Article

J. Mex. Chem. Soc. **2006**, *50(3),* 126-129

ISSN 1870-249X

Experiments and Modeling of the *Cymbopogon winterianus* Essential Oil Extraction by Steam Distillation

Eduardo Cassel,* Rubem M. F. Vargas

Laboratório de Operações Unitárias, Engineering Faculty - PUCRS, Av. Ipiranga 6681, CEP 90619-900,
Porto Alegre - RS, Brazil, Telephone + (55)(51) 3320-3653, Fax +(55)(51) 3320-3625, E-mail: cassel@pucrs.br

Dedicated to Professor Pedro Joseph Nathan

Recibido el 31 de enero del 2005; aceptado el 5 de abril del 2006.

Abstract. This work has as objective to optimize and to model the yield of the citronella essential oil extraction processes from twigs and leaves by steam distillation. The process variables evaluated in this study were extraction time, and raw material state (dry or natural). The yield is calculated from the relation between the essential oil mass obtained and the raw material mass used in the extraction and the quantitative and qualitative analyses of the oils were performed by capillary GC/MS. The experimental condition for the maximum yield, 0.942%, is the following one: extraction time, 4 h, state, natural plant, and the results obtained from the factorial experimental planning indicate that the variable that more influences the essential oil yield is the state. The modeling of these results is proposed from the description of the mass transfer from a single plate particle. Yield curves for all studied conditions were fairly well fitted using one adjustable parameter of the model and the experimental monitoring of oil composition as function of extraction time was realized in laboratory steam distillation apparatus and compared with industrial scale results.

Keywords: Citronella essential oil, steam distillation, mass transfer, mathematical model

Resumen. Este trabajo tiene como objetivo optimizar y modelar el rendimiento del proceso de extracción del aceite esencial de citronela, obtenido por destilación por arrastre de vapor a partir de hojas y ramas. Las variables del proceso evaluadas en este estudio fueron el tiempo de extracción y el estado de la materia prima (seca o natural). El rendimiento de aceite esencial es calculado a partir de la relación entre la masa de aceite y la masa de planta aromática usada en la extracción. Los análisis cuantitativo y cualitativo de los aceites fueran determinados por GC/MS. Las condiciones experimentales para el rendimiento máximo, 0,942%, son las siguientes: tiempo de extracción, 4 h; estado, planta natural; y los resultados obtenidos a partir del estudio estadístico indicaron que la variable que más influencia el rendimiento de aceite esencial es el estado de la planta. El modelado propuesto para describir la transferencia de masa del proceso de extracción está centrado en una partícula en forma de placa plana. Las curvas de rendimiento, para todas las condiciones estudiadas, fueron ajustadas usando un modelo con un parámetro ajustable y los resultados del modelado obtenidos a partir de los datos en escala de laboratorio fueron comparables con las informaciones experimentales obtenidas en escala industrial.

Palabras claves: citronela, destilación por arrastre de vapor, transferencia de masa, modelado matemático

Introduction

The essential oil from *Cymbopogon winterianus* presents repellent properties [1] and represents a significant parcel of the essential oil national production. It is possible to cultivate these aromatic plants in different geographic regions of Brazil and *C. winterianus* is resistant to climatic variation and plagues. The citronella oil doesn't present a good value in the international market, but the improvement in the extraction technology and its use as raw material could modify this scene.

The steam distillation is the traditional process to obtain essential oils from leaves and the aromatic industry use this method because is cheap when it is compared with technologically advanced methods as supercritical fluid extraction. The objective of this study is to optimize the citronella essential oil extraction process from twigs and leaves through process variables evaluation to define the best operational conditions with regard the yield and composition of the citronella essential oil considering as function of the time and raw state material (dry or natural).

The mathematical modeling of steam distillation is necessary to design industrial plant with good operational conditions. In the literature, there are some studies of oil extraction by steam and hydrodistillation. Spiro and Selwood [2] interpreted their results in terms of a model based on steady-state theory of extraction. The authors presented a on of the effect of particle size in the extraction and related the diffusion coefficient of caffeine in the coffee bean particles an being of meaningful order of the 10^{-11}m^2/s. Spiro and Page [3] studied the hydrodynamic aspects relevant kinetics and mechanism of caffeine infusion from coffee. They measured the rate of extraction of caffeine at various rotation speeds and found that the rate-determining step for extraction from coffee-coated discs was the diffusion of caffeine through the bean particle, where the diffusion coefficient of caffeine was approximately $2x10^{-11}$m^2/s. Spiro [4] reported the kinetics of extraction of ginger rhizome with dichloromethane, ethanol, 2-propanol and an acetone-water mixture. In their modeling, the extractions all proceeded in three stages: an initial "washing" stage, a fast stage and a much slower stage, with different diffusion coefficient at the stages. The diffusion coefficient was reported in the interval 10^{-13} to 10^{-12} (m^2/s) for diffusion of the soluble constituent through the particles (a slower stage) and in the interval 10^{-10} to 10^{-11} (m^2/s) to diffusion of the constituent through the Nernst layer (a fast

Table 1. Yield experimental results of the citronella essential oil using the factorial experimental planning 2^2.

Plant Sample Mass(g)	Extraction Time (h)	Essential Oil Mass (g)	Material State	% (p/p) Oil Yield
50	02	1.176	Dry	0.647
50	04	1.412	Dry	0.776
50	04	0.471	Natural	0.942
50	02	0.471	Natural	0.942

Obs.: the water concentration in natural plant is 72.50 % (p/p)

Table 2. GC/MS of citronella essential oil obtained by steam distillation

IK	Compound	%
1026	d-Limonene	1,8
1151	Citronellal	35,9
1224	Citronellole	5,2
1248	Geraniole	20,9
1264	Geranial	1,5
1346	Citronellyl Acetate	2,9
1375	Geranyl Acetate	4,0
1383	beta-Elemene	0,5
1473	Germacrene D	0,8
1499	Germacrene A	0,8
1511	delta-Cadinene	2,1
1542	Germacrene B	6,8
1614	1,10-di-epi-Cubenol	2,0
1620	1-*epi*-Cubenol	1,9
1624	gama-Eudesmol	1,2
1635	Cubenol	1,0
1637	alfa-Muurolol	2,0
1649	alfa-Cadinol	8,0
	Soma	99,3

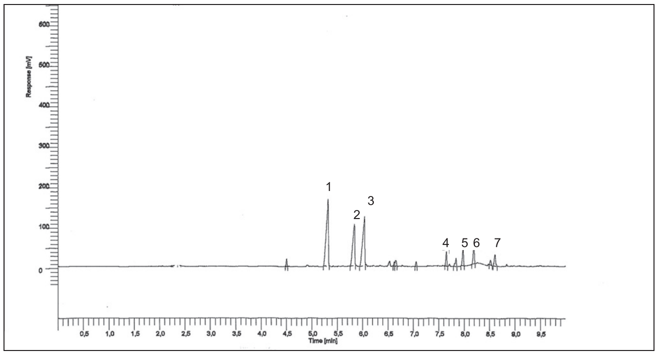

Fig. 1. GC traces of citronella essential oil obtained by steam distillation. 1 – Citronellal; 2 – alfa-Cadinol; 3 – Geraniole; 4 – Citronellyil Acetate; 5 – Citronellole; 6 – Germacrene B; 7 – Geranyl Acetate.

stage), in function of the solvent. Barton et al. [5] treated the supercritical fluid extraction of vanilla oleoresin as a chemical reaction. The authors assumed that the rate extraction was proportional to the concentration of oleoresin left in the vegetable particle and presented an expression to kinetic constant related to diffusion coefficient. Benyoussef [6] described the modeling of coriander essential oil by steam distillation using two diffusional models: the first one takes only diffusion into account, in the second of the transferred species is additionally modeled.

In this work the mathematical modeling is performed using a model based on diffusion mechanism related to mass transfer.

Experiments

The essential oils were extracted using leaves and twigs of plants collected in Viamão in the state of Rio Grande do Sul, in Southern Brazil. The experiments were conducted using the aerial part of plants. A 0.050 kg amount of sample was used for extraction. The oils were extracted on steam distillation equipment and the data of the experimental yield versus time of the citronella essential oil are showed in Table 1. The experimental results were obtained using the factorial experimental planning 2^2. The yield is calculated from the relation between the essential oil mass obtained and the raw material mass used in the extraction.

Quantitative and qualitative analyses of the oils were performed by capillary GC/MS on an Agilent 6890/HP 5973 mass selective (MS) detector system operating at 70 eV, using a HP-5MS column (cross-linked 5% phenylmethylsiloxane, 30 m length, 0.25 mm i.d. and 0.25 micron coating thickness, fused silica of stationery phase). Injector and transfer line temperatures were set at 200 ºC and 280 ºC, respectively; the oven temperature was programmed from 40º - 220 ºC, at 3 ºC/min. Helium was employed as carrier gas (1 mL/min); injection of

Table 3. Experimental Data from Steam distillation for citronella in natural state as time function.

t(min)	V(ml)	Oil mass extracted (g)
0	0	0
3.0	0.1	0.085
6.0	0.2	0.170
9.0	0.4	0.340
12.0	0.5	0.425
16.5	0.6	0.510
21.0	0.7	0.595
25.5	0.8	0.680
36.0	0.9	0.765
66.0	1.0	0.850
90.0	1.1	0.935
114.0	1.2	1.020

1ml of a 1% solution of whole essential oil in ethyl acetate, split 1:50, scan range 41-300 amu and scan time 1.0 sec. The percentage compositions were obtained from electronic integration measurements without taking into account relative response factors. Compound identification was based on a comparison of retention indices (determined relatively to the retention times of a series of *n*-alkanes from *n*-octane to *n*-eicosane) and mass spectra with those of authentic samples and with literature data [7], Table 2. The GC traces of citronella essential oil is presented in the Figure 1.

The experimental data of citronella essential oil extraction as function time is showed in Table 3. The citronella essential extraction was realized in laboratory steam distillation apparatus as time function using leaves with average thickness 5.25x10^{-4}m. In the experiments was used 0.04Kg of material and the total extraction time was 114 min

Mathematical Modeling

In this work, bearing in mind that the stage controlling process is the diffusion in the particle, we simulated steam distillation process using a model based on Fick´s law in steady-state for one-dimensional rectangle geometry, assuming that in the beginning process the soluble constituent concentration is homogeneous and constant all of particle. Furthermore, at the boundaries steam carried out all oil, therefore the oil concentration at the boundaries is very small (c_A=0). The mathematical formulation is expressed as

$$\frac{\partial^2 c_A}{\partial x^2} = \frac{1}{D}\frac{\partial c_A}{\partial t} \quad in \quad 0 \le x \le L \tag{1}$$

with initial condition

$$c_A = c_{A0} \quad in \quad t = 0 \tag{2}$$

and the boundary conditions

$$c_A = 0 \quad in \quad x = 0 \tag{3}$$

$$c_A = 0 \quad in \quad x = L \tag{4}$$

where L is the thickness of the plate and D is the effective diffusion coefficient.

Equations (1) to (4) are a Sturm Liouville problem, bearing this in mind we used the separation variable technique [8] , and the following solution was established

$$c_A(x,t) = \sum_{n=1}^{\infty} \frac{4c_{A0}}{n\pi} sen(\beta_n x) e^{-D\beta_n^2 t} \tag{5}$$

where

$$\beta_n = \frac{n\pi}{L} \tag{6}$$

with n=1,2,3… .

The mass flow as function time was obtained from the mass flux at the boundary multiplied by normal surface area resulting

$$\dot{m}_A(t) = \frac{4c_{A0}DA}{L} \sum_{n=1}^{\infty} e^{-D\beta_n^2 t} \tag{7}$$

Thus the extracted mass of soluble constituent is

$$m_A(t) = \frac{8m_{A0}}{\pi^2} \sum_{m=0}^{\infty} \frac{(1 - e^{-\frac{(2m+1)^2 \pi^2 Dt}{L^2}})}{(2m+1)^2} \tag{8}$$

and the degree extraction is defined by

$$e(t) = \frac{m_A(t)}{m_A(\infty)} = \frac{\sum_{m=0}^{\infty} \frac{(1 - e^{-\frac{(2m+1)^2 \pi^2 Dt}{L^2}})}{(2m+1)^2}}{\sum_{m=0}^{\infty} \frac{1}{(2m+1)^2}} \tag{9}$$

Results and Discussion

The essential oil compositions to different conditions were obtained with the objective to analyze the influence of the variable value in the composition of the citronella oil. These results were obtained using the factorial experimental planning 2^2. The yield is calculated from the relation between the essential oil mass obtained and the raw material mass used in the extraction.

The experimental condition for the maximum yield, 0.942x10^{-2}g/g is the following one: extraction time, 4 h, state, natural plant, and the results obtained from the factorial experimental planning indicated that the variable that more influences the essential oil yield is the state. The principal compounds identified in the citronella essential oil were: citronellal, citronellole, geraniole, geranyl acetate, and α-cadinol.

The yield curve is constructed from oil mass extracted relation to amount sample used in the extraction; in this work we used 0,04 Kg of leaves, in Table 4 the quantities used in the simulation are shown.

In the diffusional model, the parameter D was directly adjusted using the Equation 9 with one term in the series and the data from Table 4. The best value obtained was 1.60x10^{-11} m^2/s.

This parameter was estimated by minimization of the sum of square of errors between the experimental data and the prediction from model. To find the minimum, the Nelder-Mead Simplex method [9] was used with the software Matlab version 6.

The comparison between the experimental data and the mathematical model is shown in Figure 2. Analyzing the

Table 4 . Quantities used in the mathematical simulation from experimental data.

t(s)	m(g)	e	yield
0	0	0	0
180	0.085	0.0833	0.002125
360	0.170	0.1667	0.004250
540	0.340	0.3334	0.008500
720	0.425	0.4167	0.010625
990	0.510	0.5000	0.012750
1260	0.595	0.5834	0.014875
1530	0.680	0.6667	0.017000
2160	0.765	0.7500	0.019125
3960	0.850	0.8334	0.021250
5400	0.935	0.9167	0.023375
6840	1.020	1.0000	0.025500

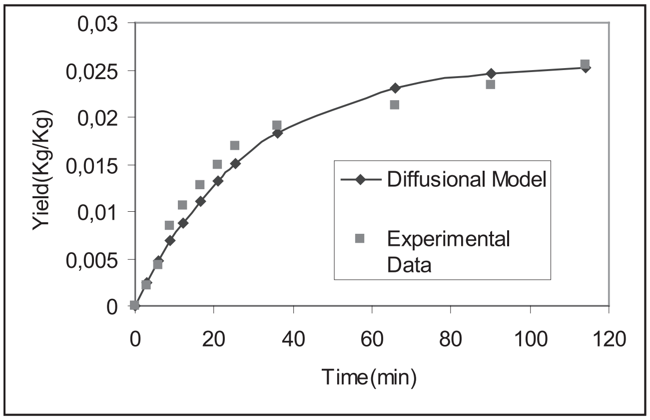

Fig. 2.- Yield curve of the citronella essential oil steam distillation: mathematical model and experimental data.

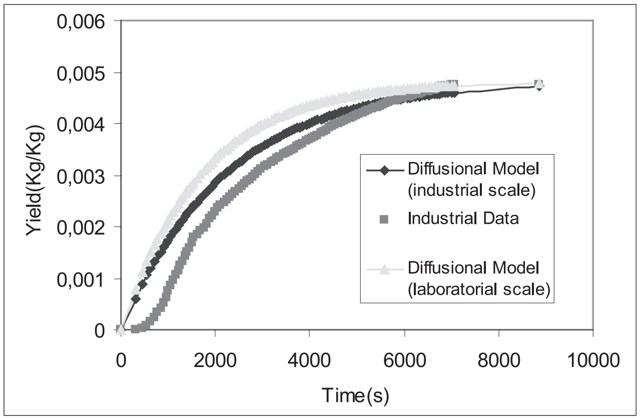

Fig. 3. Yield curve of the citronella essential oil steam distillation: mathematical models and industrial data.

Figure 2 we note that diffusional model based on mass transfer fitted very well the experimental data. The diffusional model is based on material balance across internal surface of particle assuming that the components to be extracted are uniformly distributed inside the particle and the surface resistance is negligible, that is next to reality.

To verify the confidence of the method, we extended the prevision of this model to industrial scale. The results are presented in Figure 3, where the generated curve using de parameter from laboratorial scale and industrial scale are confronted. The industrial data was adjusted using the same technique used in lab scale. In this case the best value to effective difusivitty was $1.23 \times 10^{-11} m^2/s$.

Conclusions

It is possible to verify the importance of the process variables, principally the state condition of the raw material, in the yield of the citronella essential oil by steam distillation that justify the use of the factorial experimental planning to determine the best condition to the process: natural plant. The process variable selected, natural plant and two hours were used in the experiments to obtain the yield curve.

The experimental data for citronella essential oil yields are well correlated by the diffusional model. The determination of values for the adjusted parameter agreed to available literature data in terms of order of magnitude. Finally, the model parameter evaluation, attained in this work to laboratorial scale, could be useful during the scale-up of the extraction process and/or during pilot or industrial operation to evaluate the extraction time required to obtain a given yield, as confirmed in this study.

References

1. Clay, D.V.; Dixon, F.L.; Willoughby, I. *Forestry* **2005**, *78*, 1-9.
2. Spiro, M.; Selwood, R. M. *J. Sci. Food Agric*. **1984**, *35*, 915-924.
3. Spiro, M.; Page, C. *J. Sci. Food Agric*. **1984**, *35*, 925-930.
4. Spiro, M., Kandiah, M.; Price, W. *J. Food Sci. Tech.* **1990***, 25*, 157-167.
5. Reverchon, E. *J. Supercrit. Fluids* **1997**, *10*, 1-37.
6. Benyoussef, E. H.; Hasni, S.; Belabbes, R.; Bessiere, J. M. *Chem. Eng. J.* **2002**, 85, 1-5.
7. Adams, R. P. *Identification of Essential Oil Components by Gas Chromatography/mass Spectrometry*. Allured: Illinois, **1995**.
8. Kreider, D.L., Kuller, R.G., Ostberg, D.R., Perkins, F.W. *An Introduction to Linear Analysis*. Addison-Wesley Company Inc., Massachusetts, **1966**.
9. Nelder, J.; Mead, R. *Comput. J.* **1965**, *7*, 308, 1965.