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Influence of toasting on the nutritious and thermal properties of flaxseed

P. S. Epaminondas · K. L. G. V. Araújo · A. Lima de Souza · M. C. D. Silva · N. Queiroz · A. L. Souza · L. E. B. Soledade · I. M. G. Santos · A. G. Souza

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Abstract Chemical and thermal analyses of golden and brown flaxseeds were carried out for raw and toasted seeds aiming at evaluating their nutritional and thermo-oxidative properties. Moisture, lipids, protein, soluble carbohydrates, and ash contents were quantified. Concerning lipids and proteins, in average, no meaningful differences were observed for the two varieties, being also equivalent to the literature data. The golden variety had a lower amount of fibers and a higher amount of soluble carbohydrates than the brown variety. The techniques of thermogravimetry and differential scanning calorimetry were applied for elucidating the thermal degradation process of the seeds. The toasted gold and brown seeds were more stable to thermal decomposition than the raw seeds, under oxidative conditions. Golden seeds seem to be more susceptible to oxidation than brown seeds, under toasting conditions. Finally, no meaningful advantages were observed for the golden seeds in comparison to the brown ones.

Keywords Flaxseed · Omega-3 · Toasting · Functional food · Thermal decomposition

P. S. Epaminondas · K. L. G. V. Araújo · A. L. de Souza
Programa de Pós-Graduação em Ciência e Tecnologia de Alimentos, CT, Universidade Federal da Paraíba, Campus I, João Pessoa, PB 58051-970, Brazil

P. S. Epaminondas
Instituto Federal de Educação, Ciência e Tecnologia (IFPB), Campus Sousa, Sousa, PB 58800-970, Brazil

M. C. D. Silva
Centro de Ciências Sociais, Saúde e Tecnologia, Universidade Federal do Maranhão, Campus II, Imperatriz, MA 65901-000, Brazil

N. Queiroz · A. L. Souza · L. E. B. Soledade · I. M. G. Santos · A. G. Souza (✉)
Laboratório de Combustíveis e Materiais (LACOM), Departamento de Química, CCEN, Universidade Federal da Paraíba, Campus I, João Pessoa, PB 58059-900, Brazil
e-mail: agouveia@quimica.ufpb.br

Introduction

Flaxseed is widely known as a functional food as its frequent consumption provides benefits for human health. This seed is composed by basic nutrients (minerals, vitamins, proteins, and lipids) besides chemical compounds with beneficial properties as poliphenols and tocopherols (antioxidants), Omega-3 fatty acids (antiinflammatory), fibers (laxative), and lignins (anticarcinogenic) [1–4]. Therefore, flaxseed is often applied as a diet complement for the preventive treatment of cardiovascular diseases, intestine and prostate carcinomas, diabetes, and also against obesity [3, 5–10]. Flaxseed extract can also be used in the synthesis of cyclic fatty acids [11].

Flaxseed is frequently commercialized in two basic varieties, brown and golden, having comparable nutritional attributes. In spite of this, the golden grains are preferred instead of the other variety. For both, consumers usually toast the seeds in order to restrain some anti-nutritional compounds present in flaxseed, as cyanogenic glycoside, anti-vitamin B_6, and phytic acid, despite these substances are not toxic when consumed in the recommended amounts [12]. The problem of the toasting process is the higher tendency of oxidation of some polyunsaturated fatty acids (omega-3 and omega-6) [2, 13].

Therefore, this study aims at evaluating the effects of the toasting process on the characteristics and thermo-oxidative properties of the golden and brown flaxseed varieties

by means of chemical identification and thermal analysis techniques.

Experimental

Golden and brown flaxseeds were obtained from Paraoara Alimentos Naturais (Jaboatão dos Guararapes, PE, Brazil), with commercial degree. Each variety was divided in two approximately equal parts. One of these parts was heat treated at 160 °C for 15 min (toasted seed) while the other one was used as received (raw seed). Thus, four groups of samples were obtained, being denoted as raw golden flaxseed (RGFS), raw brown flaxseed (RBFS), toasted golden flaxseed (TGFS), and toasted brown flaxseed (TBFS). Later, all samples were characterized in triplicate and thermally evaluated as described below.

The moisture and ash content were quantified by means of thermal treatment at 105 and 550 °C, respectively, under room atmosphere. The protein quantity was determined by the Micro-Kjeldahl method, using an automatic digester (Tecnal, TE-007D) and a distiller (Tecnal, TE-0363). A nitrogen to protein conversion factor of 5.41 was used as recommended for this kind of samples. The total lipid content was determined by Soxhlet extraction, using hexane and reflux periods of 6 h. All previous procedures were performed according to the methods determined by the Association of Official Analytical Chemists [14].

The soluble carbohydrates were quantified using a spectroscopic method, applying an aqueous solution of 9,10-dihydro-9-oxoanthracene as an indicator dye [15]. After solubilization, absorbance values of the solutions at 620 nm were measured in a UV-2550 ultraviolet–visible spectrophotometer (Shimadzu) and compared to the absorbance values obtained from calibration curves of standard solutions containing 5, 10, 15, 20, 25, 30, 35, and 40 g L^{-1} of glucose. The total content of fibers was calculated from difference, subtracting from 100% the sum of the contents of moisture, fats, proteins, ash, and soluble carbohydrates.

The thermogravimetric (TG) and calorimetric (DSC) curves were recorded using a SDT 2960 thermal analyzer (TA Instruments) and DSC 2920 (TA Instruments), respectively. The non-isothermal method was applied, using 10 mg of sample heated at 10 °C min^{-1} up to 600 °C. The measurements were performed using platinum crucibles and 50 mL min^{-1} of synthetic air. For the isothermal measurements, 160 °C was applied as isothermal temperature in the same experimental conditions previously described.

Results and discussion

Table 1 shows the nutritional composition of the RGFS and RBFS. The average amounts of ash and fibers were higher for the RBFS than for the RGFS samples, contrasting with the other parameters. Both samples showed adequate levels of nutrients, confirming the possibility of their use as dietary products [10]. The moisture of the RBFS (6.6%) and of the RGFS (7.2%) were lower than the maximum value (8%) specified for stored flaxseed [16] preventing biological degradation due to fungal infection. Mueller et al. [10] found a moisture amount of 7.4 and 7.3% for RBFS and RGFS, respectively. Coskuner and Karababa [17] found even lower moisture contents in flaxseed (6.1%), whereas Selvi et al. [18] reported values above the standard ones (8.3%).

Table 1 Chemical analyses for the RGFS and RBFS samples

Parameter/%	Flaxseed	
	Raw golden	Raw brown
Moisture	$7.2^{a} \pm 0.2$	$6.6^{b} \pm 0.2$
Lipids	$40.0^{a} \pm 0.7$	$38.6^{b} \pm 0.2$
Protein[A]	$23.1^{a} \pm 0.01$	$21.9^{b} \pm 0.3$
Soluble carbohydrates	$1.12^{a} \pm 0.07$	$0.91^{b} \pm 0.07$
Others/including fibers[B]	$25.7^{b} \pm 0.9$	$28.2^{a} \pm 0.3$
Ash content	$2.9^{b} \pm 0.1$	$3.8^{a} \pm 0.1$

Average and standard deviation obtained from analysis in triplicate

[A] Conversion factor used from nitrogen to protein was 5.41

[B] Determined from difference

[a, b] Different letters in the same line indicate the statistic difference in the 5% level of probability in the Student's *t* test

In this study, the average ash contents of 2.9 and 3.8% determined for the RGFS and RBFS samples, respectively were very similar to the values reported by Muir and Westcott [19] (3.4%) and Mueller et al. [10] (3.3% for RGFS and 3.5% for RBFS) and lower than the value reported by Oomah and Mazza [20] (4.8%).

The average lipid contents of the brown (38.6%) and the golden (40.0%) varieties were similar to the content obtained by Oomah and Mazza [21] (40.4%), but lower than the contents reported by Oomah and Mazza [20] in another paper (43.8%) and by Mueller et al. [10] (45.2% for RBFS and 44% for RGFS). The oil content of a flaxseed depends on the cultivation methods and on the geographical aspects of the producing region.

The protein contents obtained for the golden (23.1%) and the brown (21.9%) flaxseed varieties were similar to the values found by Mueller et al. [10] (23.3 and 23.4%, respectively) and higher than the contents reported by Oomah and Mazza [20, 21] (20.3 and 19.2%). The protein contents of this study were much higher than the values reported by Oomah et al. [22] (8.2–19.3%) but a conversion factor from nitrogen to protein of 6.25 was used by these authors which is higher than the value used in this study and also by Mueller et al. [10] and Oomah and Mazza [20, 21].

A higher content of soluble carbohydrates and a lower content of fibers were noticed for the RGFS (1.12 and 25.7%, respectively) than for the RBFS (0.91 and 28.2%, respectively). This may justify the softer flavor and texture of the golden flaxseed, compared to the brown one. The results of this study are in agreement with the average results of total carbohydrates (29.4% for RGFS and 27.8% for RBFS) reported by Mueller et al. [10].

Figure 1 shows the TG and DTG curves of the raw and toasted seeds. The results are summarized in Table 2. In all cases, four different decomposition steps were observed with no meaningful difference among the profiles of the TG curves (Fig. 1). It should be emphasized that similar values were observed for the different flaxseed parameters (Table 1) and the mass loss corresponding to the different thermal decomposition steps (Table 2), as it will be showed later.

The first mass loss step was assigned to dehydration (between 30 and 200 °C), with mass losses of 6.8% (RGFS) and 6.2% (RBFS). The higher mass loss due to dehydration observed for RGFS was in agreement with the moisture contents determined by the classical method (Table 1). By means of the final temperatures of the first step, it can be inferred that RGFS and RBFS had the same thermal stability up to 170 °C.

The toasted seeds presented, as expected, lower mass losses for the first step, 5.4% (TGFS) and 5.5% (TBFS). These seeds also had a higher final temperature (T_f) for the first decomposition step (192 and 197 °C, for the golden and brown varieties, respectively) than the raw flaxseeds (170 °C for both varieties). This behavior was due to the elimination of primary water during toasting.

Figure 2 displays the isothermal TG and DSC curves, at 160 °C, of the four samples. It can be noticed that these results agree with the TG curves shown in Fig. 1. Only the thermal losses related to the first TG step occurred at 160 °C for 2 h, suggesting that the toasting process of raw seeds, at this temperature, did not lead to nutritional losses. It was also observed that toasting led to the dislocation of the TG curves to higher temperatures (Fig. 2a), with smaller final mass losses. This behavior was due to the elimination of primary water during toasting process.

Table 2 Thermogravimetric data of the different flaxseed samples

Sample	Step	T_i/°C[a]	T_f/°C[b]	T_{pDTG}/°C[c]	Δ_m/%[d]
RGFS	First	29	170	78	6.8
	Second	170	388	314	41.9
	Third	388	469	416	24.6
	Fourth	469	625	512	23.2
	Residue	–	–	–	2.4
RBFS	First	30	170	74	6.2
	Second	170	388	349	42.9
	Third	388	471	418	22.9
	Fourth	471	634	516	23.9
	Residue	–	–	–	2.9
TGFS	First	25	192	85	5.4
	Second	192	393	375	43.2
	Third	393	480	414	27.0
	Fourth	480	611	516	21.5
	Residue	–	–	–	1.5
TBFS	First	25	197	70	5.5
	Second	197	386	361	43.3
	Third	386	466	425	22.7
	Fourth	466	611	512	24.7
	Residue	–	–	–	2.4

[a] Initial temperature

[b] Final temperature

[c] Peak temperature DTG

[d] Mass loss

According to literature, besides dehydration other different endothermic events occur at the same temperature, as starch gelatinization and protein denaturation [22–25]. Oomah et al. [22] investigating the thermal characteristics of the proteins isolated from flaxseed, observed initial denaturation temperatures varying from 85.7 to 97.1 °C.

In this study, no meaningful difference was observed among the endothermic peaks of the DSC curves (Fig. 2b) due to the toasting process, indicating that protein desaturation or starch gelatinization were not detected.

The loss of the nutritional value of the flaxseed began in the second mass loss step (Fig. 1). A sequence of exothermic events was observed, as indicated in the DSC

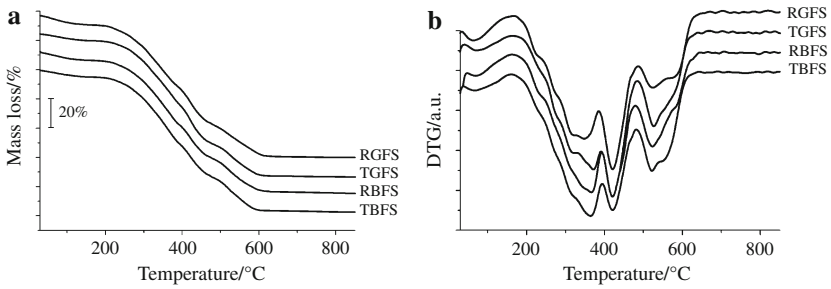

Fig. 1 TG (**a**) and DTG (**b**) curves of the raw and toasted flaxseed samples

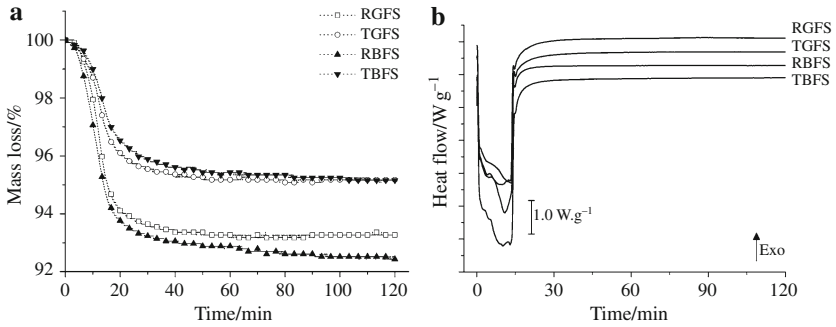

Fig. 2 Isothermal curves at 160 °C of the raw and toasted flaxseed samples. **a** TG and **b** DSC

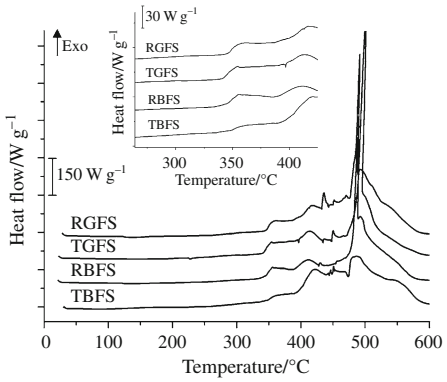

Fig. 3 Non-isothermal DSC curves for the different flaxseed samples

curves (Fig. 3), characterizing the combustion of the organic material present in the seeds.

In the second step, the meaningful mass loss of 42–43% was assigned to the carbohydrate combustion, to the beginning of hemicellulose, to the cellulose decomposition, and to the triglycerides degradation, comprising oxidation of the fatty acids [26, 27]. It should be observed that the mass loss amount of this step was similar to the lipid concentration, as shown in Tables 1 and 2. In this second step, the toasted seeds presented higher values of initial and peak temperatures than the raw ones, indicating that products with higher stability were formed delaying the decomposition [2]. We believe that these products were formed due to oxidation reactions. A higher increase in peak temperature upon toasting was observed for the golden seeds.

According to literature, line seeds have antioxidants, including secoisolariciresinol digluycoside, flavonoids, and tocopherols, which are found in shells and seed meals [10]. This protection depends on a wide variety of factors, such as system temperature and atmosphere [2]. Although toasting does not lead to the decomposition of the seeds, it degrades the endogenous antioxidants and damages the cellular structures for the lipid storage, favoring water elimination, lipase action, facilitating the oxygen attack [2, 28]. As a consequence, toasted seeds may undergo oxidation with the formation of new flaxseed degradation products, which are more resistant to thermal decomposition. In this study, these processes probably led to the formation of higher stability products detected in the second mass loss step of the TG curves.

In nuts and seeds with a higher carbohydrate contents, such as soybean [29], toasting contributes positively to the formation of antioxidant products (melanoidines) that are produced from the Maillard reaction and improve the thermo-oxidative stability [30]. However, Cämmerer and Kroh [2] pointed out that the free carbohydrates content in flaxseed is of about 1%, which is too low to produce melanoidine antioxidants that compensate such negative effects. They also stressed that the polysaccharides, available in the form of fibers, are quite stable and do not participate significantly of the Maillard reaction.

In practice, oxidation processes can occur, for instance, when previously toasted flaxseeds are utilized in feed prepared at higher temperatures, such as cakes, breads, and cookies, leading to nutritional losses. The ideal would be the ingestion of raw flaxseed, once the daily recommended intake (1–2 teaspoons per day) can not provoke toxicity [10].

The third mass loss step (23–27%) was assigned to the thermal degradation of fibers, mainly the lignin ones, while the fourth step was attributed to protein degradation (22–25%). This mass loss amount was similar to the protein content, as shown in Tables 1 and 2. According to literature, the higher thermal stability of the proteins in relation to the other compounds is due to the different protein functional groups that lead to ionic and hydrophobic interactions as well as to hydrogen bondings and disulfide linkages or disulfide–sulfydryl (SS–SH) interactions [26, 27].

Analyzing the residue contents obtained from the TG curves (Table 2), their magnitude was rather lower than the ash contents determined by classic gravimetry. This was due to the differences in the final temperature, which was 550 °C in the classic gravimetry (Table 1) and 900 °C for thermogravimetry (Table 2).

Conclusions

Brown flaxseed is nutritionally similar to the golden flaxseed and both are equally plentiful in important lipids, proteins, and fibers, conferring thus a functional activity for

both grains. The toasting process exposes the lipids and other constituents to oxidative processes, especially for golden seeds. The formation of oxidation products lead to a higher thermal stability of the toasted seeds when submitted to new thermal processes and might lead to a health risk, not yet quantified.

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