Modeling Steam Distillation of Essential Oils: Application to Lavandin Super Oil

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Steam distillation of essential oil was studied to develop a phenomenological model able to reproduce oil recovery yield vs. collected floral water volume of aromatic plants with oil glandular trichomes. The model considers three stages in the oil obtaining process: (1) thermal oil exudation from the glandular trichomes, (2) vapor–liquid equilibrium at the interface, considering individual oil components, and (3) vapor phase oil mass transfer. Oil exudation was confirmed by SEM, and first order release kinetics was assumed for this stage. Lavandin super oil steam distillation experimental data were collected at a bench scale plant, using different steam flows and bed porosities. Experimental data were used to correlate model parameters: (1) the thermal exudation rate constant (0.072 min^{-1}), and (2) the oil spots average thickness in the oil-aqueous layer (115 μm). The average oil recovery yield was 1.36 ± 0.14% w/w. The main compounds of essential oil were identified and quantified by GC/MS. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 909–917, 2008

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Introduction

Steam distillation (SD) is a modified distillation process used for the recovery of temperature sensitive materials. One of its most widespread applications is the separation of essential oils from aromatic plants.[1–6] Although this process has been widely used for several centuries, only a few attempts have been reported by chemical engineers in the search for a deeper understanding of the whole process under a phenomenological point of view.

Some of these models[7–10] have been developed for oils present in ground particles (fruits), where diffusion inside the particle is the main resistance to oil recovery. It is usual that aromatic plants present the oil located in glandular trichomes on the outer surface of the flowers and leaves,[1–3] as in the lavandin super that belongs to the *Lavandulas* family.[11]

Oil release from glandular trichomes has been considered immediate as soon as the water starts boiling.[12] This behavior has been repeatedly checked by Scanning Electron Microscopy (SEM) for the supercritical fluid extraction of some herbs.[13–17] However, one unique SEM study[11] made with steam distilled lavender flowers revealed that glandular trichomes appeared swollen, with a highly wrinkled surface and empty of essential oil, but the integrity of their cuticles was maintained.

One of most serious restrictions in all reported models is the assumption of the oil as a single component. The necessity of implementation of different volatilities for essential oil components has been suggested by previous authors.[9,12]

Lavandin super (*Lavandula angustifolia L. x latifolia L.*) is a hybrid plant resulted of a cross between spike and fine lavender. It is cultivated in fields between 700 and 1100 m high, and it thrives in drought and Mediterranean winter, although dry rocky soils are preferred. The “super” qualification comes from its high esters content in the essential oil and it is also less camphor-flavored than other lavandin vari-

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eties. Because of these characteristics, it is considered as a more refined essential oil. Unfortunately, recovery yield is lower than in the "Abrial" variety.[5,6,18]

The main objective of this article is to obtain a better understanding of lavandin super steam distillation, and has been subdivided into three specific purposes:

(a) The development of a phenomenological model able to reproduce the essential oil recovery from process variables. This model will be used in a future work to optimize process conditions and product quality.

(b) The determination of essential oil recovery yield under different process conditions: bed porosity and steam flow.

(c) The essential oil characterization and plant microhistological analysis, before and after steam distillation, to determine the effects produced by the process.

Materials and Methods

Lavandin super

Plant was supplied by COCOPE S. Coop. (Peñafiel, Spain) in August 2005. It was transported to destination in polypropylene sacks and stored in a ventilated and dry place. Average plant humidity was 53% in weight, with a heterogeneous size distribution between flowers and stems. Trying to reproduce industrial conditions, neither physical separation nor drying processes were carried out. Plant humidity was determined by weighting three samples, after drying at 100°C for a period of 24 h.

Density and refractive index

Essential oil relative density (d^{20}) was measured using a Gay Lussac type pycnometer, in compliance with UNE 84156 standard method.[19] Refractive index was determined with an ABBE refractometer (Bellingham + Stanley, Model 60/ED), in compliance with UNE 84158 standard method.[20]

Gas Chromatography Mass Spectrometry

Essential oil composition was determined by gas chromatography mass spectrometry (GC/MS) analysis, on a HP 6890GC/5973MSD Network (Agilent Tech., USA). Two (30 m $\times$ 0.25 mm $\times$ 0.25 μm) HP-5MS and DB-WAX fused silica capillary columns were used. Each sample was analyzed three times in both columns. The temperature program for the HP-5MS column was from 65°C (6 min) to 200°C, at a rate of 4°C/min. With the DB-WAX column, temperature was kept constant at 55°C for 6 min and then raised to 200°C at 4°C/min. An injection volume of 0.4 μL and a split ratio of ca. 1:200 were used. The carrier gas was helium (Carburos Metálicos S.A., Spain), with a constant flow of 0.7 mL/min. The MS scan parameters included a mass range of 35–550 m/z, a scan frequency of 20 Hz, a scan speed of 5.3 scans/s, and a detector voltage of 1.53 keV. Compounds identification was carried out with the help of the NIST98 standard mass spectral library. A standard method[21] was used to quantify compounds quantities, by total ion chromatograph (TIC) peak integration, using a threshold of 18. In peak overlapping situations, separation was accepted when suggested by software.

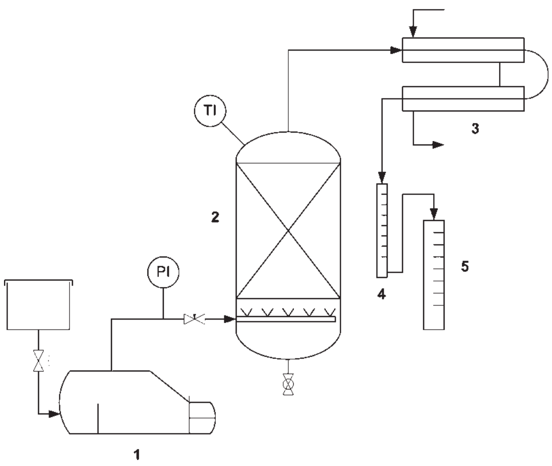

Figure 1. Scheme of bench plant: (1) boiler, (2) distiller, (3) condenser, (4) florentine, and (5) container of floral water.

Scanning electron microscopy

Microhistological analysis was done by using a JSM-T300 scanning electron microscope (SEM) (JEOL, USA), at 15 kV accelerating voltage. Random samples from each lot were divided lengthwise into four parts and the best one was sputter coated with gold before being examined.

Experimental Device

Experimental apparatus

Experiments were performed in a bench scale apparatus, which was designed and constructed at the Dept. of Chemical Engineering and Environmental Technology in the University of Valladolid (Figure 1). Saturated steam was used to operate the apparatus, which flows up to 50 g/min and a maximum operating pressure of 2.5 bar.

Steam distillation took place into a 40 L AISI 304L SS vessel (distiller), with a cross steam distributor and a rack to support the load. It was connected to a double pipe condenser (1.2 m length, 12 mm internal tube diameter, 28 mm external tube diameter). Condensate was collected into a glass florentine flask, where oil and floral water (condensate water containing most of the hydrophilic water soluble molecules from the plant that did not distil into the essential oil) were efficiently separated.

Experimental design

A 3 $\times$ 4 design matrix was selected for experimental tests, taking bed porosity (ε) and steam flow rate as process parameters. Bed porosity was calculated by the ratio between bed and apparent plant density (0.7 g/cm^3). Plan density was determined from the measured volume of a known mass of plant after air removal by pressing the syringe piston.[22] Steam flow rate was determined from floral water flow rate (Q_{fw}), instead of boiler steam, to leave out condensed water at distiller walls. Process parameters values are shown in Table 1. Plant load was 2.175 ± 0.050 kg. Steam pressure was controlled to 2.0 ± 0.2 bar. Collected essential oil and floral water volumes were recorded at different times, starting at

Table 1. Design Matrix

	Q_{fw} (cm^3/min)			
	35	25	15	10
ε				
0.721	P1	P2	P3	P4
0.762	P9	P10	P11	P12
0.805	P5	P6	P7	P8

the first floral water drop collected, until a constant volume of oil was attained (t_{sd}). The filling time of distiller (t_{fill}) was also registered. Collected oil was filtered by using a drying agent (Na_2SO_4 anhydrous, USP, Panreac Química S.A., Spain), and cold storage (6°C) in amber flasks.

Experimental Results

Steam distillation

Final essential oil yields referred to fresh plant (Y_∞) were in the range between 1.186% and 1.468% (Table 2), and no clear dependency was observed neither on steam flow nor on bed porosity. Discrepancies were associated to flowers/stem ratio differences in the loads, since all essential oil content is in the flowers.

Although final values of Y_∞ are not dependent on operating conditions, Figure 7 shows how the evolution of collected oil vs. condensed floral water volume clearly depends on the steam flow used in the process. The results show how the rate of oil recovery increases with increasing steam flow rate, at constant bed porosity. This behavior proves the influence of other stages, as well as of vapor–liquid equilibrium (VLE), on the oil recovery process, since the only dependency of the process on VLE would show a single curve when floral water volume is selected as the independent variable, even for different steam flow rates.

In Figure 8, the evolution of collected oil vs. condensed floral water volume is shown for three experiments with constant steam flow rate (35 cm^3/min) and different bed porosities. In this graph, the behavior of the three experimental curves is very similar and a dependency on bed porosity may not be confirmed. This fact may be enlightened after calculation of vapor phase mass transfer coefficients, presented later in Table 4. In the case of variable steam flow rates (Figure 7), mass transfer coefficient increased fivefold times, from 6.4 to 31.4 cm/min, for the different conditions used in the presented experiments. However, for variable bed porosity experiments (Figure 8) mass transfer coefficient increased only 15%, from 27.2 to 31.4 cm/min, because of the limited available operation range of bed porosities.

Table 2. Steam Distillation Results

	N_e	t_{fill} (min)	t_{sd} (min)	τ_o (min)	Y_∞ (%)	n_D^{20}	d_{20}^{20}
P1	26	13.00	33	0.144	1.324	1.4600	0.8911
P2	23	14.25	48	0.201	1.448	1.4590	0.8930
P3	28	25.00	56	0.335	1.419	1.4603	0.8873
P4	33	42.25	64	0.502	1.446	1.4603	0.8917
P5	23	11.66	43	0.229	1.410	1.4592	0.8940
P6	33	12.00	68	0.321	1.265	1.4586	0.8934
P7	26	15.80	83	0.535	1.186	1.4621	0.8920
P8	31	19.42	110	0.891	1.226	1.4603	0.8922
P9	24	8.58	72	0.178	1.654	1.4589	0.8955
P10	21	12.25	54	0.249	1.270	1.4607	0.8947
P11	30	16.95	92	0.415	1.468	1.4585	0.8928
P12	31	22.50	90	0.622	1.205	1.4589	0.8917

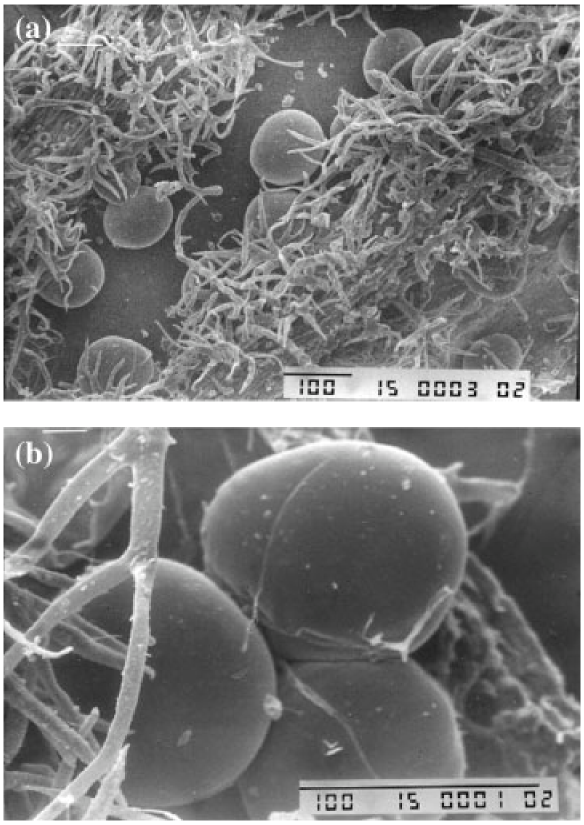

Figure 2. SEM images of the flower surface before SD: (a) with ×150 magnification and a scale of 70 μm and (b) with ×500 magnification and a scale of 20 μm.

Herbaceous material characterization (microhistology analysis)

SEM images (Figure 2) show peltate glandular trichomes[11,23] uniformly distributed on the outer surface of flowers, between files of non-glandular trichomes. No trichomes were detected onto the inner surface. The average diameter of peltate glandular trichomes was considered to be 100 μm.

After steam distillation, all observed peltate trichomes reduced their volume and looked like imploded (Figure 3), because of oil exudation by steam.

The microhistological analysis reveals the complete efficiency of the steam distillation since all examined trichomes were found affected after the process.

Chemical analysis by GC/MS

Two different columns were required in the chemical analysis by GC/MS to discriminate all detected compounds. There was overlapping of some peaks when only the HP-5MS

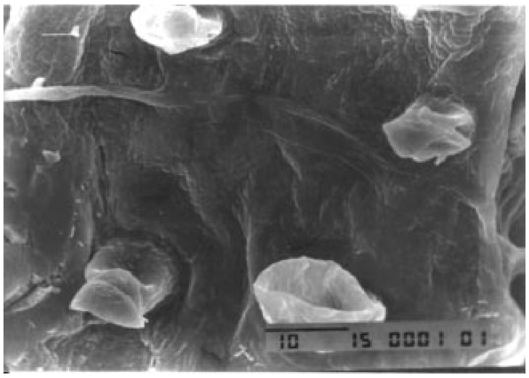

Figure 3. SEM image of the flower surface after steam distillation, with 200× magnification and a scale of 5 μm.

column was used (D-limonene and 1,8-cineole; octanone-3 and β-myrcene; and borneol and terpinen-4-ol). The same situation appeared for different compounds when only the DB-WAX column was used (linalool and linalyl acetate; α-terpineol and borneol; *cis*-β-ocimene and octanone-3). TICs for both columns are shown in Figures 4 and 5.

A list of the main components present in the lavandin super essential oil is shown in Table 3. Components were determined by experimental GC/MS and selected attending to their composition in the oil. This list was confirmed by a literature survey.[24–27] Chemical composition for each run was obtained by averaging experimental results with both columns. Compound column (N°) in Table 3 is used to identify component peak location in the TICs (Figures 4 and 5). Both isomers of β-ocimene were considered as a single peak under N° 3. The compounds selected to represent the essential oil mixture in the developed phenomenological model are numbered in column "No" of Table 3.

Only two components, linalyl acetate and linalool, represented 67% w/w of essential oil. Other components, like camphor, β-ocimene isomers, and 1,8-cineole, characterized this essential oil as corresponding to lavandin super, according to criteria suggested by Prager and Miskiewicz.[24]

Phenomenological modeling

The following assumptions were used to derive the model:

(a) The system was isothermal and isobaric.

(b) The bed of leaves and stems was considered as a batch.

(c) The porous bed formed by the plant was stable. No changes in form or disposition took place during the process.

(d) Vapor phase inside the distillation vessel was considered perfectly mixed, with constant flow rate. Oil accumulation in the vapor phase was neglected.

(e) All oil inside trichomes was extracted during the process.

(f) Four-phase system: oil inside the trichome, condensed water, free-oil outside the trichome, and vapor phase.

(g) Essential oil was considered as a mixture of 10 components. Oil composition inside trichomes (w_i^{tr}) agrees with distilled essential oil collected during the entire process. Composition was determined by GC/MS.

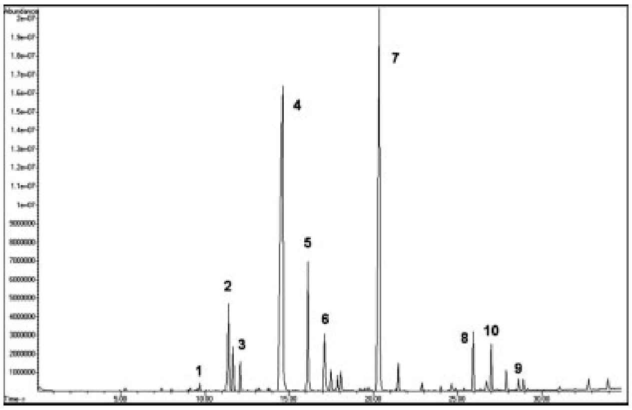

Figure 4. TIC of the run 1 (P1), with HP-5MS column.

(h) Condensed water and essential oil were completely immiscible.

(i) The steam stream fed to the distillation vessel was oil-free ($C^{\text{in}} = 0$).

Model development

Oil transport from the plant to the vapor phase was considered to take place in three-stages (Figure 6):

(i) Oil was initially inside glandular trichomes. During the process, it was heated by steam and flows out through the cuticle in a thermal exudation stage ($\dot{m}_i^{\text{tr}\to\text{os}}$). No changes in oil composition were considered at this stage.

(ii) Oil leaving the trichome and condensed water formed a two-phase layer wetting the plant. Oil components evaporated at the vapor–oil interface according to phase equilibrium.

(iii) Mass transfer of evaporated oil components took place from vapor–oil interface to the steam stream ($\dot{m}_i^{\text{os}\to\text{vp}}$).

Mathematical representation of the model for each stage:

(i) Thermal exudation of oil from the trichomes.

Oil exudation flow ($\dot{m}^{\text{tr}\to\text{os}}$) was assumed to be pseudo first order with respect to oil mass remaining inside the trichomes (G), as previously proposed by Benyoussef et al.[8]:

$$\dot{m}^{\text{tr}\to\text{os}} = -\frac{d(GW)}{dt} = K_{\text{tr}}GW \qquad (1)$$

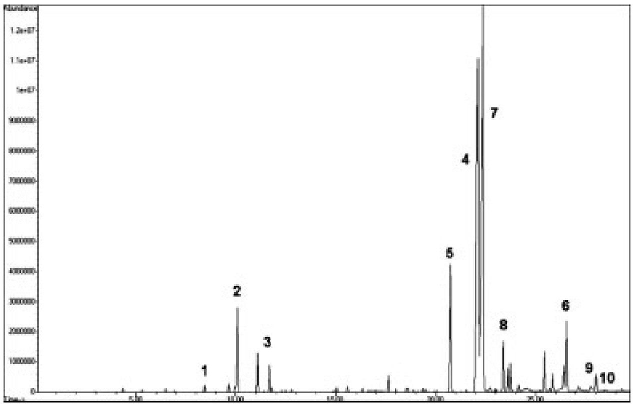

Figure 5. TIC of the run 1 (P1), with DB-WAX column.

Table 3. Essential Oil Chemical Composition (Weigh Percent), Determined by GC/MS with Two Different Columns

		Runs											
N°	Compounds	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12
	α-Pinene	0.14	0.11	0.13	0.12	0.15	0.18	0.19	0.14	0.13	0.15	0.14	0.13
	Camphene	0.09	0.08	0.09	0.08	0.10	0.12	0.14	0.11	0.09	0.11	0.10	0.10
	α-Pinene	0.16	0.11	0.13	0.13	0.15	0.18	0.17	0.13	0.12	0.13	0.13	0.13
	Octanone-3	0.16	0.09	0.12	0.08	0.03	0.04	0.09	0.14	0.08	0.11	0.08	0.08
1	β-Myrcene	0.31	0.34	0.40	0.53	0.35	0.48	0.50	0.69	0.41	0.38	0.70	0.59
	D-Limonene	0.35	0.26	0.33	0.32	0.28	0.34	0.39	0.44	0.27	0.34	0.38	0.34
2	1,8-Cineole	4.19	2.64	2.66	2.49	2.57	2.87	2.35	3.63	1.92	3.30	1.96	1.95
3	*trans*-β-ocimene	1.76	0.93	1.88	1.06	0.97	1.09	1.43	1.27	0.87	1.04	1.04	0.92
	cis-β-ocimene	1.20	0.84	1.30	1.04	0.84	1.01	1.12	1.16	0.86	0.88	1.13	0.99
4	Linalool	32.84	30.84	35.36	32.23	30.77	30.42	34.26	33.27	29.91	31.90	31.89	31.36
5	Camphor	6.94	5.99	6.07	5.95	5.93	5.84	5.12	6.84	5.24	6.71	5.29	4.90
6	Borneol	3.92	4.26	3.66	4.22	4.62	4.50	4.13	4.72	4.03	5.49	3.70	4.53
	Terpineol-4	1.10	1.01	0.91	1.17	1.27	1.10	1.04	1.05	0.95	1.24	0.82	0.95
	α-Terpineol	1.34	1.34	1.25	1.77	1.26	1.36	1.38	1.88	1.33	1.48	1.59	1.68
7	Linalyl acetate	32.98	37.68	32.15	35.26	37.35	36.61	32.14	31.05	39.91	34.13	38.14	37.30
	Neryl acetate	0.44	0.62	0.58	0.45	0.97	1.18	0.35	0.93	0.51	0.63	0.42	0.43
8	β-Caryophyllene	2.49	2.50	2.58	2.52	2.64	2.77	2.92	2.58	2.70	3.12	2.28	2.77
9	γ-Cadinene	1.00	0.22	0.82	0.25	0.30	0.26	1.41	0.24	0.27	0.24	0.92	1.08
10	Coumarine	0.88	0.97	0.90	0.63	1.25	0.99	0.73	1.12	1.38	1.34	1.33	1.10
	Total identified	92.25	90.82	91.56	90.28	91.80	91.35	89.85	91.39	90.95	92.71	92.02	91.31
	Total modeled	88.49	87.21	88.02	86.16	87.59	86.85	86.10	86.56	87.47	88.52	88.37	87.48

No composition changes were considered in the exudation stage:

$$\dot{m}_i^{\mathrm{tr}\to\mathrm{os}} = w_i^{\mathrm{tr}}\dot{m}^{\mathrm{tr}\to\mathrm{os}} \tag{2}$$

$$\sum_{i=1}^{n} w_i^{\mathrm{tr}} = 1 \tag{3}$$

Oil composition inside trichomes was assumed to be the same as essential oil recovered in the distillate along the entire process.

The initial condition is:

$$t = 0, \quad G = G_o \tag{4}$$

By integrating Eq. 1 with conditions 2 and 4:

$$G_i = G_o w_i^{\mathrm{tr}} \exp(-K_{\mathrm{tr}} t) \tag{5}$$

A filling time (t_{fill}) was required to warm up the distiller. Since steam was fed to the distillation vessel until the first floral water droplet was collected at the condenser. Remaining oil inside trichomes at this time may be calculated by:

$$G_{i,\mathrm{fill}} = G_o w_i^{\mathrm{tr}} \exp(-K_{\mathrm{tr}} t_{\mathrm{fill}}) \tag{6}$$

Equation 1 may be rewritten in terms of collected floral water (V_{fw}), by assuming constant flow (Q_{fw}), with a different initial condition:

$$Q_{\mathrm{fw}} = \frac{dV_{\mathrm{fw}}}{dt} \tag{7}$$

$$\frac{dG_i}{dV_{\mathrm{fw}}} = -\frac{K_{\mathrm{tr}}}{Q_{\mathrm{fw}}} G_i \tag{8}$$

With the initial condition:

$$V_{\mathrm{fw}} = 0, \quad G = G_{i,\mathrm{fill}} \tag{9}$$

(ii) Oil evaporation at the vapor–oil interface.

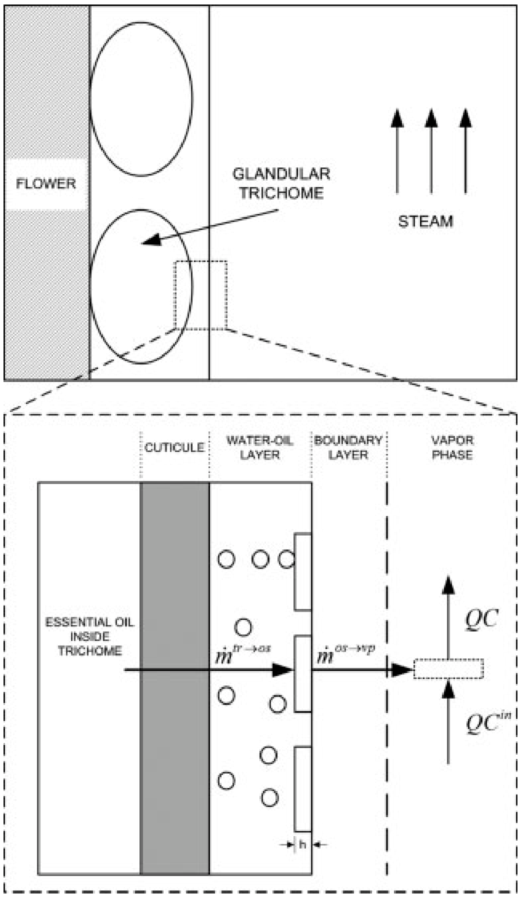

Figure 6. Oil transfer route from the trichome to the steam flow bulk.

Water and essential oil in the liquid phase were considered totally immiscible. By Dalton's law:

$$P = P_{\mathrm{w}}^{0} + P^{0,\mathrm{os}} \tag{10}$$

Vapor pressure of essential oil was calculated by Raoult's law, considering all main components present in the essential oil (Table 3):

$$P^{0,\mathrm{os}} = \sum_{i=1}^{10} x_i^{\mathrm{os}} P_i^{0} \tag{11}$$

Vapor phase composition:

$$y_i^{\mathrm{vp}} = \frac{x_i^{\mathrm{os}} P_i^{0}}{P} \tag{12}$$

$$y_{\mathrm{w}}^{\mathrm{vp}} = \frac{P_{\mathrm{w}}^{0}}{P} \tag{13}$$

Vapor pressures of oil components were evaluated by Antoine's equation.[28–31] The essential oil mass concentration in the vapor phase at the oil–vapor interface:

$$C^{*} = \frac{P^{0,\mathrm{os}} M_{\mathrm{W}}}{RT} \tag{14}$$

$$M_{\mathrm{W}} = \sum_{i=1}^{10} y_i^{\mathrm{vp}} M_{\mathrm{W}_i} \tag{15}$$

(iii) Mass transfer from the vapor–oil interface to the steam stream.

Oil components mass transfer from the interface to the steam:

$$\dot{m}_i^{\mathrm{os}\to\mathrm{vp}} = K_{\mathrm{g}} S^{\mathrm{os}} w_i^{\mathrm{vp}} (C^{*} - C) \tag{16}$$

Where C^{*} and $\{w_i^{\mathrm{vp}}\}$ were calculated from phase equilibrium.

Mass transfer coefficient from the interface to the steam (K_{g}) was calculated from flow conditions in the bed. From the numerous correlations reported in literature to calculate mass transfer coefficients in inert beds,[32] the one proposed by Rexwinkel et al.,[33] was selected. Recommended flow characteristic dimensionless groups fit correlation requirements ($Re_{\mathrm{p}} < 10$ and $Pe_{\mathrm{p}} > 100$):

$$Sh_{\mathrm{p}} = 0.3 Pe_{\mathrm{p}}^{1.3} \tag{17}$$

Essential oil diffusion coefficient in steam was averaged from five characteristic compounds present in the oil (linalool, linalyl acetate, camphor, 1,8-cineole, and β-caryophyllene). The method proposed by Fuller[34] was used. Calculated value was 6.65 cm^2/min. An average particle diameter (0.195 cm) was estimated from plant measurements. Calculated values of K_{g} are reported in Table 4.

Oil to vapor mass transfer area (S^{os}) depends on the mass of oil in the two-phase aqueous layer:

$$M^{\mathrm{os}} = S^{\mathrm{os}} h \rho_{\mathrm{eo}} \tag{18}$$

$$M^{\mathrm{os}} = \sum_{i=1}^{n} M_i^{\mathrm{os}} \tag{19}$$

where h is the oil spots average thickness in the two-phase aqueous layer. The value of h was assumed to be constant: a decrease in the mass of oil implies the reduction of the vapor phase mass transfer area.

Table 4. Operation and Model Parameters for All Data Sets

Run	U^{o} (cm/min)	Re_{p}	Pe_{p}	K_{g} (cm/min)	AAD
P1	80.9	1.37	2.37	31.4	0.093
P2	57.8	0.98	1.69	20.3	0.060
P3	34.7	0.58	1.01	10.5	0.033
P4	23.1	0.39	0.68	6.2	0.069
P5	72.4	1.22	2.12	27.2	0.070
P6	51.7	0.87	1.52	17.6	0.116
P7	31.0	0.52	0.91	9.1	0.031
P8	18.6	0.31	0.55	4.7	0.067
P9	76.5	1.29	2.24	29.3	0.073
P10	54.7	0.92	1.60	18.9	0.043
P11	32.8	0.55	0.96	9.7	0.099
P12	21.9	0.37	0.64	5.7	0.020

Mass balance of oil components in the two-phase liquid layer:

$$\frac{dM_i^{\mathrm{os}}}{dt} = \dot{m}_i^{\mathrm{tr}\to\mathrm{os}} - \dot{m}_i^{\mathrm{os}\to\mathrm{vp}} \tag{20}$$

By combination of Eqs. 1, 2, 5, 7, 16, 18, and 20:

$$\frac{dM_i^{\mathrm{os}}}{dV_{\mathrm{fw}}} = \frac{K_{\mathrm{tr}} W}{Q_{\mathrm{fw}}} G_i - \frac{K_{\mathrm{g}} M^{\mathrm{os}}}{Q_{\mathrm{fw}} h \rho_{\mathrm{eo}}} w_i^{\mathrm{vp}} (C^{*} - C) \tag{21}$$

According to initial model assumptions "d" and "e," final essential oil recovery fraction (Y_{∞}) may be related to oil mass in the plant at the beginning of the operation:

$$Y_{\infty} = \frac{M_o^{\mathrm{os}}}{W} + G_o \tag{22}$$

The mass fraction of oil which is initially ($t = 0$) outside the trichomes:

$$\omega = \left(\frac{M_o^{\mathrm{os}}/W}{Y_{\infty}} \right)_{t=0} \tag{23}$$

From Eqs. 22 and 23:

$$G_o = (1 - \omega) Y_{\infty} \tag{24}$$

Initial condition ($v_{\mathrm{fw}} = 0$) for Eq. 21 takes place at $t = t_{\mathrm{fill}}$:

$$M_i^{\mathrm{os}}\big|_{v_{\mathrm{fw}}=0} = w_i^{\mathrm{tr}} Y_{\infty} W [1 - (1 - \omega) \exp(-K_{\mathrm{tr}} t_{\mathrm{fill}})] \tag{25}$$

(iv) Vapor phase

If oil accumulation in the vapor phase is neglected and steam feed is oil-free, then:

$$\dot{m}_i^{\mathrm{os}\to\mathrm{vp}} = Q w_i^{\mathrm{vp}} C \tag{26}$$

From Eqs. 16, 18, and 26:

$$C = \left(\frac{K_{\mathrm{g}} M^{\mathrm{os}}}{Q h \rho_{\mathrm{eo}} + K_{\mathrm{g}} M^{\mathrm{os}}} \right) C^{*} \tag{27}$$

(v) Condensed oil.

Mass balance to the collected essential oil (M_i^{sd}), after condensation in the florentine:

$$\frac{dM_i^{\mathrm{sd}}}{dV_{\mathrm{fw}}} = \frac{Q w_i^{\mathrm{vp}} C}{Q_{\mathrm{fw}}} \tag{28}$$

From Eqs. 27 and 28:

$$\frac{dM_i^{\mathrm{sd}}}{dV_{\mathrm{fw}}} = \left(\frac{K_g M^{\mathrm{os}} Q}{Q_{\mathrm{fw}}(Qh\rho_{\mathrm{eo}} + K_g M^{\mathrm{os}})}\right) w_i^{\mathrm{vp}} C^* \tag{29}$$

$$M^{\mathrm{sd}} = \sum_{i=1}^{n} M_i^{\mathrm{sd}} \tag{30}$$

Initial condition:

$$M_i^{\mathrm{sd}}\Big|_{v_{\mathrm{fw}}=0} = 0 \tag{31}$$

Results and parameters optimization

Simulation results were obtained by simultaneous integration of Eqs. 8, 21, and 29. This system of $3n$ ODEs was solved using the Euler method, with an integration step equal to 1 cm^3 of floral water. VBA programming language in Microsoft® Office Excel 2003 spreadsheet (Microsoft Co., USA) was used for integration.

Model parameters selected for optimization were h and K_{tr}. These values should depend only on plant characteristics and so, they were considered unique values for all the experiments. Although attempts were made to include ω value in parameter optimization, finally it was discarded and set to a fixed value of 0.01, because of its low influence.

Parameters optimization of experimental oil yields $(Y_{i,j}^{\mathrm{exp}})$ collected at different floral water volumes (V_{fw}) was done simultaneously for all data sets. The selected objective function (FO) was the average absolute deviation in yield values (AAD), for all data sets:

$$\mathrm{FO} = \sum_{j=1}^{l} N_{e,j} \cdot \mathrm{AAD}_j \tag{32}$$

$$\mathrm{AAD}_j = \frac{1}{N_{e,j}} \sum_{i=1}^{N_{e,j}} |Y_{i,j}^{\mathrm{exp}} - Y_{i,j}^{\mathrm{cal}}| \tag{33}$$

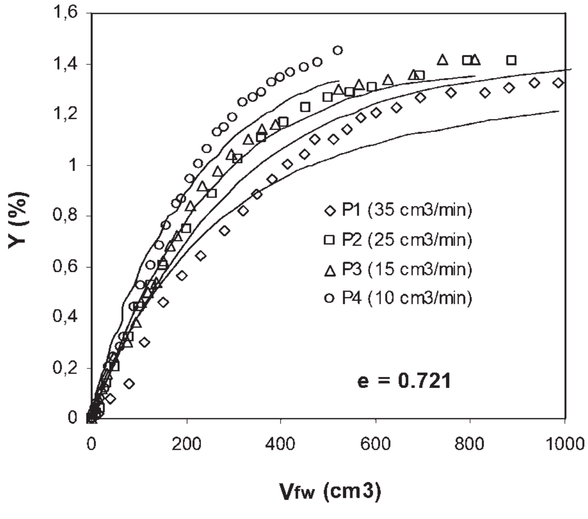

Figure 7. Comparison between experimental and simulated data, at fixed bed porosity vs. floral water volume.

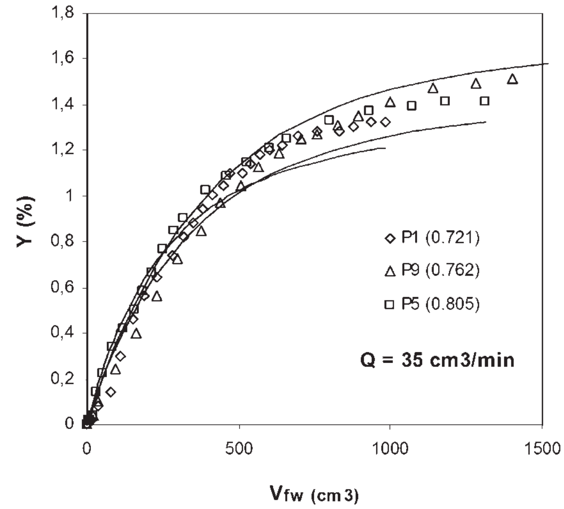

Figure 8. Comparison between experimental and simulated data, at fixed floral water flow vs. floral water volume.

Obtained values for optimized parameters were as follows: $K_{\mathrm{tr}} = 0.072$ min^{-1} and $h = 115$ μm.

Simulation results may be graded as acceptable, considering a natural product has been processed. Furthermore, simulation results got dramatically worse when any of the stages (exudation or vapor phase mass transfer) were neglected, since both are controlling stages at some point during the process.

Experimental and calculated recovery yields vs. accumulated floral water volume are shown in Figures 7 and 8 for different experimental sets with fixed bed porosity or steam flow, respectively. The model can predict the evolution of the process at all conditions (Figures 7b and 8b).

A detailed examination of simulation results shows how oil mass transport from the trichomes to the vapor phase is initially controlled by both stages: thermal exudation and vapor phase mass transport. However, at the end of the steam distillation process, only the vapor phase mass transport controls the kinetics of oil recovery. Phase equilibrium also influences the evaporated oil mass flow, since C^* changes during the process. The evaporation of lighter components is favored because of their higher vapor pressures, causing accumulation of heavier components in the liquid phase, which decreases driving force for vapor phase mass transfer rate $(C^* - C)$.

Conclusions

A phenomenological model for lavandín super steam distillation has been developed by considering three serial stages: (1) thermal exudation from the trichomes, (2) oil evaporation at the vapor–oil interface, and (3) mass transfer from the vapor–liquid interface to the steam bulk. Experimental data of oil recovery yield vs. collected floral water were measured to validate model implementation. The model reproduces experimental data with acceptable precision, for different operation conditions (bed porosity and steam flow).

Two model parameters were calculated by experimental data correlation: thermal exudation rate constant ($K_{tr} = 0.072\ min^{-1}$) and the oil spots average thickness in the oil-aqueous layer ($h = 115\ \mu m$). These parameters are characteristic of lavandín super and should not depend on operation conditions.

Scanning electron microscopy was used to confirm how the essential oil present in the peltate glandular trichomes of the flowers outer surface is released by contact with steam, decreasing their volume, but maintaining the integrity of their cuticles. This evidence was used in the phenomenological model development to associate a kinetic resistance to oil exudation from trichomes.

The lavandin super essential oil was obtained with an average global yield of 1.36 ± 0.14% w/w on wet basis, in 12 runs at bench scale, using different steam flows and bed porosities. Steam distilled oil was identified positively by GC/MS, density and refractive index measured values. The main identified compounds were as follows: linalool (29.9–35.4%), linalyl acetate (31.1–39.9%), camphor (4.9–6.9%); 1,8-cineole (1.9–4.2%), borneol (3.6–4.7%), and β-caryophyllene (2.3–3.1%). This chemical composition was initially used in the simulation to calculate the phase equilibrium at the oil-aqueous interface.

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Notation

AAD_j = average absolute deviation in yield values for data set "j," % g/g
C = essential oil mass concentration in the vapor phase, g/cm^3
C^* = vapor essential oil mass concentration at the oil–vapor interface, g/cm^3
d^{20} = essential oil relative liquid density, dimensionless
d_p = average particle diameter, cm
D = oil–steam diffusion coefficient, cm^2/min
G = oil mass inside the trichomes per mass of fresh plant, g/g
h = oil spots average thickness in the two-phase aqueous layer, cm
K_g = mass transfer coefficient, cm/min
K_{tr} = exudation kinetic constant, min^{-1}
l = number of experimental data sets
$\dot{m}$ = oil mass flow, g/min
M = mass, g
M_W = molecular weight, g/mol
n = number of components in the essential oil (10 in this article)
$N_{e,j}$ = number of experimental points of a data set "j"
P = pressure, kPa
P° = vapor pressure, kPa
$Pe_p = U^\circ d_p/D$ is the interstitial Peclet Number
Q = steam volumetric flow, cm^3/min
Q_{fw} = floral water liquid volumetric flow, cm^3/min
R = universal gas constant
$Re_p = U^\circ d_p/\nu$ is the interstitial Reynolds Number
S = mass transfer area, cm^2
$Sh_p = K_g d_p/D$ is the particle Sherwood number
t = time, min
T = temperature, °C
t_{sd} = required time to complete oil distillation, min
U° = interstitial fluid velocity, cm/min
V_{fw} = collected floral water liquid volume, cm^3
w_i = mass fraction, g/g
W = fresh plant mass, g
x_i = liquid mole fraction
y_i = vapor mole fraction
Y = essential oil recovery yield, on fresh plant basis, % g/g

Greek letters

ε = bed porosity
ρ_{eo} = essential oil liquid density at 20°C, g/cm^3
ν = kinematical viscosity, cm^2/min
τ_o = void distiller residence time, min
ω = initial mass oil fraction outside the trichomes

Superscripts

exp = experimental value
cal = calculated value
fill = instant when the first floral water droplet is collected at the florentine
i = i-th component of the essential oil
in = steam stream fed to the distillation vessel
j = j-th experimental data set
os = oil spots in the two-phase aqueous layer wetting the plant
sd = collected essential oil
tr = glandular trichomes
vp = vapor pressure

Subscripts

∞ = time when all essential oil is collected at the florentine
fill = filling time of distiller
fw = liquid floral water
o = initial value ($t = 0$)
w = water

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