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THERMAL ANALYSIS OF THE RICE AND BY-PRODUCTS

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Abstract

The thermogravimetry (TG) is a technique used in the quality control of foods. In this work the moisture and ash contents in the rice and by-products (bran and husk), the thermal stability and the gelatinization process by conventional, thermogravimetric and calorimetric methods were studied. The moisture and ash contents obtained by TG and conventional methods did not present significant differences. The rice presented higher starch content, while the bran presented higher protein content. The thermogravimetric data presented the following thermal stability order: rice>bran>husk. The calorimetric curves indicated the gelatinization of the starch. The kinetic parameters were compatible.

Keywords: DSC, rice, TG

Introduction

Thermal analysis plays an important role in the quality control of food [1–3]. The rice is the second cereal most cultivated in the world. There are two species of rice cultivated in the world, Asian (*Oryza sativa L.*) and African (*Oryza glaberrima Steud*). Brazil produces about 11 million tons of the Asian rice, the largest producer in South America [4, 5].

During processing, after the grains are separated from residues and peeled, the following fractions are obtained: rice, bran and husk [6]. The bran is a by-product obtained by milling the rice, constituting 7–8% of the grain; it is composed of husk, small portions of pericarp and germ. According to the American Association of Control Official of Foods, the bran should contain at least 11% proteins, 10% fat and less than 15% fibers. In order to reach these amounts the bran should not contain more than 20% husk, because its high silica content could cause intestinal lesions [7, 8].

Refining the rice an appreciable amount of husks is removed and taken to accumulation, about 2.5 million tons that constitutes a problem for industrial processing [6]. These husks do not have commercial interest and cause serious pollution problems.

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The ash, denominated residual, is obtained without temperature control and exposition time [9].

Thermal analysis constitutes a group of techniques of great interest in the characterization of foods. Thermogravimetry (TG) has been used with success in chemistry and also in other areas such as: nutrition, ceramics, metallurgy, biochemistry and pharmacology. Differential scanning calorimetry was used to study the gelatinization process of the starch, which is a molecular rearrangement and causes irreversible changes in its properties [10, 11].

The calculation of kinetic data is based on the following equation:

$$g(\alpha)=\frac{A}{\phi}\int_0^T e^{-E/RT}\mathrm{d}T \quad (1)$$

where α – decomposed fraction, T – sample temperature, ϕ – heating rate, E – activation energy, A – pre-exponential factor and R – gas constant.

The first term of Eq. (1) is easy to solve, whereas, the integral of the exponential does not present an exact solution, even so, various approximations for the calculation of this integral have been proposed, originating from different methods for the calculation of kinetic parameters. These solutions are classified on the basis of mathematical method employed. Various equations of integration and approximation methods were proposed, such as Coats–Redfern, Madhusudanan, Horowitz–Metzger and Van Krevelen [12–15].

In this work the moisture and ash contents in the rice and by-products (bran and husk), the thermal stability and the gelatinization process were studied by conventional, thermogravimetric and calorimetric methods.

Experimental

The rice and by-products were collected in a processing industry, located in Pernambuco State.

The conventional analysis in ovens was according to the Normas Analíticas do Instituto Adolfo Lutz [16], 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 4 h. In the ash analysis, the samples were carbonized on a Bunsen burner, followed by incineration in a furnace, QUIMIS, at 600°C during 6 h.

The analyses of the protein and the starch were realized by Kjeldahl' method and Volumetric method, respectively, according to the Normas Analíticas do Instituto Adolfo Lutz [16].

The percentage values obtained by conventional method were the mean results of three determinations for each sample.

The thermogravimetric curves were obtained in a thermobalance, Shimadzu TGA-50, in air atmosphere at 20 mL min^{-1}, using an alumina cell, mass 19 mg and heating rate 10°C min^{-1} up to 950°C.

The calorimetric curves were obtained in a differential scanning calorimeter, Shimadzu DSC-50, in the temperature range of 25–300°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 by dilution of water with rice, resulting in solutions containing water 50% (*w*/*w*) [11].

Results and discussion

Moisture and ash contents

The conventional method combined the direct determination of moisture and ash contents, incinerating the residue obtained in the moisture determination. The knowledge of the moisture content is important because it is related to the deterioration control during the storage and the ash content indicates the amount of minerals.

In a general way, the values of the moisture content obtained by TG correlated well with the values obtained by the conventional method (Table 1).

The absolute error was calculated, which is the difference between the measured value (thermogravimetric) and the accepted value (conventional) [17]. The absolute error found in the moisture content was 0.010, 0.011 and 0.003 for the rice, bran and husk, respectively. In the case of the ash content, the absolute error was 0.008, 0.016 and 0.006 for the rice, bran and husk, respectively. The percentages obtained by TG were higher, due to the shorter time of analysis.

Table 1 Moisture and ash contents of the samples

Methods	Samples	Moisture/%	Ash/%
Conventional	rice	12.0	0.4
	bran	9.8	4.3
	husk	9.0	17.5
Thermogravimetric	rice	13.0	1.2
	bran	10.9	5.9
	husk	9.3	18.1

Starch and protein contents

Table 2 presents the starch and protein contents of the rice and the bran. The percentage values of the starch and the protein were the mean results of three determinations for each sample.

Table 2 Starch and protein contents of the rice and the bran

Samples	Starch/%	Protein/%
Rice	74.92±0.35	7.64±0.23
Bran	41.64±0.01	13.70±0.16

The results of the rice presented higher starch content, while the bran presented higher protein content. The standard deviation indicated comparable values.

Thermogravimetry (TG)

The profile of the thermal decomposition of the rice and by-products presented similar characteristics with three events of thermal decomposition (Figs 1–3).

The thermogravimetric curves of the rice, bran and husk presented the first event of thermal decomposition in the temperature intervals of 36–257, 30–136 and 28–133°C, respectively, which corresponds to dehydration of samples. The second and third events were consecutive and corresponded to the decomposition process in the temperature intervals of 257–672, 255–627 and 214–538°C for the rice, bran and husk, respectively. The rice presented, in these events, decomposition with mass loss of 85.8% remaining

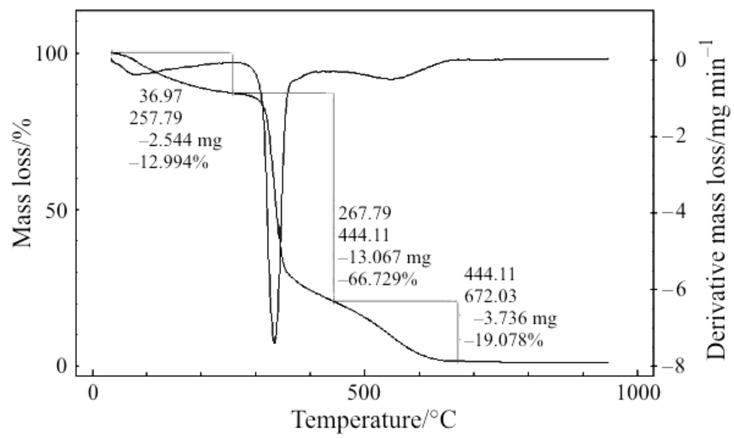

Fig. 1 TG and DTG curves of rice

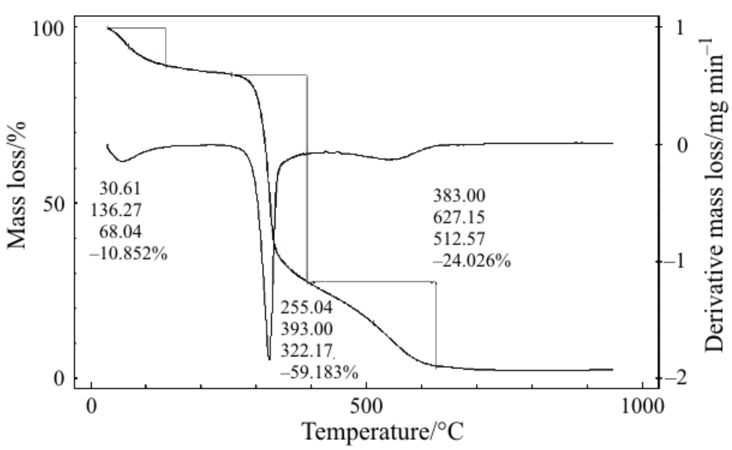

Fig. 2 TG and DTG curves of bran

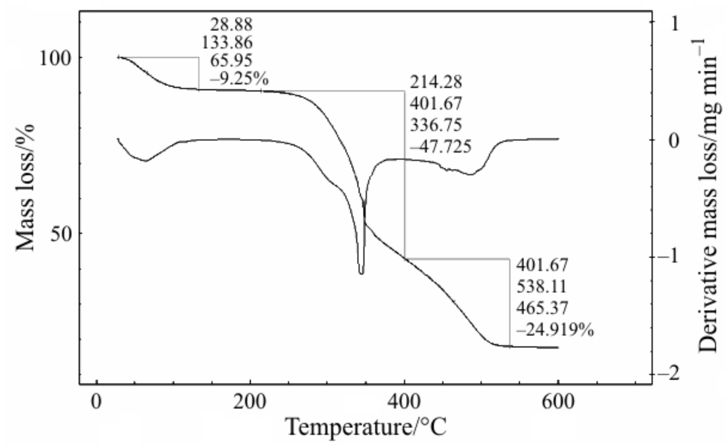

Fig. 3 TG and DTG curves of husk

only 1.2% ash. The husk presented ash content of 18.1% it was constituted 99% silica [9]. The bran presented characteristics among rice and husk, due to their composition.

Kinetic study

The kinetic model that better adjusted to experimental data was the kinetic model F1, based in the reaction order, which was calculated by Coats–Redfern method [12], in the interval of decomposed fraction $0.90 \geq \alpha \geq 0.10$.

The determination of the kinetic parameters (*n* – reaction order; *E* – apparent activation energy; *A* – pre-exponential factor) of the first event of process of the thermal decomposition of samples (Table 3) was realized according to the expressions proposed by Coats–Redfern (CR), Madhusudanan (MD), Horowitz–Metzger (HM) and Van Krevelen (VK) [12–15].

The values of the kinetic parameters obtained by integral and approach methods were compatible. The values obtained by approach methods were higher than the values obtained by integral methods due to different mathematical treatments.

Table 3 Kinetics parameters

Samples	Kinetic parameters	Kinetic models			
		CR	MD	VK	HM
Rice	E/kJ mol^{-1}	43.44	43.63	48.56	53.18
	A/s^{-1}	$7.46 \cdot 10^3$	$8.86 \cdot 10^3$	$6.17 \cdot 10^9$	$6.14 \cdot 10^5$
	n	1.62	1.62	1.86	2.10
Bran	E/kJ mol^{-1}	59.08	58.81	66.78	72.88
	A/s^{-1}	$1.29 \cdot 10^7$	$1.25 \cdot 10^7$	$2.82 \cdot 10^{13}$	$4.55 \cdot 10^9$
	n	2.39	2.37	2.75	3.07
Husk	E/kJ mol^{-1}	76.09	74.86	81.96	88.75
	A/s^{-1}	$8.35 \cdot 10^9$	$5.53 \cdot 10^9$	$8.63 \cdot 10^{15}$	$8.96 \cdot 10^{11}$
	n	2.10	2.05	2.23	2.39

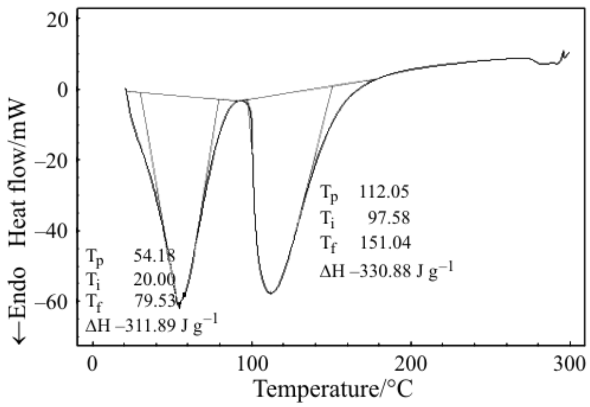

Fig. 4 Calorimetric curve of the rice

Differential scanning calorimetry (DSC)

The calorimetric curves of the rice and bran presented two endothermic transitions. In the DSC curve of rice (Fig. 4) the first endothermic transition corresponded to the gelatinization of the starch (peak 54.2ºC; enthalpy 311.89 J g^{-1}) and the second endothermic transition corresponded to the vaporization of the water (peak 112.1ºC; enthalpy 330.88 J g^{-1}). In the DSC curve of the bran the first endothermic transition corresponded to the gelatinization of the starch (peak 53.5ºC; enthalpy 276.99 J g^{-1}) and the second endothermic transition corresponded to the vaporization of the water (peak 108.1ºC; enthalpy 853.69 J g^{-1}).

Conclusions

The moisture and ash contents obtained by thermogravimetric method were compatible with the results obtained by the conventional method. The thermogravimetric method presented advantages, such as shorter time of execution and smaller amount of sample.

The thermogravimetric curves of the rice, bran and husk presented similar thermogravimetric profiles, with three events of thermal decomposition. The rice presented higher moisture content, while the husk presented higher ash content. The results indicated the following thermal stability order: rice>bran>husk.

The calorimetric curves of the rice and the bran presented two endothermic transitions, confirming the gelatinization of the starch.

The CR and MD integral methods gave similar results, while the HM and VK approach methods showed kinetic parameter values somewhat higher than those for CR and MD methods, due to different mathematical treatments.

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