Thermal Characterization of the Favelone Derivatives (Cnidoscolus Quercifolius) by Thermogravimetry and Differential Scanning Calorimetry

José Carlos Oliveira Santos^{1*}, Lionete Dantas Nunes¹, Sylvia Berenice Puzinski Nóbrega¹, José Pires Dantas¹, Antonio Gouveia Souza²

Abstract

A thermal analysis has been applied to characterization of food and food products. Taking into account the problems of desertification and agricultural practices able to provide income to the population at the semi-arid region of Northeastern Brazil, this work presents the results of the chemical, thermal and kinetic characterization by thermogravimetry and differential scanning calorimetry of the seed derivatives of favelone (*cnidoscolus quercifolius*), aiming at the application of these materials as an alternative of food source for animals and for the human population at this brazilian region.

Keywords: Favelone, *cnidoscolus quercifolius*, TG, DSC, semi-arid

¹ Departamento de Química, Centro de Ciências e Tecnologia, Universidade Estadual da Paraíba, UEPB, Av. das Baraúnas 351, Campus Universitário, Bodocongó, 58109-753, Campina Grande, Paraíba, Brazil.

² Departamento de Química, Centro de Ciências Exatas e da Natureza, Universidade Federal da Paraíba, Campus I, Cidade Universitária, 58059-900, João Pessoa, Paraíba, Brazil.

* Author for correspondence: E-mail: zecarlosuepb@yahoo.com.br
Phone/Fax: 55-83-33153352

Introduction

The semi-arid region of Northeastern Brazil faces 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 (Figure 1), locally known as favelone, deserves its prominence, among of the 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 Northeastern Brazilian. 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 favelone: in semi-arid lands of low fertility. Previous studies indicate a good perspective for the utilization of these materials as human and animal food and, thus, the possibility of their industrialization [2, 3].

Figure 1 – *Cnidoscolus quercifolius* plant.

Therefore, this work aims a characterization of the seed derivatives of *cnidoscolus quercifolius*, hereinafter called favelone, 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 foods.

Materials and Methods

Materials

The seeds of favelone were collected in experimental unities of EMBRAPA (Brazilian governmental organization for agriculture research) of various regions of the Paraíba state, Brazil.

The samples of flour, peel and almond were obtained at different particle sizes, denominated as A and B, whose mean particle sizes are respectively 1.19 cm and 1.64 cm.

The favelone seed oil was extracted according to the procedure used by Ahmad [4], and its analysis regarding the fatty acid composition was carried out according to the methodology of American Oil Chemists Society (AOCS) [5].

Chemical characterization

The moisture, ash, carbohydrate, nitrogen and the protein contents of the solid samples (flour, almond and peel) can be determined by standardized methods, as utilized by the Adolfo Lutz Institute [6], and by thermogravimetric curves [7]. The values obtained by such standardized methods are the mean results of three determinations for each sample.

The fatty acid compositions were determined using a gas chromatograph equipped with flame ionization detector. The following conditions were used: carrier gas: helium (1 mL/min); atmosphere: synthetic air (400 mL/min); column pressure: 11.5 psi; injection mode: split; injector temperature: 250 °C; detector temperature: 280 °C; column: HP-INNOWA; and temperature program: 120 °C (1 min) and increase of 8 °C/min up to 210 °C (55 min).

The moisture, color, density, acidity value, iodine value, saponification value and viscosity of the oils were determined according to AOCS methods [5]. The rheological behavior of each sample was evaluated (rheometer Brookfield, LV-DVII) at room temperature (25 °C), using different shear rates. The parameter values obtained by conventional methods are the mean results of three determinations for each oil sample.

Thermal analysis

The TG/DTG curves were obtained with the purpose of studying the thermal stability and obtaining the moisture and ash contents of the favelone seed derivatives. It was used a thermobalance (Shimadzu, TGA-50), under air atmosphere (30 mL/min), using an alumina crucible, in non-isothermal conditions. The TG/DTG curves were obtained using a sample mass of 10.0 ± 0.5 mg, heating rate of $10\text{ }^{\circ}\text{Cmin}^{-1}$, at the 25 – 800 $^{\circ}\text{C}$ temperature range.

The DSC curves were determined with the objective to study the enthalpic transitions regarding the thermal decomposition of the favelone seed derivatives, under nitrogen atmosphere (50 mL/min). A differential scanning calorimeter (Shimadzu, DSC-50) was employed, operating at the temperature range from room temperature up to 500 $^{\circ}\text{C}$, with a heating rate of $10\text{ }^{\circ}\text{Cmin}^{-1}$. From the DSC data, were determined the specific heat capacities of the favelone seed. Such DSC data were obtained from DSC curves performed both for the investigated samples and for alumina, the reference material.

The heat capacities of the favelone derivatives were determined from the data obtained by DSC. The calculations were based on implementation of the temperature program. The oil samples were heated at a rate of $5\text{ }^{\circ}\text{Cmin}^{-1}$ up to 30 $^{\circ}\text{C}$ during five minutes. Then, they were heated at a rate of $10\text{ }^{\circ}\text{Cmin}^{-1}$ up to 200 $^{\circ}\text{C}$ during five minutes.

The following ratio was used to calculate the heat capacities:

$$c = \frac{m_0 c_0}{m} \cdot \frac{S_3 - S_1}{S_2 - S_1} \quad (1)$$

where c_0 and c are the specific heat of the reference material and of the favelone derivatives, respectively; m_0 and m refer to the mass of rice bran oil samples and of the reference material, respectively, and S_1 , S_2 and S_3 are the thermal displacements of the DSC in relation to the blank, reference and sample, respectively [8].

Curso de Balanceamento de Equações Químicas
Contato com www.empresa.tchequimica.com

Chemical analysis

The moisture and ash contents for the favelone seed (Figure 2) derivatives obtained by the standardized and thermogravimetric methods, at different particle sizes, are listed in Table 1, for a comparative analysis.

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

Figure 2 – Favelone seeds

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

Favelone 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 the derivatives of favelone 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

The favelone 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 aspects of the use of the favelone seed derivatives in human food.

The favelone seed flour is rich in mineral salts (ash) and proteins and it can be an alternative for human food, depending on the aforementioned toxicological study. The protein value of the flour is concentrated in the almond. Thus, to obtain a protein richer food, it is necessary to raise the almond proportion the composition.

In terms of oil yield, it should be stressed that it varies between 35 and 50 weight percent of the whole seed. The chemical composition of the fatty acids present in the favelone seed oil is listed in the Table 3.

Table 3 – Fatty acid composition for the favelone 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

The favelone seed oil is highly similar to other edible vegetable oils [9], regarding the their fatty acids composition, e.g., the predominance of linoleic acid. The moisture content, acidity value, saponification value, color, density, and iodine value of the favelone oil, obtained by conventional methods, are listed in Table 4.

Table 4 – Physical and chemical parameters of the favelone seed oil

Parameters	Results
Moisture (%)	0.452
Color	1.0
Density (g/cm ³)	0.9125
Viscosity (mPa.s)	44.0
Saponification value (mg KOH/g)	280.73
Acidity value (mg KOH/g)	0.108
Iodine value (g I/ 100 g)	110.00

The favelone oil parameters, Table 4, are similar to those reported by other authors [8, 9], mainly for the moisture and acidity contents. This oil has a high potential of achieving the required standards for human consumption as edible oil, due to their low moisture and low acidity and high saponification value.

In the refining process, the favelone seed oil presents some advantageous features, for instance, its low free acidity (within the range admitted in the edible vegetable oil standard) and the absence of need of clarification. It presents 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 been used for frying, it did not cause smoke formation and maintained the food without any change in the aroma and flavor.

After eight months of storage, the favelone seed oil was shown to keep its perfect conservation conditions and it did not present rancidity, maintained unchanged its organoleptic quality.

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

Thermal analysis

The thermal decomposition behavior of the favelone seed derivatives varies according to the type of the derivative. The thermogravimetric behavior of the favelone seed oil (Figure 3) displays three decomposition steps between 220 – 550 °C, indicating a high stability, when compared with other edible vegetable oils [9, 10].

Figure 3 – TG/DTG curves of the favelone seed oil.

The thermogravimetric profile of the favelone flour samples showed one dehydration step (water loss) step between 25 - 120 °C, and two thermal decomposition steps, related to the loss of their constituents at the 180 - 680 °C range, of 69.3 and 21.7 % mass loss, respectively (Figure 4). The remaining residue (ash) at 800 °C is roughly of 4 %.

Figure 4 – TG curves of the favelone seed solid derivatives at different particle sizes.

Table 5 contains the TG/DTG data of the analyzed samples. The peel samples presented one dehydration step between 25 - 140 °C, and two steps of thermal decomposition, related the constituent loss at the 170 - 610 °C, presenting mass losses of

42.0 and 46.3 %, respectively. The residue (ash) remaining at 800 °C varied from 2 to 3%.

Table 5 – Thermogravimetric data of the favelone seed derivatives

Favelone derivatives	1 st step		2 nd step		3 rd step	
	T _p (°C)	%W	T _p (°C)	%W	T _p (°C)	%W
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 %W = weight loss

The almond samples presented similar thermal characteristics, with one step of dehydration between 25 - 160 °C, and two steps of decomposition for proteins, carbohydrates and lipids at the range from 180 °C to 700 °C. The decomposition mass losses were of 71.0 and 19.6 %, respectively. The residue (ash) remaining at 800 °C was of about 4 %.

The favelone seed oil presented three thermal decomposition steps between 90 and 500 °C (Table 6), indicating high thermal and oxidative stabilities, when compared with other edible vegetable oils [10]. The oil sample presented an exothermic event with a peak temperature of 115 °C, corresponding to its oxidation. The other two events correspond to the decomposition of its constituents.

Table 6 – Molar decomposition enthalpy (ΔH_D , J/g°C) obtained by DSC

Derivatives	1 st step	2 nd step	3 rd 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

The DSC curves of the favelone seed derivatives presented different profiles, in

which can be observed endothermic transitions, (Figure 5), corresponding to the decomposition of their principal constituents (water, lipids, carbohydrates and proteins).

Figure 5 – DSC curves of the solid derivatives of the favelone seed at different particle sizes.

From the total integration of DSC curves for the thermal decomposition process of the favelone seed derivatives at the 25 - 500 °C range, can be estimated their mean calorific values (cal/g). The values obtained were: oil (75.6), flour A (328.7), flour B (354.2), peel A (158.9), peel B (188.0), almond A (297.3) and almond B (281.9). These values are similar to the ones of other foods utilized for human use [2]. Table 6 contains the values of the decomposition enthalpy for the samples investigated by DSC.

Heat capacity (C_p)

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 favelone seed derivatives are listed in Table 7.

Table 7 – Specific heat capacities of the favelone seed derivatives

Favelone seed derivatives	C_p (J/g°C)				
	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	—	—

For most of the samples, the specific heat capacity values did not substantially vary as a function of temperature.

Conclusions

The study of the thermal analytical properties of the favelone seed derivatives contributes to a better understanding of the probable chemical changes of these materials when exposed to high temperatures. The favelone seed oil advantages of high percentage of fatty materials, easy laboratory extraction, color, acidity, conservation and aroma and flavor, coupled to the potential use of the favelone seed flour as a human food supply, due to its high protein contents, encourage a detailed study on the feasibility of the industrial favelone seed processing. Further studies are needed to investigate the presence of toxins in the favelone seed derivatives.

According to the herein described results, the favelone seed derivatives present

thermodynamic properties similar to the ones of other foods utilized for human use, as well as an acceptable calorific value. The present work contributes to the incorporation of the favelone to the economy of the semi-arid region of Northeastern 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.

References

1. BEZERRA, G. E., *Favela – Seu aproveitamento como forrageira*, Boletim Técnico, 30:1 (1972) 71-78.
2. LIMA, J. L. S., *Plantas forrageiras das caatingas*, edited by Embrapa, Petrolina, 1986, 44p.
3. DUQUE, J. G., *O Nordeste e as lavouras xerófilas*, edited by ESAM, Mossoró, 1980, 337p.
4. AHMAD, M. U., Hussain, S. K., Osman, S. M., *Extraction of oils: a review*, Journal American Oil Chemists Society 58:3 (1988) 673-679.
5. AOCS, *Official methods and recommended practices of the American Oil Chemist's Society*, edited by D. Firestone, v.1. Champaign, 1994.
6. LUTZ, A., *Normas Analíticas do Instituto Adolfo Lutz*, São Paulo, 1985, 210p.
7. AMORIM, J. A., Santos, J. C. O., Souza, A. G., *Thermal analysis of rice and by-products*, Journal of Thermal Analysis and Calorimetry 75:2 (2004) 393-398.
8. SANTOS, J. C. O., Santos, M. G. O., Souza, A. G., Conceição, M. M., *Comparative study of specific heat capacity determined by differential scanning calorimetry and microwave oven*, Journal Thermal Analysis and Calorimetry 79:2 (2005) 345-349.
9. SANTOS, J. C. O., Souza, A. G., Santos, I.M.G., Conceição, M. M., *Thermoanalytical, kinetic and rheological parameters of edible vegetable oils*, Journal Thermal Analysis and Calorimetry 75:2 (2004) 419-428.
10. SANTOS, J. C. O., Souza, A. G., Prasad, S., Santos, I.M.G., *Thermal stability and kinetic study of thermal decomposition of commercial edible oils by thermogravimetry*, Journal of Food Science 67:4 (2002) 1393-1398.