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EXTRACTION OF CITRONELLA (*Cymbopogon nardus*) ESSENTIAL OIL USING SUPERCRITICAL CO_2: EXPERIMENTAL DATA AND MATHEMATICAL MODELING

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Abstract - Citronella essential oil has more than eighty components, of which the most important ones are citronellal, geranial and limonene. They are present at high concentrations in the oil and are responsible for the repellent properties of the oil. The oil was extracted using supercritical carbon dioxide due to the high selectivity of the solvent. The operational conditions studied varied from 313.15 to 353.15 K for the temperature and the applied pressures were 6.2, 10.0, 15.0 and 180.0 MPa. Better values of efficiency of the extracted oil were obtained at higher pressure conditions. At constant temperature, the amount of extracted oil increased when the pressure increased, but the opposite occurred when the temperature increased at constant pressure. The composition of the essential oil was complex, although there were several main components in the oil and some waxes were presented in the extracted oils above 10.0 MPa. The results were modeled using a mathematical model in a predictive way, reproducing the extraction curves over the maximum time of the process.

Keywords: Citronella oil; Geraniol; Empirical model; Extraction modes.

INTRODUCTION

Essential oils are concentrated essences extracted from different parts of plants, containing hundreds of substances, but typically with the prevalence of one, two or three of them that really characterize the fragrance (Mendes *et al*., 2007).

Industrial interest in essential oils is due to their application as fragrances in perfumes, as flavor additives for use in food products or even as pharmaceutical products. In the case of citronella species, for example, the components present in the oil are responsible for the desirable repellent characteristics of the plant against mosquitoes (Katz *et al*., 2008; Simic *et al*., 2008). Numerous plants and derived products, in particular essential oils, have been investigated and described as potential natural sources of insect repellent. Trongtokit *et al*. (2005) compared the repellent efficiency of 38 essential oils against mosquito bites, including the species *Aedes aegypti*. Among other essential oils, citronella oil was the most effective and provided 2 hours of repellency. Wong *et al*. (2005) studied five commercial plant extracts, including citronella, and showed that it is effective in deterring the infestation of cartons containing muesli and wheat germ by red flour beetles. Moreover, Olivo *et al*. (2008) proved that citronella oil has other effects, such as the

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*To whom correspondence should be addressed control of cattle ticks, the most important active principles being citronelal and geraniol. Nakahara *et al*. (2003) studied the chemical composition of citronella oil and its antifungal activity. The crude essential oil markedly suppressed the growth of several species of *Aspergillus*, *Penicillium* and *Eurotium*. The most active compounds among the 16 volatiles examined, consisting of 6 major constituents of the essential oil and 10 other related monoterpenes, were citronellal and linalool.

Currently, there are plant-based insect repellents on the market that contain essential oils from one or more of the following plants: citronella (*Cymbopogon nardus*), cedar (*Juniper virginiana*), eucalyptus (*Eucalyptus maculata*), geranium (*Pelargonium reniforme*), lemon-grass (*Cymbopogon excavatus*), peppermint (*Mentha piperita*), neem (*Azadirachta indica*) and soybean (*Neonotonia wightii*). Most of these essential oil-based repellents tend to give short-lasting protection for less than 2 h (Choochote *et al*., 2007). Citronella oil has demonstrated good efficacy against 44 mosquitoes in concentrations ranging from 0.05 % to 15 % (w/v) alone or in combination with other natural or commercial insect repellent products (Sakulku *et al*., 2009 apud Fradin, 1998). Olivo *et al*. (2008) apud Shasany *et al*. (2000) confirmed that this characteristic of the oil is due to the presence of four main components, citronelal, eugenol, geraniol and limonene.

Reis *et al*. (2006) studied the effect of drying at different temperatures (323.15, 333.15 and 343.15 K) on the composition of the essential oil of citronella extracted by hydrodistillation. The results showed a slight change in the composition for some components, but the drying did not influence the composition of the main components. The yield of the extraction was approximately 9.4 %, defined as the ratio between the mass of essential oil extracted and the initial mass of citronella used in the experimental tests.

According to Reverchon and De Marco (2006), the extraction of compounds from natural sources is the most widely studied application of supercritical fluids (SCFs), with several hundreds of published scientific papers. Indeed, supercritical fluid extraction (SFE) has immediate advantages over traditional extraction techniques: it is a flexible process due to the possibility of continuous modulation of the solvent power/selectivity of the SCF and it allows the elimination of polluting organic solvents and of the expensive post-processing cost of solvent elimination from the extracts.

Because of this motivation, this work has as its objective the study of essential oil extraction from citronella species using supercritical carbon dioxide to produce an extract free of solvent and concentrated in the active components of the oil, with attention to the efficiency and the composition of the extracted oil. The extraction with supercritical fluid has potential as an alternative technology with the objective of minimizing energy and the use of organic and pollutant solvents. In this work, the supercritical solvent used is carbon dioxide because of its atoxicity, low cost, volatility and low critical properties.

MATERIALS AND METHODS

Materials

The experiments were conducted using approximately, 6 g of dried leaves, 0.03 m in size, at ambient temperature,. The leaves were harvested in the Botanical Garden of the Universidade Federal Rural do Rio de Janeiro (UFRuralRJ). The citronella type used was *citronella of Ceilão*. The CO_2 (minimum purity of 99.9 %) was from Linde Gases S.A. (Rio de Janeiro).

Experimental Procedure

The extraction was performed in an experimental apparatus containing a high pressure pump, a stainless steel extractor with a capacity of 42.0 cm^3, a micrometric valve for sampling, a thermostatic bath (± 0.1 K, Lab-Line Instrument, Inc.; Melrose Park Illinois) to control the temperature, a manometer and a rotameter to measure the flow rate of CO_2. The flow diagram of the experimental apparatus is presented in Figure 1 (from Mendes, 2002).

The experimental procedure starts with the adjustment of the temperature in the heating bath. The experimental procedure was done in the semi-batch mode and carbon dioxide was fed with a volumetric flow rate of 0.155 $cm^3\ s^{-1}$ during the extraction time of 3600 seconds. When the pump reached the desired pressure and the system stabilized in a steady – state mode, the extraction was initiated with sampling, using a micrometric valve. The oil was collected in tubes of 15.0 cm^3.

A salt and ice bath (temperature equal to 263.15 K) was placed on in the high pressure pump head with the objective of ensuring that the solvent was in the liquid state.

The extracted oil was weighed on analytical balance with a precision of 1×10^{-4} g.

The operational conditions investigated were 313.15, 313.15 and 353.15 K for the temperature and 6.2, 10.0, 15.0 and 18.0 MPa, for the pressure.

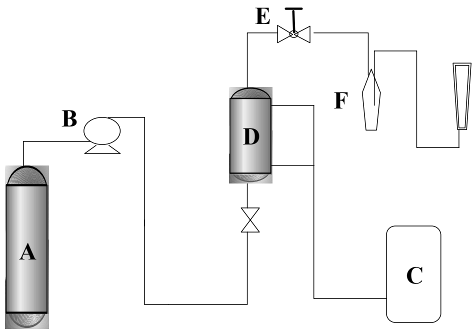

Figure 1: Flow diagram of the experimental apparatus, where A - CO_2 cylinder; B - high pressure pump; C - heating bath; D - extractor; E - micrometric valve; F - raffinate; G - rotameter.

Chromatographic Analysis

The extracts obtained from the supercritical fluid extraction were analyzed using gas chromatography (HP – 6890 Series System) coupled to a mass spectrometer (5973 MSD) using the Wiley 275 library (Adams, 1993). A DB-5 capillary column DB-5 (30 m long, 0.25 mm internal diameter, 0.25µm film thickness) was utilized with temperature limits from 213.15 K to 598.15 K. The flow of the carrier gas was 1.0 ml/min and the temperature programming varied from 353.15 K to 573.15 K at 279.15 K/min, with the injector temperature of 563.15 K and detector temperature of 583.15 K.

RESULTS AND DISCUSSIONS

A total of 12 experiments were performed, varying the conditions of temperature and pressure. The results are presented in Table 1.

The yield (Y) is presented as the ratio between the mass of extracted oil and the mass of leaves fed into the extractor. This formula was the same used by Reis *et al.* (2006). The best value of the yield was 2.2 % at 353.15K and 18.0 MPa of pressure. Although this is a low value, compared to 9.40 % obtained by Reis *et al.* (2006), it is important to remember that, in the process using supercritical carbon dioxide, the extract does not have residual solvent, which could justify its application to produce more pure oil. Moreover, the traditional processes using organic solvents extract all of the components without selectivity in relation to the major components. Reis *et al.* (2006) extracted the essential oil using a Clevenger apparatus (hydrodistillation with extraction with heptane and drying of the organic fraction with magnesium sulfate), using the same methodology described in Radünz *et al.* (2002).

Figure 2 shows that the quantity of extracted oil increases with increasing pressure, at constant temperature. This reflects the increase in the carbon dioxide density and, consequently, the increase of its solvent power.

As observed with other raw materials (Vargas *et al.*, 2010), practically all the oil was extracted in the first 30 minutes of extraction. This indicates that the majority of the oil was probably present near the surface of the leaves.

The quantity of solvent consumed during the extraction can be calculated and verified as the ratio between the extracted oil mass and the consumed mass of carbon dioxide, M_E/M_{CO2}. Chrastill (1982) called this variable the operational solubility because of the similarity of this ratio to the concept of solubility, which is however a thermodynamic property. Table 2 shows how the ratio M_E/M_{CO2} varies as a function of the density of the solvent. Table 2 also shows the extracted mass (ME) and the quantity of CO_2 consumed. Figure 3 shows the behavior of the variables presented in Table 2.

In a general manner, Table 2 shows that the extracted mass increased with increasing CO_2 density. Therefore, a cross-over effect can be observed in the extraction curves in Figure 3 at 313.15 and 333.15 K, probably due to the increase in the vapor pressure of the solutes, contrasting with the decrease in the CO_2 density. Another possibility might be the extraction of other components together with the oil.

Table 1: Extracted mass (ME) and yield (Y) of extraction as a function of temperature (T) and pressure (P)

Experiment number	P (MPa)	T (K)	ME (g)	Y*%
1	6.2	313.15	0.0145	0.24
2		333.15	0.0068	0.11
3		353.15	0.0074	0.12
4	10.0	313.15	0.0306	0.50
5		333.15	0.0285	0.47
6		353.15	0.0122	0.20
7	15.0	313.15	0.0545	0.90
8		333.15	0.1316	2.18
9		353.15	0.0776	1.25
10	18.0	313.15	0.0488	0.81
11		333.15	0.1110	1.83
12		353.15	0.1245	2.06

* Yield (Y, %) is the ratio between the mass of extracted oil and the initial mass of citronella leaves fed into the extractor

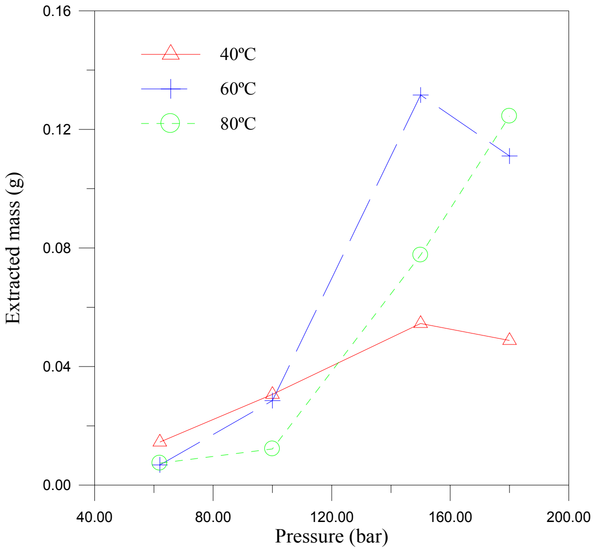

Figure 2: Extracted mass of oil as a function of pressure

Table 2: Variation of M_E/M_{CO2} as a function of the density of solvent

ME (g)	MCO$_2$ (g)	M_E/M_{CO2} x 10^4	D (g cm^{-3})
0.0074	64.31	1.2	0.1151
0.0068	73.36	0.93	0.1313
0.0145	89.08	1.6	0.1585
0.0122	124.43	0.98	0.2228
0.0285	164.73	1.7	0.2949
0.0776	240.95	3.2	0.4313
0.1245	296.26	4.2	0.5304
0.1316	339.02	3.9	0.6069
0.0306	343.77	0.89	0.6154
0.111	378.60	2.9	0.6778
0.0545	436.10	1.2	0.7807
0.0488	456.25	1.1	0.8168

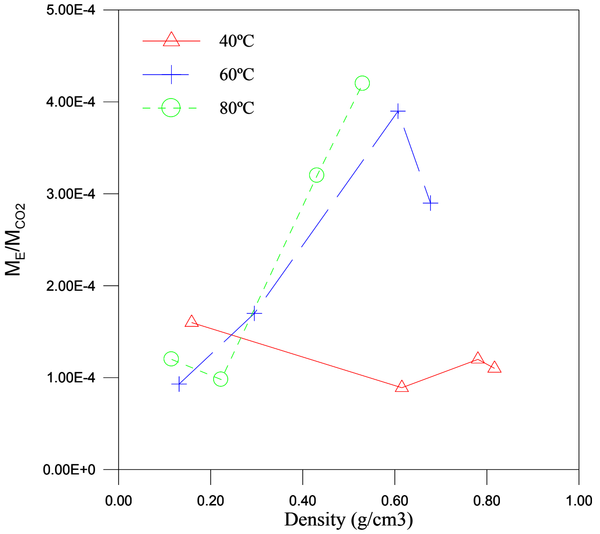

Figure 3: M_E/M_{CO2} as a function of carbon dioxide density

At 353.15 K the same behavior was not observed, which probably indicates that other components are being solubilized with increasing temperature. Thus, the extracted mass increases, but in part due to the solubilization of other chemical components that could potentially inhibit the essential oil extraction or change the original characteristics of the oil.

In general, at pressures higher than 10.0 MPa, other components present in the plant are extracted in addition to essential oil. This fact could be verified by the variation of the color of the extract obtained. At greater pressures, the extract is darker. At lower pressures, the color of the raffinate was yellow, while at higher pressures the color was green. When the pressure was increased, the intensity of the color and the amount of extracted material increased. The co-extraction of waxes was also observed by Carlson *et al*. (2001) in the extraction of lemongrass (*Cymbopogon citratus*) essential oil with dense carbon dioxide.

Figure 4 shows the chromatogram of the citronella oil obtained at 353.15 K and 18.0 MPa, indicating the relative abundance of the substances and their retention times. The identification of each component in the extract is indicated in Table 3, corresponding to the numbers of each peak in Figure 4. The Wiley library, used to identify the components, only confirms the presence of any component if the spectral match has a probability (P) higher than 70%.

To compare the selectivity of the process, Figure 5 shows the results of the chromatographic analysis of the extract obtained at 313.15K and 62.0MPa. Each identified component is listed in Table 4.

The results indicated a higher selectivity in the essential oil extracted at the higher temperature and pressure, as evidenced by the number of components present in the chromatograms. This behavior could be observed by comparing Figure 4 and Figure 5 and further certified in Tables 3 and 4.

The compositions of the citronella oil extracted under two different operational conditions, presented in Tables 3 and 4, indicate that these oils can be used as repellent with numerous applications because of the presence of citronellal, citronelol, geraniol and eugenol.

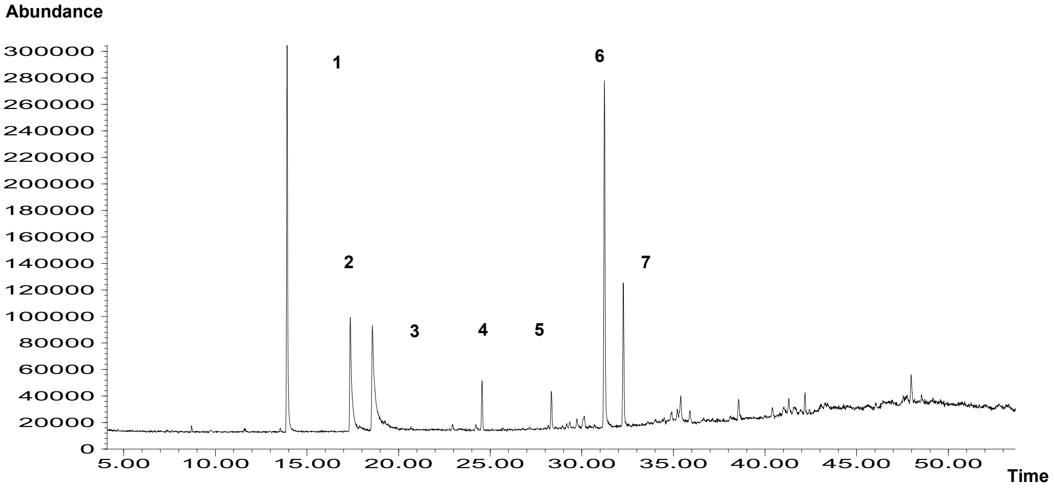

Figure 4: Chromatogram of the essential oil extracted with supercritical carbon dioxide at 353.15K and 18.0MPa

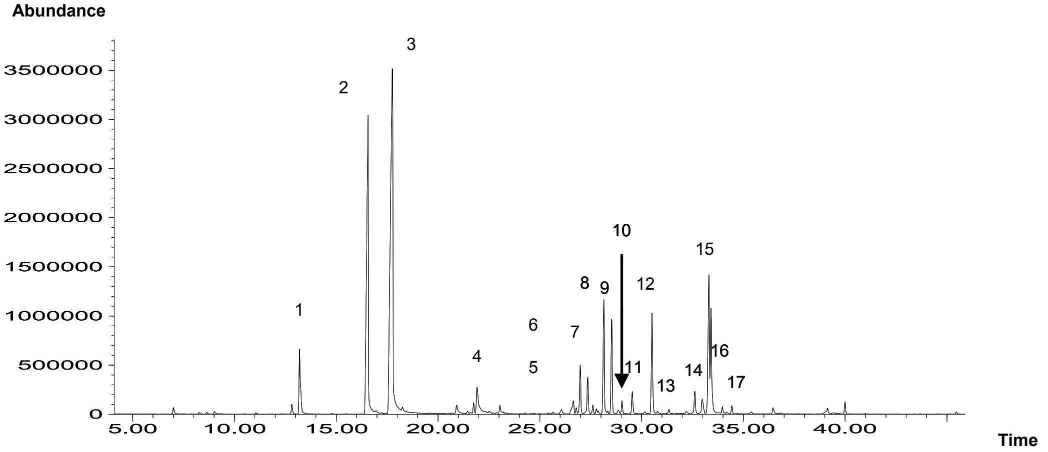

Figure 5: Chromatogram of the essential oil extracted with supercritical carbon dioxide at 313.15K and 62.0MPa

Table 3: Identification of the components present in the chromatogram in Figure 4

Identification	Components	P (%)
1	Citronellal	98
2	Citronellol	95
3	Geraniol	86
4	β-Elemene	95
5	Germacrene-D	99
6	Elemol	83
7	Germacredien-5-ol	91

Table 4: Identification of the components presents in the chromatogram in Figure 5

Peak	Components	P (%)	Peak	Components	P (%)
1	Citronellal	98	10	α-morfene	97
2	Citronellol	98	11	δ-cadinene	99
3	Geraniol	95	12	α-cadinene	98
4	eugenol	98	13	elemol	91
5	α-amorfene	98	14	γ-eudesmol	98
6	Germacrene-D	98	15	t-cadinol	90
7	β-selinene	99	16	β-eudesmol	99
8	α-selinene	98	17	α-eudesmol	99
9	α-muuorele	98			

MATHEMATICAL MODELING

A simple model was applied to fit the extraction results of citronella oil. The model was proposed by Naik and Lentz (1988) and it does not consider interactions between the solute and the solid matrix. This model was also applied by Esquível *et al.* (1999), Silva *et al.* (2008), and to *Jatropha curcas* oil (Pereira, 2009). The model is represented by Equation (2) and has only two adjustable parameters, e_{lim} and b:

$$e = e_{lim}\left(\frac{t}{b+t}\right) \qquad (1)$$

where e is the ratio of the mass of oil extracted at time t (s) to the initial mass of solute-free feed (kg of oil/kg of solute-free feed) and e_{lim} is the e value for an infinite extraction time or the maximum amount of solute initially present in the matrix. The ratio e_{lim}/b corresponds to the initial slope of the extraction curve versus time.

The model was used to represent the extraction behavior. The value of e_{lim}, taken from the conventional hidrodistillation method extraction, was 9.4% of oil in citronela leaves (Reis *et al.*, 2006).

Table 5 shows the empirical model parameter, b, and the calculated efficiency (e_{calc} - %) for all the operational conditions. Although the b parameter does not have a physical meaning, it is possible to see its variation as a function of the pressure.

The behavior of the efficiency (%) as a function of the time, at 6.2, 10.0, 15.0 and 18.0MPa for all temperatures, confirms the fact that almost all the oil had been extracted by half the time of the process. The presence of the oil on the surface of the leaves favours the convection mechanism as opposed to diffusion. As suggested by Sovová (1994), the extraction process occurs in three stages and they are controlled by either a convective or diffusion mechanisms, with a transition between them.

The results show that 313.15K is the best temperature, with no great differences in the efficiency at 333.15 and 353.15K. The results at 10.0MPa are in accord with the behavior observed in the experimental results. At 15.0MPa, the best efficiency was found at 333.15K, as can also be seen at 18.0MPa. Moreover, there were no great differences between 333.15 and 353.15K in relation to efficiency.

Table 5: Empirical model parameter, b, and calculated efficiency, %, for all operational conditions

	P (MPa)							
	6.2		10.0		15.0		18.0	
T (K)	b (s)	e_{calc}	b (s)	e_{calc}	b (s)	e_{calc}	b (s)	e_{calc}
313.15	137146.7	0.27	63520.4	0.56	33914.6	1.00	38000.0	0.89
333.15	299034.1	0.12	68771.3	0.52	11952.8	2.40	14900.0	2.02
353.15	271743.3	0.14	163652.8	0.22	23467.2	1.38	13000.0	2.25

CONCLUSIONS

This work had as its objective the use of supercritical carbon dioxide to extract the essential oil of citronella. Different operational conditions were investigated using 6.0×10^{-3} kg of the plant in the extractor. The best condition was found to be 353.15K and 18.0MPa with the maximum efficiency of the process in relation to the quantity of extracted mass. Besides the better value of efficiency, this operational condition showed good selectivity compared to other conditions. A high selectivity was obtained at 353.15K and 18.0MPa, with a more pure essential oil concentrated in the active main components. At 18.0MPa and 353.15K, seven components were presented, while at 62.0MPa and 313.15K there were seventeen components. The model used to predict the extraction behaviour showed a similar behaviour for all experimental conditions. This result suggests that the process is controled by the convection mechanism. The composition of the essential oil obtained using supercritical carbon dioxide indicates that the oil can be used for its antimicrobial, antifungal and repellency activities.

NOMENCLATURE

ME	Extracted mass	kg
Eff.	Efficiency of extraction as a function of temperature	%
T	Temperature	K
P	Pressure	MPa
D	Density	$kg.m^{-3}$
MCO_2	consumed mass of CO_2	kg
e	kg of oil/kg of solute-free feed	(-)
b	parameter of empirical model	s
t	time	s
e_{lim}	e value for infinite extraction time or the maximum amount of solute present	kg/kg
e_{calc}	calculated e value	kg/kg

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