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Thermal and kinetic studies of white lupin (*Lupinus albus*) oil

Gustavo Guadagnucci Fontanari[1] · Marcelo Kobelnik[2] · Marcelo Rodrigues Marques[1] · José Alfredo Gomes Arêas[1] · Bruno Trevizan Franzin[3] · Iêda Aparecida Pastre[4] · Fernando Luis Fertonani[4]

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Abstract The aim of this work was to evaluate the thermal and kinetic behavior of white lupin (*Lupinus albus*) oil obtained from its seeds. White lupin is a seed from the *Lupinus albus* species, and it presents physicochemical and physiological functional properties and is rich in fiber, protein, and lipids with a great application potential. Oil was extracted from the seeds, and its fatty acid profile indicates predominantly monounsaturated fatty acids (~65%). Thermo-gravimetry, derivative thermo-gravimetry, and differential scanning calorimetry (DSC) were used to characterize the thermal behavior of the oil fraction at high temperatures, showing a good thermal stability between 222 and 230 °C and a large heat delivery at $T = 400$ °C. Additionally, DSC was performed from 25 to −60 °C, in which the crystallization behavior was verified. The kinetic behavior of the thermal decomposition was evaluated from several β values and mass samples (5 and 20 mg) under nitrogen and oxygen atmospheres to comparisons of the data.

✉ Gustavo Guadagnucci Fontanari
gufontanari@gmail.com

✉ Marcelo Kobelnik
mkobelnik@gmail.com

[1] Departamento de Nutrição Faculdade de Saúde Pública, Universidade de São Paulo (FSP/USP), São Paulo, Brazil

[2] Centro Universitário do Norte Paulista (UNORP), São José do Rio Preto, SP, Brazil

[3] Departamento de Química Analítica, Instituto de Química, Universidade Estadual Paulista (Unesp), Araraquara, SP, Brazil

[4] Departamento de Química e Ciências Ambientais, Instituto de Biociências, Letras e Ciências Exatas, Universidade Estadual Paulista (Ibilce/Unesp), São José do Rio Preto, SP, Brazil

Keywords Lupin oil · Fatty acids composition · Thermal behavior · Transition phase

Introduction

Vegetable oil is recognized as world commodity. In the past years, the oil consumption has increased. On the other hand, recent data have shown a low growth in total oil production. Thereby there is a trend of the lack of this resourse to satisfy global demand, being necessary to find other unconventional oils at lower prices [1, 2]. The Vegetable oil is recognized as world commodity and as alternative, lupin is a legume commonly consumed in Mediterranean countries, but also in Australia, South Africa, and South America. The lupin planting can easily adapt to different climates and also grow for the purpose of fixing nitrogen in the soil [3]. This legume has aroused interest in several areas of research because it presents large amounts of fiber, protein, and lipids in its composition. In relation to the protein, lupin has around 30–37% great potential for human food use, when comparable to 40% of protein and approximately 20% of oil present in soybean [4]. Studies show that this protein has hypocholesterolemic and hypoglycemic effect [5–7] and also presents functional and physicochemical properties when incorporated into food systems [8–10].

However, there has been little discussion about the lupin oil composition and its healthy characteristics [2, 11, 12]. In addition to protein and fiber, the lupin also features around 11–18% oil in its composition [13, 14], presenting great potential of the application, but this is underexplored and its properties and behavior thermal are little known. Thermal stability to oxidation is an important parameter for vegetable oils, they provide values that allow better control for the oil processing, and the data can be used for

correlation with the time for the storage of these products. Thus, thermal analysis techniques have been used to evaluate and establish the thermo-oxidative parameters of oils and vegetable fats [14–16], targeting sustainable development, replacement for depleting fossil oil resources and development of new foods with health claims [17–19].

In this work, the aim was to evaluate the lipid profile, the thermal and kinetic behavior of the oil obtained from white lupin (*Lupinus albus*) seeds. The results of the present study improve the knowledge on this oil, including its crystallization behavior and thermal behavior. The kinetic evaluation was based on three experimental TG curves, according to recommendations of ICTAC [20]. Nevertheless, the experimental data were obtained with two mass samples in nitrogen and oxygen atmospheres, in order to determine the effect of this change on the results and also on the kinetic behavior [21–23]. Moreover, the activation energy (E_a/kJ mol^{-1}) data were obtained of the TG/DTG curves applying the iso-conversional method proposed by Capela, Capela and Ribeiro [23].

Experimental

Materials

The mature seeds of a sweet variety of white lupin (*Lupinus albus*) were obtained from IAPAR (Agronomic Institute of Paraná), Londrina, PR, Brazil. Alkaloids were removed by soaking the seeds in water at 50 °C, three times a day, for 5 days. Afterward the seeds were oven-dried at 50 °C and pulverized in a hammer grinder with a 0.4-mm sieve [24]. The lupin oil was obtained, with *n-hexane* (analytical reagent), in an extraction bath at ambient temperature. The *n-hexane* phases were removed and concentrated in a rotary evaporator.

Methods

Lipid profile

Fatty acid profile of the oil extracted from lupin was determined using the method of Folch et al. [25], followed by lipid methylation to produce fatty acid methyl esters according to Hartman and Lago [26]. The fatty acids' determination was carried out on GC-2010 Gas Chromatograph Shimadzu, Tokyo, Japan, fitted with a SP2560 fused silica column (100 m × 0.25 mm I.D., film thickness × 0.20 µm by Supelco). The oven temperature was programmed to rise from 100 to 235 °C at the rate of 10 °C min^{-1} under the following conditions: carrier gas H_2 (2.5 mL min^{-1}), split ratio 50:1, flame ionization detector (FID) 250 °C. The peaks of fatty acids were identified by comparison with the retention time of a standard mixture of fatty acids methyl esters (37 FAME Mix 47,885, Supelco). The results were expressed as a percentage of the area of each peak over the total area of all fatty acids in the chromatogram.

Thermal analysis

TG/DTG and DSC curves were obtained from a SDT 2960 and a DSC 2910, both from TA Instruments, respectively. The TG/DTG curves were carried out using sample sizes of about 10 mg in an α-alumina crucible with heating rates of $\beta = 5$, 10 and 20 °C min^{-1} under nitrogen and oxygen atmosphere with flow of 100 mL min^{-1}. The evaluation of the oxidative behavior was performed with the evaluation of DSC curve, which was carried out under an oxygen flow of 100 mL min^{-1} and heating rate of 20 °C min^{-1}, with a mass sample of about 5 mg, placed in an open aluminum crucible. For the transition phase study, the DSC curves were obtained from DSC1 Stare from Mettler Toledo, with mass sample was about 5 mg in an aluminum crucible with cover and cooled in the range of (25 °C $\leq \Delta T \leq$ −60 °C) and subsequently heated in the range of (−60 °C $\leq \Delta T \leq$ 25 °C), both at a cooling/heating rate of 1 °C min^{-1} under nitrogen atmosphere (flow rate 100 mL min^{-1}).

Kinetic methodology

The ICTAC Kinetics Committee has recommended conditions to obtain kinetic data for thermo-analytical curves [20]. It is important to note that this Committee suggests three or more curves, because it has been considered that statistics require three minimal quantities of TG curves. Thus, this recommendation is followed in this paper because the uses of three curves are not a limiting condition for the kinetic study. Moreover, this would not affect the work, but allows the discussion and preparation of new work by us and other authors. We also consider appropriate to use more than one sample mass and also purge gas in order to favor an interpretation of kinetic data as much as possible.

Kinetic evaluation was carried out according to a previously reported protocol analysis. This procedure allows there producibility and comparison of the data with the literature [14, 16, 18, 27]. Therefore, the kinetic analysis was carried out under non-isothermal conditions, considering the integral kinetic equation defined by

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

where $\beta = \mathrm{d}T/\mathrm{d}t$ 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.

The kinetic parameters are obtained by fitting Eq. (1) to experimental data. As a consequence, the evaluation of the integral on the right side of Eq. (1), known as temperature integral, is required. A difficulty results from the fact that this integral does not have an exact analytical solution. Thus, it is convenient to approximate the integral of the temperature for some function that yield suitable estimates to these kinetic parameters.

In this work, the kinetic parameters are obtained using an iso-conversional method on approximation to the temperature integral based on the convergent of a Jacobi fraction, proposed by Capelaet al [23]. This approximation is a rational function, given by the following equation:

$$\int_{x}^{\infty} \frac{\exp(-z)}{z^2} \mathrm{d}z = \frac{\exp(-x)}{x} \frac{x^3 + 14x^2 + 46x + 24}{x^4 + 16x^3 + 72x^2 + 96x + 24} \tag{2}$$

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 for temperature (T_α), values for activation energy (E_α) and values for pre-exponential factor (A_α).

Replacing the integral in Eq. (1) by the approximation given in Eq. (2) obtains the following expression for heating rate β as function of the $x_\alpha = 10^3/RT_\alpha$:

$$\beta = \frac{\exp(B_\alpha - E_\alpha z_\alpha)}{x_\alpha} \frac{E_\alpha^3 z_\alpha^3 + 14E_\alpha^2 z_\alpha^2 + 46E_\alpha z_\alpha + 24}{E_\alpha^4 z_\alpha^4 + 16E_\alpha^3 z_\alpha^3 + 72E_\alpha^2 z_\alpha^2 + 96E_\alpha z_\alpha + 24}, \tag{3}$$

where the activation energy is in kJ/mol^{-1} and the parameter B_α is defined as:

$$B_\alpha = \ln\left(\frac{10^3 A_\alpha}{Rg(\alpha)}\right) \tag{4}$$

The estimates of the E_α and B_α can be obtained by the nonlinear fitting of Eq. (3) to the β values as a function of x_α.

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:

$$\hat{A}_\alpha = \frac{R}{10^3} \exp(\hat{B}_\alpha) g(\alpha) \tag{5}$$

Results and discussion

Table 1 shows the results of the fatty acid composition of *Lupinus albus* oil obtained in this work by gas chromatography analysis. In comparison with data of Table 1, Sbihi et al. [2] showed the a high content of essential fatty acids and monounsaturated fatty acids (MUFA) in lupin seeds, being the oleic acid predominant in the *Lupinus albus* oil.

The oil profile obtained in the present work to this variety contains higher amounts of oleic and lower amounts of linoleic acid compared with several authors that found values ranged about 50–60% oleic acid and 16–23% linoleic acid. These differences from Sbihi HM [2] results are explained by environment and planting conditions [12, 28]. For example, the *Lupinus termis*, from Egypt soil, the major fractions fatty acid was oleic acid (41.9%) followed by linoleic acid (23.4%) [11], in Saudi Arabia soil, the major fraction was the same profile with 44.93% for oleic acid and 26.25% of linoleic acid for *Lupinus albus* [12].

The content of oleic fatty acid obtained (Table 1) is similar to that found in olive oil [29]. Olive oil is recommended for consumption because it promotes benefits to health presenting physiological functional properties, mainly on cardiovascular system, attributed to monounsaturated fats in its composition, as oleic acid [30]. In Brazil, the soybean oil is the most consumed; however, it presents the linoleic fatty acid as a major component (approximately 54%) and its oleic fatty acid fraction corresponds to only 22% of its total composition [17].

Other dominant fractions were linoleic and linolenic acids among other fatty acids. These two fatty acids are considered essential because they cannot be synthesized in the body and must be obtained from the diet.

In humans, both fatty acids use the same enzymes and compete with each other for enzyme availability, because of that, the balance of n-6/n-3 fatty acids plays an important role in maintaining homeostasis and human normal

Table 1 Fatty acid composition of lupin (*Lupinus albus*) oil; obtained in the present work by chromatography method[b]

Fatty acid	Mean value[a]/%
Palmitic (C16:0)	10.3 ± 0.08
Stearic (C18:0)	2.4 ± 0.07
Arachidic (C20:0)	0.9 ± 0.06
Behenic (C22:0)	2.6 ± 0.07
Oleic (C18:1 n9)	60.2 ± 0.08
Cis-11-Eicosenoic (C20:1 n9)	3.5 ± 0.07
Erucic (C22:1 n9)	1 ± 0.07
α-Linolenic (C18:3 n3)	6.1 ± 0.06
Linoleic (C18:2 n6c)	13 ± 0.08

[a] Mean ± standard deviation

[b] (Chromatograph method: Folch et al. [25] and Hartman and Lago [26])

development [31]. It has been estimated that the present Western diet is imbalanced in n-3 fatty acid consumption.

During evolution, there was a balance in the intake of n-6 and n-3 with a ratio of n-6/n-3 = 1. In this context, the lupin emerges useful for nutritional purposes because of its low ratio of n-6/n-3 = 2 [31]. Thus, the lupin (*Lupinus albus*) oil presents a great potential for industrial processing and can be extracted for human consumption in culinary preparations.

It is well known that the distinction between the thermal characteristics of various vegetable oils is due, mainly to differences in the distribution of fatty acids in the sample. Thus, the complexity of the thermal profiles of vegetable oils can vary due to the principal constitutes.

Figures 1 and 2 show TG/DTG curves of lupin oil with different mass of 5 and 20 mg obtained under different atmospheres: oxygen and nitrogen. Figure 1 shows four steps of mass loss under oxygen atmosphere in agreement with DTG curve, for a mass sample of 5 mg. The first mass loss step occurs between $(195 \leq \Delta T \leq 365)$ °C with overlapping reactions, as confirmed by DTG curves. These overlapped mass losses correspond to a total mass loss of 45.86%. The DTG curve shows other three mass loss steps, which occur between: 1—first step for $(365 \leq \Delta T \leq 405)$ °C with a mass loss of 19.07%; 2—second step for $(405 \leq \Delta T \leq 455)$ °C with a mass loss of 16.33%; and 3—third step for $(455 \leq \Delta T \leq 556)$ °C with a mass loss of 16.89%. These steps are corroborated by DTG curves, with $T_{peaks} = 320$, 380, 428 and 477 °C, all of them are sharp peaks except $T_{peak} = 320$ °C, that shows as large peak profile.

Figure 2 shows TG/DTG curves obtained for the extracted lupin oil under nitrogen atmosphere and 20 mg of oil sample. The thermal behavior shows two loss steps occurring in: 1—first step for $(207 \leq \Delta T \leq 323)$ °C with a mass loss of 4.53%; and 2—second step for

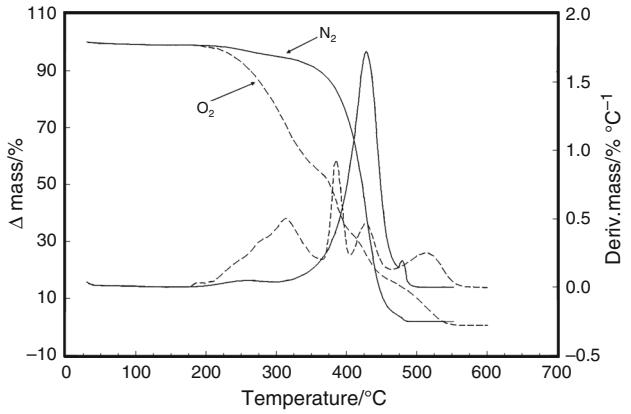

Fig. 1 TG/DTG curves of lupin oil with mass of 5 mg in oxygen and nitrogen atmospheres; heating rate of 20 °C min^{-1}; gas flow of 100 mL min^{-1}

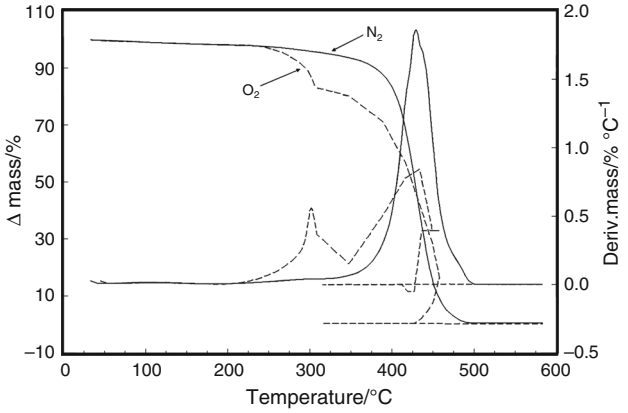

Fig. 2 TG/DTG curves of lupin oil with mass of 20 mg in oxygen and nitrogen atmospheres; heating rate of 20 °C min^{-1}; gas flow of 100 mL min^{-1}

$(323 \leq \Delta T \leq 485)$ °C with a mass loss of 91.71%. The first mass loss step was ascribed to oil evaporation or as "*smoke point*" as it is commonly known in science of food. In this fact, the temperature at which enough volatile compounds "*emerge*" from the oil and the smoke becomes clearly visible.

At this temperature range, $(207 \leq \Delta T \leq 323)$ °C are released from the oil, volatile compounds such as free fatty acids and short-chain degradation products of oxidation. This event is characterized by slow kinetic process and associated with a low mass loss and was ascribed to the gaseous materials elimination from the sample [32].

This same behavior was not observed under oxygen atmosphere, due to the oxidation reaction occurring between the volatile species and oxygen. In nitrogen atmosphere was observed a small peak in DTG curve at $T_{peak} = 478$ °C suggesting a carbonaceous residue formation effectively observed for 5 mg samples.

Furthermore, Fig. 2 shows TG/DTG curves obtained for oil mass of 20 mg, in nitrogen atmosphere (Fig. 2). The thermal behavior for 20 mg mass oil is very similar to that obtained for sample mass of 5 mg under the same atmosphere. By the other side, the TG/DTG profiles obtained under oxygen atmosphere are so different from curves carried out with 5 mg.

TG/DTG curves, in oxygen atmosphere, show two steps of mass losses: 1—fist step for $(220 \leq \Delta T \leq 310)$ °C with a mass loss of 17,50%; and 2—second step for $(310 \leq \Delta T \leq 318)$ °C with a mass loss of 82,50% and shows an overlap of other three subsequent steps. This overlapped step shows an instantaneous heat release, moving instantaneously the sample temperature by ~135 to 455 °C, and immediately returning to the furnace temperature at 320 °C. This instantaneously temperature sample changes were ascribed to the combustion of the heavy fraction oil and are in agreement with DSC curve,

Fig. 3 that shows an intense and characteristic instantaneously oxidation peak.

The DSC curve shown in Fig. 3 was performed with sample mass of 5 mg in oxygen atmosphere and shows two large exothermic events between 160 and 350 °C. These events can be ascribed to the removal of volatile oils fractions in corroboration with TG/DTG curves in Fig. 1. Besides, in the temperature range of $(300 \leq \Delta T \leq 500)$ °C, we can see an intense, curved and well-defined exothermic peak, characteristic of an intense heat release. This peak was ascribed to the combustion of the heavy fraction of the oil, which is corroborated by TG curve (Fig. 1).

Nevertheless, these oils were also evaluated by DSC analysis with cooling and re-heating in a nitrogen atmosphere, which are shown in Fig. 4. During the cooling, the oils sample exhibited two well distinguishable events between $(0 \leq \Delta T \leq -7)$ °C and from $(-36 \leq \Delta T \leq -55)$ °C. The first event was ascribed to the rearrangement of the fatty acids in the sample, which cause the deviation of the baseline [16, 33]. The second exothermic reaction was ascribed to the crystallization step of the oleic acid specie, which is the major constituent of this oil. Nevertheless, these events should be evaluated by X-ray diffraction to be better elucidated.

Figure 4 shows the heating step of this oil, and we can observe a melting complex behavior in the temperature range $(-33 \leq \Delta T \leq 10)$ °C. This behavior appears due to the overlapping of the endothermic melting process considering the complex nature of the oil constitution (Table 1). However, using only DSC technique there is no way to determine the effective origin of each peak among the overlapped melting peaks in this temperature range $(-33 \leq \Delta T \leq 10)$ °C. Therefore, in this temperature range, the melting of two or more fatty acids can occur simultaneously, resulting in broad or overlapping melting peaks in DSC curve [33].

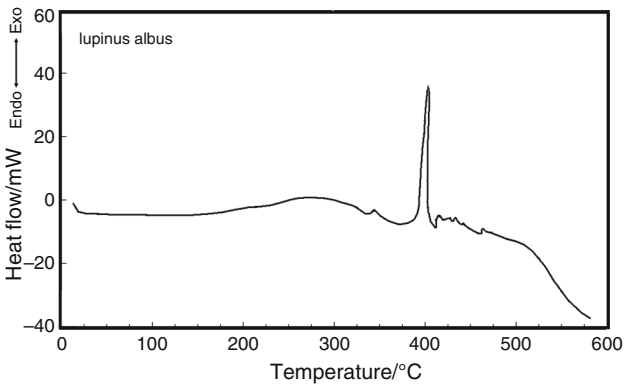

Fig. 3 DSC curve of lupin oil mass of 5 mg in oxygen atmosphere, aluminum crucible and heating rate of 20 °C min^{-1}; gas flow of 100 mL min^{-1}

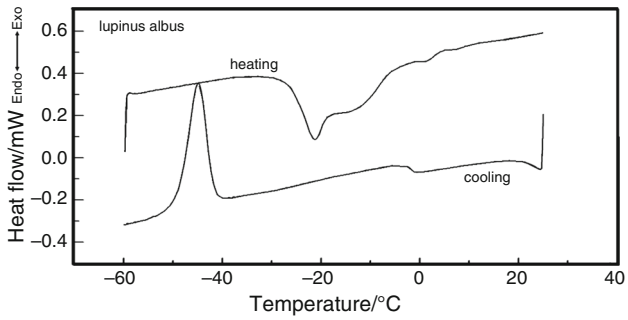

Fig. 4 DSC curves of under heating and cooling between 25 and −60 °C; mass sample was 5 mg; heating rate of 1 °C min^{-1} in nitrogen atmosphere; gas flow of 100 mL min^{-1}

Kinetic parameters

The kinetic parameters of the thermal decomposition of this oil were evaluated from DTG curves obtained in nitrogen and oxygen gases purge. Figure 5 shows the thermal behavior of the lupin oil in nitrogen atmosphere for different values of $(5 \leq \beta \leq 15)$ °C min^{-1}. The TG/DTG curves were obtained in triplicate for the kinetic purposes as suggested in the literature.

The lupin oil thermal behavior shows mass loss occurring in two steps as previously shown (Fig. 1), in nitrogen atmosphere. The first step of loss mass occurs in the temperature range of $(185 \leq \Delta T \leq 280)$ °C, which was ascribed to the as "*smoke point*" process of the oil during the heating, as aforementioned, and the second step occurs in the temperature range of $(280 \leq \Delta T \leq 500)$ °C which shows only one thermal decomposition process, without evidences in DTG curve about overlapping reactions. However, there is an exception seen during the mass loss end step wich is possible to observe that there was the formation of a shoulder, suggesting an additional reaction.

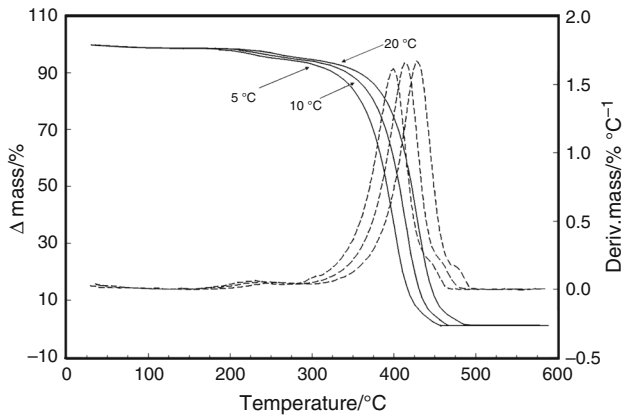

Fig. 5 TG/DTG curves of lupin oil showed heating rate of 5, 10, and 20 °C min^{-1}; mass sample of 5 mg in nitrogen atmosphere; gas flow of 100 mL min^{-1}

Furthermore, the activation energy of the first mass loss step, ($185 \leq \Delta T \leq 280$) °C, of all β values used to kinetic studies was not calculated because this reaction was suggested as evaporation process and not as thermal decomposition. Thus, only the second mass loss step was used to do the kinetic investigations.

Figure 6 shows the distribution of the heating rate (β) in function of the $1000/RT_{\alpha}$ of the second decomposition stage for sample of 5 mg of lupin oil (under nitrogen streaming), where it can be observed the adjustment of the variation for activation energy (E_a) and also the correlation coefficient (r) values. The average values of the E_a of the kinetics data obtained from TG curves are summarized in Table 2, and the graphical representation of the activation energy (E_a) *versus* conversion degree (α) values for lupin oil is shown in Fig. 7.

As aforementioned, the distinction between the thermal characteristics of various vegetable oils is due mainly to differences in the distribution of fatty acids in the sample. Thus, the complexity of the thermal profiles of vegetable oils can vary due to the amount of the main components.

So, the evaluation of the samples under nitrogen and oxygen can help with more information on the interpretation of the kinetic behavior of this sample [15, 16, 18].

In nitrogen atmosphere studies, we can see that for sample of 20 mg, after the $\alpha = 0.1$, the activation energy shows a stable profile in the activation energy, and likewise, for sample of 5 mg, the kinetic behavior maintains the same feature on the extension of conversion degree (α).

This fact suggests that there was no change in behavior kinetic during the mass loss. Nevertheless, the E_a kinetic value obtained for a mass sample oil of 20 mg is higher than that obtained for 5 mg, which can be ascribed to the difference in the amount of sample used to obtain each of the TG/DTG curves.

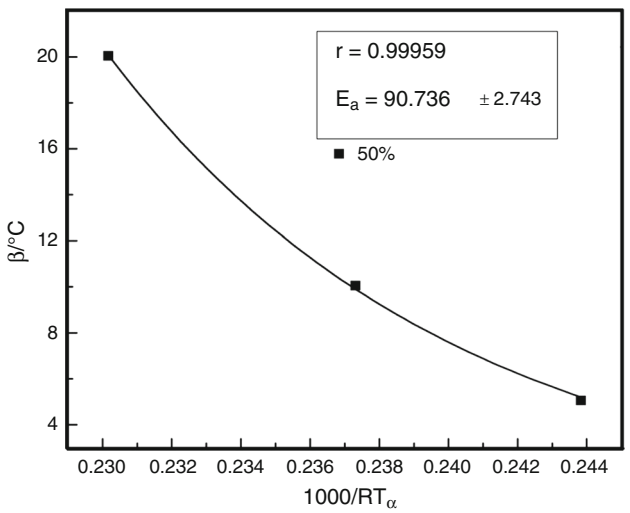

Fig. 6 Diagram of dispersion of β versus degree conversion ($\alpha - 50\%$) with the adjustment functions of the lupin oil for first decomposition step with 5 mg in nitrogen atmosphere

Table 2 E_a/kJ mol^{-1} and correlation coefficient (r) for the thermal decomposition step in different atmospheres

Compound	Sample mass	[a]E_a/kJ mol^{-1}	[a]r
Lupin oil	5 mg (nitrogen)	88.61 ± 0.02	0.99952
	20 mg (nitrogen)	94.30 ± 0. 14	0.99139
	5 mg (oxygen)	52.22 ± 0.12	0.99912
	20 mg (oxygen)	63.46 ± 0.10	0.99499

[a] Average

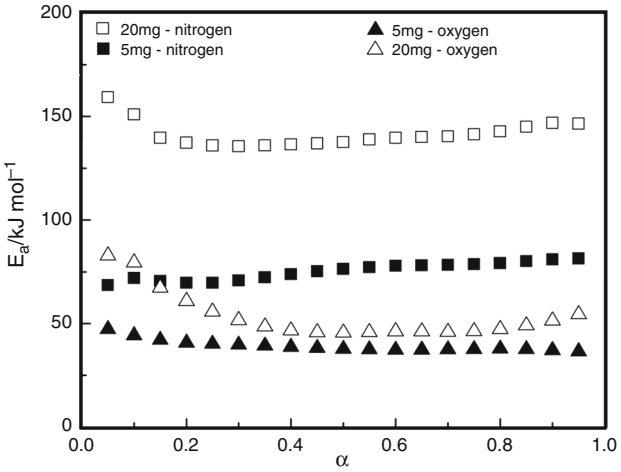

Fig. 7 The calculated E_a/kJ mol^{-1} as a function of α for lupin oil under oxygen and nitrogen atmospheres

By the other side, the studies carried out under oxygen atmosphere, for oil samples mass of 5 and 20 mg they can also be seen that there are tendencies of the activation energy remain stable and approximately equal throughout the extent of the degree of conversion, $0.3 \leq \alpha \leq 0.8$.

Besides, the nonvolatile species oxidation by the oxygen atmosphere from temperature range of ($280 \leq \Delta T \leq 500$) °C may be favorable to the formation of products of low activation energy when compared with nitrogen atmosphere. This fact also was not observed in the previous work [27], for bicuíba oil (*Virola bicuhyba*) where the studied oil showed a wide variation in the composition of fatty acids.

Conclusions

The lupin oil presents lipid profile similar to other sources of oils, as olive oil, and can be of great potential use for human consumption. The values of chromatographic analyses (gas chromatography) reveal the predominance of

the monounsaturated oleic fatty acid (n-9). In the present work, an experimental investigation has been conducted to examine the effect of several conditions used to evaluate the lupin oil. The TG curves have shown the thermal behavior and also exhibit a comparison of this oil in two atmospheres, both conditions demonstrating the differences in trends of mass losses. DSC curves of the cooling of this oil reveal one main crystallization stage and during the heating they demonstrated overlapping peaks ascribed to the melting of the fatty acids presents in the sample. Furthermore, the thermal studies carried out on non-isothermal TG provide a comparison of the oil behavior during thermal analysis as well as allow that it can be seen from the resemblance between the two different mass samples, with a better evaluation of kinetic parameters. Finally, these findings provide to the literature technical information that assist in processing on the lupin, especially this obtained oil, enabling its use in food and other possible applications.

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References

1. Nehdi IA, Sbihi H, Tan CP, Al-Resayesa SI. Evaluation and characterisation of Citrullus colocynthis (L.) Schrad seed oil: comparison with Helianthus annuus (sunflower) seed oil. Food Chem. 2013;136(2):348–53.
2. Sbihi H, Nehdia IA, Tanb CP, Al-Resayes SI. Bitter and sweet lupin (Lupinus albus L.) seeds and seed oils: a comparison study of their compositions and physicochemical properties. Ind Crops Prod. 2013;49:573–9.
3. Cazzato E, Laudadio V, Stellacci AM, Tufarelli V. Influence of sulphur application on protein quality, fatty acid composition and nitrogen fixation of white lupin. Eur Food Res Technol. 2012;235(5):963–9.
4. Liu K. Chemistry and nutritional value of soybean components in soybeans: chemistry, technology, and utilization. Boston: Springer; 1997. p. 25–113.
5. Sirtori CR, Lovati MR, Manzoni C, Castiglioni S, Duranti M, Magni C, Morandi S, D'Agostina A, Arnoldi A. Proteins of white lupin seed, a naturally isoflavone-poor legume, reduce cholesterolemia in rats and increase LDL receptor activity in HepG2 cells. J Nutr. 2004;134(1):18–23.
6. Bettzieche A, Brandsch C, Schmidt M, Weisse K, Eder K, Stangl GI. Differing effect of protein isolates from different cultivars of blue lupin on plasma lipoproteins of hypercholesterolemic rats. Biosci Biotechnol Biochem. 2008;72(12):3114–21.
7. Fontanari GG, Batistuti JP, Cruz RJ, Saldiva PHN, Arêas JAG. Cholesterol-lowering effect of whole lupin (Lupinus albus) seed and its protein isolate. Food Chem. 2012;132(3):1521–6.
8. Jayasena V, Nasar-Abbas SM. Development and quality evaluation of high-protein and high-dietary-fiber pasta using lupin flour. J Texture Stud. 2012;43(2):153–63.
9. Castilho F, Fontanari GG, Batistuti JP. Avaliação de algumas propriedades funcionais das farinhas de tremoço doce (Lupinus albus) e feijão guandu (Cajanus cajan (L) Millsp) e sua utilização na produção de fiambre. Food Sci Technol (Campinas, Braz). 2010;30:68–75.
10. Xu J, Mohamed A. Thermal and rheological properties of Lupinus albus flour. J Am Oil Chem Soc. 2003;80(8):763–6.
11. Hassanein MM, El-Shami SM, El-Mallah MH. Investigation of lipids profiles of Nigella, lupin and artichoke seed oils to be used as healthy oils. J Oleo Sci. 2011;60(3):99–107.
12. Alamri MS. Characterization of lupin seed oils extracted from bitter and sweet types. Pak J Food Sci. 2012;22:161–7.
13. Martinez-Villaluenga C, Frias J, Vidal-Valverde C. Functional lupin seeds (Lupinus albus L. and Lupinus luteus L.) after extraction of alpha-galactosides. Food Chem. 2006;98(2):291–9.
14. Marques MR, Fontanari GG, Kobelnik M, Freitas RAMS, Arêas JAG. Effect of cooking on the thermal behavior of the cowpea bean oil (Vigna unguiculata L. Walp). J Therm Anal Calorim. 2015;120(1):289–96.
15. Kobelnilk M, Fontanari GG, Cassimiro DL, Ribeiro CA, Crespi MS. Thermal behavior of coffee oil (Robusta and Arabica species). J Therm Anal Calorim. 2014;115(3):2045–52.
16. Kobelnik M, Cassimiro DL, Dias DS, Ribeiro CA, Crespi MS. Thermal behavior of araça oil (Psidium cattleianum Sabine). J Therm Anal Calorim. 2012;108(3):1281–6.
17. Samyn P, Schoukens G, Vonck L, Stanssens D, Abbeele HV. Quality of Brazilian vegetable oils evaluated by (modulated) differential scanning calorimetry. J Therm Anal Calorim. 2012;110(3):1353–65.
18. Kobelnik M, Cassimiro DL, Dias DS, Ribeiro CA, Crespi MS. Thermal behavior of jerivá oil (Syagrus romanzoffiana). J Therm Anal Calorim. 2011;106(3):711–5.
19. Stewart KK, Whitake JR. r. Modern methods of food analysis, ed. Springer Netherlands. Ift Symposium Basic Series, 1983, New Orleans. 1984, New Orleans.
20. Vyazovkin S, Chrissafis K, Lorenzo MLD, Kogad N, Pijolate M, Roduitf B, Sbirrazzuolig N, Suñolh JJ. ICTAC Kinetics Committee recommendations for collecting experimental thermal analysis data for kinetic computations. Thermochim Acta. 2014;590:1–23.
21. Kobelnik M, Bernabé GA, Ribeiro CA, Capela JMV, Fertonani FL. Decomposition kinetics of iron (III)-diclofenac compound. J Therm Anal Calorim. 2009;97(2):493–6.
22. Souza JL, Kobelnik M, Ribeiro C, Capela J, Crespi M. Kinetic study of crystallization of PHB in presence of hydroxy acids. J Therm Anal Calorim. 2009;97(2):525–8.
23. Capela JV, Capela M, Ribeiro C. Rational approximations of the Arrhenius integral using Jacobi fractions and gaussian quadrature. J Math Chem. 2009;45(3):769–75.
24. Fontanari GG, Martins JM, Kobelnik M, Pastre IA, Arêas JAG, Batistuti JP, Fertonani FL. Thermal studies on protein isolates of white lupin seeds (Lupinus albus). J Therm Anal Calorim. 2012;108(1):141–8.
25. Folch J, Lees M, Sloane-Stanley G. A simple method for the isolation and purification of total lipids from animal tissues. J Biol Chem. 1957;226(1):497–509.
26. Hartman L, Lago RC. Rapid preparation of fatty acid methyl esters from lipids. Lab Pract. 1973;22(6):475–6.
27. Kobelnik M, Fontanari GG, Soares RAM, Figueiredo AG, Ribeiro CA. Study of the thermal behavior of bicuíba oil (Virola bicuhyba). J Therm Anal Calorim. 2014;115(3):2107–13.

28. Boschin G, D'Agostina A, Annicchiarico P, Arnoldia A. Effect of genotype and environment on fatty acid composition of Lupinus albus L. seed. Food Chem. 2008;08(2):600–6.
29. Choudhury N, Tan L, Truswell AS. Comparison of palmolein and olive oil: effects on plasma lipids and vitamin E in young adults. Am J Clin Nutr. 1995;61(5):1043–51.
30. Covas M-I. Olive oil and the cardiovascular system. Nutr Pharmacol. 2007;55(3):175–86.
31. Simopoulos A. Evolutionary aspects of diet: the omega-6/omega-3 ratio and the brain. Mol Neurobiol. 2011;44(2):203–15.
32. Ismail R. Palm oil and palm olein frying applications. Asia Pac J Clin Nutr. 2005;14(4):414.
33. Marangoni AG, Aurand TC, Martini S, Ollivon M. A probabilistic approach to model the nonisothermal nucleation of triacylglycerol melts. Cryst Growth Des. 2006;6(5):1199–205.