

Thermal behavior of araçá oil (*Psidium cattleianum* Sabine)

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Abstract The araçá is a well-known fruit, which belongs to the Myrtaceae family, *Psidium cattleianum* Sabine species, frequently found in the southern region of Brazil. The extraction of araçá oil was carried out from seeds, and the fatty acid profile of this oil indicates the predominant presence of linoleic acid (81.38%). Thermogravimetry, derivative thermogravimetry, and differential scanning calorimetry (DSC) were used to characterize this oil. In addition, this oil was evaluated by DSC from 25 to -60 °C, where the crystallization behavior was verified. Details concerning thermal decomposition as well as data of kinetic parameters of these stages have been described here. The kinetic behavior of the thermal decomposition was evaluated from several heating rates with mass samples of 5 and 20 mg in open crucibles under nitrogen and synthetic air atmospheres.

Keywords Araçá oil · Thermal behavior · Kinetic parameters · Crystallization

Introduction

The araçá is a well-known fruit, which belongs to the Myrtaceae family, *Psidium cattleianum* Sabine species,

and is frequently found in the southern region of the Brazil as a native tree. This fruit is not used industrially, but it is commonly used in juice or jam preparations [1, 2]. This fruit is between 1.5 and 2.5 cm in diameter, possesses succulent pulp and a pleasant flavor as well as having a great amount of seed. The study of this oil is of growing interest nowadays because it can be used for both human consumption and other industrial purposes such as cosmetics and varnishes.

In this study, we report the extraction of araçá oil and its thermal characterization as well as its fatty acid profile. This oil was investigated by simultaneous TG/DTG, chromatographic analysis, and DSC. The results of this study improve the knowledge on this oil including its crystallization behavior and thermal decomposition which was carried out on two mass samples in nitrogen and synthetic air atmospheres. Thus, these variables were to determine the changes on obtained results as well as on the kinetic behavior. Furthermore, the isoconversional method is used not only as a way of obtaining reliable and consistent kinetic information, but also because it avoids the use of explicit kinetic models [3–9]. Thus, the activation energy (E_a /kJ mol $^{-1}$) data were obtained applying the isoconversional method proposed by Capela and Ribeiro [10].

Experimental

The fruit (red species) was collected in Ponta Grossa city, localized in Paraná state, Brazil. The seeds were separated from the pulp manually and dried at ambient temperature. This seeds are similar those of the *Psidium guajava* L. A fine powder was obtained by grinding the seeds in a blender. The oil was obtained, with *n*-hexane (analytical reagent), in an extraction bath at ambient temperature. The

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n-hexane was removed and concentrated in a rotary evaporator.

The fatty acid composition was analyzed as previously described by AOCS [11]. The fatty acid composition of this oil was obtained in a gas chromatography (GC) using a GC 3900 model, from Varian (Walnut Creek, USA), equipped with an injector temperature of 250 °C and with a flame-ionization detector, with a capillary column of fused silica CP-Sil 88 (0.20 mm × 60 m) and film thickness of 0.20 μm. The column temperature was held at 90 °C for 4 min⁻¹, with heating rates ranging from 10 °C min⁻¹ up to 195 °C, and maintained in isotherm during 16 min⁻¹ with a flow rate of hydrogen of 30 mL min⁻¹. The injection volume was 1.0 μL and split injection ratio was 1:30.

Simultaneous TG/DTA and DSC curves were obtained from a SDT 2960 and a DSC 2910, both from TA Instruments. The TG/DTG curves were obtained using mass samples of about 5 and 20 mg in an α-alumina crucible with heating rates of 5, 10, and 20 °C min⁻¹ under a nitrogen and synthetic air atmospheres (100 mL min⁻¹) from 30 to 650 °C. The DSC curves were performed with a mass sample of about 5 mg, but placed in an open aluminum crucible, under a synthetic air flow of 50 mL min⁻¹ and heating rate of 20 °C min⁻¹. For the crystallization study, the DSC curve was obtained from DSC1 Star^e from Mettler Toledo. The mass sample was about 5 mg in an aluminum crucible with a lid and cooled from 25 to -60 °C and subsequently heated from -60 to 25 °C, both at a heating rate of 5 °C min⁻¹.

Kinetic methodology

To perform the kinetic analysis under non-isothermal conditions is usually considered the integral kinetic equation, defined by

$$\beta = \frac{AE}{Rg(\alpha)} \int_{E/RT}^{\infty} \frac{\exp(-z)}{z^2} dz, \quad (1)$$

where $\beta = dT/dt$ is a constant heating rate (T is the temperature and t is the time), $g(\alpha)$ is the integral form of the reaction model as function of the extent of reaction α , A is the pre-exponential factor, E is the activation energy, and R is the gas constant.

Estimates of the kinetic parameters are obtained by fitting Eq. 1 to experimental data. As consequence, is required the evaluation of the integral on the right side of the Eq. 1, known as temperature integral. However, the results from these integral do not have an exact analytical solution. Thus is convenient to approximate the integral of temperature to some function that yields suitable estimations to these kinetic parameters.

In this study, the kinetic parameters are obtained through isoconversional method using an approximation to the temperature integral based on the convergent of a Jacobi fraction, proposed by Capela and coworkers [7]. This approximation is a rational function, given by the following equation:

$$\int_x^{\infty} \frac{\exp(-z)}{z^2} dz = \frac{\exp(-x)}{x} \frac{x^3 + 14x^2 + 46x + 24}{x^4 + 16x^3 + 72x^2 + 96x + 24}. \quad (2)$$

A characteristic experimental curve presents the conversional fraction, α , as a function of the temperature for a given heating rate, β . For each fixed value of α , there are corresponding values T_x for temperature, values E_a for activation energy, and values A_x for pre-exponential factor.

Replacing the integral in Eq. 1 by the approximation given in Eq. 2 is obtained by the following expression for heating rate β as function of the $x_x = 10^3/RT_x$:

$$\int_x^{\infty} \frac{\exp(-z)}{z^2} dz = \frac{\exp(-x)}{x} \frac{x^3 + 14x^2 + 46x + 24}{x^4 + 16x^3 + 72x^2 + 96x + 24} \quad (3)$$

where the activation energy is in kJ mol⁻¹ and the parameter B_x is defined as:

$$B_x = \ln \left(\frac{10^3 A_x}{Rg(\alpha)} \right). \quad (4)$$

The estimates of the E_a and B_x can be obtained by the non-linear fitting of the Eq. 3 to the β values as function of x_x [10].

Once the $g(\alpha)$ function has been determined for each conversional fraction α , the estimation of the Arrhenius pre-exponential factor can be obtained from Eq. 4 and is given by following equation:

$$\hat{A}_x = \frac{R}{10^3} \exp(\hat{B}_x) g(\alpha). \quad (5)$$

Results and discussion

The oil content in the arapa seed was around 12%, with a greenish-yellow color. Table 1 presents the results of the fatty acid composition of arapa oil obtained by CG analysis. The linoleic acid is predominant, which is an essential oil for human consumption and, therefore, useful for nutritional purposes.

Simultaneous TG/DTA and DTG curves of arapa oil in a synthetic air atmosphere are shown in Fig. 1. The first mass loss occurs between 194 and 335 °C which corresponds to a loss of 31.94%. The second mass loss occurs between 335

Table 1 Fatty acid composition of araça oil

Fatty acid	Percentage by weight ^a
Araquidic (C20:0)	0.29 ± 0.01
Stearic (C18:0)	4.19 ± 0.23
Linoleic (C18:2 n6)	81.38 ± 0.11
Araquidic (C20:0)	0.29 ± 0.01
Palmítico (C16:0)	6.36 ± 0.06
Oléico (C18:1 n9)	7.48 ± 0.06

^a The value in the table represents the mean ± standard deviation of triplicate analyses

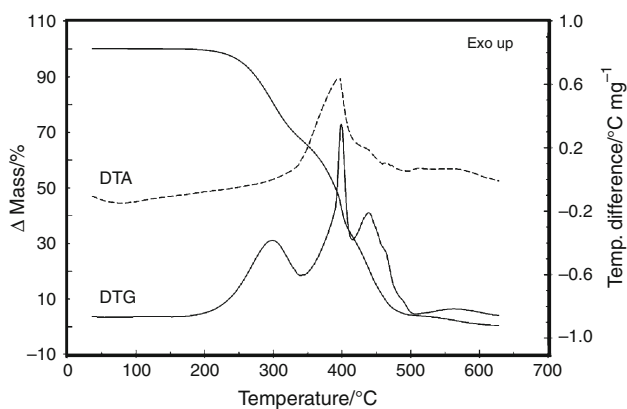


Fig. 1 Simultaneous TG/DTA and TG/DTG curves of araça oil with mass sample of 20 mg in synthetic air atmosphere and heating rate of 20 °C min⁻¹

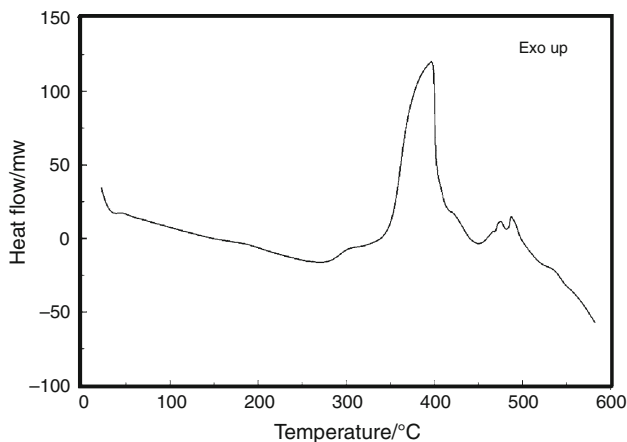


Fig. 2 DSC curve of araça oil with mass sample of 20 mg in synthetic air atmosphere and heating rate of 20 °C min⁻¹

and 410 °C (35.90%) and shows an exothermic peak in DTA curve. This reaction is in agreement with the DSC curve, as showed in Fig. 2. Furthermore, this reaction was attributed to the combustion of this oil. According to the DTG curve, the third and fourth mass loss occurs between

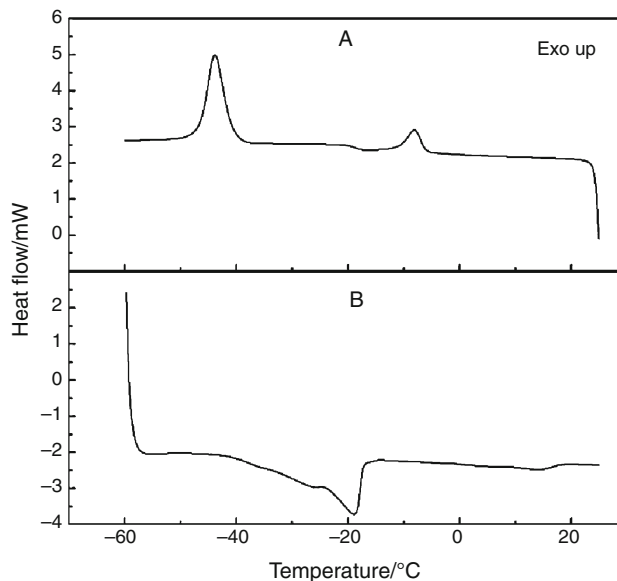


Fig. 3 DSC curve of araça oil: **a** cooling and **b** heating. The mass sample was 5 mg, with heating rate of 5 °C min⁻¹ in nitrogen atmosphere

410 and 500 °C and between 500 and 620 °C, both corresponds to losses of 28.07 and 3.21%, respectively. After thermal decomposition, there was the formation of a small quantity of carbonaceous residue.

Figure 3 shows the DSC curves of cooling and heating of araça oil in a nitrogen atmosphere. During the cooling, the oil exhibited two well distinguishable exothermic events between -8 and -45 °C. These events were attributed to the crystallization of saturated and unsaturated acids, respectively. However, this interpretation is made with caution, because there are mixtures of saturated and unsaturated fatty acids, due not only to the proportions but also to the sum of minor constituents of this oil. Two reasons can be attributed to the deviation of the baseline localized between -18 and -20 °C during cooling. First, it can be due to the crystallization of the fractions of the minor constituents and second, it can be attributed to the solid-to-solid or liquid-solid transition, which is due to the rearrangement of the crystals of fatty acids into more stable forms [12, 13]. Furthermore, a similar event occurs during the heating process between 17 and 20 °C, which can be due to the final solid-liquid transition of the fatty acids. Nevertheless, these events should be evaluated by X-ray diffraction to be elucidated.

The heating process is more complex than cooling, due to the exhibition of multiple endothermic events in the range from -40 to 17 °C. The endothermic reaction observed from -40 to -17 °C is attributed to the melting stage, which is due to the overlapping reactions of the different saturated and unsaturated fatty acids.

Kinetic parameters

The kinetic parameters of the thermal decomposition of this oil were evaluated from DTG curve obtained in nitrogen and synthetic air atmospheres, as shown in Figs. 4 and 5, respectively. For the analysis in nitrogen atmosphere, the mass loss occurs in two stages without evident overlapping reactions, whereas in synthetic air the mass loss occurs in more than one stage. Thus, the kinetic evaluation in synthetic air was made for the first stage of decomposition.

In Fig. 6, the distribution of the heating rate (β) in function of the $1000/RT_\alpha$ of the first decomposition step for 5 mg is shown under nitrogen atmosphere. It can be observed the adjustment of the variation for E_a and also the correlation coefficient (r) values, shown inside of this Figure. Thus, the average values of the activation energy (E_a) of the kinetics data obtained from TG curves are shown in Table 2. The graphical of the activation energy (E_a) versus conversion degree (α) values with mass samples of 5 and 20 mg are shown in Fig. 7.

For evaluation under nitrogen atmosphere, for the first stage of thermal decomposition, we can see that for both sample masses, the activation energy maintains the same feature and is invariable on the extension of conversion degree (α). Nevertheless, in second stage of thermal decomposition, the activation energy for mass of 20 mg is higher than 5 mg, but the behavior of the activation energy versus conversion degree (α) has the same feature. This increase in activation energy is associated to the mass sample.

For evaluation under a synthetic air atmosphere, it can also be seen that there are tendencies of the plots to maintain the same features on the extension of conversion degree (α). Furthermore, it is also clear that the values of activation energy are invariable for both masses, which

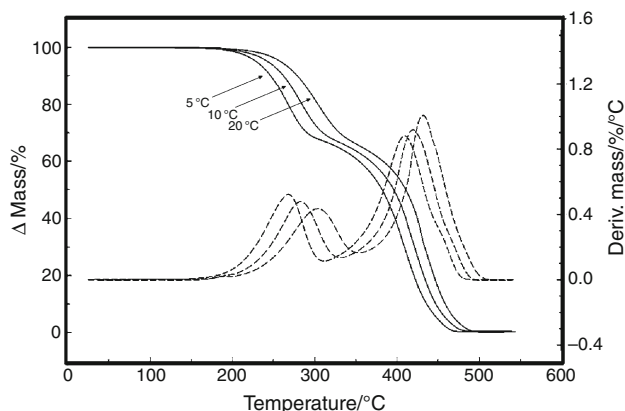


Fig. 4 TG/DTG curves of araça oil with heating rate of 5, 10, and 20 °C min⁻¹, mass sample of 20 mg in nitrogen atmosphere

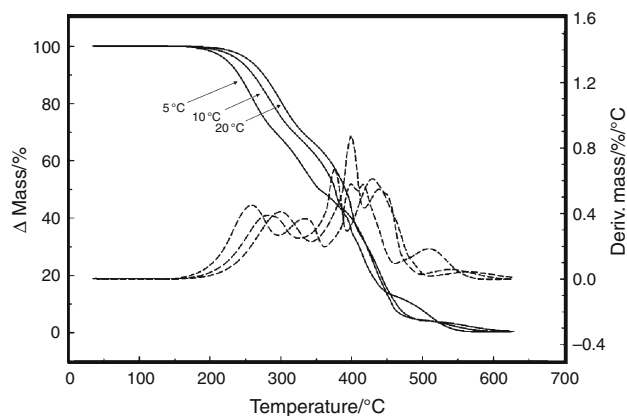


Fig. 5 TG/DTG curves of araça oil with heating rate of 5, 10, and 20 °C min⁻¹, mass sample of 20 mg in synthetic air atmosphere

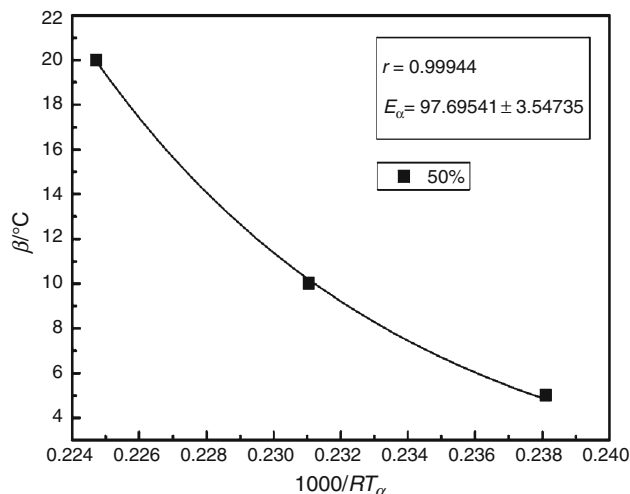


Fig. 6 Diagram of dispersion of β versus degree conversion (α —50%) with the adjustment functions of the araça oil for first decomposition stage with 5 mg in nitrogen atmosphere

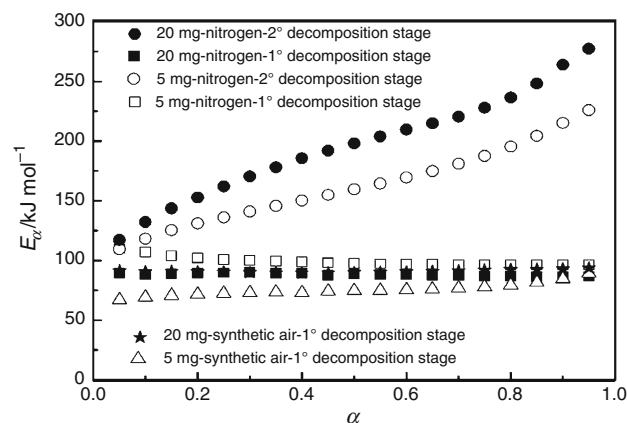
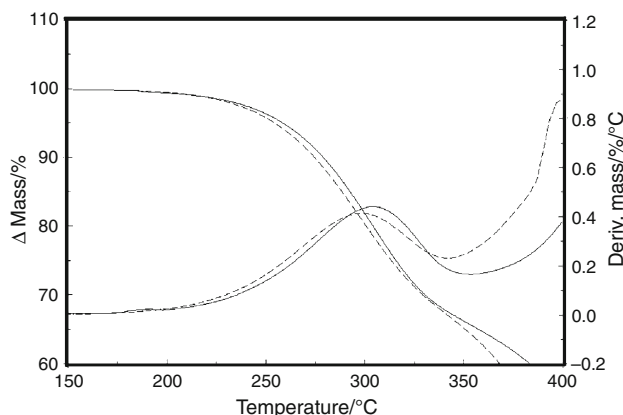


Fig. 7 The calculated E_a /kJ mol⁻¹ as a function of α for araça oil in the first and second decompositions steps

Table 2 E_a /kJ mol⁻¹ and correlation coefficient (r) for the thermal decomposition stages

Compound	Sample mass	E_a /kJ mol ⁻¹	r
Araçá oil	5 mg (nitrogen)	99.38 ± 0.04	0.99935
	1° decomposition stage		
	20 mg (nitrogen)	88.18 ± 0.01	0.99931
	1° decomposition stage		
	5 mg (nitrogen)	162.55 ± 0.20	0.99775
	2° decomposition stage		
	20 mg (nitrogen)	196.44 ± 0.22	0.99992
	2° decomposition stage		
	5 mg (synthetic air)	75.56 ± 0.07	0.99460
	1° decomposition stage		
Araçá oil	20 mg (synthetic air)	90.96 ± 0.01	0.98940
	1° decomposition stage		

**Fig. 8** TG curves of seed araçá oil with mass sample of 20 mg in synthetic air (solid curve) and nitrogen (dash dot curve) atmospheres with heating rate of 20 °C min⁻¹

also indicates that it can be regarded as a single-stage reaction.

Usually, a comparison of the results under different atmospheres is not common. Evidently, this occurs because the reactions are under an air atmosphere, which favors the occurrence of oxidation reactions. However, the kinetic behavior here studied reveals that the first stage of the thermal decomposition of this oil under both atmospheres are similar, which can indicate that the sample has the same reaction. Furthermore, the evaluation of the kinetic data leads to an unequivocal interpretation, because the reactions produced in synthetic air probably are another, and therefore, are not the same as produced under a nitrogen atmosphere. Recently, we evaluated the thermal characterization of jervá oil, but were not observed the similar thermal behavior like here reported [9]. Nevertheless, the jervá oil showed varied fatty acids composition, while the araçá oil has predominantly only linoleic acid. Thus, when

TG curves of araçá oil obtained in nitrogen and synthetic air atmospheres are compared, only for mass sample of 20 mg and heating rate of 20 °C min⁻¹ as shown in Fig. 8, suggest that the first stage of the thermal decomposition is the same, because the thermal behaviors are similar. Besides, if the others heating rates and mass samples of 5 and 20 mg are also considered, it can be seen that they all have the same behavior. Therefore, considering the mass precision of the instrument, the product of the reaction would not be the same. To rectify this suggestion, it would be necessary to carry out an analysis coupled with instruments in the TG system to detect the products formed during the reaction, which is beyond our means.

Conclusions

The araçá oil has high linoleic acid content, which makes it useful for human consumption. The thermal studies carried out on non-isothermal TG in nitrogen and in air provide a comparison and understanding of the araçá oil behavior during thermal analysis. DSC curves of the cooling and heating of this oil reveal two crystallization stages and overlapping reactions attributed to the melting of the fatty acids.

Moreover, it can be seen from the resemblance between the two different mass samples, that a better evaluation of kinetic parameters is permitted. Besides, in synthetic air, the activation energy is low and this indicates that the oxidation process favors a decrease of the activation energy.

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