Modeling the kinetics of essential oil hydrodistillation from plant materials

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Abstract

The present work deals with the modeling of the kinetics of essential oils extraction from plant materials by water and steam distillation. The experimental data were obtained by studying the hydrodistillation kinetics of essential oil from juniper berries. The literature data on the kinetics of essential oils hydrodistillation from different plant materials were also included into the modeling. A physical model based on simultaneous washing and diffusion of essential oil from plant materials were developed to describe the kinetics of essential oils hydrodistillation, and two other simpler models were derived from this physical model assuming either instantaneous washing followed by diffusion or diffusion with no washing (*i.e.*, first-order kinetics). The main goal was to compare these models and suggest the optimum ones for water and steam distillation and for different plant materials. All three models described well the experimental kinetic data on water distillation irrespective of the type of distillation equipment and its scale, the type of plant materials and the operational conditions. The most applicable model is the one involving simultaneous washing and diffusion of the essential oil. However, this model was generally inapplicable for steam distillation of essential oils, except for juniper berries. For this hydrodistillation technique, the pseudo first-order model was shown to be the best one. In a few cases, a variation of the essential oil yield with time was observed to be sigmoidal and was modeled by the Boltzmann sigmoid function.

Keywords: diffusion, modeling, physical models, steam distillation, washing, water distillation.

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Essential oils are secondary metabolites of aromatic plants that are formed by all plant organs, such as buds, flowers, leaves, stems, twigs, seeds, fruits, roots, wood or bark. They are stored in secretory cells, cavities, canals, epidermic cells or glandular trichomes. At present, about 3000 essential oils are known, but only 10% of them are commercially important [1]. According to their chemical composition, essential oils are natural, complex mixtures of volatile compounds present at quite different concentrations and have a strong aroma and flavor. These mixtures are usually characterized by two or three major compounds at fairly high concentrations (20–70%), while the other compounds are present in trace amounts. For example, α-pinene (38––54%), limonene (16–18%) and myrcene (9–19%) are the major compounds of *Juniper communis* essential oil, which is 70–80% of the essential oil [2]. Generally, these major compounds determine the biological properties of essential oils [1].

The essential oil from a plant or its parts has an identifiable aroma, flavor or other feature of that plant or part that is of practical use. Essential oils and their individual components are used as food and drink flavorings, perfumes, deodorants, pharmaceuticals, pesticides, *etc*. Their use is determined by their specific chemical, physical and sensory properties. It is obvious that the content, composition and character of essential oils extracted from different plant species, the same plant species or from different parts of a plant species could differ to each other due to different geographical locations, climate, soil factors as well as plant organ, age and vegetative stage.

The production of essential oil involves several, closely connected steps. The raw plant material is obtained by manual collection of wild plant populations or by the harvesting of cultivated plants in the stage of development that gives the best yield of the essential oil having the desired features. The raw plant materials are used as fresh or after drying in the dark, sun or convective dryers, and some of them are comminuted before further processing. The state of the employed raw plant material significantly influences the yield, composition and features of the essential oil that can be extracted. The essential oil is usually present in the

raw plant material at a low concentration and a high performance separation method is employed to recover it in a high yield. Both traditional and novel methods, such as hydrodistillation, solvent extraction or supercritical carbon dioxide extraction, are used for essential oil recovery. Like the pretreatment of the raw plant material (drying, comminution, etc.), the recovery method applied affects the yield, composition and character of the obtained essential oil. Sometimes, a particular feature is reinforced by eliminating unwanted fractions or by extracting desired fractions of the essential oil through further processing employing physical or chemical methods. Due to the novel separation techniques, essential oils are regarded as industrial raw materials for the production of the individual compounds or fractions with particular flavor and aroma characteristics.

Each of the traditional essential oil separation methods has its particular advantages and disadvantages. Solvent extraction produces extracts that contain solvent residues and non-volatile waxy components. The extracting solvents are usually toxic and flammable, while their recovery entails additional costs and environmental risks. Although hydrodistillation provides essential oils in low yields containing several byproducts of the distillation process, this method is most frequently used for essential oil extraction from raw plant materials. The essential oil is extracted at temperatures lower than the boiling points of its constituents, enabling the separation of thermo-sensitive compounds. Hydrodistillation, which provides good quality essential oil, is operated in a relatively simple and safe manner and is environmentally friendly. The advantages of this method are also that the volatile constituents are condensed into water, and the steam displaces atmospheric oxygen protecting the volatiles from oxidation. Its disadvantages are a high-energy consumption and heating the raw plant material to high temperatures. Compared with supercritical carbon dioxide extraction, which is technologically more advanced, hydrodistillation is much cheaper with respect to the capital cost. It is performed as a water, steam or water-steam distillation.

In the laboratory, a Clevenger-type apparatus is normally used for extracting essential oils from raw plant materials, while at the pilot or industrial level, different types of distillation units (distillers) with or without direct steam supply are employed. Hydrodistillation under atmospheric pressure remains the most widely employed technique for the extraction of essential oil on the industrial level because of its economic viability [3]. Other types of distillation have also been tried for extracting the essential oil from raw plant materials, such as vacuum distillation of essential oil

from heated pulverized plant materials, known as "dry" distillation [4] and water distillation under vacuum [3].

There have been numerous studies dealing with the yield, composition and biological activities of essential oils obtained by hydrodistillation from different plant species grown all over the world. However, the kinetics of essential oil hydrodistillation has been studied to a much smaller extent despite its importance not only for the fundamental understanding but also for operation, optimization, control and design of industrial hydrodistillation processes. Kinetic models along with essential oil yield and composition are important for hydrodistillation processes from both technological and economical viewpoints.

Surveys of the reports on the kinetics of water and steam distillation of essential oil are given in Tables 1 and 2, respectively. Aerial parts and leaves were mainly employed as the raw plant materials in these studies, although other plant organs, such as flowers, seeds, fruits, peals and branches with needles and wood, were also used. Intact and fresh raw plant materials are more rarely used than processed ones. After harvesting, the raw plant materials are usually dried to preserve/conserve their qualities. To protect the sensitive constituents, low drying temperatures (30 to 50 °C) are most frequently applied. Small quantities of collected plant materials are naturally dried in the field or in a well-aired, dark and dry place at room temperature, while large quantities of raw plant materials on the industrial scale are convectively dried by warm air in special dryers, corresponding to the plant parts to be dried. After drying, the plant material is comminuted (chopped, milled, ground, etc.).

Water and steam distillations are mainly used for extracting essential oils from aerial parts, leaves, flowers, seeds, fruits, needles, peals and wood (Tables 1 and 2, respectively), while the employment of water-steam distillation has not yet been reported. The kinetics of hydrodistillation process as well as the oil yield and composition were the main subjects of the studies performed. In several studies, various kinetic models were presented. The maximum essential oil yield and the duration of hydrodistillation to attain it varied from one plant material to another and on the applied operational conditions.

When using a water distillation, the plant material is completely immersed in water in a heated still. On the laboratory scale, the apparatus according to Clevenger was usually employed to perform water distillation under atmospheric pressure, and a reduced pressure was used in only one study. Different solid-to-water ratios up to 1:50 g/mL were applied in the studies. The suspension was usually held at the boiling temperature (about 100 °C), although a water distillation can be performed under vacuum at a reduced temperature. The

Table 1. Literature survey on studying the kinetics of water distillation of essential oils from plant materials; na – not available

Plant/part	Technique/level	Operating conditions	Essential oil yield	Objective of study	Reference
Lavender (*Lavandula angustifolia*); flowers	50 g/3 L of buffered aqueous medium (pH 7.0).	100°C, 15 min to 7 h	1.61%, 2 h	Kinetics of the essential oil constituents	Morin *et al*. [5]
Ridolfia segetum, flowers, fresh	Clevenger; 500 g/500 mL of distilled water	B.p., up to 150 min	5.0%, 1.5 h	Kinetics; composition and antibacterial activity of the oil	Jannet and Mighri [6]
Common lavender (*Lavandula officinalis*); flowers, dried and milled (d_p=0.5 mm)	Clevenger; 15 g/150 mL of water or cohobation water	B.p., up to 240 min	5.73 mL/100 g	Kinetics; composition and antimicrobial activity of the oil	Stanojević *et al*. [7]
Wild marigold (*Target es minuta*); flowering tops, fresh	Clevenger; 500 g Portable distillation unit; 2 kg/8 kg of water	B.p., 3 h B.p. under vaccum (to 225 mmHg), up to 3.5-4.5 h	1.56%, 3 h 0.91-1.16%, about 3 h	Kinetics; oil yield and composition; kinetic model.	Babu and Kaul [3]
Sage (*Salvia officinilis*), flowers, leaves and stems, dried	Clevenger 400 g of plant sample / 5 dm³ of water	B.p., 2 h	Flower: 1.8% Leaf: 2.0% Stem: 0.4%	Kinetics; oil yield	Veličković *et al*. [8]
Savory (*Satureja hortensis*, *Satureja montana*); dried aerial parts	Clevenger; 1:20 w/w (6 or 30 g of plant materials)	B.p., 4 h	3.1% for *S. hortensis*, 0.7% for *S. montana*, 3 h	Kinetics; oil yield	Rezvanpanah *et al*. [9]
Spearmint (*Mentha spicata*); leaves, fresh	na; 100 g/? g of water	B.p., up to 3 hours	0.89%, 2 h	Kinetics; composition vriation with time	Benyoussef *et al*. [10]
Eucalyptus cinerea, leaves, fresh and dried 24 h at ambient conditions	Clevenger; 4 kg/8 L of water	B.p., up to 8 h	2.56% (fresh leaves), 2.87% dried leaves, 8 h	Effect of drying on the kinetics and the oil composition; modeling by the Langmuir equation	Babu and Singh [11]
Rosemary (*Rosemarinus officinalis*); leaves	na	B.p., up to 2 h	0.44%, 2 h.	Kinetics; modeling (diffusional model based on the Fick's second law)	Boutekedjiret *et al*. [12]
Rosemary (*Rosmarinus officinalis*); leaves	Clevenger; 500 g/3 L of water	B.p., up to 1.5 h	0.35%, 1.5 h	Kinetics; oil composition	Bousbia *et al*. [13]
Thyme (*Thymus vulgaris*); aerial parts, dried.	Clevenger; 60 g/1.2 L of water	B.p., up to 4 h	2.39%, 4 h.	Kinetics; oil composition	Golmakani and Rezaei [14]
Creeping thyme (*Thymus serpyllum*); herba, dried, crushed (<1 mm)	Unger; 1:10, 1:20, 1:30, 1:40 and 1:50	B.p., up to 3 h	0.8-1.0%, 3 h	Kinetics; modeling (a phenomenological model including intact and broken plant cells)	Sovová and Aleksovski [15]
Shirazi thyme (*Zataria multiflora*); aerial parts, dried	na[a]; 30 g/0.5 L of water	B.p., up to 4 h.	3.23% , 3.64% (salted, 1% NaCl), 60 min.	Kinetics; oil yield, composition and properties	Gavahian *et al*. [16]
Lemon grass (*Cymbopogon citratus*); leaves.	na; 250 g/2 L of water.	B.p., up to 45 min	0.84% (v/w), 45 min.	Kinetics; process optimization	Silou *et al*. [17]
Cherry laurel (*Prunus laurocerastis* L. var. serbica Pančić); leaves	Clevenger; 0.5 kg/5 kg of water	B.p., up to 2.5 h	0.432% (v/w), 2.5 h	Kinetics; oil composition	Stanisavljević *et al*. [18]
Coriander (*Coriandrum sativum* L.); seeds	Clevenger; 60 g.	B.p., up to 9 h	0.057%, 9 h	Modeling (difussional model and model based on first order kinetics)	Benyoussef *et al*. [19]
Cumin (*Cuminum cyminum*); seeds, ground	Clevenger; 200 g (small batch)	B.p., up to 5 h	3.4-3.8% (small batch), 5h	Kinetics; oil yield; modeling (model based on first order kinetics)	Sowbhagya *et al*. [20]

Table 1. Continued

Plant/part	Technique/level	Operating conditions	Essential oil yield	Objective of study	Reference
Celery (*Apium graveolens* Linn.); seeds, milled	Clevenger; 200 g (small batch)	B.p., up to 5 h	1.8–2.2% (small batch), 5 h	Kinetics; oil yield; modeling (model based on first order kinetics)	Sowbhagya *et al.* [21]
Fennel (*Foeniculum vulgare*); seeds, crushed	Clevenger; 25 g/200 mL	B.p, up to 20 min; 300 W	2.12% (v/w), 20 min	Kinetics; modeling (model including washing and diffusion)	Kapas *et al.* [22]
Parsly (*Petroselinum crispum*); seeds, intact, non-fermented	Clevenger; 2000 mL	B.p., up to 270 min	2.17% (v/w), 270 min	Kinetics; effects of different hydrodistillation techniques on the oil yield	Stanković *et al.* (2004)
Parsly (*Petroselinum crispum*); seeds.	Clevenger	B.p., up to 270 min	3.28% (v/w) intact; 4.51% (v/w) crushed; 270 min	Kinetics; effects of seed fermentation on the oil yield	Stanković *et al.* [23]
Intact, feremented at 28 °C for 4 h	20 g/200 mL	–	–	–	–
	20 g/300 mL	–	–	–	–
	20 g/400 ml	–	–	–	–
	20 g/500 ml	–	–	–	–
Intact, feremented at 30 °C for 4 h	20 g/400 ml	–	–	–	–
Crushed, feremented at 28 °C for 4 h	20 g/400 ml	–	–	–	–
Parsly (*Petroselinum crispum*); seeds	Clevenger	B.p., up to 270 min	–	–	Stanković *et al.* [24]
Juniper (*Juniperus communs* L.); berries, dried, milled	Clevenger; 364 or 1000 g; 1:3 or 1:10 g/mL	B.p., up to 100 min; 150-700 W	0.56-1.68% (v/w), 90 min	Kinetics; modeling (model based on washing and diffusion)	Milojević *et al.* [2]
Abies grandis, *Picea abies*, *Pinus sylvestris*, *Pseudotsuga menzi-esii*, branches with needles, chopped; *Juniper communis*, fruits, ground	Unger; 100 g/300 mL of water; for some experiments, the plant materials were microwave-pretreated (10 min)	na	0.53-1.68% (v/w), 2 h	Kinetics; oil yield	Miletić *et al.* [26]
Lime (*Citrus latifolia* Tanaka); peals, dried, whole/milled (2 mm)	Clevenger; 60 g	B.p., up to 8 h	3.4% (v/w), 5 h	Kinetics; oil yield and composition	Atti-Santos *et al.* [27]
Lemon (*Citrus limon*), peals, fresh	Clevenger; 200 g/2 L of water	B.p., up to 3 h	0.21%, 3 h	Kinetics; oil yield, composition and antimicrobial activity	Ferhat *et al.* [28]
Agarwood (*Aquilaria crasna*), wood, dried, comminuted, sieved (0.7 cm)	3 kg/27 kg of water; wood was soaked in water for 7 days	Operating temperature: 80, 100 and 120 °C; up to 64 h	0.046-0.061%, 64 h	Kinetics; oil yield and composition; modeling (model based on washing and diffusion)	Pornpunyapat *et al.* [29]

Table 2. Literature survey on studying the kinetics of steam distillation of essential oils from plant materials; na – not available

Plant/part	Level	Operating conditions	Essential oil yield	Objective of study	Reference
Lavender (*Lavandula angustifolia*); flowers, dried	50 g per batch	na	8.75%, 1.5 h	Kinetics; yield an composition of the essential oil	Chemat *et al.* [30]
Sage (*Salvia offici-nilis*), flowers, leaves and stems, dried	Clevenger 400 g per batch	2 h	Flower: 1.6 Leaf: 1.7% Stem: 0.2%	Kinetics; oil yield	Veličković *et al.* [8]

Table 2. Continued

Plant/part	Level	Operating conditions	Essential oil yield	Objective of study	Reference
Lavandin super (*Lavandula angusti-folia x latifolia*); aerial parts, fresh	Bench scle unit; 2175 g per batch	Steam pressure: 2 bar	1.186–1.468%	Kinetics; modeling (a phenomenological model)	Cerpa *et al*. [31]
Aniseed (*Pimpinella anisum*); leaves, dried	Pilot plan, 2 and 5 kg per batch	140 and 200 kPa; steam flow rate: 6 kg/h; up to 2.5 h	2.55%, 2.5 h	Kinetics; modeling of steam distillation; oil yield	Romdhane and Tizaoui [32]
Thyme (*Thymbra spicata*); leaves, dried; whole: 2.05 mm; ground: 0.50 and 1.00 mm	150 g per batch	Steam of athmospheric pressure, flow rate: 0.64 and 1.03 L/h; up to 2.5 h	1.3%, 2.5 h	Effects of milling, process time and steam flow rate on essential oil yield and composition; kinetics	Hanci *et al*. [33]
Rosemary (*Rosemarinus officinalis*); leaves	na	Steam of atmospheric pressure	1.2%, 2 h	Kinetics; modeling (diffusional model based on the Fick's second law)	Boutekedjiret *et al*. [12]
Lavander (*Lavandula angustifolia*), flowers; Artemisia (*Artemisia annua*), leaves	750 g per batch	na	6-10%, 5 h 0.3-0.9%, 4 h	Kinetics; oil yield and composition	Masango [34]
Artemisia judaica, aerial parts (flowers, leaves and small stems), fresh	1 kg per batch	na	1.42%, 2 h	Kinetics; oil yield and composition	Charchari and Hamadi [35]
Rosemary (*Rosmarinus officinalis*); leaves and caulis together, dried (lot A) and fresh (lot B).	Pilot plant, 9.9–23.0 (lot A) and 8.6–29.9 kg (lot B) per batch	Steam pressure: 3 bar; steam flow rate: 0.89 and 0.75 kg/min for lots A and B, respectively	Mean 0.62% and 0.49% for lots A and B, respectively	Economic evaluation of an industrial steam distillation; kinetics; oil yield and composition	Mateus *et al*. [36]
Citronella (*Cymbopogon winterianus*); aerial parts (leaves and twigs), dried and fresh	50 g per batch	na	0.776%, 4 h (dried) 0.942%, 2 h (fresh)	Kinetics; oil yield and composition; process optimization; modeling (difusional model based on the Fick's second law)	Cassel and Vargas [37]
Baccharis anomala, Baccharis dentata, Baccharis uncinella, aerial parts (leaves and twigs)	200 g per batch	na	0.06% (v/w), 0.05% (v/w), 0.24% (v/w), 40 min	Kinetics; oil yield and composition; modeling (model of Sovova based on mass transfer fundamentals)	Xavier *et al*. [38]
Rosemary (*Rosmarinus officinalis*), basil (*Ocimum basilicum*), lavender (*Lavandula dentate*), fresh leaves	213-313 g per batch	Steam pressure: 1.01.bar; steam flow 3.4 mL/min; 213-313 g; no pre-processing of leaves	0.51%, 0.38%, 0.32%, 30 min	Kinetics; oil yield and composition; modeling (diffusional model)	Cassel *et al*. [39]
Lemon grass (*Cymbopogon* spp.), leaves, chopped or unchopped; 70-1000 kg	Pilot plant	Steam flow rate: 12-16 L/h	0.31-0.53% (v/w), 5 h	Kinetics at pilot scale; modeling (model based on first order kinetics)	Kaul *et al*. [40]
Peppermint (*Mentha piperita*), leaves, dried, crushed	Steam distillation	Steam pressure: 1 atm (100 °C)	na	Kinetics of oil constituent distillation	Ammann *et al*. [41]

produced water steam and the essential oil leave the hot suspension, condense and are collected and separated by decantation. Two products are obtained – the essential oil and the condensed water containing water-soluble constituents of the essential oil, known as floral water or hydrosol. The plant materials are usually comminuted to decrease the particle size and to increase the particle surface area.

When employing a steam distillation, the plant material is placed in a still and steam is forced to pass through the material and the essential oil is released from the plant material. Different batches of plant materials and steam flow rates are used on scales from laboratory to industrial. The pressure of steam is usually greater than atmospheric pressure; hence, the operational temperature is higher than 100 °C. The steam containing the essential oil is cooled down, collected and separated into two products – the essential oil and the floral water. Water-steam distillation is a combination of the previous two methods. The plant material is immersed in water in a still, which is heated, and steam is fed into the suspension.

During a hydrodistillation, the increase of temperature causes an increase of pressure within the plant organs containing the essential oil. Once the pressure increases above a certain level, the cell walls break and the essential oil is released. A part of the essential oil is released from the external surfaces of the plant particles, but the remaining part must diffuse from the interior of the plant particles to their external surfaces. Then, the steam carries away the essential oil from the external surface of plant particles. This mechanism is the basis for modeling the kinetics of essential oil hydrodistillation processes.

The present work deals with the modeling of the kinetics of the extraction of essential oils from a number of plant materials and their parts by hydrodistillation (water and steam distillation). The experimental data were obtained by studying the hydrodistillation kinetics of the essential oil from juniper berries using a pilot distillation unit. In addition, data on the kinetics of the hydrodistillation of essential oils collected from the literature (Tables 1 and 2) were included in the modeling. A three-parameter physical model was developed assuming simultaneous essential oil washing and diffusion processes. Two simpler exponential models, the first assuming instantaneous washing followed by diffusion of essential oil and the second assuming only diffusion of essential oil, were derived from the three-parameter model. Furthermore, a sigmoid model was used to describe the kinetics of essential oils deviating from the exponential pattern. The main goal was to compare these physical models and suggest the optimum ones for the two methods of hydrodistillation and for different plant materials.

Modeling of the kinetics of essential oils hydrodistillation

Model of simultaneous washing and diffusion

The mathematical model describing the kinetics of essential oil hydrodistillation is derived for a batch distillation vessel in which a plant material and water are added. For water distillation of the essential oil, the plant material is immersed in water, while for steam distillation the plant material as a porous bed is placed on a perforated plate above the water. The produced water vapor (stem) heats the plant material and carries the essential oil from the external surface of the plant particles. The mixture of water and essential oil vapors is condensed in a heat exchanger and then separates into the floral water and the essential oil. In the case of water distillation the floral water is usually returned to the distillation vessel.

The mathematical model is based on the following assumptions:

i) in the case of water distillation, the suspension in the distillation vessel is perfectly mixed. In the case of steam distillation, the porous bed of plant material is considered as a batch and is stable, with no changes in form or disposition during the process, and the vapor phase flow is plug flow, with a constant rate;

ii) the essential oil is considered as a single component;

iii) plant particles are isotropic, equal in size, shape and initial essential oil content;

iv) the effective coefficient of diffusion through plant particles is constant;

v) there is no resistance to the mass transfer of essential oil from the external surfaces of the plant particles;

vi) the essential oil and the floral water are completely immiscible;

vii) a fraction of the essential oil is located at the external surfaces of the plant particles, *f*, and the rest is uniformly distributed in the plant particles, (1-*f*);

viii) the isolation of essential oil occurs via two simultaneous mechanisms: a) "washing" of the essential oil from the external surfaces of the plant particles and b) the diffusion of essential oil from the interior of the plant particles towards their external surfaces. The kinetics of both processes is assumed to be the first order with respect to the essential oil in the plant particles:

$$-\frac{dq_p}{dt} = kq_p \qquad (1)$$

where q_p is the average concentration of essential oil in the plant particles (g/100 g) at time *t*, and *k* is the process rate constant. Each process has a different rate constant: the diffusional process is much slower than

the washing and is responsible for limiting the overall extraction process rate.

ix) The amount of the essential oil available for hydrodistillation corresponds to the amount of the essential oil distilled off until saturation:

$$q_{po} = q_\infty \tag{2}$$

where q_{po} is the initial average concentration of essential oil in the plant particles, and q_∞ is the amount of essential oil distilled off until saturation (in g/100 g of the plant materials).

By integrating Eq. (1), the following equations are derived for washing and diffusion, respectively:

$$\frac{q_{p1}}{q_\infty} = e^{-k_1 t} \tag{3}$$

and

$$\frac{q_{p2}}{q_\infty} = e^{-k_2 t} \tag{4}$$

where k_1 and k_2 are the rate constants for washing and diffusion processes, respectively.

Based on the assumption *vii)*, the total amount of essential oil remained in the plant particles until time *t* is as follows:

$$\frac{q_p}{q_\infty} = f \frac{q_{p1}}{q_\infty} + (1-f) \frac{q_{p2}}{q_\infty} \tag{5}$$

or:

$$\frac{q_p}{q_\infty} = f e^{-k_1 t} + (1-f) e^{-k_2 t} \tag{6}$$

The amount of essential oil recovered until time *t*, *q*, is connected to the amount of the essential oil present in the plant particles at the same time by the following equation:

$$q = q_\infty - q_p \tag{7}$$

By combining Eqs. (6) and (7), the following equation is derived:

$$\frac{q}{q_\infty} = 1 - f e^{-k_1 t} - (1-f) e^{-k_2 t} \tag{8}$$

Analyzing the hydrodistillation apparatus as a whole, Milojević *et al.* [2] showed that a direct relationship between the amount of the essential oil collected in the separator, divided by the amount of the plant material, and the essential oil yield from the plant material in the distillation vessel with the time delay. Therefore, Eq. (8) describes the variation of the dimensionless content of essential oil extracted from the plant material with the progress of extraction. The

parameters of Eq. (8) can be calculated by fitting this equation to the experimental q/q_∞ ratios and minimizing the sum of the squared deviations between the experimental and calculated ratios.

Sovova and Aleksovski [15] have derived a kinetic expression basically the same to Eq. (8) from a phenomenological model for water distillation of essential oil for both particles with homogeneously distributed essential oil and particles with part of the essential oil deposited on their surface. In the former case, the essential oil from intact cells diffuses slowly to the particle surface, and in the latter case, the essential oil located in the cells with broken walls is rapidly extracted (washed out). According to the phenomenological model of Sovova and Aleksovski, the parameter *f* is the fraction of broken plant cells, while its two other parameters are time constants corresponding to the reciprocal values of the rate constants for washing and diffusion, k_1 and k_2. The phenomenological model has been already tested for water distillation of essential oil from creeping thyme and intact coriander seeds [15].

Model of instantaneous washing followed by diffusion

The developed model can be further simplified by assuming that washing is very fast and occurs instantaneously ($k_1 \to \infty$), so Eq. (8) becomes:

$$\frac{q}{q_\infty} = 1 - (1-f) e^{-k_2 t} \tag{9}$$

Equation (9) is the same to the kinetic expression developed by Milojević *et al.* [2], where *f* is the washing coefficient, corresponding to the washable part of the essential oil that can be extracted, and k_2 is the coefficient of slow essential oil distillation. The model has been experimentally verified for the extraction of the essential oil from cherry juniper berries [2], laurel leaves [18], fennel seeds [22] and agarwood [29] by water distillation.

Model of pseudo-first order kinetics

If no washing of the essential oil occurs (*f* = 0), then Eq. (9) becomes a simple exponential function:

$$\frac{q}{q_\infty} = 1 - e^{-k_2 t} \tag{10}$$

This is the logarithmic equation based on the assumption of pseudo first-order kinetics with respect to the essential oil remaining in the plant material and is frequently used model for both water and steam distillations. For instance, the first-order kinetics was used to model the essential oil extraction from leaves of thyme (*Thymbra spicata* L.) [33], lemon grass (*Cymbopogon* spp.) [40], celery (*Apium graveolens* Linn.) [21] and cumin (*Cuminum cyminum* L.) [20] seeds by

steam distillation, as well as from flowers of lavender (*Lavandula angustifolia* Mnch) by water distillation [5].

Sigmoid model

The kinetics of water and steam distillation of essential oils from some plant materials have been observed to deviate from the above-mentioned exponential kinetic models. An almost linear increase during the initial period of the water distillation of parsley seeds was noticed [23], while a sigmoid variation of the essential oil yield with time was observed for various plant materials exposed to either water or steam distillation, such as the aerial parts of *Artemisia judaica* [35], the flowers, leaves and stems of common sage [8], lavender flowers and leaves [34], as well as rosemary leaves and caulis [36]. In these cases, the variation of the essential oil yield from its lowest, A_1, to the highest, A_2, asymptotic value can be described by a Boltzmann sigmoid curve:

$$\frac{q}{q_\infty} = \frac{A_1 - A_2}{1 + \exp\left(\dfrac{t - t_0}{T_1}\right)} + A_2 \qquad (11)$$

Since $A_1 = 0$ at $t = 0$ and $A_2 = 1$ when $t \to \infty$, Eq. (11) becomes:

$$\frac{q}{q_\infty} = 1 - \frac{1}{1 + \exp\left(\dfrac{t - t_0}{T_1}\right)} \qquad (12)$$

where t_0 is the time at which the essential oil yield is halfway between the lowest and the highest value and T_1 is the steepness of the curve, which corresponds to the diffusion time constant. This model has not been used yet for the purpose of modeling the kinetics of essential oil hydrodistillation.

EXPERIMENTAL

Plant material

Mature juniper berries, originating from the Moutain Kopaonik, Leposavić, Serbia, were used. The berries were comminuted immediately before the pilot hydrodistillation by a hammer mill (5 kW).

Water distillation

The water distillation was performed in a pilot distillation unit. The comminuted berries (10 kg) were placed in the distillation vessel and distilled water (30 L) was added. The floral water flow rate was 46 mL/min. The essential oil was collected at different times and the volume recorded.

Steam distillation

The same pilot distillation unit was employed to recover the essential oil from juniper berries by steam distillation. The comminuted berries (3 kg) were placed on a perforated plate, above the distilled water (10 L). The thickness of the juniper bed was about 30 mm. The floral water rate was 30 mL/min. The volume of the essential oil collected at different times was recorded.

Literature data

The published experimental data on the kinetics of hydrodistillation of essential oil from different plant materials were included into comparing the kinetic models. Tables 1 and 2 summarize the plant materials, the technique and the operating conditions used in the studies on water and steam distillation of essential oil, respectively.

Estimation of the parameter values

Values of the parameters of Eqs. (8)–(10) and (12) were estimated by a computer program using all measured values of the q/q_∞ ratio. The computer program employs the Levenberg-Marquardt algorithm, which combines the Gauss-Newton method and the steepest descent method, to adjust the parameter values in the iterative procedure. The "best-fit" parameter values were estimated by minimizing the deviation between the predicted and actual values of the q/q_∞ ratio.

Goodness of fit

The criterion used to evaluate the goodness of fit of each model was the mean relative percentage deviation between the predicted and actual values of the q/q_∞ ratio, *MRPD*, which is defined as follows:

$$MRPD = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{(q/q_\infty)_{\mathrm{pi}} - (q/q_\infty)_{\mathrm{ai}}}{(q/q_\infty)_{\mathrm{ai}}} \right| \qquad (13)$$

where subscripts p and a denote predicted and actual, respectively.

RESULTS AND DISCUSSION

Hydrodistillation of juniper essential oil

The variations of the normalized juniper essential oil yields with the progress of the water and steam distillation processes are shown in Figure 1. The initial essential oil extraction was faster by steam than by water distillation. However, the essential oil yield and the process duration were larger for water than for steam distillations. A techno-economic analysis should be performed to distinguish whether water or steam distillation is more suitable for the recovery of the essential oil from juniper berries on a commercial scale.

According to the mean relative percentage deviation (*MRPD*) values (Tables 3 and 4), the model based on simultaneous washing and diffusion fits better the

experimental data than the model based on instantaneous washing followed by diffusion especially for the steam distillation. The pseudo-first order model appears to be the worst one because of the largest *MRPD* values. The values of the parameters of the employed models for water and steam distillation of essential oil from juniper berries are presented in Tables 3 and 4. Values of the rate constants k_1 and k_2 indicate that both diffusion and washing during steam distillation of juniper berries were faster than those during water distillation, and the difference was greater for washing than for diffusion. However, the fraction of washed essential oil was larger for the juniper berries subjected to water distillation. Compared to the laboratory water distillation of juniper berries [2] (Table 4), the pilot water distillation is characterized by smaller values of the rate constants k_1 and k_2, indicating a slower process, which is probably due to more efficient heating applied in the former case.
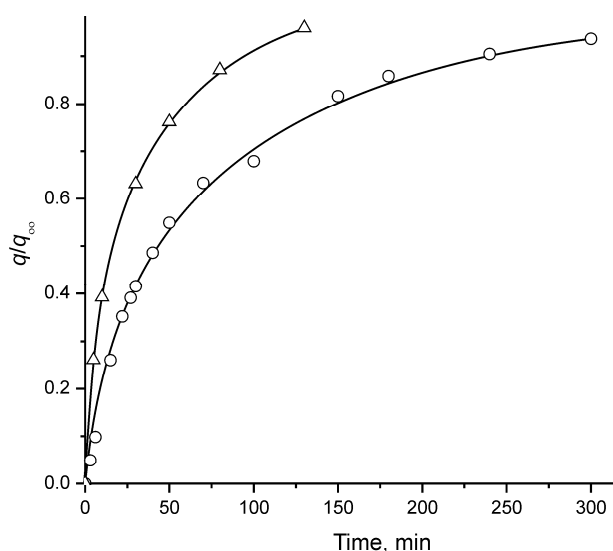

Figure 1. Variation of q/q_∞ with time during water and steam distillation of essential oil from ground, dried juniper berries (water distillation: ◯; solid batch: 10 kg; solid/liquid ratio: 1:3; floral flow rate: 46 mL/min; steam distillation: △; solid batch: 3 kg; steam flow rate: 30 g/mL).

The results for water and steam distillation of the essential oil from rosemary leaves can also be employed for comparing the two techniques. The results confirmed that the diffusion rate through the plant particles was much smaller for water (0.019 min^{-1}, Table 3) than for steam (0.154 min^{-1}, Table 4) distillation [11]. The same was also observed for dried thyme leaves (0.010-0.020 min^{-1} [15] and 0.030–0.052 min^{-1} [33] for water and steam distillation presented in Tables 3 and 4, respectively. However, the diffusion rate constants for water and steam distillation of the essential oil from lavender flowers were approximately the same (about 0.050 min^{-1}) [5,30].

Water and steam distillation of essential from various plant materials

The results of the application of the simplified physical models for modeling the kinetics of essential oil extraction from different plant materials by water and steam distillation are summarized in Tables 3 and 4, respectively.

Water distillation

All the employed models fitted the kinetics of the experimental water distillation data quite well, independent of the type of distillation equipment and its scale, the type of plant and the plant part, and the operational conditions. The applicability of a model improved with its complexity, and the best model was the most complex model of simultaneous washing and diffusion, Eq. (8), involving the simultaneous washing and diffusion of the essential oil. As a rule, the lowest *MRPD*-values between the predicted and experimental values of the essential oil yield were observed with this model. In some cases, the fit did not converge for unknown reasons or for the over parameterization of the fitting model. In addition, in a few cases, it was observed that the rate constants k_1 and k_2 were very similar. In such cases, the simpler models were used to fit the experimental data. The worst model was shown to be that based on the pseudo-first order kinetics, Eq. (10). The model of Milojević and coworkers involving instantaneous washing followed by diffusion of the essential oil through the plant particles, Eq. (9), was

Table 3. Parameters of the kinetic models based on essential oil washing and/or diffusion: water distillation

Reference	Plant	q_∞ g/100 g	Pseudo-first order, Eq. (10)		Instantaneous washing and diffusion, Eq. (9)			Simultaneous washing and diffusion, Eq. (8)			
			$k_2\times10^3$ min^{-1}	MRPD %	$k_2\times10^3$ min^{-1}	f	MRPD %	f	$k_1\times10^3$ min	$k_2\times10^3$ min	MRPD %
Morin et al. [5]	Lavender, flowers	1.61	54.0	±5.1	46.1	0.406	±1.1	0.456	268.8	48.3	±0.2
Stanojević et al. [7]	Common lavender, flowers, dried	5.73[a]	30.5	±12.5	27.7	0.284	±11.2	0.773	70.9	16.0	±3.5
Jannet and Mighri [6]	*Ridolfia segetum*, flowers, fresh	5.0	38.7	±10.5	35.5	0.213	±2.7	0.669	73.0	25.1	±1.3

Table 3. Continued

Reference	Plant	q_∞ g/100 g	Pseudo–first order, Eq. (10)		Instantaneous washing and diffusion, Eq. (9)			Simultaneous washing and diffusion, Eq. (8)			
			$k_2\times10^3$ min^{-1}	MRPD %	$k_2\times10^3$ min^{-1}	f	MRPD %	f	$k_1\times10^3$ min	$k_2\times10^3$ min	MRPD %
Babu and Kaul [3] Wild marigold, aerial parts	Vaccum distilled	0.91	23.3	±6.5	–	–	–	0.091	220.8	16.7	± 5.4
	Distilled at NTP	1.56	19.5	±7.4	18.5	0.032	± 3.2	0.019	22222.2	20.8	± 3.7
Rezvanpanah et al. [9]	*Satureja hortensis*, aerial parts, dried	3.1	21.3	±14.4	17.5	0.359	7.3	0.200	1091.7	20.1	± 9.7
	Satureja montana, aerial parts, dried	0.7	20.8	±11.0	17.3	0.333	± 5.9	0.100	6493.5	20.0	± 14.7
Gavahian et al. [16]	Shirazi thyme, aerial parts, dried	3.23[a]	127.2	±7.1	126.4	0.016	± 6.7	0.254	561.8	98.2	± 3.5
Golmakani and Rezaei [14]	Thyme, aerial parts, dried	2.39	53.8	±3.0	51.6	0.098	± 7.5	0.558	89.4	41.1	± 3.9

Reference	Particle size, mm	Liquid/ solid ratio, g/mL	q_∞ g/100 g	$k_2\times10^3$ min^{-1}	MRPD %	$k_2\times10^3$ min^{-1}	f	MRPD %	f	$k_1\times10^3$ min	$k_2\times10^3$ min	MRPD %
Sovova and Aleksovski [15] Thyme, aerial parts, dried	0.1	1:10	0.790	12.0	±19.1	8.8	0.283	±9.5	0.506	43.5	13.6	±1.5
		1:20	0.794	11.9	±17.3	9.4	0.222	±10.5	0.048	140.1	20.7	±2.2
		1:30	0.772	9.7	±10.4	–	–	–	1.0	–	–	–
		1:40	0.747	9.9	±15.4	9.3	0.055	±8.1	1.0	–	–	–
		1:50	0.687	10.1	±15.0	9.6	0.0.41	±13.7	1.0	–	–	–
	0.25	1:10	0.820	9.9	±12.9	9.1	0.094	±7.5	0.105	0.234	109.18	±3.5
		1:20	0.824	10.3	±8.4	9.6	0.081	±11.9	1.0	–	–	–
		1:30	0.815	9.6	±10.7	9.2	0.049	±7.4	1.0	–	–	–
		1:40	0.747	9.5	±19.0	–	–	–	1.0	–	–	–
		1:50	0.687	10.3	±23.1	9.9	0.030	±21.6	1.0	–	–	–
	0.315	1:10	0.858	12.5	±7.5	12.3	0.024	±6.4	1.0	–	–	–
		1:20	0.927	17.3	±7.4	16.4	0.085	±2.4	1.0	–	–	–
		1:30	0.815	11.4	±10.8	11.3	0.009	±7.6	1.0	–	–	–
		1:40	0.747	9.2	±15.4	8.6	0.059	±9.3	1.0	–	–	–
		1:50	0.687	7.9	±17.8	7.8	0.016	±15.4	1.0	–	–	–
	0.4	1:10	0.944	19.4	±10.5	15.7	0.316	±6.4	0.108	2304.1	25.5	±0.9
		1:20	0.961	21.9	±6.5	20.3	0.147	±4.9	0.175	2500.0	21.3	±2.0
		1:30	0.901	15.7	±5.3	15.2	0.049	±7.9	1.0	–	–	–
		1:40	0.841	13.0	±11.3	10.8	0.200	±13.3	1.0	–	–	–
		1:50	0.833	12.2	±5.2	11.2	0.096	±14.7	1.0	–	–	–
	0.5	1:10	0.880	13.0	±15.7	10.1	0.296	±7.0	0.425	56.8	8.1	±1.9
		1:20	0.913	15.2	±10.5	13.1	0.224	±6.9	0.131	7812.5	16.6	±2.0
		1:30	0.880	15.4	±11.8	12.7	0.246	±7.7	0.226	93.0	17.3	±1.0
		1:40	0.856	14.2	±14.3	11.0	0.276	±9.6	0.295	81.3	15.6	±0.6
		1:50	0.800	11.3	±13.3	9.3	0.186	±11.6	0.291	58.5	9.9	±1.9
	0.63	1:10	0.875	15.7	±14.1	12.0	0.317	±8.6	0.097	47619.0	24.1	±1.9
		1:20	0.910	18.8	±12.3	14.6	0.349	±8.8	0.097	1730.1	27.6	±0.9
		1:30	0.867	14.0	±8.9	12.3	0.155	±7.9	0.114	3745.3	15.1	±4.4
		1:40	0.850	13.6	±11.4	11.4	0.196	±9.8	0.086	15384.6	18.1	±2.1
		1:50	0.858	16.6	±7.2	16.3	0.027	±13.0	0.004	2681.0	19.0	±6.3
	0.8	1:10	0.858	12.4	±7.3	10.9	0.160	±3.9	1.0	–	–	–
		1:20	0.893	13.8	±11.6	11.4	0.24	±3.0	1.0	–	–	–
		1:30	0.858	13.8	±7.4	12.7	0.112	±6.6	0.058	1869.2	17.3	±2.7

Table 3. Continued

Reference	Plant	q_∞ g/100 g	Pseudo–first order, Eq. (10)		Instantaneous washing and diffusion, Eq. (9)			Simultaneous washing and diffusion, Eq. (8)			
			$k_2\times10^3$ min⁻¹	MRPD %	$k_2\times10^3$ min⁻¹	f	MRPD %	f	$k_1\times10^3$ min	$k_2\times10^3$ min	MRPD %
	1:40	0.858	11.5	±16.9	8.9	0.273	±6.7	0.293	139.9	8.5	±0.9
	1:50	0.858	13.1	±8.5	11.9	0.121	±10.6	0.012	2681.0	19.0	±4.8
1.0	1:10	0.840	14.2	±13.5	11.1	0.267	±9.3	0.131	65.3	22.2	±1.3
	1:20	0.848	11.4	±10.3	10.1	0.154	±7.5	0.040	2932.6	19.1	±6.6
	1:30	0.800	9.5	±8.3	8.7	0.090	±6.7	0.043	12820.5	9.9	±3.2
	1:40	0.800	9.5	±8.6	8.5	0.117	±15.3	1.0	–	–	–
	1:50	0.800	11.3	±13.3	9.3	0.186	±11.6	0.076	58.5	9.9	±7.0
Benyouseff et al. [10]	Spearmint, leaves, fresh	0.89	22.7	±14.6	18.7	0.242	12.5		–	–	–
Babu and Singh [11]	Fresh	2.56	9.39	±5.7	8.53	0.236	±2.9	0.524	22.9	6.4	±1.0
Eucalyptus cinerea, leaves	Dried	2.87	8.75	±4.2	8.81	0.134	±1.6	0.377	24.6	5.9	±0.4
Boutekedjiret *et al.* [12]	Rosemary, leaves	0.44	68.7	±2.4	67.5	0.010	±0.30	0.943	75.3	10.4	±2.3
Stanisavljević et al. [18]	Cherry laurel; leaves	0.43[a]	38.7	±11.8	34.2	0.294	±6.6	0.779	85.6	18.2	±1.7
Bousbia *et al.* [13]	Rosemary, leaves	0.35	19.35	±8.4	–	–	–	–	–	–	–
Silou *et al.* [17]	Cut, 1000 W	0.36[a]	90.1	±29.7	–	–	–	–	–	–	–
Lemon grass	Cut, 1500 W	0.28[a]	69.0	±24.8	–	–	–	–	–	–	–
	Ground 1000 W	0.64[a]	73.9	±9.3	–	–	–	–	–	–	–
Benyouseff et al. [19]	Corriander seeds	0.0566	5.20	±5.4	–	–	–	0.024	170.9	4.0	±2.7
Sowbhagya *et al.* [20], Cumin seeds	Powder	1.92[a]	63.4	±3.5	57.3	0.327	±1.0	0.752	111.6	42.5	±0.1
	Flakes	2.19[a]	56.2	±4.1	54.6	0.054	±3.8	0.544	4830.9	25.6	±1.3
Sowbhagya et al. [21], Celery seeds	Powder	1.320[a]	44.8	±1.7	–	–	–	–	–	–	–
	Flakes	1.623[a]	40.6	±5.3	35.2	0.315	±3.5	–	–	–	–
Kapas et al. [22]	Fennel seeds, crushed	2.12[a]	22.4	±28.1	3.4[b]	0.084[a]	na[c]	0.867	250.0	149.9	±5.8
Milojević et al. [2], Juniper berries, dried	1:3 g/mL; 0.13 mL/min	0.56	22.5	±7.4	–	–	–	–	–	–	–
	1:3 g/mL; 3.6 mL/min	1.52	38.2	±17.4	36.1	0.134	±9.0	0.443	107.8	8.6	±1.5
	1:3 g/mL; 10.0 mL/min	1.68	50.6	±10.6	50.3	0.199	±6.5	0.820	82.2	13.4	±2.2
	1:3 g/mL; 11.7 mL/min	1.68	56.4	±9.7	51.7	0.212	±5.1	0.172	247.5	56.1	±1.6
	1:10 g/mL; 10.0 mL/min	1.51	115.4	±22.3	89.3	0.549	±14.7	0.709	332.2	15.0	±4.6
This work	Juniper berries, dried	1.33[a]	10.2	±16.7	8.0	0.350	±5.9	0.364	50.7	7.9	±5.5
	Batch of 10 kg, 1:3 kg/L; floral water rate: 46 mL/min										
Miletić *et al.* [26]	*Abies grandis*, wooded greenery	0.65[a]	26.8	±9.1	–	–	–	0.073	1712.3	11.9	±2.3
	Picea abies, branches with needles, fresh	0.63[a]	30.9	±13.1	–	–	–	0.189	8.1	8.2	±5.9
	Pinus sylvestris, branches with needles	0.53[a]	33.4	±3.7	–	–	–	0.039	3759.4	26.2	±2.0
	Juniper berries, dried, microwave pretreated	1.68[a]	21.5	±32.2	–	–	–	0.195	27777.8	24.3	±1.1
	Juniper berries, dried	1.50[a]	32.9	±2.8	–	–	–	–	–	–	–
	Pseudotsuga menziesii, branches with needles	0.75[a]	26.4	±5.0	–	–	–	–	–	–	–
Atti-Santos *et al.* [27]	Lime, peals, dried	3.48[a]	8.7	±5.5	8.43	0.040	±5.4	0.187	699.3	6.8	± 2.8
Ferhat et al. [28]	Lemon, peals, fresh	0.21	11.6	±7.9	–	–	–	–	–	–	–

[a] mL/100 g; [b] The value taken from the original paper; [c] Not available

Table 4. Parameters of the kinetic models based on essential oil washing and/or diffusion: steam distillation

Reference	Plant	q_∞ g/100 g	Pseudo first–order, Eq. (10)		Instantaneous washing and diffusion, Eq. (9)		
			$k_2\times10^3$ min^{-1}	MRPD %	f	$k_2\times10^3$ min^{-1}	MRPD %
Chemat *et al.* [30][a]	Lavender; flowers, dried	8.75	52.5	±4.6	0.030	51.2	± 3.4
Cerpa *et al.* [31], Lavandin super, aerial parts, fresh; floral water flow 35 ml/min	Bed porosity						
	0.721	1.324	131.3	±16.0	–	–	–
	0.762	1.654	84.3	±27.8	–	–	–
	0.805	1.410	114.0	±7.9	–	–	–
Hanci et al. [33], Thyme, dried leaves; steam flow rate: 0.64 L/h	Mean particle size, mm						
	2.05	1.33[d]	55.4	±3.2	0.173	51.6	±2.6
	1.00	1.00[d]	48.1	±4.3	0.172	44.3	±3.7
	0.50	1.00[d]	31.4	±4.2	0.109	29.7	±5.5
Steam flow rate: 1.03 L/h	2.05	1.6[d]	53.4	±3.6	0.139	50.9	±17.9
	1.00	0.9[d]	47.9	±6.2	–	–	–
	0.50	0.8[d]	39.9	±2.1	–	–	–
Cassel and Vargas [37]	*Cymbopogon* leaves; laboratory	2.55	30.0	±13.0	0.191	26.0	±5.0
Xavier *et al.* [38] *Baccharis anomala*, aerial parts	Autumn	0.040	70.8	±18.7	–	–	–
	Winter	0.042	64.1	±18.5	–	–	–
Baccharis dentata, aerial parts	Autumn	0.027	73.4	±9.5	–	–	–
	Winter	0.037	40.1	±22.0	–	–	–
Baccharis uncinella, aerial parts	Autumn	0.163	87.7	±5.8	–	–	–
	Winter	0.182	65.1	±18.5	–	–	–
Cassel *et al.* [39]	Rosemary, leaves	0.51	16.6	±4.9	0.128	15.56	±6.4
	Basil, leaves	0.38	17.4	±17.9	–	–	–
	Lavender, leaves	0.32	12.0	±30.9	–	–	–
Boutekedjiret *et al.* [12][b]	Rosemary, leaves	1.20	154.4	±4.2	0.480	110.8	±2.6
Koul *et al.* [40], Lemon grass	100 kg,unchopped, tight packing, 12–15 L/h	0.31[d]	12.2	±9.4	–	–	–
	86 kg,unchopped, loose packing, 12–15 L/h	0.49[d]	10.8	±17.5	–	–	–
	70 kg, chopped, loose packing, 12 L/h	0.55[d]	15.0	±5.1	–	–	–
	70 kg, chopped, loose packing,15 L/h	0.47[d]	14.5	±21.1	–	–	–
	1000 kg, unchopped, loose packing, 125 L/h	0.57[d]	18.5	±4.0	–	–	–
	1000 kg, unchopped, loose packing, 140 L/h	0.52[d]	18.8	±9.8	–	–	–
	1000 kg,unchopped, loose packing, 160 L/h	0.53[d]	18.8	±11.8	–	–	–
Romdhane and Tizaoui [32] Aniseed; steam preasure/batch	1.4 kPa/2 kg	1.9	18.7	±4.3	–	–	–
	2.0 kPa/2 kg	2.1	25.8	±5.8	–	–	–
	2.0 kPa/5 kg	2.0	20.7	±8.7	–	–	–
This work[c]	Juniper berries, dried	0.73[d]	25.5	±19.7	0.265	22.1	±6.4
	Batch of 3 kg; bed thickness: 3 cm; steam flow rate: 30 mL/min						

[a]Equation (8) was applicable with a very small value of the fraction of broken plant cells (f = 0.030; k_1 = 9.80 min^{-1}; k_2 = 0.0522 min^{-1}); [b]Eq. (8) was applicable with a very large value of the fraction of broken plant cells (f = 0.901; k_1 = 0.240 min^{-1}; k_2 = 0.0163 min^{-1}); [c]Eq. (8) was applicable with the following parameters: f = 0.299, k_1 = 0.200 min^{-1} and k_2 = 0.0215 min^{-1} (MRPD :±0.3%); [d]mL/100 g

applicable only in the latter stage of water distillation and deviated from the experimental data in the initial period.

When the model involving the simultaneous washing and diffusion of the essential oil was applied to the distillation of the essential oil from flowers [5–7], a medium to large fraction of washed essential oil (0.46 to 0.77) was observed. The washing rate constant was 3 to 5 times larger than the diffusion rate constant, indicating that the washing was much faster than the diffusion. Thus, for water distillation of essential oils from flowers, washing is more important than diffusion. The fraction *f* was larger and the rate constants were lower for dried lavender flowers than for fresh ones, indicating that drying increases the availability of the essential oil for washing by rupturing the cell walls but decreases the rates of washing and diffusion, probably because of in-take of the solvent by the dry plant material followed by washing and diffusion through the liquid within the plant particles. Large, but similar values of fraction *f* were found for the fresh flowers of *L. officinalis* and *R. segetum* [6,7]; moreover, the values of the washing and diffusion rate constants were similar for these two flowers. Small to medium values of fraction *f* (up to 0.52) were determined for essential oil recovery from the aerial parts and leaves of different plants by water distillation [3,9–11,13–18]. The application of vacuum during the water distillation of wild marigold increased the fraction *f* and dramatically increased the washing rate constant, probably due to the reduced vapor pressure of the essential oil [3]. Values of the diffusion rate constant, k_2, determined for the different types of plant materials were mainly of the same order, about 0.01 to 0.02 min^{-1}, although, some plant materials had smaller and others higher values of this rate constant under certain operating conditions. The phenomenological model was generally applicable for essential oil extraction from large particles (> 0.5 mm) of thyme, independent of the solid-to-liquid ratio, while the exponential pseudo-first order model could be employed for small plant particles [15]. Smaller values of fraction *f* were observed for larger plant particles of the aerial parts of thyme, which were connected to the smaller degree of plant material comminution. This is in accordance to the very small values of fraction *f* observed for the largest plant particles (1.0 mm). Approximately the same values of model parameters were determined for fresh and dried *E. cinerea* leaves [11].

The model based on the first-order kinetics was found to be applicable for modeling the kinetics of water distillation of the essential oil from almost all the studied plant materials, as the *MRPD* was generally less than ±20% with a few exceptions, such as lemon grass, fennel seeds and juniper berries. The diffusion rate constants for the essential oils from the aerial parts of wild marigold, *S. hortensis* and *S. montana* and the leaves of spearmint and rosemary were approximately the same (about 0.020 to 0.023 min^{-1}). Significantly higher values of the diffusion rate constant were found for aerial parts of shirazi thyme (0.127 min^{-1}) and thyme (0.054 min^{-1}) from Iran, the leaves of cherry laurel (0.040 min^{-1}) and rosemary (0.069 min^{-1}), and lemon grass (0.070 to 0.090 min^{-1}). The diffusion rate constants for flowers, being between 0.030 and 0.054 min^{-1}, were also higher than those for most of the aerial parts and leaves. However, smaller values (generally less than 0.015 min^{-1}) were determined for the aerial parts of thyme (collected from Macedonia) and the leaves of spearmint and *E. cinerea*. The effects of plant particle size and solid-to-liquid ratio in the case of the water distillation of the essential oil from the aerial parts of thyme were observed to be very complex. The values of the diffusion rate constant for fresh and dried leaves of *E. cinerea* were similar. As expected, cumin and celery seeds in the form of powder and flakes showed much higher values of the diffusion rate constant (0.040 to 0.063 min^{-1}) than intact coriander seeds (0.005 min^{-1}). Higher values of the diffusion rate constant were found for powdered seeds than for flakes due to the better degree of seed disintegration. In the case of juniper berries, the diffusion rate constant increased with increasing the floral flow rate and with decreasing solid-to-liquid ratio. According to the diffusion rate constant at a solid-to-liquid ratio of 1:3 g/mL, the comminution of dried juniper berries using a blender (0.023 to 0.056 min^{-1}) was more efficient than using a hammer mill (0.010 min^{-1}), as can be concluded from Tables 3 and 4, respectively. The rate of essential oil diffusion was increased after microwave pretreatment of dried juniper berries. The diffusion rate constant for the peals of lime and lemon were among the lowest ones (0.009 and 0.012 min^{-1}).

Steam distillation

For steam distillation, generally, the model based on the first-order kinetics, Eq. (10), appears to be the best model for all types of plant materials included in the present study [12,31–33,37–40]. The bed porosity seems not to influence the diffusion rate constant in the case of fresh aerial parts of lavandin super. The steam flow rate did not affect the diffusion rate constant for the distillation of essential oil from dried thyme leaves and lemon grass. However, surprisingly, the diffusion rate constant decreased with decreasing plant particle size, independently of the steam flow rate. It was observed that the diffusion rate constant for lemon grass increased with increasing the batch size from 100 to 1000 kg, but chopping and dense packing did not affect the diffusion rate constant. The increase

in steam pressure in the distillation of aniseed increased the diffusion rate constant.

The phenomenological model based on the simultaneous washing and diffusion was not applicable for the steam distillation of essential oils from plant materials, except from lavender flowers, rosemary leaves and juniper berries (Table 4). In the first two cases, either a very small (f = 0.03) or a very large (f = 0.90) value of the fraction f was determined, indicating that the kinetics of essential oil distillation was rather "pure" exponential.

It is also interesting that a washing stage was not observed for most of the plant materials included in the analysis. When the washing was a part of the kinetic model (flowers of lavender as well as leaves of thyme, *Cymbopogon* and rosemary), the lowest value of the washing coefficient f was found for dried flowers of lavender (0.03). Its values were mainly between 0.11 and 0.19, indicating that diffusion through plant material is a more important stage than washing. The diffusion rate constant was of the same order for flowers and leaves.

Sigmoid model

The parameters of the sigmoid kinetic model for water and steam distillation are presented in Tables 5 and 6, respectively. Approximately the same values of the diffusion time constant were observed for water and steam distillation of the essential oil of the flowers, leaves and stems of common sage [8]. However, the

time constant was larger for water (10.4 to 14.1 min) than for steam (6.6 to 8.8 min) distillation, indicating that the latter was faster than the former (Table 5). Smaller values of the diffusion time constant were determined for water distillation of crushed than of intact parsley seeds, regardless of whether the seeds were fermented or not [23–25]. However, the solid-to-liquid ratio did not affect the diffusion rate constant for water distillation of the essential oil from parsley seeds [24,25]. The steam flow rate greatly influenced the diffusion time constant for essential oils obtained from lavender flowers and Artemisia leaves by steam distillation (Table 6) [34]. With increasing steam flow rate, the diffusion time constant decreased, indicating the enhancement of the essential oil distillation rate [34].

CONCLUSIONS

Three physical models for describing the kinetics of the hydrodistillation of essential oil from different plant materials were compared in the present paper. These models were 1) a pseudo first-order model (logarithmic model), 2) an instantaneous washing followed by diffusion model and 3) a model based on simultaneous washing and diffusion. Although all models are applicable for the water distillation of essential oils, the model based on simultaneous washing and diffusion is the best choice for describing the kinetics of essential oil recovery from any type of plant material and on any scale. In the case of steam distillation, the best model is

Table 5. Parameters of the sigmoid kinetic models: water distillation

Reference	Plant	t_0 / min	T_1 / min	MRPD / %
Veličković *et al.* [8], Common sage	Flowers	30.00	12.06	±5.1
	Leaves	33.44	14.08	±3.2
	Stems	27.59	10.37	±5.1
Stanković *et al.* [23]	Parsley, seeds, intact	105.98	39.98	±5.8
Stanković *et al.* [24], Parsley, seeds, intact, fermented (28 °C, 4 h);	Solid/liquid ratio, g/ml			
	1:10	81.23	35.15	±7.2
	1:15	75.22	33.22	±5.9
	1:20	74.46	34.82	±7.0
	1:25	74.87	33.70	±7.1
Intact, fermented (30 °C, 4 h)	1:20	74.87	33.70	±7.1
Crushed, fermented (30 °C, 4 h)	1:20	53.98	25.12	±5.9
Stanković *et al.* [25], Parsley, seeds, intact	Solid/liquid ratio, g/ml			
	1:10	95.24	38.78	±6.4
	1:15	103.05	43.37	±8.3
	1:20	81.83	37.82	±6.5
	1:25	92.25	40.22	±7.8
Crushed	1:10	60.81	29.37	±7.6
	1:15	60.50	32.50	±14.7
	1:20	51.77	27.67	±8.2
	1:25	53.46	26.70	±8.2

Table 6. Parameters of the sigmoid kinetic models: steam distillation

Reference	Plant	t_0 / min	T_1 / min	MRPD / %
Veličković *et al.* [8], Common sage	Flowers	20.01	7.66	±7.8
	Leaves	21.98	8.80	±12.3
	Stems	21.28	5.59	±14.7
Masango [34], Lavander, flowers	Steam flow rate, ml/min			
	2	49.67	19.06	±2.3
	4	22.17	8.80	±2.6
	20	4.83	2.25	±4.5
Artemisia, leaves	2.5	33.52	10.12	±2.9
	5	17.39	5.58	±3.1
	20	4.74	2.01	±3.9
Charchari and Hamadi [35]	*Artemisia judaica*, aerial parts, fresh	41.43	8.95	±4.8
Mateus *et al.* [36], Rosemary, leaves and caulis	Dried plant	5.58	2.40	±8.3
	Fresh plant	4.54	1.91	±4.0

the pseudo-first-order model, while the model based on simultaneous washing and diffusion was non-applicable except in the case of a few plant materials. For certain plant materials, however, only the sigmoidal model fitted the experimental data. Further studies involving a number of operational variables should be performed to derive a general model applicable to all plant materials from laboratory to the industrial scale.

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IZVOD

MODELOVANJE KINETIKE HIDRODESTILACIJE ETARSKOG ULJA IZ BILJNIH MATERIJALA

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Rad se bavi modelovanjem kinetike ekstrakcije etarskog ulja iz biljnih materijala primenom destilacija vodom i vodenom parom. Eksperimentalni podaci dobijeni su proučavanjem kinetike hidrodestilacije etarskog ulja ploda kleke. Literaturni podaci o kinetici hidrodestilacije etarskog ulja iz različitih biljnih materijala su, takođe, uključeni u modelovanje. Za opisivanje kinetike hidrodestilacije etarskog ulja razvijen je fizički model koji je zasnovan na istovremenom ispiranju i difuziji etarskog ulja iz biljnog materijala. Iz ovog modela izvedena su dva prostija modela od kojih je prvi zasnovan na trenutnom ispiranju praćenim difuzijom a drugi na difuziji bez ispiranja (tj.na kinetici prvog reda). Glavni cilj je bio poređenje ovih modela i predlaganje optimalnog za destilacije vodom i vodenom parom I za različite biljne materijale. Sva tri modela opisuju dobro eksperimentalne kinetičke podatke u slučaju destilacije vodom nezavisno od tipa destilatora i njegove veličine, tipa biljnog materijala i procesnih uslova, ali je najbolji model koji uključuje istovremeno ispiranje i difuziju etarskog ulja. Ovaj model je, međutim, neprimenljiv za vodeno-parnu destilaciju etarskog ulja, izuzev za etarsko ulje ploda kleke. Za ovu destilaciju etarskog ulja najbolji je kinetički model pseudo-prvog reda. U slučaju nekoliko biljnih materijala, promena prinosa etarskog ulja sa vremenom je sigmoidna, pa je modelovana Bolcmanovom sigmoidnom funkcijom.