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Thermal Characterization of Orange, Lemongrass, and Basil Essential Oils

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In this work, it was performed the thermoanalytical characterization of three essential oils (Orange, Lemongrass, and Basil) using techniques of thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC). Thermogravimetry analysis provided information on essential oil thermal stability. TG/DTG data were correlated to Arrhenius equation to provide evaporation kinetic parameters, including: activation energy (Ea), and frequency factor (A). DSC analyses were conducted over a temperature range from -150 to 300°C and showed the presence of endothermic peaks related to the process of evaporation for all these three oils. Differently from Orange and Lemongrass oils that showed only one phase change (vaporization), the DSC profile of Basil essential oil revealed three thermal events: two endothermic peaks due to melting and vaporization, and an exothermic peak attributed probably to a change in the solid structure before melting. 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. In this work, it was performed the thermoanalytical characterization of three essential oils (Orange, Lemongrass, and Basil) using techniques of thermogravimetry and differential scanning calorimetry. The

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obtained data were used to calculate activation energy (Ea) and enthalpy (ΔHvap) of evaporation for the studied essential oils. 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 take to new technological developments able 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 ($kJ.mol^{-1}$)	Material	Ea ($kJ.mol^{-1}$)	ΔHvap ($kJ.mol^{-1}$)
Cinnamon oil	45.10[a]	-	Linalool	65.64[a]	52.12[a]
	51.05[b]	-		46.12[b]	39.67[b]
Lemon oil	35.61[c]	-	Lavender oil	27.99[c]	-
	32.93[c]	-		26.32[c]	-
	31.79[d]	-		33.05[d]	-
Cineole	39.64[a]	41.22[a]	Limonene	37.87[a]	39.44[a]
	38.17[b]	34.54[b]		41.60[b]	36.38[b]
Clove oil	36.74[b]	49.15[b]	Citral	43.71[b]	48.72[b]
Eucaliptus oil	31.19[b]	39.92[b]	Cinamaldehyde	50.79[a]	52.63[a]
	-	-		47.94[b]	50.50[b]
Lynalyl Acetate	40.44[b]	45.68[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/DTG 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. 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 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), the calculi are based in the following kinetic equation:

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

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

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

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

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

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

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

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

2.4 Differential scanning calorimetry
The DSC essential oil profile was determined using a differential scanning calorimeter, model 823E from Mettler Toledo. Ten milligram samples were placed in aluminium crucibles. 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 calculated by peak area integration of DSC profiles and the results were compared with the estimated 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 oils. A typical TG/DTG plot for Orange oil is shown in Figure 1. The TG/DTG profiles showed only one evaporation stage 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 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 behavior, i.e., zero-order kinetics as showed in Figure 1. Therefore, to determine evaporation kinetic parameters, essential oils evaporation was considered a zero-order process. A typical Arrhenius plot for the calculation of activation energy is showed in Figure 2. The essential oil kinetic parameters determined from TG data are shown in Table 2.

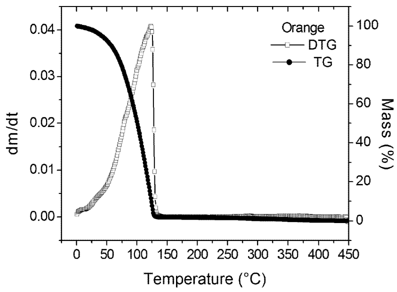

Figure 1: A typical TG/DTG plot of orange oil profile

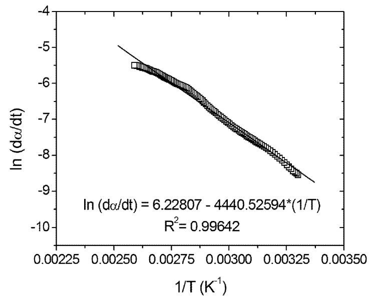

Figure 2: A typical Arrhenius plot for the calculation of the activation energy

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 showed in Figures 3, 4, and 5, 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 were 42.37 and 67.12 $J.g^{-1}$, respectively.

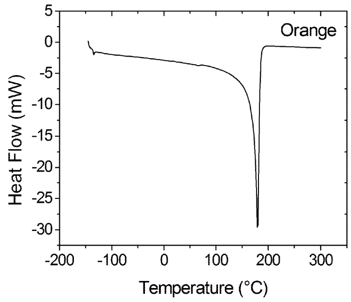

Figure 3: DSC Orange oil profile

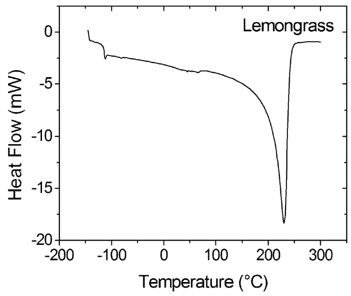

Figure 4: DSC Lemongrass oil profile

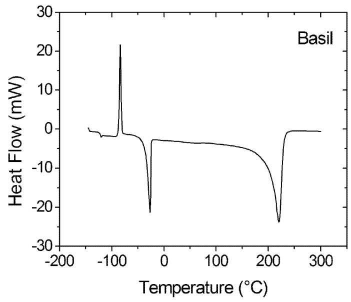

Figure 5: DSC Basil oil profile

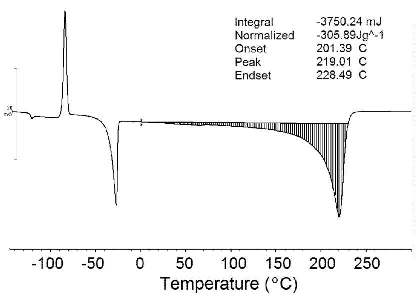

Figure 6: A typical area integration for the calculation of vaporization enthalpy.

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 calculated by DSC were compared with estimated vaporization enthalpies of essential oils major components, which values are presented in Table 3. A typical area integration of vaporization peak from DSC Basil oil profile is shown in Figure 6. 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.

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

4. Conclusions

In this work, it was performed the thermoanalytical characterization of three essential oils (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.

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