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Calorimetric and kinetic parameters of manioc derivatives

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Abstract

The present work had as an objective the determination of calorimetric and kinetic parameters of the manioc derivatives seeking to contribute for thermal characterization of these products. Calorimetric curves were obtained in a Shimadzu DSC, model DSC-50, and thermogravimetric curves in a Shimadzu thermobalance, model TGA-50. The kinetic parameters, activation energy (E), reaction order (n) and frequency factor (A) were obtained by the methods of Coats–Redfern, Madshudanan, Horowitz–Meltzger and Van Krevelen. The calorimetric results shows sharply that the gelatinization of the starch only happened in the liophilized gum and sour manioc flour products. The kinetic data showed values of activation energy for the four methods that suggest the following order of stability of the products: sour manioc flour > liofilized gum > tapioca > cassava flour. The analysis of the data reveals clearly that the products tapioca and cassava flour, previously processed in the temperature post-gelatinization, are less stable when compared with the liophilized gum and the sour manioc flour. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Manioc derivatives; DSC; TG

1. Introduction

Thermal methods are very important in the characterization of nutritious products, supplying significant analytical data for the industrial processing at the time of useful life of the victuals. The basic contributions of these methods result in mathematical models for determination of the heat propagation in the victuals and of the kinetics of the degradative reactions (Maillard, lipidic oxidation, enzymatic, proteins denaturation, etc). In the past years, several works done have been trying to describe the thermal behavior of varied victuals [1–8] In this work, we have determined the calorimetric and kinetic parameters of manioc derivatives seeking to contribute for its thermal characterization.

2. Experimental

Samples of fresh gum, sour manioc flour, thermic processed gum (Tapioca) and cassava flour were collected in the trade of the city of João Pessoa – Paraíba, Brazil. The liophilized gum was obtained starting from the fresh gum dehydrated in a freeze dryer HLTO, model FD3. The granulometry of the samples was obtained in sieves with diameter of 60 mesh (0.250 mm).

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The DSC curves were obtained with a Shimadzu differential scanning calorimeter – model DSC-50, in a temperature range of 25–200°C using an aluminum panin, with a heating rate of 10°C/min, under nitrogen atmosphere with flow of 50 ml/min. The samples used in DSC were prepared by dilution of water with each one of the derivatives, resulting in solutions containing water 10, 20, 40 and 50% (weight/weight). The TG curves were obtained in a Shimadzu thermobalance model TGA-50, using an alumina pan, with the heating rate of 10°C/min in a temperature range of 25–900°C, and an atmosphere of air with flow of 20 ml/min. The amount of the sample was of 10 mg. The TG and DSC curves were analyzed with the aid of the TASYS software from Shimadzu.

The kinetic parameters, activation energy, reaction order and frequency factor were obtained across thermogravimetric data by the methods of Coats–Redfern (CR) [9], Madhusudanan (MD) [10], Horowitz–Metzger (HM) [11] and Van Krevelen (VK) [12].

3. Results

Table 1 shows the values of temperatures and heat of phase transitions of those derived of cassava. Sour manioc flour presents two phase transitions. The temperature of the first phase transition increases with the water content in the sample. The second transition does not show alteration in the value of the peak temperature with the increases in the water content. The liophilized gum shows two peaks of phase transition in the samples containing 10 and 20% of water (w/w), with variation in the temperature of the peak transition. In the samples with 40 and 50% of water was just verified one transition. The tapioca and the cassava flour just present a phase transition, where the peak temperatures stay relatively unaffected in the samples with 10 and 20% of water and they show variations for larger values when the suspensions were prepared with 40 and 50% of water. The heat of phase transition, generally, decrease with the water content except for cassava flour.

Table 1
Calorimetric behavior of the cassava derivatives

Product	Phase transitions			
	First		Second	
	Tp (°C)	*E* (J/g)	Tp (°C)	*E* (J/g)
Sour Manioc Flour : Water (w/w)				
90 : 10	62.3	826.5	103.4	56.0
80 : 20	68.5	47.2	10.2	278.5
60 : 40	96.4	186.1	–	–
50 : 50	108.5	597.7	–	–
Liophilized Gum : Water (w/w)				
90 : 10	56.9	55.0	105.4	27.4
80 : 20	63.0	201.2	102.4	126.4
60 : 40	81.5	365.5	–	–
50 : 50	114.2	251.7	–	–
Tapioca : Water (w/w)				
90 : 10	120.1	1.170.0	–	–
80 : 20	123.4	1.140.0	–	–
60 : 40	112.4	889.7	–	–
50 : 50	114.5	426.1	–	–
Cassava Flour : Water (w/w)				
90 : 10	110.6	655.4	–	–
80 : 20	115.2	668.0	–	–
60 : 40	156.0	697.1	–	–
50 : 50	131.9	848.9	–	–

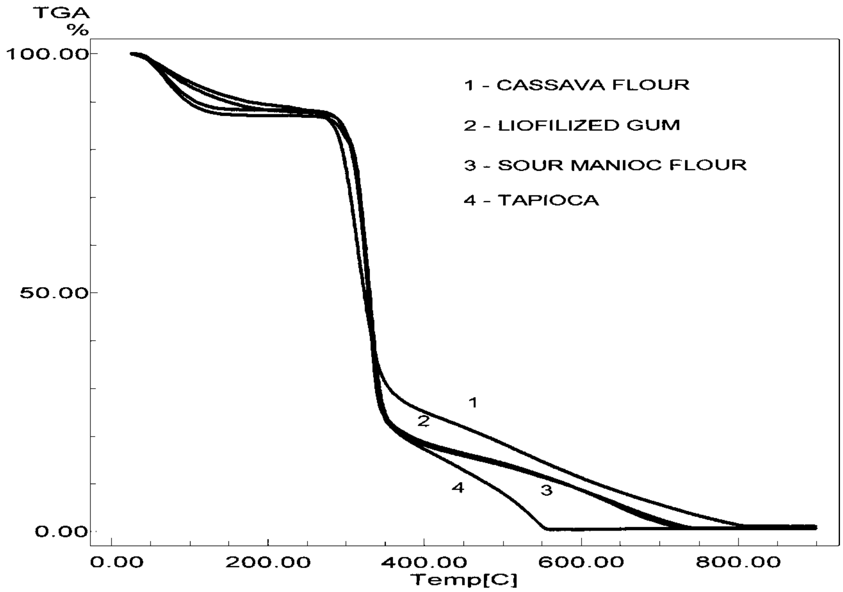

Fig. 1. TG curve of the manioc derivatives.

The profile of the thermodecomposition of those derivatives of cassava presented similar characteristics, showing 04 decomposition stages (Fig. 1). The thermogravimetric data allowed to calculate the kinetic parameters in a temperature range of 160–345°C, using a strip of the decomposed fraction of 0.25–0.80. The values of the kinetic parameters: reaction order (n), activation energy

Table 2
Kinetic parameters of those derived of the cassava calculated starting from the dynamic thermogravimetric data in the reason of heating of 10°C/min

Product	Methods			
	CR	MD	HM	VK
Sour manioflour				
n	1.6	1.3	1.6	1.6
E (kJ/mol)	327.2	298.7	319.4	328.4
A (s^{-1})	3.95 E + 26	1.12 E + 24	6.28 E + 27	1.85 E + 32
Liophilized gum				
n	1.7	1.5	1.8	1.9
E (kJ/mol)	253.2	232.0	276.1	289.4
A (s^{-1})	2.76 E + 20	6.49 E + 18	1.41 E + 22	2.05 E + 26
Tapioca				
n	1.1	1.1	1.2	1.1
mE (kJ/mol)	238.0	236.4	258.8	225.4
A (s^{-1})	5.22 E + 18	3.86 E + 18	3.30 E + 20	1.39 E + 23
Cassava flour				
n	2.0	2.2	2.2	2.1
E (kJ/mol)	201.4	215.7	222.3	220.1
A (s^{-1})	7.79 E + 16	1.72 E + 17	7.60 E + 17	1.40 E + 23

(E) and frequency factor (A) are presented in the Table 2.

4. Discussion

The calorimetric data shows clearly the difference among them cassava derivatives containing water 10% (Fig. 2), submitted to thermal processing with temperatures above 100°C. The sour manioc flour, dehydrated in solar dryer and the gum liophilized evidenced the presence of the starch in its native form because they presented phase transitions, respectively, in the temperatures of 62.3° and 56.9°C, characteristics of the starch gelatinization. As the water content

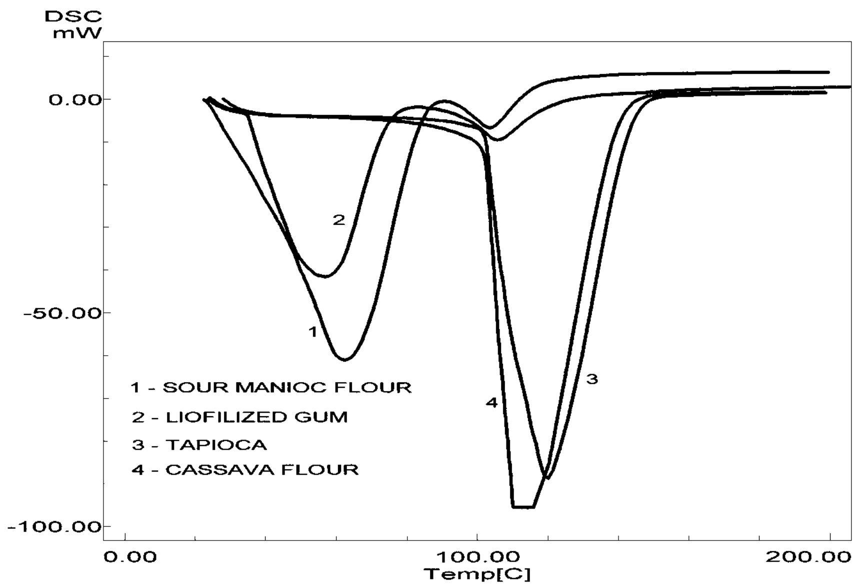

Fig. 2. DSC curves of the manioc derivatives containing water 10% (w/w).

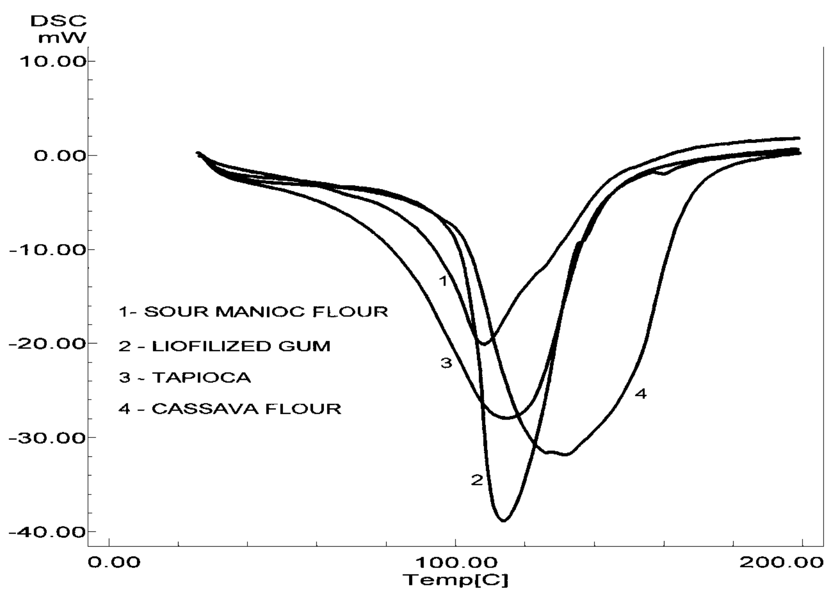

Fig. 3. DSC curves of the manioc derivatives containing water 50% (w/w).

increases it shows displacement of the gelatinization process of the starch in such a way that melts with the second transition, resulting in only one phase transition (Fig. 3). The products tapioca and cassava flour that are processed with temperatures larger than 100°C, presented only one phase transition which was attributed to water vaporization.

The values of the kinetic parameters obtained by the different integral and approach methods showed coherence with the respective mathematical models. The activation energy for approach methods of Horowitz–Metzger and Van Krevelen are larger than those for integral methods of Coats–Redfern and Madhusudanan.

The comparison of the activation energy of those manioc derivative (Table 2) with the TG curves (Fig. 1) suggest the following order of stability of the products: sour manioc flour > liofilized gum > tapioca > cassava flour.

5. Conclusions

The calorimetric parameters allowed to differentiate the derivatives of the cassava. The sour manioc flour and the liophilized gum present phase transitions characteristics of the starch gelatinization.

The kinetic parameters show that derivatives of the cassava dehydrated with low temperatures (sour manioc flour and liophilized gum) present values larger of activation energy compared with derivatives submitted to thermal processing with temperatures larger than 100°C (tapioca and cassava flour), suggesting thermal stability larger for sour manioc flour and liophilized gum.

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