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THERMAL ANALYSIS OF THE POWDER AND THE BRAN OF ALGAROBA

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Abstract

The powder and the bran of algaroba pods, submitted to drying temperatures of 55, 65, 75, 85, 95 and 105°C, were studied by conventional and thermogravimetric methods. The dynamic thermogravimetric curves of the samples indicated the following thermal stability order: 105>55>65>95>85>75ºC. The powder and the bran of algaroba pods, dried at 55°C, presented protein content higher and isothermal thermogravimetric profiles comparable. The calorimetric curves of samples, dried at 55°C, indicated the gelatinization of starch.

Keywords: algaroba, gelatinization, isothermal

Introduction

Algaroba [*Prosopis juliflora* (SW) D. C.] is a leguminous vegetable species, un-oily, native of arid and semi-arid regions of the Americas, Africa and Asia, presenting an admirable range of adaptation. This species is used for the production of wood, charcoal, alcohol, molasses, human and animal food, apiculture, reforestation, garden-making and shading, rendering it a cultivar of social and economic value [1]. In the Brazilian northeast, these xerophytes, introduced in the beginning of the 40's, with the objective of animal feeding and to be used for reforestation, currently appears to be a possible alternative as a human food-source [2].

This plant produces large quantities of green beans of excellent palatability and good digestibility, containing 25–28% glucose, 11–17% starch, 7–11% proteins, 14–20% organic acids, pectin and other substances. Thus, algaroba contains about 43%

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sugars and starch, constituting an excellent fattening food, besides being relatively rich in proteins. It possesses about 3.75% ash content and the moisture content varies from 16–20% [3].

Thermal analysis constitutes a group of techniques of great interest in food characterization, since it provides relevant data for industrial processing [4, 5]. The analytical possibilities of thermogravimetry in the quality control of food has aroused the interest of research workers due to the reduction of the required sample quantity and the analysis time [6]. The amounts of moisture and ash in green beans of algaroba are quality parameters. The moisture content is used in biological control during storage and commercialization of the products and the ash content is used to indicate the quantity of minerals [7].

When starch is heated with water a gelatinization process occurs, which can be measured by differential scanning calorimetry. Gelatinization occurs at a temperature within the range of 50–70°C, depending on the variety of the starch and its origin. The gelatinization of starch is a molecular rearrangement and causes irreversible changes in its properties, such as: swelling of granules, fusion of initial crystals, loss of birefringency and dissolution of starch [8].

In this work had been studied the powder and the bran of algaroba pods, submitted to drying temperatures of 55, 65, 75, 85, 95 and 105°C, by conventional gravimetry, dynamic/isothermal thermogravimetric and calorimetric methods.

Experimental

Samples

The algaroba pods samples were collected from the Algaroba Green Bean Processing Unit for animal food, located in São Bento Farm, in the Coxixola municipality, Paraíba State. The samples were submitted to drying in a sterilization and drying oven, Olidef CZ, at temperatures of 55, 65, 75, 85, 95 and 105°C. They were ground in a bladed grinder, Marconi. Two products of algaroba pods were obtained the powder corresponding to the ground product, and the bran corresponding to the remainder (retained by the grinder sieve). The products were sieved through Granutest sieves, of 0.25 mm opening, corresponding to 60 mesh, to make the samples used as uniform as possible.

Conventional analysis

The conventional analysis in ovens was according to the Normas Analíticas do Instituto Adolfo Lutz [9], with each sample of 5 g, weighed in porcelain crucible, using an analytical balance Shimadzu, Libror AEL–40 SM.

The moisture analysis was done by dry heat in a sterilization and drying oven, Olidef CZ, at 105°C until constant mass, during about 4 h. Then, the samples were cooled in desiccator and weighed. In the ash analysis, the samples were carbonized on a Bunsen burner, followed by incineration in a furnace, Quimis, at 600°C for a period of 6 h and then they were cooled in a desiccator and weighed.

The percentage values of moisture and ash, obtained by the conventional gravimetric method, were the mean results of three determinations for each sample.

The moisture analysis by infrared radiation was done on a balance, Ohaus MB200, using about 10 g of the samples at a constant temperature of 105°C. The percentage values were the mean results of three determinations for each sample.

The protein analysis were realized by Kjeldahl' method, according to the Normas Analíticas do Instituto Adolfo Lutz.

Thermal analysis

The dynamic thermogravimetric curves were obtained in a thermobalance, Shimadzu TGA-50, in an atmosphere of flowing air at 20 mL min^{-1}, using an alumina crucible and a heating rate of 10°C min^{-1}. Sample masses varied between 10.0 and 10.5 mg, and the temperature was scanned up to 900°C and held for 20 min. The isothermal thermogravimetric curves were obtained at the temperatures of 150, 160, 170, 180 and 190°C for 120 min.

In the thermogravimetric method, the moisture and ash content was a mean result of three parallel determinations for each sample.

The DSC curves were obtained in a differential scanning calorimeter, Shimadzu DSC-50, in the temperature range of 25–200°C, using an aluminum pan, a heating rate of 10°C min^{-1} and a nitrogen atmosphere at 50 mL min^{-1}. The samples used in DSC were prepared with the addition of water to the powder and bran of algaroba pods, resulting in samples containing 10% of water (mass/mass) [10–12].

Results and discussion

Moisture and ash contents

The moisture (16–20%) and ash (3.75%) contents of algaroba cited earlier were obtained from natural algaroba pods, without passing through any thermal treatment. In this work, the pods were subjected to thermal treatment at temperatures of 55, 65, 75, 85, 95 and 105°C, before treatment to obtain the powder and bran only then were the moisture and ash contents determined.

Table 1 presents the moisture and ash contents of the powder and bran of algaroba, obtained by conventional gravimetric, dynamic thermogravimetric and infrared radiation (moisture) methods. In general, the values for the water content obtained by thermogravimetric and infrared radiation methods, and the values for the ash content obtained by the thermogravimetric method are well correlated with the values obtained by conventional gravimetric methods, for the two samples studied at diverse drying temperatures. The standard deviations of the amounts of moisture and ash of the powder and the bran of algaroba pods, obtained by conventional gravimetric and infrared radiation methods, were larger than those for the thermogravimetric method, suggesting that the last is the most precise method.

Table 1 Percentages of moisture and ash of samples, obtained by different methods

Drying temp.	Samples	Moisture conv./%	Moisture TG/%	Moisture IR/%	Ash conv./%	Ash TG/%
55°C	powder	4.13±0.12	4.54±0.002	4.00±0.43	3.58±0.065	3.18±0.064
	bran	4.49±0.24	3.68±0.003	5.10±0.31	2.98±0.017	2.72±0.007
65°C	powder	4.12±0.08	4.43±0.009	3.90±0.51	3.49±0.011	3.50±0.010
	bran	3.32±0.08	3.09±0.004	3.20±0.28	3.14±0.052	2.47±0.050
75°C	powder	4.01±0.00	4.43±0.002	3.87±0.54	3.34±0.015	2.48±0.010
	bran	3.15±0.05	3.09±0.003	3.10±0.24	3.42±0.020	2.72±0.005
85°C	powder	2.31±0.01	2.26±0.008	2.40±0.27	3.36±0.069	2.33±0.002
	bran	2.13±0.15	2.89±0.007	2.80±0.27	3.15±0.043	2.12±0.001
95°C	powder	1.53±0.04	1.73±0.035	1.80±0.17	3.45±0.064	1.41±0.030
	bran	1.65±0.03	2.69±0.002	1.60±0.11	3.13±0.011	1.77±0.002
105°C	powder	0.99±0.05	1.06±0.032	1.10±0.11	3.57±0.061	2.12±0.040
	bran	1.35±0.03	2.68±0.001	1.50±0.12	3.09±0.011	2.33±0.006

Some lack of reproducibility is observed in the dynamic thermogravimetric method, probably, due to heterogeneity of bran (peel, seed, fiber) and could also be related, both for the bran and the powder, with the mass of the samples used in the analysis, which varied between 10.0 and 10.5 mg. The difference in sample mass between the techniques is large, since in conventional analysis it was 5.0 g, whereas in thermogravimetric analysis it was 10.0 mg. The maximum temperature to which the samples were exposed was 900°C in thermogravimetric method and in the conventional gravimetric method only up to 600°C. At 600°C the sulfates, carbonates, phosphates, silicates (mineral residues) still remain and at 900°C these substances are decomposed into their respective oxides, results in a diminution of the ash content obtained by thermogravimetry.

Protein content

Table 2 presents the protein contents of the powder and the bran of algaroba at the drying temperatures of 55, 65, 75, 85, 95 and 105°C. The percentages of protein of the powder and the bran of algaroba decreased with the increase of the drying temperatures. The samples dried at 55°C presented the highest protein content.

Thermal analysis

The dynamic thermogravimetric curves of the thermal decomposition of the powder and the bran of algaroba pods, at the drying temperatures 55, 65, 75, 85, 95 and 105°C, presented three (powder) and four events (bran). The first event was attributed to dehydration of the samples, and the remaining events were attributed to the thermal decom-

position of carbohydrates and proteins present in the samples. The results indicated the following thermal stability order: 105>55>65>95>85>75ºC.

Table 2 Percentages of protein of the powder and the bran of algaroba

Drying temperatures/°C	Protein	
	Powder/%	Bran/%
55	8.84	9.51
65	8.44	8.66
75	8.42	8.53
85	8.12	8.41
95	8.02	8.28
105	7.87	8.07

The isothermal thermogravimetric curves of the powder and the bran of algaroba pods, dried at 55°C, were obtained at the temperatures of 150, 160, 170, 180 and 190°C. The isothermal profiles indicated one step of thermal decomposition at the temperatures of 150, 160, 170 and 180°C and two steps at the temperature of 190°C. In this temperature, it could be verified that in the first step there was a fast mass loss and in the second step a slow mass loss, probably due to decomposition of different substances (Figs 1–2).

Gelatinization

Table 3 presents the transition temperatures of the starch, powder and bran of the algaroba pods, with their respective enthalpy variations, determined from the peak areas corresponding to the gelatinization and water vaporization, analyzed in the differential scanning calorimeter. The gelatinization temperature (T_1) is within the interval cited in the literature. In relation to the water vaporization temperature (T_2) comparing the values of the powder and the bran at each drying temperature, it is observed

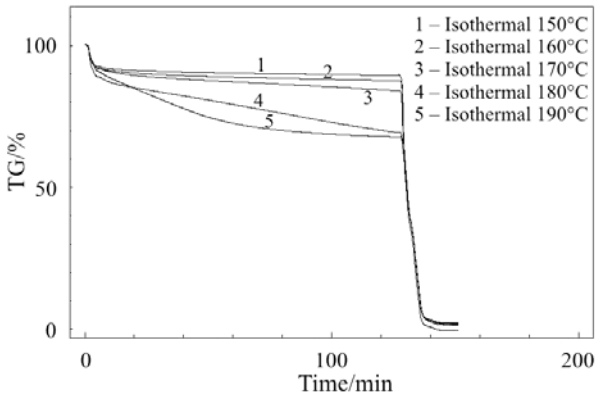

Fig. 1 Isothermal thermogravimetric curves of the powder of algaroba dried at 55 ºC

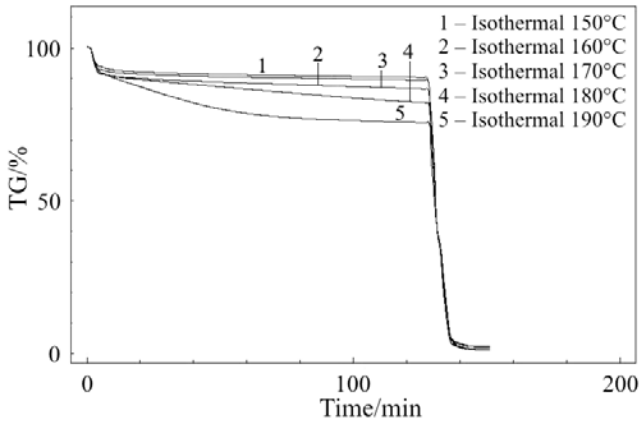

Fig. 2 Isothermal thermogravimetric curves of the bran of algaroba dried at 55ºC

that the T_2 values for the bran are higher, due to heterogeneous nature of the sample. The values of the enthalpies water vaporization (ΔH_2) increased with increase in drying temperature, probably because of the sample being more dehydrated.

Table 3 Starch gelatinization and water vaporization temperatures and enthalpies

Drying temp./°C	Samples	[a]T_1/°C	[b]ΔH_1/J g^{-1}	[c]T_2/°C	[d]ΔH_2/J g^{-1}
55	powder	60	357	107	380
	bran	54	487	124	346
65	powder	–	–	98	570
	bran	–	–	109	1130
75	powder	–	–	115	632
	bran	–	–	117	1191
85	powder	–	–	108	799
	bran	–	–	131	1242
95	powder	–	–	88	1040
	bran	–	–	89	1260
105	powder	–	–	117	1074
	bran	–	–	122	1327

[a]Temperature of starch gelatinization; [b]Enthalpy of gelatinization; [c]Temperature of water vaporization; [d]Enthalpy of vaporization.

The starch gelatinization peak appears only in the samples dried at 55°C. Even with this previous heating, the starch structure did not alter. Two peaks are observed in this curve, the first is related to the gelatinization and the second to the water va-

porization. The gelatinization peak does not appear in the other curves, because the samples had been subjected to previous heating that had modified the starch structure. In the DSC curves for the samples with drying temperatures 65, 75, 85, 95 and 105°C, only one peak relating to the vaporization of water is observed.

Conclusions

The moisture and ash contents of the powder and the bran of algaroba pods obtained by conventional gravimetric, thermogravimetric and infrared radiation methods were comparable for the drying temperatures studied.

The variation in the protein content of the powder and the bran of algaroba pods indicated the influence of the drying temperatures in the protein contents. The samples dried at 55°C presented the highest protein content.

The dynamic thermogravimetric curves of the powder and the bran of algaroba pods indicated the following thermal stability order: 105>55>65>95>85>75ºC. The samples dried at 55°C presented comparable isothermal thermogravimetric profiles.

The calorimetric curves of the powder and the bran of algaroba pods, dried at 55°C, presented characteristics phase transitions for the starch gelatinization.

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