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STUDY OF ESSENTIAL OILS EVAPORATION USING THERMOANALYTICAL TECHNIQUES

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In this work, it was carried out the study of three essential oils evaporation (orange, lemongrass, and basil) using techniques of thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC). TG/DTG curve profiles provided information on essential oil thermal stability, revealing the same thermal behavior for all these three essential oils; it means only one evaporation stage and a quick mass loss in function of time and temperature. TG/DTG data were correlated to Arrhenius equation to provide evaporation kinetic parameters, including: activation energy (Ea), and frequency factor (A). DSC curve profiles showed endothermic peaks related to the process of evaporation from which vaporization enthalpy was evaluated. DSC results are in agreement with TG/DTG data that showed the rate of evaporation increases in the following order: lemongrass, basil, and orange. The importance of thermal characterization of essential oils is to drive new technological developments to supply the market demand for new products.

1. INTRODUCTION

Essential oils thermal characteristics determine their application as ingredients in perfumes and in food formulations. For their use in perfumes, for example, one important property is volatility, which is the tendency of a material to vaporize. There must be a balance between the ingredients that leave readily the formulation and those that make the fragrance lasts for more time. So, the rates of evaporation play an important role determining the sensorial characteristics of a fragrance (Aggarwal et al., 1997). Limited data are available to describe the thermal characteristics of essential oils. Some studies have indicated that essential oils vaporization can affect the air quality when they are used indoors, especially under poor ventilation (Hsiu-Mei et al., 2010; Hua-Hsien et al., 2009). Other studies have proposed the encapsulation of fragrance materials to promote the chemical stabilization and the controlled release of the entrapped materials, prolonging their sensory characteristics (Sansukcharearnpon et al., 2010; Choi et al., 2009). Hence, to know the rate of evaporation is important to determine applications for these substances. Evaporation is the process in which a substance changes from liquid to vapour state and it can be studied by means of thermogravimetry using inert atmosphere. In a thermogravimetry analysis, the sample is placed in a very accurate balance located inside a furnace. During a controlled heating program, the mass sample is monitored and the vaporized mass is calculated subtracting the sample mass at time t from sample mass at time t-1. Thermogravimetry has been used to evaluate thermal behaviour of fatty acids (Shen and Alexander, 1999), oxidative stability and antioxidants effects on linseed oil (Rudnik et al., 2001), thermal stability and thermal decomposition kinetics of commercial edible oils (Santos et al., 2002), thermal decomposition of native, blended and enzyme interesterified oils (Debnath et al., 2011) and oxidation kinetics of genetically modified vegetable oils (Adhvaryu et al., 2000). It has also been applied in the study of pharmaceuticals evaporation (Lerdkanchanaporn and Dollimore, 2000), thermal degradation (Saha and Goshal, 2005), and to determine physical properties as vapor pressure and vaporization enthalpy (Wright et al., 2004; Hazra et al., 2002; Hazra et al., 2004). Regarding DSC applications, Lim et al. (2010) used the technique to differentiate among two types of pitaya (*Hylocereus cacti*) seed oils; Pardauil et al. (2011) to determine

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oxidative stability of vegetables oils from Amazonian area; Cevallos et al. (2010) to study encapsulated flavors release, and Liolios et al. (2009) to estimate antioxidant activity of carvacrol/thymol and carvacrol/ γ-terpinene, which are the two main components of oregano (*Origanum dictamnus*) essential oil, before and after their encapsulation in liposome. This technique can also be used to detect vegetable oils adulteration (Chiavaro et al., 2008, Torrecilla et al., 2011). In this work, kinetic evaporation of orange, lemongrass, and basil essential oils were studied by means of thermogravimetry analysis system, using a dynamic method of temperature and an inert atmosphere of nitrogen. Activation energy (Ea) and frequency factor (A) from Arrhenius equation were calculated from linear fit of obtained data. DSC was used to complement thermoanalytical characterization of orange, lemongrass, and basil essential oils, allowing identifying thermal events comprised inside the temperature range studied, and to estimate vaporization enthalpy (ΔHvap). Indeed, this paper is the extended version of the work presented at ICheap-10 Conference (Martins et al., 2011). Activation energy and enthalpy of evaporation published in the literature for other essential oils are reported in Table 1. A more detailed knowledge on essential oils vaporization can drive new technological developments to supply the market demand for new products.

Table 1: Literature values of Ea and ΔHvap for several essential oils

Material	Ea ($kJ.mol^{-1}$)	ΔHvap ($kJ.mol^{-1}$)
Cinnamon oil	45.10[a]	-
Lemon oil	35.61[c]	-
	31.79[d]	-
Cineole	39.64[a]	41.22[a]
	38.17[b]	34.54[b]
Clove oil	36.74[b]	49.15[b]
Eucaliptus oil	31.19[b-]	39.92[b]
Lynalyl Acetate	40.44[b]	45.68[b]
Linalool	65.64[a]	52.12[a]
	46.12[b]	39.67[b]
Lavender oil	27.99[c]	-
	26.32[c]	-
	33.05[d]	-
Limonene	37.87[a]	39.44[a]
	41.60[b]	36.38[b]
Citral	43.71[b]	48.72[b]
Cinamaldehyde	50.79[a]	52.63[a]
	47.94[b]	50.50[b]
Orange oil	38.86[b]	-

[a] Hazra et al. (2002), [b] Hazra et al. (2004), [c] Hua-Hsein et al. (2009), [d] Hsui-Mei et al. (2010)

2. MATERIALS AND METHODS

2.1 Essential oils

The following essential oils were used in the experiments: Orange (*Citrus sinensis*, Brazil), Lemongrass (*Cymbopogon flexuosus*, India), and Basil *(Ocimum basilicum*, Vietnam).

2.2 Thermogravimetry

TG analyses were conducted in a thermogravimetric analyser; model TGA-50 from Shimadzu (Japan). Data was collected in the temperature range from room temperature to 350°C. The equipment recorded TG and DTG data simultaneously. DTG means derivative plot of TG curve. The heating rate was 10°C/ min. Dry nitrogen was used as a purge gas at a flow rate of 50 mL/min. The sample mass used was nearly to 10.0 mg.

2.3 Evaporation kinetic

Sample mass variation by temperature data obtained by TG/DTG was used to determine evaporation kinetic parameters. According to Zhang et al. (2009), calculations are based in the following kinetic equation:

$$\frac{d\alpha}{dt} = k.(1-\alpha)^n \tag{1}$$

where α corresponds to the amount of vaporized material, n is the apparent reaction order and K is the rate constant. K depends on temperature following Arrhenius equation:

$$k = A.exp(-\frac{Ea}{RT}) \tag{2}$$

where A is the frequency factor, Ea corresponds to the activation energy, and R the gas constant. Considering equations 1 and 2, and taking the natural logarithm the following expression is derived

$$ln\left(\frac{d\alpha}{dt}\right) = \left[ln\, A.(1-x)^n\right] - \frac{Ea}{RT} \tag{3}$$

Thus, plotting $ln\left(\frac{d\alpha}{dt}\right)$ versus $\left(\frac{1}{T}\right)$, and correlating the values by the least-square method to obtain a straight line, the slope will provide the activation energy after being multiplied by R.
For zero-order reactions (n = 0), the equation becomes

$$ln\frac{d\alpha}{dt} = ln\, A + (-\frac{Ea}{RT}) \tag{4}$$

and the intercept of this equation will be equivalent to ln A.

α, the amount of vaporized material, is defined as:

$$\alpha = \frac{(m_0 - m_t)}{(m_0 - m_f)} \quad (5)$$

In which,:
m_o corresponds to sample initial mass,
m_t corresponds to the sample mass at time t, and
m_f corresponds to sample final mass.

Thus,

$$\frac{d\alpha}{dt} = \frac{-\frac{dm}{dt}}{m_o - m_f} \quad (6)$$

and the value of $\left(\frac{dm}{dt}\right)$ is provided by DTG plot.

2.4 Differential scanning calorimetry

Differential scanning calorimetry can be defined as the technique that allows the measurement of heat flow rate difference among a sample and a reference submitted to the same controlled temperature program. In this work, the DSC essential oil profile was determined using a differential scanning calorimeter, model 823E from Mettler Toledo. The instrument was calibrated using indium (Melting point 156.6C; ΔH_f = 28.45J/g). Ten milligram samples were placed in 40 µL hermetically sealed aluminium crucibles. An empty pan was used as reference. The samples were analyzed under a flow of nitrogen gas (40 mL/min). A dynamic scan was performed at a heating rate of 10°C/min over a temperature range of -150 to 300°C. Evaporation enthalpies were estimated by peak area integration of DSC profiles and the results were compared with the calcuated vaporization enthalpy of essential oils major components.

3. RESULTS

3.1 Thermogravimetric profile

TG/DTG curve profiles revealed the same thermal behavior for orange, lemongrass, and basil essential oils as can be seen in Figures 1, 2, and 3. The rate of evaporation can be read directly from dm/dt plots. The TG/DTG profiles showed only one stage of evaporation and a quick mass loss in function of time and temperature, the graphics do not show a plateau indicating thermal stability; conversely, the mass lost begins at temperatures around the room temperature and the evaporation ends at 118.1, 166.7 e 164.2°C for orange, lemongrass, and basil essential oils, respectively.

3.2 Evaporation kinetic

For a reaction to be considered an evaporation process, it is imperative that the mass loss according to the time or temperature be a zero order process. DTG data have an important role in determining reaction order. According to Hazra et al. (2002), the DTG curve for a zero order kinetic is characterized by an abrupt curve return from the maximum point to the baseline. All oils presented in this work showed this behaviour, i.e., zero-order kinetics as shown in Figures 1, 2, and 3. Therefore, to determine evaporation kinetic parameters, essential oils evaporation was considered a zero-order process. A typical orange oil Arrhenius plot for the calculation of activation energy is shown in Figure 4. The essential oil kinetic parameters determined from TG/DTG data are shown in Table 2.

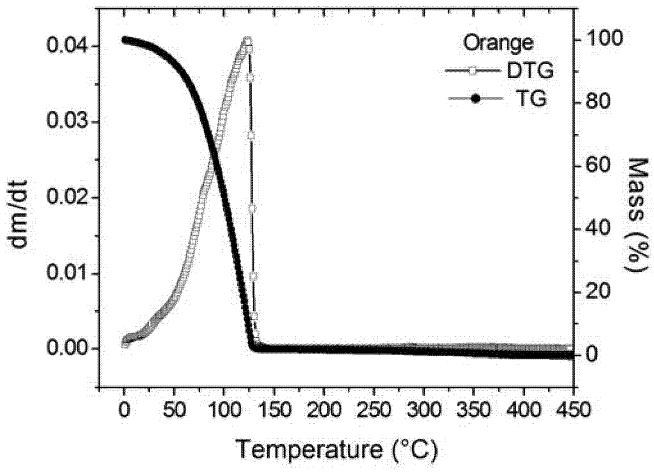

Figure 1: TG/DTG plot of orange oil profile

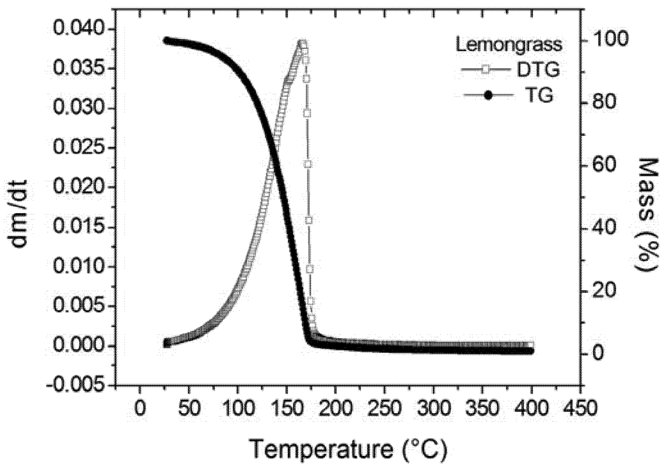

Figure 2: TG/DTG plot of lemongrass oil profile

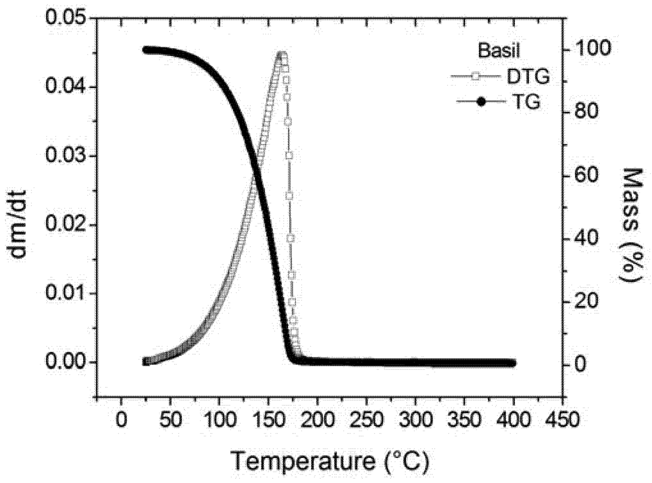

Figure 3: TG/DTG plot of basil oil profile

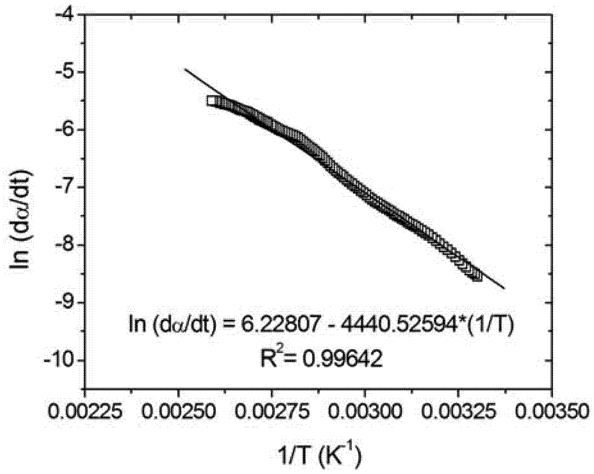

Figure 4: A typical orange oil Arrhenius plot for the calculation of the activation energy

Table 2: Evaporation kinetic parameters of essential oils

Parameters	Orange	Lemongrass	Basil
Ea (kJ.mol^{-1})	38.24	37.72	39.63
A (s^{-1})	728.58	120.83	220.72

The values of activation energy obtained in this work are in agreement with literature data (Table 1). Small variations in activation energy are associated with different heating rates employed during TG experiments (in general higher heating rates, lower activation energy) and different essential oils compositions that differs in function oil extraction process, harvest time, etc.

3.3 Calorimetry profile

DSC curve profiles of orange, lemongrass, and basil oils are shown in Figures 5, 6, and 7, respectively. All of them showed endothermic peaks related to the process of evaporation at 179°C, 230°C, and 220°C, respectively. Differently from orange and lemongrass oils that showed only one phase change, vaporization, the DSC profile of basil oil revealed an exothermic peak at -84°C attributed to a change into the solid structure before melting, and an endothermic peak at -27°C related to melting. Solid restructuration and melting enthalpies for basil oil, calculated by area integration, were 42.37 and 67.12 J.g -1, respectively.

Essential oils usually show predominant substances in their compositions. In this work, limonene comprises 90% of orange oil, citral 66% of lemongrass oil, and methyl chavicol 84% of basil oil. Thus, essential oils evaporation enthalpies estimated by DSC were compared with calculated vaporization enthalpies of essential oils major components, which values are presented in Table 3. The vaporization enthalpy calculation was carried out considering Trouton's rule depicted by the formula:

$$\Delta H_{vap} = T_b\,[36{,}6 + 8{,}314\,ln(T_b\,)] \quad , \qquad (7)$$

in which T_b corresponds to normal boiling point.

Calculated and estimated vaporization enthalpies showed comparable values. Higher purity of the oil concerning its major substance, closer it is essential oil enthalpy of the pure substance vaporization enthalpy. A typical area integration of vaporization peak from DSC basil oil profile is shown in Figure 8.

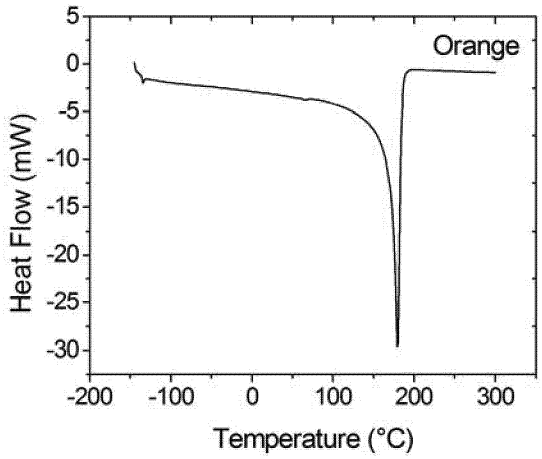

Figure 5: DSC orange oil profile

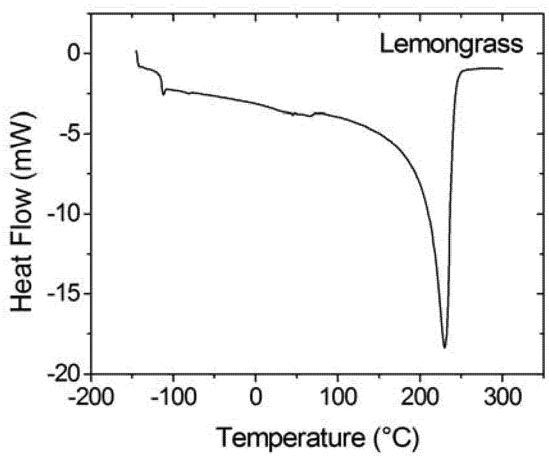

Figure 6: DSC lemongrass oil profile

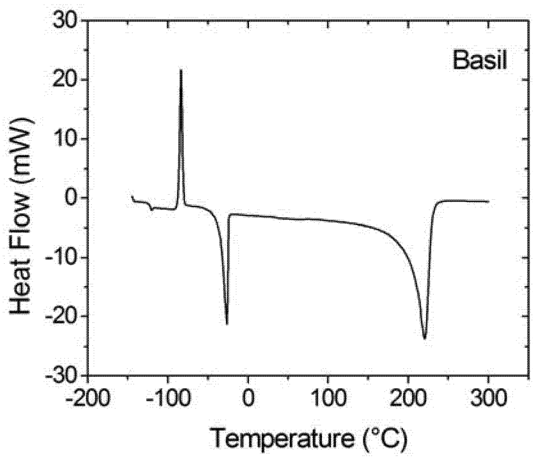

Figure 7: DSC basil oil profile

Table 3: Estimated and calculated vaporization enthalpy

Oil	ΔHvap ($J.g^{-1}$)	Main Substance	ΔHvap ($J.g^{-1}$)	ΔHvap ($kJ.mol^{-1}$))
Orange	277.39	Limonene	288.08	39.25
Lemongrass	336.02	Citral	291.28	44.34
Basil	305.89	Methyl chavicol	290.09	42.99

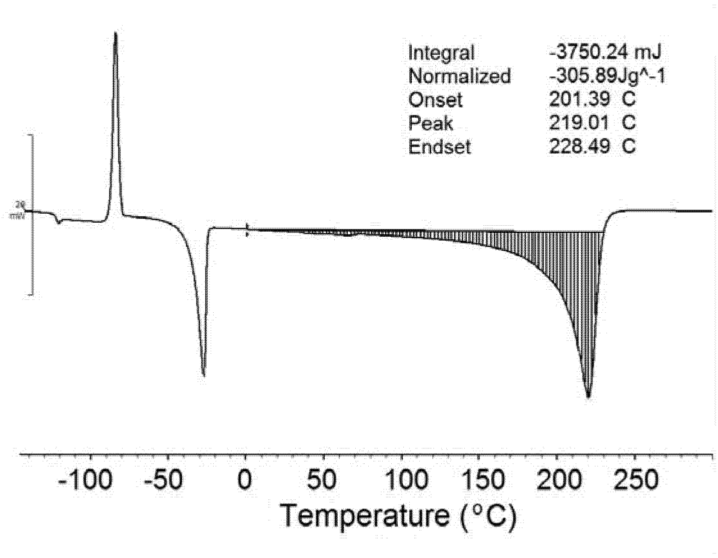

Figure 8: A typical area integration for the calculation of vaporization enthalpy

4. CONCLUSIONS

In this work, it was performed the study of three essential oils evaporation (orange, lemongrass, and basil) using techniques of thermogravimetry and differential scanning calorimetry. TG/DTG data were correlated to Arrhenius equation to provide evaporation kinetic parameters. Activation energies for orange, lemongrass, and basil were 38.24, 37.72 e 39.63 $kJ.mol^{-1}$ and the frequency values were 728.58, 120.83, and 220.72 s^{-1}, respectively. DSC analyses showed endothermic peaks related to the process of evaporation for all oils studied. Differently from orange and lemongrass oils that showed only one phase change (vaporization), the DSC profile of basil essential oil revealed three thermal events: an exothermic peak probably due to a solid restructuration before melting, an endothermic peak related to melting, and an endothermic peak related to vaporization. Enthalpy of vaporization calculated by DSC for orange, lemongrass, and basil were 277.39, 336.02, and 305.89 $J.g^{-1}$, respectively. These results are in agreement with TG/DTG data that showed the rate of evaporation increases in the following order: lemongrass, basil, and orange. Activation energy values and enthalpies of evaporation were comparable with previous data published in the literature for other essential oils finding good agreement among them.

5. ACKNOWLEDGEMENTS

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