashemi-Moghaddam et al. (2013) evaluated the performance of MAHD for the extraction of Eucalyptus EO, obtaining important reductions in processing time, as well as a significant increment in the obtained yield, in comparison with the conventional HD (10 min vs. 3 h and 1.72% vs. 0.29%, respectively).

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Despite all their advantages, these new technologies are not easily scalable at an industrial level due to their high cost of installing equipment, operation, and maintenance. Thus, traditional SD and HD methods remain the most widely used for essential oil extraction in the industry (Jaimand et al., 2020; Valderrama and Ruiz, 2018; Masango, 2005). Traditional methods are based on simple mechanisms such as selective vaporization of a volatile component. For instance, SD is used to recover temperature-sensitive materials as EO by injecting steam directly into the sample (Cerpa et al., 2008; Božović et al., 2017), wherein steam, known as "steam trawl," breaks the raw material pores and releases the EO from them. This vapor is then condensed, and the EO can be collected (Cerpa et al., 2008). The SD has been used to extract EO from different plants such as rosemary (Farhat et al., 2017; Jaimand et al., 2020), lavender (Périno-Issartier et al., 2013), thyme (Benmoussa et al., 2016), and basil (Cassel et al., 2009). A process variation of SD is HD (Okoh et al., 2010), wherein unlike SD, the plant matrix is submerged directly in water inside a container, and the mixture is brought to a boil (Mahian and Sani, 2016). EO is evaporated with the water, and subsequently, the vapors are liquefied in a condenser to recover the separated EO. The HD time depends on the material plant being processed (Okoh et al., 2010). HD has been used to extract EO from orange peel (Allaf et al., 2013), thyme (Golmakani and Rezaei, 2008), rosemary (Okoh et al., 2010), lavender (Périno-Issartier et al., 2013), and Eucalyptus (Ghaffar et al., 2015; Hashemi-Moghaddam et al., 2013) to name a few.

Reyes-Jurado et al. (2015) discussed that plants' low concentration of essential oils requires high-performance extractions to achieve larger yields. Therefore, there is a great interest in improving extraction methods and optimizing processing parameters. This last objective can be achieved through mathematical modeling. The response surface methodology has been typically used to determine the significant effects of different process variables on the interest responses, along with their possible interactions (Mitić et al., 2019). In this approach, quadratic polynomial equations based on statistical analysis of experimental designs are utilized to determine the best combination of the operation parameters. This kind of model can be found in Putri et al. (2019) for MADH, where microwave power, solid/liquid ratio, and material size were optimized for the extraction of EO from canaga flowers and patchouli, and in Galadima et al. (2012) for optimizing the process conditions during the extraction of Eucalyptus EO via SD.

Furthermore, different authors have described the extraction kinetics of EO by steam distillation and hydro-distillation through mass transfer models (Cassel and Vargas, 2006; Cassel et al., 2009). For instance, Xavier et al. (2011) developed a model based on broken and intact cells by assuming that the oil from broken cells is rapidly extracted, whereas the oil from intact cells diffuses slowly to the surface of the raw material. Benyoussef et al. (2002) modeled the extraction of coriander essential oil using SD through two diffusional models. The first one considered only the diffusion inside the pores, whereas the second one added the rate of oil dissolution from the solid phase into the fluid filling the pores. Sovová and Aleksovski (2006) used a mathematical model that considers two types of particles; i) entire leaves with a part of the solute deposited on the surface, ii) ground particles with an initial homogeneous solute distribution. Cerpa et al. (2008) developed a model considering three stages in the extraction process: thermal oil exuded from the glandular trichomes, vapor-liquid equilibrium at the interface, and mass transfer in the vapor phase.

All the mentioned models aim to describe the extraction mechanisms by considering different factors such as geometry, shape, density, moisture content, solid content, water volume, etc. The effect of stirring and particle size on the extraction yield and extraction rate has also been discussed elsewhere (Franco-Vega et al., 2016, 2019). In addition, less complex models based on dynamic behavior may be helpful to understand the dynamic characteristics of the process; this last approach has previously been used to describe extraction kinetics of EO (Franco-Vega et al., 2019).

As stated above, steam distillation and hydrodistillation techniques remain the most used industrial applications, mainly due to their technological maturity and ease of operation. However, these conventional techniques present high energy demands for steam production, so there is a great interest in optimizing the operation parameters. The effect of steam flow trajectories during the extraction of essential oils in conventional steam distillation has been discussed in Valderrama and Ruiz (2018), showing that a trade-off between yield and energy consumption does not necessarily imply a constant trajectory of steam flow rate. For systems wherein the vapor source is external, it can be pretty easy to adjust the steam flowrate as proposed by those authors. However, for systems like hydrodistillation where the steam production depends on process variables (as the solid:liquid ratio, stirring, heating distribution, etc.), it is crucial to define how such parameters affect the extraction yield. Besides, it should be helpful to describe the effect of such parameters on the extraction mechanisms through mathematical models that can be further used for process optimization.

The present research aims to evaluate the effect of solid/liquid ratio and stirring speed on heating velocities, steam generation rates, and cooling requirements as well as on the obtained yield during the extraction of eucalyptus EO through HD and then compare them to that obtained for a system with direct injection of steam. Both temperature profiles and extraction kinetics were fitted to two mathematical models: i) a simple dynamic model to evaluate heating velocities and ii) a more complex model that describes the extraction stages to elucidate the related phenomenological mechanisms. The meaning of model parameters was discussed for both approaches.

2. Materials and methods

2.1. Plant materials

Eucalyptus (*Eucalyptus urograndis*) leaves were used to extract the EO, purchased from Hierbas Medicinales SA de CV, a local supplier in Puebla, Mexico. The dry leaves were separated from the branches; whole leaves were used in the extraction by SD due to the system arrangement. For hydrodistillation, where the sample is completely immersed in water, the leaves were ground in a domestic mill for 1.5 min to maximize plant material and contact area. The powder obtained measured an average particle size of 268 ± 13 μm (Blue Wave, Microtrac, USA) and had a moisture content of 6.37% ± 0.02% (according to the official AOAC method 930.15, 2005).

2.2. Extraction of eucalyptus essential oil (EO) by using direct steam injection

Two different arrangements with a direct steam injection to extract essential oil from whole eucalyptus leaves were used as a comparison basis. The first was a hydrodistillation system with direct steam supply into the wetted matrix (HDS); the second was a steam drag through dry plant material (SD). In HDS, the steam is bubbled into the wetted plant (solid:liquid ratio of 1: 0, 1: 1, or 1: 2 g/ml) contained in a three-neck round bottom flask (Figure 1a). In the second arrangement, two flasks are connected in series; the steam is supplied in the first flask (the three-neck round bottom) and then rose through to the second one where the dry plant is contained (Figure 1b).

For both cases, 100 g of whole eucalyptus leaves were processed because the amount of plant material was constrained by the system volume. Steam was supplied using a pressurized steam generator (Sussman, USA) with a steam flowrate ranged between 6.1 to 8.8 g/min. It is worthy of mention that such variations are attributable to intermittencies in the steam generator. In both cases, the energy consumption was calculated using steam tables. A condenser was used to recover the EO through which cold water was circulated (3 °C condenser inlet temperature), and a graduated glass receiver was used to collect the extracted EO. The extraction time was set at 120 min for each sample, long enough

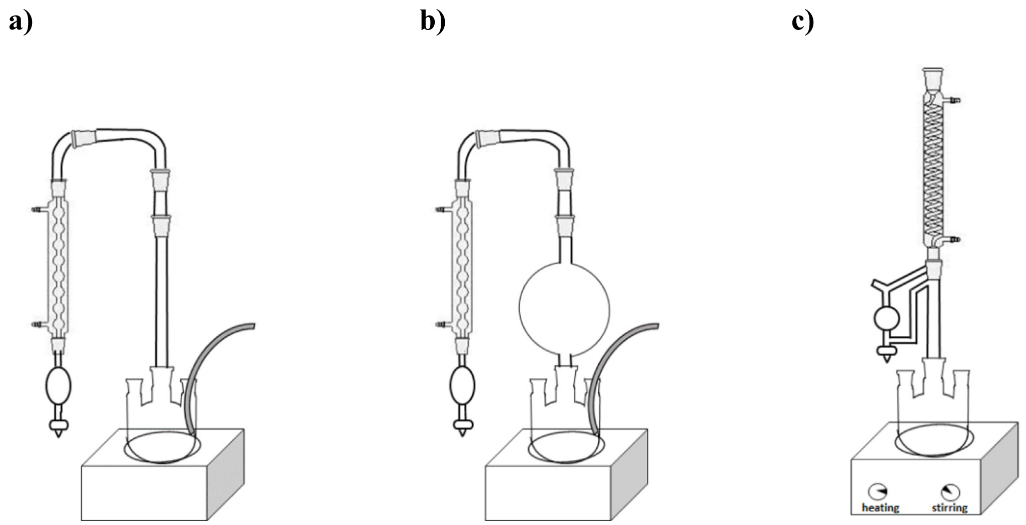


Figure 1. a) Hydrodistillation system with direct steam supply into the wetted matrix (HDS) equipment scheme. b) Direct SD with dry plant material equipment scheme. c) Conventional hydro-distillation (HD) equipment scheme.

for a steady state behavior for tested conditions. The capacity of the steam generator constrained extraction time and system temperature. All of the experiments were carried out in duplicate.

2.3. *Hydrodistillation (HD) extraction of eucalyptus essential oils (EO) with electric heating: temperature profiles and steam generation*

Conventional HD was performed in a three-necked round bottom flask with a volume of 3 L heated by a heating mantle with stirring (480 W, 60 Hz) (Prendo, Mexico), attached to a condenser and graduated trap (Figure 1c). A sample of 200 g of eucalyptus powder was mixed with distilled water in a beaker using three different solid/liquid ratios (1: 1, 1: 3, or 1: 5 g/ml), considering three different stirring speeds (0, 200 or 400 rpm), and the extraction time was set at 90 min in each of the processes studied. For most cases, processing time triplicated the time required to achieve the boiling temperature, being long enough to achieve a steady state. All of the experiments were carried out in duplicate.

A condenser was used to obtain the EO by HD cold water circulated (3 °C condenser inlet temperature), and a graduated glass receiver was used to collect the extracted EO. Once the process started, the temperature of the system rose until the sample began to boil, at which point the water vapor along with the oil began to rise and was condensed using a thermostatically controlled water bath (PolyScience/PolyScience Inc., Illinois, USA) to keep the cooling system at 3 °C and then extraction was started. The time required to reach the boiling temperature (90 °C–94 °C at 590 mmHg, mean atmospheric pressure in Puebla, Mexico) was recorded as t_{cut}, which varies depending on the conditions of the solid/liquid ratio and stirring speed used in each experiment. The EO volume collected was recorded at different times during all the experiments by reading the graduated glass receiver. After each extraction, the obtained EO was dried with anhydrous sodium sulfate, weighed on an analytical balance, and then stored at 4 °C in dark vials until analyzed.

2.4. *Performance indicators during hydrodistillation processes*

The extraction yield was expressed as the percentage ratio of the mass of EO extracted to the mass of the amount of sample used (Li et al., 2012). In each extraction process, different temperatures were recorded: the sample temperature in the flask, the temperature of the tube where the steam rises during boiling and extraction, and the inlet and outlet temperatures of the cooling water in the condenser. The temperature difference (ΔT_c) recorded within the cooling system was used to solve the energy balance (equation 1), to calculate the steam flow rate for the different operating conditions.

$$Qc = \dot{M}_w Cp_w \Delta T_c = \lambda_s \dot{M}_s \tag{1}$$

where Qc is the heat transferred from vapor to cooling water; $\dot{M}_w$ is the water flow (3.30 kg/min) coming from the water bath; Cp_w denotes the specific heat (4.18 kJ/K kg); ΔT_c is the temperature difference between the inlet and outlet temperatures of the cooling system; λ_s is the latent heat of vaporization (2257 kJ/kg); $\dot{M}_s$ denotes the steam flow.

The energy consumption for each gram of EO obtained was calculated using the output power of the heating mantle and the operational extraction time (kJ/g EO) (Chemat and Cravotto, 2013. This operational time is when the maximum amount of EO has been recovered since the remaining time was considered a non-productive period (Franco-Vega et al., 2019).

The environmental impact of the conventional HD extraction process was calculated using the standard Eco-Indicator 99 (EI99), which describes the total environmental load of a process considering the results of the life cycle analysis. The scale of this method is in Ecopoints (PT), wherein one PT (point) is representative of one thousandth of the annual environmental load of an average European inhabitant (Goedkoop et al., 1999). In this case, the main contributors are the amount of water required during the process for each gram of EO obtained (w, kg/g EO) and the specific energy consumption (E, kJ/g EO) as described in Eq. (2).

$$E99 = 0.026{*}w + 46{*}E \tag{2}$$

2.5. *Statistical analysis*

A factorial design was used to analyze the effect of the extraction process variables (solid/liquid ratio and stirring speed) during the HD extraction of Eucalyptus EO. The experimental design consisted of 11 experiments, determined by the 2^3 full factorial design with two replicates of the central point (Table 1). The experiments were carried out by duplicate, and the obtained data were analyzed using Minitab 19 (Minitab Inc., State College, PA, USA).

Table 1. Factorial design utilized to evaluate the effect of selected conventional hydro-distillation (HD) processing conditions (coded and uncoded).

Experimental Run	Processing conditions (coded)		Processing conditions (uncoded)	
	solid/liquid ratio	Stirring speed	Solid/liquid ratio (g/ml)	Stirring speed (rpm)
A	-1	0	1:1	200
B	0	0	1:3	200
C	-1	1	1:1	400
D	1	-1	1:5	0
E	1	1	1:5	400
F	1	0	1:5	200
G	-1	-1	1:1	0
H	0	-1	1:3	0
I	0	1	1:3	400
J	0	0	1:3	200
K	0	0	1:3	200

2.6. Mathematical modeling of hydrodistillation (HD)

As previously discussed, several mathematical models have proposed to describe the mechanisms governing the process behavior, and most of them consider a direct supply of steam. For the HD process considered here, steam is generated by heating the water content within the plant inside the flask, using an electric mantle, so that heating profiles play an important role during the process. Heating profiles and extraction kinetics were described using a second-order dynamic model reported elsewhere (Franco-Vega et al., 2019). The experimental data were fitted to the model in Eq. (3):

$$x(t) = K \cdot u(t)\left[1 - \left(1 + \frac{t - t_{cut}}{\tau}\right)e^{\frac{-(t-t_{cut})}{\tau}}\right] \tag{3}$$

where x(t) is the time-dependent output variable, in this case, the temperature increment in the vessel and tube, as well as the obtained yield, and u(t) is the input variable (in this case, the energy supplied). This dynamic model has three parameters: (a) K represents the final gain in steady state for each output, using the initial value as a reference; (b) t_{cut} represents the delay in the response; (c) the *effective time* constant τ, that indicates the change velocity. This model was utilized to describe extraction kinetics and heating profiles to identify the time at which vaporization began and the velocity of steam production.

Furthermore, as the primary goal of this paper is to assess the effect of steam production velocity during hydrodistillation, experimental data were also fitted to the model developed by Cerpa et al. (2008). Cerpa's model considers three stages in the oil extraction process: (i) thermal oil exudation from the glandular trichomes (or oil content inside the plant material), (ii) vapor-liquid equilibrium at the interface, considering individual oil components, and (iii) oil mass transfer in the vapor phase. In this work, the state space adaptation of Cerpa's model, developed by Valderrama and Ruiz (2018), was solved to describe the extraction kinetics. The state vector (x) and the manipulated inputs (u) are defined as follows:

$$x = [\dot{x_1}\dot{x_2}\dot{x_3}]^T = \left[G, M^{os}, M^{sd}\right]^T \ \ and \ \ u = S \tag{4}$$

where $\dot{x_1} = G$ is the oil mass inside trichomes per mass of fresh plant [g/g] (stage I); $\dot{x_2} = M^{\circ s}$ is the oil mass in aqueous layer [g] (stage II); $\dot{x_3} = M^{sd}$ is the oil mass collected [g] (stage III); $u = \text{S}$ is steam volumetric flow in [cm^3/min].

Following Eq. (5) describe the state space representation.

$$\begin{aligned} x_1^{\cdot} &= -K_{tr}Wx_1, \\ \dot{x}_2 &= K_{tr}Wx_1 - \frac{K_gC^*x_2}{h\rho_{eo}}\left[1 - \left(\frac{K_gx_2}{uh\rho_{eo} + K_gx_2}\right)\right], \\ \dot{x}_3 &= \frac{K_guC^*x_2}{(uh\rho_{eo} + K_gx_2)}, \end{aligned} \tag{5}$$

All the model parameters are assumed constants except the mass transfer coefficient K_g, which varies with the steam volumetric flow (S) according to Eq. (6) (Valderrama and Ruiz, 2018). W is the fresh plant mass, K_{tr} (min^{-1}) is a parameter that represents the exudation kinetic constant, which can be approached to the slope of the initial extraction rate (linear behavior).

$$K_g = 4.7 * 10^4(S - 74400) + 31.4, \tag{6}$$

where C* is the oil mass concentration-equilibrium (0.002 g/cm^3); *h* refers to the oil spots average thickness (115 × 10^{-4} cm); ρ_{eo} is the EO liquid density (0.983 g/cm^3); $\dot{x_1}$ (0) is the initial oil mass fraction inside the plant material; $\dot{x_2}$ (0) is the initial oil mass in the aqueous layer; $\dot{x_3}$ (0) is the initial oil mass collected.

2.7. Chemical composition

Once the EO was obtained by HD, its chemical composition was analyzed. An Agilent Technologies 6850 N gas chromatograph (Palo Alto, CA, USA) equipped with an Agilent 5975 C mass spectrometer detector (Palo Alto, CA, USA) was used for this. The flow rate of the carrier gas (helium) was set at 1.1 ml/min. The derivatives were separated on an HP-5MS fused silica column (Agilent J&W, USA) (30 μm, 0.25 mm id, and 0.25 μm film thickness). The injector was held at a temperature of 300 °C and operated in the 10: 1 split mode. The column temperature was held at 60 °C for 2 min and then increased to 250 °C at 10 °C/min. The mass spectra of EO constituents were compared with those reported in the National Institute of Standards and Technology (Stein, 1990).

3. Results and discussion

3.1. Effect of process variables on the efficiency of eucalyptus EO extraction processes

To establish the comparison basis for the HD process here considered, two systems with direct steam supply were initially tested (as described in section 2.2). Table 2 presents the results obtained in the HDS and SD, wherein the best condition in terms of yield was HDS using a solid/liquid ratio of 1:2 (1.06 ± 0.27%) with a vapor flow of 6.7 ± 0.8 g/min. Furthermore, the lowest yield (0.63 ± 0.01%) was obtained at a solid/liquid ratio of 1:0 and a vapor flow of 8.6 ± 0.1 g/min.

Franco-Vega et al. (2019, 2016) showed that particle size and agitation play an essential role in yield and rate of extraction during microwave-assisted extraction since those conditions improve heat distribution. A powder sample and three stirring speeds (0, 200, or 400 rpm) were evaluated in this study. Table 3 shows the yield, specific energy consumption, and Eco-Indicator 99, resulting after each extraction. For the HD process, maximum yield (1.19% ± 0.01%) was obtained from the process variables of experiment E (Table 3), processed at the highest tested conditions for agitation (400 rpm) and solid/liquid ratio (1:5 g/ml). This yield is higher than those obtained in the arrangements with direct steam injection (Table 2). Conversely, the extraction time and the heating and cooling requirements were notably lower than in the HDS and SD systems.

Moreover, poorer tested conditions of the HD process (0.60% ± 0.1%) were observed at the intermediate value of solid/liquid ratio and agitation (1:3 g/mL and 200 rpm). During the HD process at a solid/liquid ratio of 1:1, no EO was obtained; thus, performance parameters such as

Table 2. Eucalyptus essential oil (EO) yield, energy consumption, steam generation and Eco-Indicator 99 (EI-99) for the direct steam extraction processes.

Process	solid/liquid ratio	Yield (%)	Q heating energy (kJ)/g EO)	Q cooling energy (kJ)/g EO)	Steam generated (g/min)	EI99 (mPT/g EO)
HDS	1:0	0.63±0.01	2570.7±47.7	2322.7±43.1	8.6±0.1	98.6±2.6
	1:1	0.64±0.10	2208.6±306.5	1995.5±276.9	6.6±0.1	85.3±24.5
	1:2	1.06±0.27	2148.3±11.7	1941.0±10.5	6.7±0.8	50.9±13.2
SD		0.89±0.01	2794.7±129.8	2525.1±117.3	8.8±0.2	78.2±13.8

Table 3. Eucalyptus essential oil (EO) yield, energy consumption, steam generated, ΔT in cooling system, and standard Eco-Indicator 99 (EI99) for studied HD extraction processes.

Experimental Run	Yield (%)	Q heating energy (kJ)/g EO)	Q cooling energy (kJ)/g EO	S Steam generated (g/min)	ΔT cooling system	EI99 (mPT/g EO)
A	*	*	*	*	*	*
B	0.60±0.10	1851.9±31.9	1605.7±43.0	11.1±0.1	2.6±0.5	42.2±0.7
C	*	*	*	*	*	*
D	1.16±0.02	1052.4±69.5	957.0±77.2	11.6±0.1	2.7±0.1	19.2±1.4
E	1.19±0.02	931.5±12.4	869.4±128.2	10.7±0.1	2.8±0.2	16.9±0.3
F	1.13±0.04	961.3±26.1	925.4±33.2	12.3±0.1	2.9±0.2	18.2±0.7
G	*	*	*	*	*	*
H	0.61±0.07	1774.0±6.9	1203.4±78.6	8.7±0.6	1.9±0.1	40.1±0.1
I	0.68±0.03	1826.8±46.4	1624.9±160.0	11.3±0.8	2.1±0.2	40.5±1.9
J	0.66±0.01	1834.3±27.8	1683.7±89.2	12.0±0.3	2.4±0.1	41.2±0.0
K	0.68±0.03	1806.0±74.3	1669.8±3.6	11.4±0.8	2.6±0.1	41.3±4.0

[*] No EO was obtained for experiments with solid/liquid ratio of 1:1; therefore, performance parameters as energy requirements and environmental impact were not computed.

energy requirements and environmental impact were not computed since yield was ≈0.

The obtained yields in this work are in the range reported in the literature for essential oils from different eucalyptus species. Da Silva et al. (2020) reported an extraction yield of 1.03% from E. *urograndis* obtained by HD during four hours. Ghaffar et al. (2015) reported an average yield of 1.84% (w/w) of EO obtained via HD from seven species of Eucalyptus (*E. citriodora, E. melanophloia, E. crebra, E. tereticornis, E. globulus, E. camaldulensis, and E. microtheca*), while Boukhatem et al. (2014) analyzed the extraction of EO from 10 species of Eucalyptyus by SD (*E. alba, E. camaldulensis, E. citriodora, E. deglupta, E. globules, E. propinqua, E. saligna, E. tereticornis, E. urophylla and E. robusta*), obtaining yields between 0.2–1.9 % (w/w). Hashemi-Moghaddam et al. (2013) reported extraction yields of 1.72% and 0.29% (w/w) during the EO extraction of *E. microtheca* by MAHD and HD, respectively, while Gupta et al. (2013) attained yields around 1.2% (w/w) for MAHD and 0.91% (w/w) for HD during the extraction of EO from *E. citriodora*.

For HD, analysis of the factorial design was performed to evaluate the effects of tested variables on EO yield. The statistical analysis results showed that neither the stirring speed nor its interaction significantly impacts ($p > 0.10$) on yield, which depends only on the solid-liquid ratio used. The uncoded model (Eq. 7) explained more than 95% of the variability of the data. The maximum yield was obtained at a solid/liquid ratio of 1:5.

$$\text{Yield (\%)} = -\,0.3698 + 0.3857\ (\text{liquid/solid ratio}) - 0.01593\ (\text{liquid/solid ratio})^2 \tag{7}$$

The solid/liquid ratio was expressed as liquid/solid to avoid fractional values of the parameter in the equation.

As the polynomial model suggests, the solid:liquid ratio is strongly linked to heating velocity because the output of the heating source is constant, so the water content controls the temperature rise and vapor generation rates.

As previously stated, the primary sources of environmental impact considered in this research are water consumption and energy requirements; thus, it is clear that environmental impact values (Tables 2 and 3) greatly depend on energy efficiency (both heating and cooling) and solid/liquid ratios. From the obtained results, the experiments with the higher solid/liquid ratio (1:5) were the most efficient in terms of yield, but the Eco-Indicator takes values between 16.9 ± 0.3 and 19.24 ± 1.4 mPT/g EO, due to high water consumption and energy requirements. However, there is a clear advantage in environmental impact compared to HDS and SD (50.87 ± 13.18 and 78.17 ± 13.82 mPT/g EO, respectively). As noticed, setting operating conditions must consider the obtained yield, energy requirements, cooling capacity, and environmental impact.

3.2. Effect of process variables on steam generation, heating rate, and extraction kinetics

As mentioned above, the steam extractions were carried out with a steam flow rate between 6.6 and 8.8 g/min. In these cases, the delay in heating is minimized because the steam injection accelerates the process to get the first drop of oil (approximately 5 min). Conversely, HD must consider a heating time between 7.5 and 24 min (depending on the amount of water) until achieving boiling temperature to obtain the first drop of EO. Table 3 shows steam generation and the difference in temperature of the cooling system for each experiment of the HD processes. Figure 2 shows the heating profiles, both in the vessel and in the tube at the system top, and the extraction kinetics of EO for selected experiments. Figure 2a presents the heating profile of experiment I (1:3 g/ml and 400 rpm), whereas Figure 2b presents the heating profile of experiment E, which corresponds to the same stirring speed but with a larger quantity of water (1:5 g/ml). Power input of the electric mantle remained constant in both cases. Figure 2a and 2b include two temperature profiles: the recorded data within the vessel (gray dots) and the temperature measurement at the system top (tube connected to the condenser), marked with blue triangles. The delay in the vapor production matches the time required to achieve the boiling temperature value in the vessel, and the start of EO extraction, as shown in Figure 2c and 2d of experiments I and E.

Table 4 depicts the parameters of the dynamic model (equation 3) for the heating rates and the extraction kinetics for each experiment of HD. The lower values of $\tau_{\text{vessel heating}}$ and $\tau_{\text{tube heating}}$ (high heating speeds) are

Table 4. Parameters of the dynamic model to describe heating profiles and extraction kinetics.

Experiment	$t_{cut\ tube}$ (min)	$t_{cut\ mass}$ (min)	τ_{tube} (min^{-1})	τ_{vessel} (min^{-1})	τ_{mass} (min^{-1})	R^2_{vessel}	R^2_{tube}	R^2_{mass}
A	*	*	*	*	*	*	*	*
B	10.0	13.0	1.49	2.04	16.66	0.997	0.998	0.973
C	*	*	*	*	*	*	*	*
D	20.0	23.0	3.40	2.94	7.93	0.989	0.975	0.989
E	22.0	23.0	1.57	3.72	6.64	0.994	0.992	0.995
F	24.0	25.0	0.91	6.10	5.53	0.894	0.997	0.989
G	*	*	*	*	*	*	*	*
H	9.0	13.0	1.70	1.65	14.95	0.997	0.994	0.972
I	10.0	12.0	1.91	1.59	19.91	0.996	0.997	0.985
J	10.0	13.0	1.88	1.69	16.66	0.994	0.994	0.956
K	7.5	14.0	1.82	1.69	18.16	0.994	0.955	0.955

[*] No essential oil was obtained for experiments with solid/liquid ratio of 1/1.

favored by low solid/liquid ratios. In contrast, lower values of τ_{mass} (high speeds of mass transfer) are observed for the highest quantity of water (1:5 g/ml), which corresponds to the highest yield obtained. As one might expect, the delay in the extraction process (t_{cut}) increases as the solid/liquid ratio increases. The $t_{cut\ tube}$ value represents the moment when steam production begins and, a few minutes later, the first drop of EO is obtained ($t_{cut\ mass}$). Figure 2 shows that a smooth rise in heating is linked with a higher mass transfer, resulting in a higher obtained yield. According to the dynamic responses, the time constants are directly related to process velocity. For HD, better results are obtained for more significant amounts of steam at lower heating velocities. The amount of Eucalyptus EO obtained in this work by HD was higher than those reported by Hashemi-Moghaddam et al. (2013), Gupta et al. (2013), and Da Silva et al. (2020) (0.29%, 0.9%, and 1.03%, respectively), which demonstrate the importance of optimizing the process parameters related to heating velocities and steam generation.

3.3. Effect of process variables on extraction mechanisms

In order to describe the effect of process conditions on the extraction mechanisms, data were also fitted to the mathematical approach described in Valderrama and Ruiz (2018). Table 5 shows the model parameters; the steam volumetric flow (S) fluctuates between 14,458.26 and 20,513.01 cm^3/min, depending on each experiment. Figure 3 presents the extraction behavior of the three monitored states for the selected experiments; x_1 decreases as the EO leaves the plant into the system, whereas x_2 increases quickly over the first minutes until it reaches a maximum and then tends to diminish, indicating that most of the oil is collected during the first minutes of the process. A higher accumulation of EO in this aqueous layer favors the extraction. The maximum values of EO accumulation during this state for the different experiments are presented in Table 5. As can be observed, larger values of x_2 correspond to higher yields, being noticeable the effect of the water content. Finally, the behavior of the state x_3 represents the transport of EO to the vapor phase. Cerpa et al. (2008) explained that oil mass transport from the trichomes to the vapor phase was initially controlled by thermal exudation and vapor phase mass transport; however, only the vapor phase mass transport controls the kinetic extraction at the end of the extraction process.

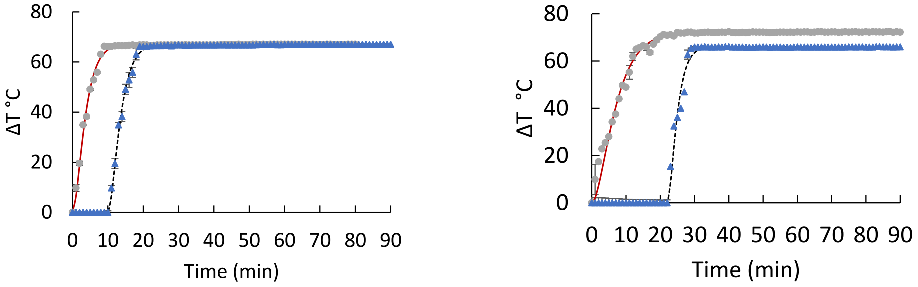
The overall results show that Cerpa's model for HD optimization can describe the effect of different process conditions on the extraction mechanisms. Additionally, it is shown how the dynamic model can simplify the description of the general process kinetics. As previously stated, the exudation kinetic constant K_{tr} can be related to the slope of the initial extraction rate, whereas the time constant (τ) of the dynamic model (equation 3) is related to extraction speed. As both parameters reflect similar mechanisms, we decided to assess the possible correlation between them using τ^{-1} as the initial guess for K_{tr}.

Figure 4 depicts the fit of the dynamic model (red line) and the model used by Cerpa et al. (2008) with two different values for the K_{tr} parameter: as first guess $K_{tr} = 1/\tau_{mass}$ (blue line), alternatively K_{tr} is equal to the slope of the initial extraction rate (black line). In both cases, the K_{tr} values are higher (higher extraction rate) for the experiments carried out with a solid/liquid ratio of 1:5 g/ml, which corresponds to the best yield obtained. Both K_{tr} values fitted very well the experimental data, although the second one shows a higher R^2. This observation can be explained since the dynamic model requires only one parameter to describe the extraction rate, whereas Cerpa's model provides the extraction kinetics by a system of three differential equations with two rate parameters. Furthermore, a second-order dynamic model is typically obtained by

Table 5. Cerpa's Model parameters to describe the extraction mechanisms during hydrodistillation.

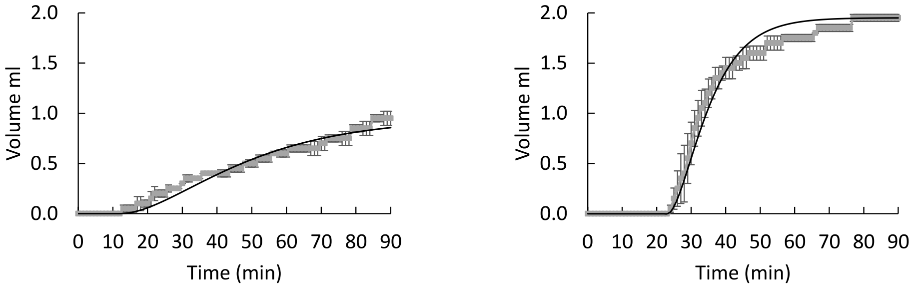
Experimental Run	$K_{TR} = 1/\tau$ (min^{-1})	R^2	K_{TR} (min^{-1})	R^2	X_1 (0) (ml)	X_2max (ml)	S (cm^3/min)
A	*	*	*	*	*	*	*
B	0.060	0.925	0.043	0.958	0.850	0.045	19050.33
C	*	*	*	*	*	*	*
D	0.126	0.954	0.085	0.988	1.950	0.166	19368.41
E	0.151	0.962	0.090	0.994	1.950	0.209	17835.65
F	0.181	0.964	0.100	0.995	1.850	0.199	20513.01
G	*	*	*	*	*	*	*
H	0.067	0.921	0.040	0.960	0.800	0.070	14458.26
I	0.050	0.921	0.025	0.975	0.950	0.038	18936.39
J	0.060	0.891	0.050	0.919	0.800	0.036	20040.00
K	0.055	0.911	0.045	0.932	0.900	0.039	19038.00

[*] No essential oil was obtained for experiments with solid/liquid ratio of 1/1.



a) 1:3 g/ml, 400 rpm

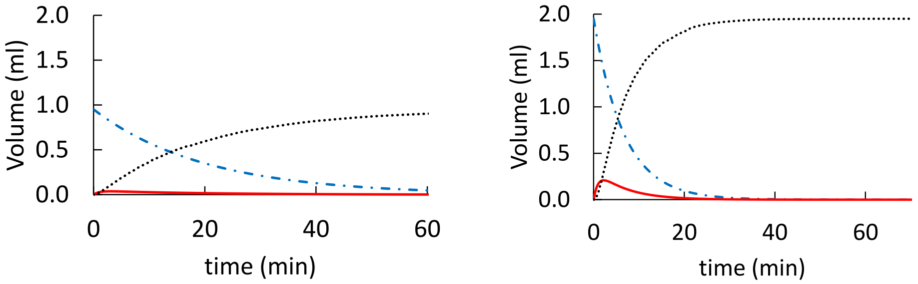
b) 1:5 g/ml, 400 rpm



c) 1:3 g/ml, 400 rpm

d) 1:5 g/ml, 400 rpm

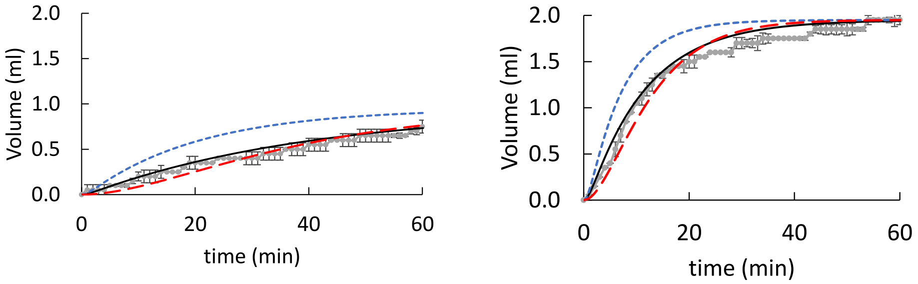
Figure 2. Heating rates and extraction profiles during extraction of eucalyptus essential oil by hydro-distillation (HD): a) and b) heating profiles; c) and d) extraction kinetics. Experimental data in markers (gray dot-vessel temperature, blue triangle-tube temperature, orange square-extracted oil volume) and dynamic model fit in solid lines.



a) 1:3 g/ml, 400 rpm

b) 1:5 g/ml, 400 rpm

Figure 3. Description of extraction stages during HD by Cerpa model. x_1, thermal oil exudation from the glandular trichomes (dashed blue line); x_2, vapor-liquid equilibrium at the interface (solid red line); and x_3, vapor phase oil mass transfer (dashed black line).



a) 1:3 g/ml, 400 rpm

b) 1:5 g/ml, 400 rpm

Figure 4. Performance of the Dynamic model (dashed red line) and the Cerpa model using two different values for K_{tr} parameter: $K_{tr} = 1/\tau_{mass}$ (dashed blue line), and K_{tr} equal to the slope of the initial extraction rate (solid black line).

Table 6. Main compounds (%) of eucalyptus essential oil obtained by conventional hydro-distillation (HD).

Constituent	HD Area (%)
α-Pinene	2.12
β-Pinene	0.18
Sabinene	0.67
1,8-Cineole	41.60
4-Terpineol	2.79
γ-Terpinene	0.50
Linalool	0.26
2-Cyclohexen-1-o'1, methyl 4 - (1-methylethyl)	1.41
Terpinen-4-ol	2.79
Carvacrol	0.14
Allo-aromadendrene	4.47
Spathulenol	21.65
Ledene oxide -(II)	4.25
**Other minor components*	19.96

[*] The % area of "other minor components" corresponds to the sum of the minor constituents that were poorly identified and individually represented less than 1% of the total area.

coupling two first-order systems; thus, the time constant for second-order systems is always greater than those related to the first-order systems (see Figure 4).

Both the dynamic model and the model proposed by Cerpa et al. (2008) reproduce experimental data with acceptable precision ($R^2 > 0.90$) for different operation conditions (solid/liquid ratio and agitation speed) and are helpful to describe the HD extraction process.

3.4. Chemical composition

Finally, the GC/MS analyses indicate the presence of 55 compounds representing 90.98% of the sample obtained by HD. The main compounds for the obtained essential oil are reported in Table 6. As can be observed, 1,8-cineole, also known as eucalyptol, was the predominant component (41.6 %). Similar compositions have been reported in the literature for EO obtained from the same Eucalyptus variety (Goldbeck et al., 2014; Da Silva et al., 2020). Goldbeck et al. (2014) reported that 1, 8 Cineol (36.18%), α-pinene (17.45%), β-Pinene (0.28%), 4-terpineol (0.33%) and spathulenol (1.87%) were the highest principal components in these EOs. Da Silva et al. (2020) reported the presence of 1, 8 Cineol (41.34%), α-pinene (27.66%), β-Pinene (0.18%), linalool (0.22%), g-Terpinene (0.25%), 4-terpineol (0.8%) and spathulenol (0.38%).

4. Conclusions

In this study, the effect of operating conditions for the extraction of Eucalyptus EO by hydrodistillation on different performance indicators was evaluated and compared to those obtained for systems that use direct steam injection, HDS and SD. It has been shown that Eco-indicator (EI99) can be used as a global performance parameter because it considers the energy and water requirements to obtain 1 g of essential oil. Overall, the results indicate that the selected operating parameters strongly affect the steam flow rate, extraction mechanisms, and yield. The effect of the evaluated conditions on the extraction kinetics was described in terms of the parameters of two mathematical models. It has shown how large amounts of steam delivered at low rate improve mass transfer and extraction rate. The obtained results provide the basis for future research work on optimizing EO extraction processes wherein the heating profiles are dominant, such as those obtained via microwave or ohmic heating.

Declarations

Author contribution statement

Elizabeth Lainez-Cerón: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

María Teresa Jiménez-Munguía: Analyzed and interpreted the data; Wrote the paper.

Aurelio López-Malo: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Nelly Ramírez-Corona: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

Allaf, T., Tomao, V., Besombes, C., Chemat, F., 2013. Thermal and mechanical intensification of essential oil extraction from orange peel via instant autovaporization. Chem. Eng. Process: Proc. Intensif. 72, 24–30.

AOAC, 2005. Official Methods of Analysis, eighteenth ed. Association of Official Analytical Chemists, Arlington, VA, USA.

Badwaik, L.S., Borah, P.K., Deka, S.C., 2015. Optimization of microwave assisted extraction of antioxidant extract from *Garcinia pedunculata* Robx. Separ. Sci. Technol. 50 (12), 1814–1822.

Benmoussa, H., Elfalleh, W., Farhat, A., Bachoual, R., Nasfi, Z., Romdhane, M., 2016. Effect of extraction methods on kinetic, chemical composition and antibacterial activities of Tunisian *Thymus vulgaris*. L. essential oil. Separ. Sci. Technol. 51 (13), 2145–2152.

Benyoussef, E.-H., Hasni, S., Belabbes, R., Bessiere, J.-M., 2002. Modélisation du transfert de matiére lors de l'extraction de l'huile essentielle des fruits de coriandre. Chem. Eng. J. 85 (1), 1–5.

Boukhatem, M.N., Amine, F.M., Kameli, A., Saidi, F., Walid, K., Mohamed, S.B., 2014. Quality assessment of the essential oil from *Eucalyptus globulus* Labill of Blida (Algeria) origin. Int. Lett. Chem. Phys. Astron. 17 (3), 303–315.

Božović, M., Navarra, A., Garzoli, S., Pepi, F., Ragno, R., 2017. Essential oils extraction: a 24-hour steam distillation systematic methodology. Nat. Prod. Res. 31 (20), 2387–2396.

Cassel, E., Vargas, R.M., 2006. Experiments and modeling of the *Cymbopogon winterianus* essential oil extraction by steam distillation. J. Mex. Chem. Soc. 50 (3), 126–129.

Cassel, E., Vargas, R.M.F., Martinez, N., Lorenzo, D., Dellacassa, E., 2009. Steam distillation modeling for essential oil extraction process. Ind. Crop. Prod. 29 (1), 171–176.

Cerpa, M.G., Mato, R.B., José Cocero, M., 2008. Modeling steam distillation of essential oils: application to lavandin super oil. AIChE J. 54 (4), 909–917.

Chemat, F., Cravotto, G., 2013. Microwave-assisted Extraction for Bioactive Compounds. Springer, New York.

Da Silva, P.P.M., de Oliveira, J., dos Mares Biazotto, A., Parisi, M.M., da Glória, E.M., Spoto, M.H.F., 2020. Essential oils from Eucalyptus staigeriana F. Muell. ex Bailey and Eucalyptus urograndis W. Hill ex Maiden associated to carboxymethylcellulose coating for the control of Botrytis cinerea Pers. Fr. and Rhizopus stolonifer (Ehrenb.: Fr.) Vuill. in strawberries. Ind. Crop. Prod. 156, 112884.

Farhat, A., Benmoussa, H., Bachoual, R., Nasfi, Z., Elfalleh, W., Romdhane, M., Bouajila, J., 2017. Efficiency of the optimized microwave assisted extractions on the yield, chemical composition and biological activities of Tunisian *Rosmarinus officinalis* L. essential oil. Food Bioprod. Process. 105, 224–233.

Franco-Vega, A., Ramírez-Corona, N., López-Malo, A., Palou, E., 2019. Studying microwave assisted extraction of *Laurus nobilis* essential oil: static and dynamic modeling. J. Food Eng. 247, 1–8.

Franco-Vega, A., Ramírez-Corona, N., Palou, E., López-Malo, A., 2016. Estimation of mass transfer coefficients of the extraction process of essential oil from orange peel using microwave assisted extraction. J. Food Eng. 170, 136–143.

Galadima, M.S., Ahmed, A.S., Olawale, A.S., Bugaje, I.M., 2012. Optimization of steam distillation of essential oil of *Eucalyptus tereticornis* by response surface methodology. Niger. J. Bas. Appl. Sci. 20 (4), 368–372.

Ghaffar, A., Yameen, M., Kiran, S., Kamal, S., Jalal, F., Munir, B., Jabbar, A., 2015. Chemical composition and in-vitro evaluation of the antimicrobial and antioxidant activities of essential oils extracted from seven Eucalyptus species. Molecules 20 (11), 20487–20498.

Goedkoop, M., Spriensma, R., Effting, S., Collignon, M., 1999. The Eco–Indicator 99. A Damage Oriented Method for Life Cycle Impact Assessment (Methodology Report–Methodology Annex–Manual for Designers).

Goldbeck, J.C., do Nascimento, J.E., Jacob, R.G., Fiorentini, Â.M., da Silva, W.P., 2014. Bioactivity of essential oils from Eucalyptus globulus and Eucalyptus urograndis against planktonic cells and biofilms of Streptococcus mutans. Ind. Crop. Prod. 60, 304–309.

Golmakani, M.T., Moayyedi, M., 2015. Comparison of heat and mass transfer of different microwave-assisted extraction methods of essential oil from *Citrus limon* (Lisbon variety) peel. Food Sci. Nutr. 3 (6), 506–518.

Golmakani, M.T., Rezaei, K., 2008. Comparison of microwave-assisted hydro-distillation with the traditional hydro-distillation method in the extraction of essential oils from *Thymus vulgaris* L. Food Chem. 109 (4), 925–930.

Grand View Research Inc, 2021. US Essential Oil Market Size, Share & Trends Analysis Report by Product (Eucalyptus, Lemon), by Application (Flavors, Fragrances), and Segment Forecasts, 2016–2024. (Accessed 21 March 2021).

Gupta, D., Shah, M., Shrivastav, P., 2013. Microwave-assisted extraction of *Eucalyptus citriodora* oil and comparison with conventional hydro distillation. Middle East J. Sci. Res. 16 (5), 702–705.

Hashemi-Moghaddam, H., Kalatejari, A., Afshari, H., Ebadi, A.H., 2013. Microwave accelerated distillation of essential oils from the leaves of *Eucalyptus microtheca*: optimization and comparison with conventional hydro-distillation. Asian J. Chem. 25, 5423–5427.

Hashemi-Moghaddam, H., Mohammadhosseini, M., Basiri, M., 2015. Optimization of microwave assisted hydro-distillation on chemical compositions of the essential oils from the aerial parts of *Thymus pubescens* and comparison with conventional hydro-distillation. J. Essent. Oil Bear. Plants 18 (4), 884–893.

Jaimand, K., Rezaee, M.B., Mirza, M., Nadery, M., Karimi, S., Ashtiany, S., Behrad, Z., 2020. Optimization of essential oil extraction conditions for *Rosmarinus officinalis* L. on a laboratory and semi-industrial scale. J. Med. Plants By-prod. 9 (Special), 29–34.

Karakaya, S., El, S.N., Karagozlu, N., Sahin, S., Sumnu, G., Bayramoglu, B., 2014. Microwave-assisted hydrodistillation of essential oil from rosemary. J. Food Sci. Technol. 51 (6), 1056–1065.

Li, X.J., Wang, W., Luo, M., Li, C.Y., Zu, Y.G., Mu, P.S., Fu, Y.J., 2012. Solvent-free microwave extraction of essential oil from *Dryopteris fragrans* and evaluation of antioxidant activity. Food Chem. 133 (2), 437–444.

Mahian, R.A., Sani, A.M., 2016. Essential oils in Food Systems: a systemic review. Int. J. Pharmtech Res. 9 (6), 409–416.

Masango, P., 2005. Cleaner production of essential oils by steam distillation. J. Clean. Prod. 13 (8), 833–839.

Mitić, M., Tošić, S., Pavlović, A., Mašković, P., Kostić, D., Mitić, J., Stevanović, V., 2019. Optimization of the extraction process of minerals from *Salvia officinalis* L. using factorial design methodology. Microchem. J. 145, 1224–1230.

Navarrete, A., Mato, R., Cocero, M., 2012. A predictive approach in modeling and simulation of heat and mass transfer during microwave heating. Application to SFME of essential oil of *Lavandin Super*. Chem. Eng. Sci. 68 (1), 192–201.

Okoh, O.O., Sadimenko, A.P., Afolayan, A.J., 2010. Comparative evaluation of the antibacterial activities of the essential oils of *Rosmarinus officinalis* L. obtained by hydrodistillation and solvent free microwave extraction methods. Food Chem. 120 (1), 308–312.

Périno-Issartier, S., Ginies, C., Cravotto, G., Chemat, F., 2013. A comparison of essential oils obtained from lavandin via different extraction processes: ultrasound, microwave, turbohydro-distillation, steam and hydro-distillation. J. Chromatogr. A 1305, 41–47.

Putri, D.K.Y., Dewi, I.E.P., Kusuma, H.S., Mahfud, M., 2019. Extraction of an essential oil from fresh cananga flowers (*Cananga odorata*) using solvent-free microwave method. J. Chem. Technol. Metall. 54 (4), 793–802.

Reyes-Jurado, F., Franco-Vega, A., Ramirez-Corona, N., Palou, E., López-Malo, A., 2015. Essential oils: antimicrobial activities, extraction methods, and their modeling. Food Eng. Rev. 7 (3), 275–297.

Sereshti, H., Rohanifar, A., Bakhtiari, S., Samadi, S., 2012. Bifunctional ultrasound assisted extraction and determination of *Elettaria cardamomum Maton* essential oil. J. Chromatogr. A 1238, 46–53.

Sovová, H., Aleksovski, S.A., 2006. Mathematical model for hydrodistillation of essential oils. Flavour Fragrance J. 21 (6), 881–889.

Stein, S.E., 1990. National Institute of Standards and Technology (NIST) Mass Spectral Database and Software. USA.

Valderrama, F., Ruiz, F., 2018. An optimal control approach to steam distillation of essential oils from aromatic plants. Comput. Chem. Eng. 117, 25–31.

Xavier, V.B., Vargas, R.M.F., Cassel, E., Lucas, A.M., Santos, M.A., Mondin, C.A., Sartor, T., 2011. Mathematical modeling for extraction of essential oil from *Baccharis* spp. by steam distillation. Ind. Crop. Prod. 33 (3), 599–604.