Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 271–275

THERMAL ANALYSIS IN SUSTAINABLE DEVELOPMENT
Thermoanalytical study of faveleira seeds (*Cnidoscolus Quercifolius*)

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Taking into account the problems of desertification and agricultural practices able to provide income to the population at the semi-arid region of North-East Brazil, this work presents the results of the chemical and thermal characterization by TG and DSC of the seed derivatives of *Cnidoscolus quercifolius*, hereinafter called faveleira, aiming at the application of these materials as an alternative of food source for animals and for the human population at this region. The faveleira seed derivatives present thermodynamic properties similar to the ones of other foods utilized for human use, as well as an acceptable calorific value. According to TG and DSC results, was verified that the faveleira derivatives presents good thermal and oxidative stabilities.

Keywords: *Cnidoscolus quercifolius, DSC, faveleira, semi-arid, sustainable development, TG*

Introduction

The semi-arid region of North-East Brazil faces to the problems of desertification and unfeasibility of the economic exploitation of exotic cultures. Thus, it is necessary to make efforts, of course including the deepening of research activities, of exploiting species adapted to the Brazilian semi-arid region [1].

The *Cnidoscolus quercifolius* species, locally known as faveleira, deserves its prominence, among other plants of this region. Due to its resistance to the dry environment and its scattering over a remarkable area of the semi-arid region of North-East Brazil. Consequently, there is the potential of huge amounts of raw material, for the extraction process of the oil and flour by industries. Other factor of great importance is the local of occurrence of the faveleira: in semi-arid lands of low fertility, which present small interest for an economical exploitation of the existing cultures. Previous studies indicate a good perspective for the utilization of these materials as human and animal food and thus, the possibility of their industrial utilization [2, 3].

Therefore, this work aims to characterize the seed derivatives of *Cnidoscolus quercifolius*, hereinafter called faveleira, in terms of their chemical and thermal properties (TG/DSC), with the purpose of the application of these materials as an alternative for human and animal food.

Experimental

Samples

The seeds of faveleira were collected in experimental unities of EMBRAPA (Brazil governmental organization for agriculture research) of various regions of the Paraíba state, Brazil. Flour, peel and almond samples were obtained at different particle sizes, denominated as A and B, whose mean particle sizes are 1.19 and 1.64 cm, respectively. The faveleira seed oil was extracted according to the procedure used by Ahmad [4] and the fatty acid composition was analysed according to the methodology of AOCS, American Oil Chemists Society [5].

Chemical characterization

The moisture, ash, carbohydrate, nitrogen and protein content of the solid samples (flour, almond and peel) can be determined using standardized methods by Adolfo Lutz Institute [6] and according to their TG curves [7]. The data of standardized methods as a results of three parallel measurements.

The fatty acid compositions were determined using gas chromatograph equipped with flame ionization detector. The experimental conditions were the following: helium carrier gas (1 mL min^{-1}) and synthetic air atmosphere (400 mL min^{-1}) was used. The column pressure was 80 kPa and split injection mode

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1388–6150/$20.00

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Springer, Dordrecht, The Netherlands

was applied using HP-INNOWA column. The injector temperature was 250°C and the temperature of the detector was 280°C. The temperature was 120°C for 1 min and then it was increased with 8°C min^{-1} up to 210°C (55 min).

The moisture (%), color, density (g cm^{-3}), acidity value (mg KOH g^{-1}), iodine content (g I 100^{-1} g^{-1}), saponification number (mg KOH g^{-1}) and viscosity (mPa s) of the oils were determined according to AOCS methods [5]. The rheological behavior of each sample was evaluated using a Brookfield, LV-DVII rheometer at 25°C, applying different shear rates. All the results obtained by conventional methods are the means of three measurements for each oil samples.

Thermal analysis

The TG/DTG curves were recorded to study the thermal stability and to determine the moisture and ash contents of the faveleira seed derivatives. A Shimadzu TGA-50 thermobalance and alumina crucibles was used. The TG/DTG curves were recorded using 10.0±0.5 mg sample mass at heating rate of 10°C min^{-1} under air purging (30 mL min^{-1}) all along in the 25–800°C temperature range.

The DSC curves were recorded to determine the enthalpies of the thermal decomposition of the faveleira seed derivatives, under nitrogen atmosphere (50 mL min^{-1}). A Shimadzu DSC-50 differential scanning calorimeter was employed, operating from room temperature up to 500°C, at a heating rate of 10°C min^{-1}. From the DSC data, the specific heat capacities of the faveleira seed were determined.

Results and discussion

Chemical analysis

The moisture and ash contents for the faveleira seed derivatives obtained by standardized and TG methods, for different particle sizes are collected in Table 1.

The nitrogen, protein and carbohydrate content of the faveleira seed derivatives are listed in Table 2.

The faveleira seeds have been used for cattle food and there is no report of human intoxication due to its use. On the other hand, no conclusive scientific study was yet undertaken to confirm the toxicity of the use of the faveleira seed derivatives in human food. The faveleira seed flour is rich in mineral salts (ash) and proteins and it can be an alternative human food, depending on the aforementioned toxicological study. The protein content of the flour is concentrated in the almond. Thus, to obtain a protein rich food, it is necessary to raise the amount of the almond in the mixture. In terms of oil yield, it should be stressed that it varies between 35 and 50 mass% of the whole seed. The chemical composition of the fatty acids present in the faveleira seed oil are listed in Table 3.

The faveleira seed oil is very similar to other edible vegetable oils [9], regarding their fatty acids composition, e.g., the predominance of linoleic acid. The moisture content, acidity, saponification number, color, den-

Table 1 Moisture and ash contents (%) of the faveleira seed derivatives

Faveleira derivatives	Thermogravimetric method		Standardized method	
	moisture	ash	moisture	ash
Flour A	4.1	4.2	3.7	3.4
Flour B	5.8	4.1	5.9	4.0
Peel A	6.7	2.0	6.4	2.3
Peel B	7.9	2.9	7.7	2.8
Almond A	4.6	3.9	4.6	3.5
Almond B	4.8	3.9	5.1	4.0

Table 2 Nitrogen, protein and carbohydrate contents (%) of derivatives of faveleira seed

Derivatives	Nitrogen/%	Protein/%	Carbohydrate/%
Flour A	8.4	52.50	23
Flour B	6.7	41.87	23
Peel A	2.2	13.75	12
Peel B	2.6	16.25	12
Almond A	9.2	57.50	34
Almond B	9.8	61.25	34

Table 3 Fatty acid composition of the faveleira seed oil

Fatty acids	Composition/%
Palmitic acid	22.0
Linoleic acid	41.6
Stearic acid	30.5
Myristic acid	1.3
Oleic acid	0.8
Saturated	53.8
Unsaturated	42.4
Total	96.2

Table 4 Physico-chemical parameters of the faveleira seed oil

Parameters	Results
Moisture/%	0.4520
Color	1.0000
Density/g cm^{-3}	0.9125
Viscosity/mPa s	44.0000
Saponification value/mg KOH g^{-1}	280.7300
Acidity value/mg KOH g^{-1}	0.1080
Iodine value/g I 100^{-1} g^{-1}	110.0000

sity and iodine content of the faveleira oil obtained by conventional methods are listed in Table 4.

The properties of faveleira oil (Table 4) are similar to those reported by other authors [8, 9], with special regard to their moisture and acidity contents. This oil has a high potential of achieving the required standards for human consumption as edible oil due to its low moisture and low acidity and high saponification number.

In the refining process, the faveleira seed oil presents some advantageous features, for instance, its low free acid content (within the range admitted in the edible vegetable oil standard) and the absence of need of clarification. It has a yellow color, color value of 1.0 desirable for the edible vegetable oil. Such oil also displays a Newtonian rheological behavior and it can easily be extracted in a laboratory.

The aroma and the flavor encourage the use as edible oil. After being used for frying, it does not cause smoke formation and maintains the food without any change in its aroma and flavor content. After eight months of storage, the faveleira seed oil was shown to keep its perfect conservation conditions and it did not present rancidity, maintained unchanged its organoleptic quality.

The aforementioned advantages of faveleira seed oil are the high percentage of fatty materials, easy laboratory extraction, color, acidity, conservation of aroma and flavor, coupled to the potential use of the faveleira seed flour as a human food supply, due to its high protein contents, encourage a detailed study on the feasibility of the industrial faveleira seed processing.

Thermal analysis

The thermal decomposition behavior of the faveleira seed derivatives varies depending on the type of the derivative. The thermogravimetric behavior of the faveleira seed oil (Fig. 1) displays three decomposition steps between 220–550°C, indicating a high stability, when it is compared to other edible vegetable oils [8, 9]. The TG profile of the faveleira flour samples showed water loss between 25–120°C, and two thermal decomposition steps, related to the loss of their constituents in the range of 180–680°C causing 69.3 and 21.7% mass losses, respectively (Figs 2a and b). The residue (ash) at 800°C is about 4%.

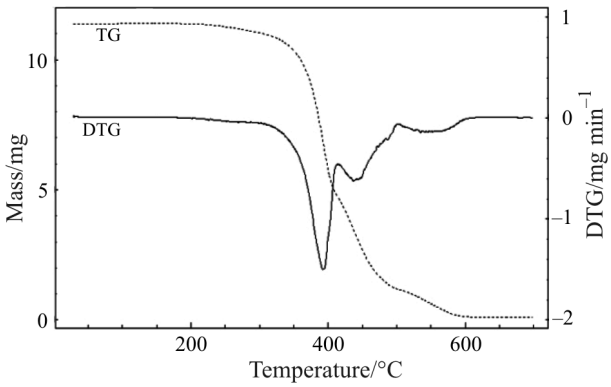

Fig. 1 TG/DTG curves of the faveleira seed oil

The numerical values taken from the TG curves are listed in Table 5.

The peel samples presented one dehydration step between 25–140°C, two steps related to the thermal decomposition between 170–610°C, exhibiting 42.0 and 46.3% mass losses, respectively. The residue (ash) remains at 800°C is about 2–3%. The almond samples exhibit similar thermal characteristics, with one dehydration step between 25–160°C, and two decomposition steps for proteins, carbohydrates and lipids in the range of 180–700°C. The mass losses upon decomposition were 71.0 and 19.6%, respectively. The residue (ash) remains at 800°C was about 4%. The faveleira seed oil presented three thermal decomposition steps between 90 and 500°C, indicating its high thermal stabilities, when it was compared to other edible vegetable oils [9]. The other two events correspond to the decomposition of its constituents.

The DSC curves of the faveleira seed derivatives exhibit different profiles, in which endothermic transitions can be observed (Figs 3a and 3b), corresponding to the decomposition of their main constituents (lipids, carbohydrates and proteins).

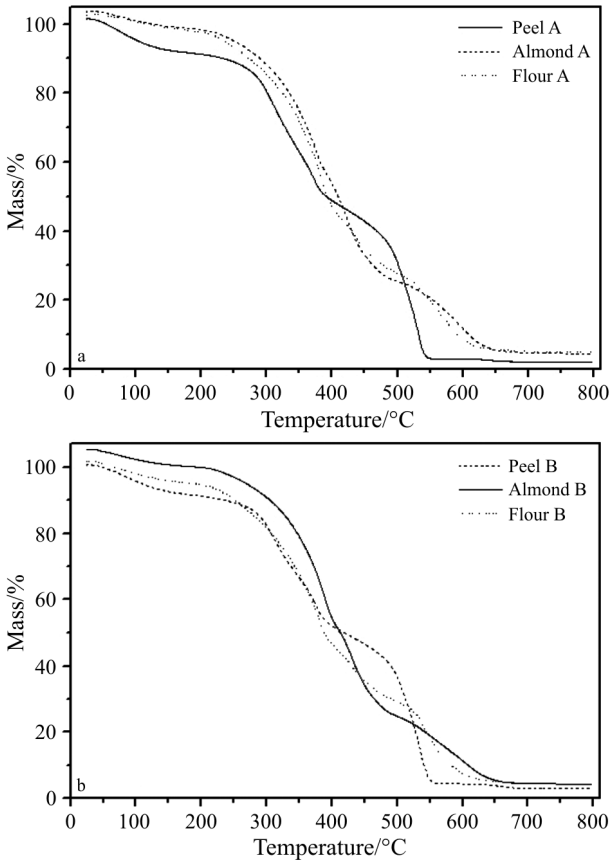

Fig. 2 TG curves of the faveleira seed solid derivatives at different particle sizes: a – 1.19 cm, b – 1.64 cm

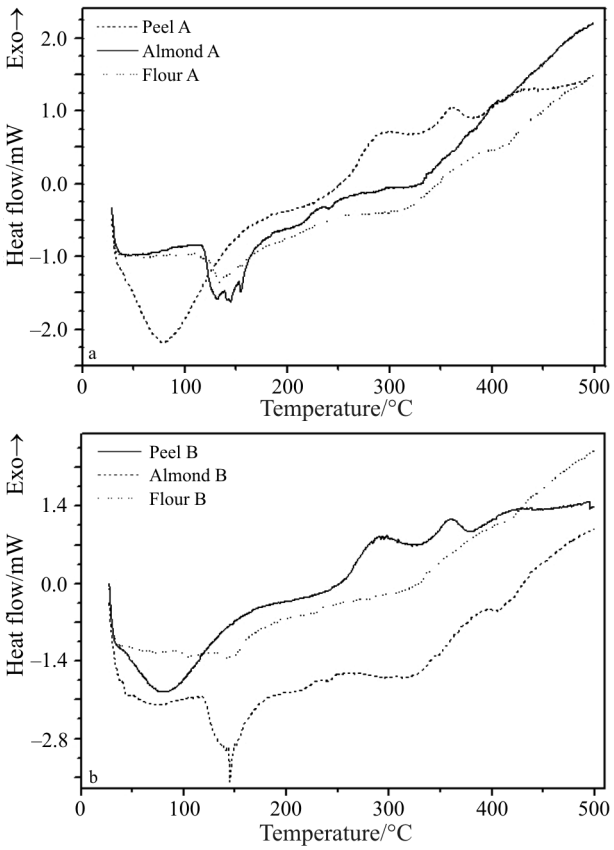

Fig. 3 DSC curves of the solid derivatives of the faveleira seed at different particle sizes: a – 1.19 cm, b – 1.64 cm

From the total integration of DSC curves concerning to the thermal decomposition process of the faveleira seed derivatives in the 25–500°C range, their mean calorific values can be estimated (kJ g^{-1}). The values obtained were: oil (0.32), flour A (1.37), flour B (1.48), peel A (0.66), peel B (0.79), almond A (1.24) and almond B (1.18). These values are similar to the ones of other foods utilized for human use [2]. The decomposition enthalpy values for the samples investigated by DSC are summarized in Table 6.

Heat capacity (C_p) measurements

The specific heat capacities of liquid phase (oil) and solid phase (almond and flour) samples were determined according to the previously described method. The specific heat capacity values of the faveleira seed derivatives are listed in Table 7. For most of the samples, the specific heat capacity values did not vary substantially with the temperature.

Table 5 Thermogravimetric data of the faveleira derivatives

Faveleira seed derivatives	1st step		2nd step		3rd step	
	T_p/°C	Δm/%	T_p/°C	Δm/%	T_p/°C	Δm/%
Oil	385.2	59.5	446.0	30.9	547.9	9.5
Flour A	106.6	4.8	371.7	68.9	564.6	21.3
Flour B	91.4	6.7	365.5	64.7	556.4	24.0
Peel A	87.7	9.6	332.1	45.0	512.2	43.3
Peel B	91.8	9.2	336.2	43.1	519.1	44.9
Almond A	96.3	5.1	380.7	70.7	583.1	19.7
Almond B	88.2	5.0	386.7	71.5	575.4	19.2

*T_p=peak temperature and Δm mass loss in %.

Table 6 Molar decomposition enthalpy (ΔH_D/J mol^{-1}) obtained by DSC

Derivatives	1st step	2nd step	3rd step
Oil	0.71	0.05	12.80
Flour A	39.44	42.31	6.46
Flour B	28.05	29.38	9.74
Peel A	520.20	16.42	16.09
Peel B	490.33	26.27	18.68
Almond A	60.21	12.33	1.77
Almond B	49.29	50.52	8.22

Table 7 Specific heat capacities of the faveleira seed derivatives

Faveleira seed derivatives	C_p/J g^{-1} °C^{-1}				
	40°C	60°C	80°C	100°C	120°C
Oil	1.625	1.689	1.702	1.806	1.834
Flour A	0.948	0.826	0.800	–	–
Flour B	0.978	0.867	0.851	–	–
Almond A	0.996	0.930	0.907	–	–
Almond B	0.994	0.856	0.836	–	–

Conclusions

The study of the thermoanalytical properties of the faveleira seed derivatives contributes to a better understanding of the chemical changes of these materials when they are exposed to increasing and/or high temperatures. According to the herein described results, the faveleira seed derivatives present thermodynamic properties similar to those of other foods utilized for human use, as well as an acceptable calorific value. According to TG and DSC results, was verified that the faveleira derivatives presents good thermal and oxidative stabilities.

The present work contributes to the incorporation of the faveleira to the economy of the semi-arid region of North-East Brazil, for the production of flour for human use, of almond for the production of edible vegetable oil and for the production of other derivatives for animal use. Besides, further studies are needed to investigate the presence of toxins in the faveleira seed derivatives.

Acknowledgements

The authors acknowledge to CNPq and FAPESQ/PB for financial support.

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