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ISOTHERMAL KINETIC STUDY OF CORN AND ITS DERIVATIVES

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Abstract

The thermogravimetric procedures applied to quality control of foods attain the global analysis of quality of the product, through the determination of quality parameters and the thermal stability of products. The kinetic parameters such as order of reaction, apparent activation energy, pre-exponential factors and the thermal decomposition rate constant were determined for the samples of corn and its derivatives by applying isothermal thermogravimetry, utilizing the Arrhenius law. This method presented excellent results as verified with the coherence and data adjustment. The rate constant values showed the expected performance from the chemical point of view.

Keywords: corn, isotherms, kinetics

Introduction

Corn (*Zea mays*) is composed of carbohydrates (about 83%), proteins, fatty compounds, minerals salts, water and small quantities of vitamins and enzymes [1, 2].

The analytical methods conventionally utilized for the evaluation of food quality are generic and in most cases merely indicative of quality. These methods are costly and require a long time for execution, taking about 20 h of uninterrupted work. It is, therefore, necessary to apply new methods to food quality control, such as thermal analysis, which furnishes reproducible results at reduced costs.

Thermal analysis constitutes a group of techniques of great interest for the characterization of foods, as it relates relevant food data to the industrial process, decreasing analysis time and the sample quantity required for obtaining the kinetic parameters [3, 4].

Thermogravimetry is a thermal analytical technique by which the variation in mass is measured as a function of temperature or of time. This technique has been ap-

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plied with great success not only in chemistry but also in other areas such as foods, ceramics, metallurgy and pharmacology [5, 6].

Environmental factors (light, humidity and heat) constitute important parameters for the study of thermal stability of foods. The determination of thermal stability and of the ideal storage conditions of food products is of fundamental importance to guarantee the quality of these products. Kinetic factors, such as temperature and time may lead to the decomposition of the constituents, forming new compounds which, in many cases, are harmful to health.

Reaction rate is defined as a function of the decomposed fraction (α), which corresponds to the relation between mass loss in a time (t) and loss of total mass for a given stage of reaction [7, 8]. The kinetic study of thermal decomposition, utilizing the isothermal method, is based on the following expression:

$$v=\mathrm{d}\alpha/\mathrm{d}t=k(T)f(\alpha) \tag{1}$$

where v – reaction rate; t – reaction time; α – decomposed fraction; k –rate constant; T – sample temperature.

This work consisted in the study of the isothermal thermoanalytic profile of corn and its derivatives and the determination of the kinetic parameters such as: order of reaction (n), rate constant of thermal decomposition (k), apparent activation energy (E_a) and pre-exponential factor (A) through isothermal thermogravimetric analysis, utilizing the method of Arrhenius law.

Materials and methods

Samples of corn and its derivatives *hominy, gritz, vitamilho (pre-cooked flour) and bran*, were obtained from the Refinações de Milho Brasil Ltda., Campina Grande, Paraíba, Brazil.

The hominy is obtained by removing corn embryo. Gritz is obtained from hominy milling using a roll mill in a continuous process. Vitamilho is obtained from gritz floculation using a pre-cooking process in a flake mill. Bran is a corn sub-product, mainly constituted by embryo and skin.

A thermobalance, Shimadzu TGA-50, was utilized to obtain the isotherms in air atmosphere having a flow of 20 mL min^{-1}, heating rate of 10°C min^{-1} and temperature range of 190–250°C (except bran, which had a temperature range of 140–200°C). The samples were packed in alumina packages containing a mass of 12.8 mg and of 60 mesh size.

The samples were introduced in the furnace at room temperature, pre-heated at a rate of 50°C min^{-1} up to the desired temperature. Then, the temperature was raised at a rate of 10°C min^{-1} and was kept at this temperature for 360 min. Later, the sample was heated up to 900°C [9, 10].

The kinetic parameters such as order of reaction, apparent activation energy, pre-exponential factor and rate constant were determined for the corn samples and its derivatives by isothermal method, obeying the Arrhenius law [11]. For a reaction of zero order, a mass graph in function of time should be plotted by the equation:

$$m=m_0-kt \tag{2}$$

For a reaction of first order, a graph of logarithmic of mass in function of time should be plotted by the following equation:

$$\ln m=\ln m_0-kt \tag{3}$$

For a reaction of second order, a graph of the inverse of mass in function of time should be plotted by the following equation:

$$\frac{1}{m}=\frac{1}{m_0}+kt \tag{4}$$

where m – mass; m_0 – initial mass; t – time.

The repetition of the calculation of the rate constants at different temperature permits the calculation of the activation energy and the pre-exponential factor from the Arrhenius equation in the linearized form [12]:

$$\ln k=\ln A-\frac{E}{RT} \tag{5}$$

Results and discussion

The dynamic thermogravimetric curves of corn and its derivatives (Fig. 1) reveals three steps of thermal decomposition, in the temperature range varying from 27 to 600°C. The first step was attributed to water loss by the sample, in the temperature range 27–150°C; the second step corresponds to the thermal decomposition of carbohydrates (starch, amylose, amylopectin), occurring in the temperature range from 250–400°C (except bran, for which the temperature range was 200–400°C). The third step corresponds to the secondary thermal decomposition of carbohydrates of low molecular mass and fibers, the temperature range of which was 400–600°C, leaving the residue over 600°C, in the form of ash, attributed to mineral salts.

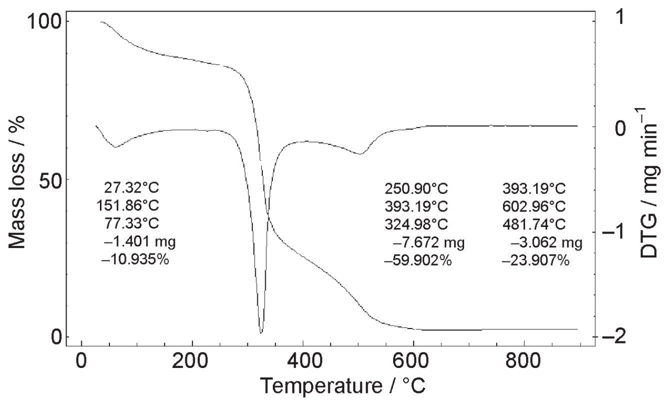

Fig. 1 Dynamic TG curve of corn

The isothermal temperatures for the corn, hominy, gritz and vitamilho were 190–250 and 140–200°C for bran. For bran, the initial temperature was much lower than those for other samples, probably due to its composition.

In isothermal thermogravimetric curves of corn and its derivatives a similar profile was observed for the samples (Fig. 2).

The isothermal thermoanalytic profile demonstrated that corn, hominy, gritz and vitamilho presented only one step of thermal decomposition in the temperatures 190,

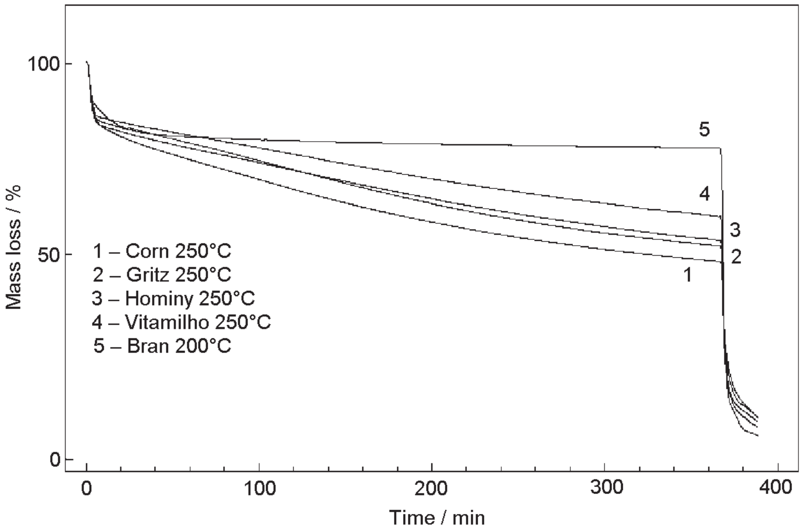

Fig. 2 Isotherm TG curves of corn and derivatives

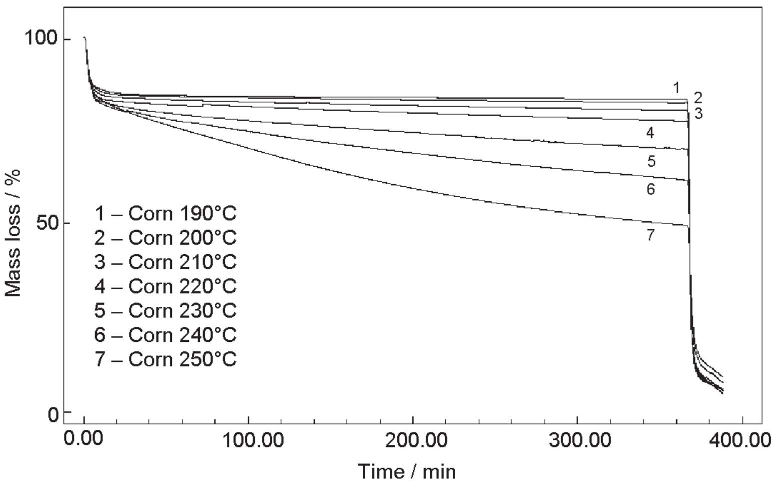

Fig. 3 Isotherm TG curves of corn 190–250°C

200, 210, 220, 230, 240 and 250°C (Fig. 3). The isothermal thermoanalytic profile for bran revealed a thermal decomposition step in the temperatures 140, 150 and 160°C and two steps of thermal decomposition in the temperatures 170, 180, 190 and 200°C. In these temperatures, it could be verified that in the first step there was a fast mass loss and in the second step an extremely slow mass loss, probably due to the decomposition of different substances.

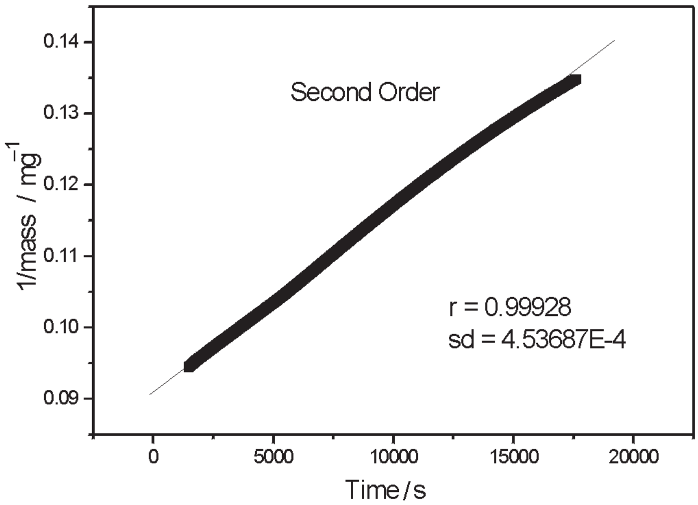

Fig. 4 Inverse of mass in relation to the reaction time of corn 250°C

Kinetic parameters were calculated, by using the decomposed fraction (α) from 0.10 to 0.90, for the temperatures of thermal decomposition of corn and its derivatives corresponding to the beginning of decomposition of carbohydrates (second step of dynamic thermogravimetric profile).

Table 1 Kinetic parameters of isothermal decomposition of corn and its derivatives

T/°C	n	k/s^{-1}	r	E_a/kJ mol^{-1}	A/s^{-1}
Corn				119.8	2.09E+07
190	2	7.85E-07	0.9937		
200	2	1.32E-06	0.9936		
210	2	2.11E-06	0.9951		
220	2	2.90E-06	0.9989		
230	2	8.17E-06	0.9977		
240	2	1.37E-05	0.9992		
250	2	2.76E-05	0.9993		

Table 1 Continued

T/°C	n	k/s^{-1}	r	E_a/kJ mol^{-1}	A/s^{-1}
Hominy				88.9	9.87E+03
190	2	1.32E-06	0.9408		
200	2	1.47E-06	0.9699		
210	2	2.08E-06	0.9917		
220	2	2.67E-06	0.9974		
230	2	4.37E-06	0.9991		
240	2	8.37E-06	0.9996		
250	2	2.01E-05	0.9997		
Gritz				135.6	5.95E+08
190	2	4.43E-07	0.9493		
200	2	5.76E-07	0.9920		
210	2	9.87E-07	0.9972		
220	2	2.32E-06	0.9974		
230	2	4.12E-06	0.9994		
240	2	9.02E-06	0.9998		
250	2	2.36E-05	0.9995		
Vitamilho				107.7	6.26E+05
190	2	6.72E-07	0.9402		
200	2	6.97E-07	0.9797		
210	2	1.30E-06	0.9934		
220	2	1.67E-06	0.9899		
230	2	3.23E-06	0.9993		
240	2	6.94E-06	0.9999		
250	2	1.59E-05	0.9998		
Bran				106.2	3.29E+07
140	2	1.47E-06	0.9958		
150	2	2.46E-06	0.9912		
160	2	4.03E-06	0.9877		
170 (1st step)	2	9.68E-06	0.9971		
170 (2nd step)	2	3.00E-06	0.9673		
180 (1st step)	2	1.84E-05	0.9965		
180 (2nd step)	2	3.04E-06	0.8833		
190 (1st step)	2	4.13E-05	0.9957		
190 (2nd step)	2	3.13E-06	0.9388		
200 (1st step)	2	6.05E-05	0.9903		
200 (2nd step)	2	3.49E-06	0.9708		

T – temperature; n – order of reaction; k=rate constant of thermal decomposition reaction; r – linear correlation coefficient; E_a – apparent activation energy; A – pre-exponential factor

Isothermal thermogravimetric data revealed a better linear regression in the graph of the inverse of mass in relation to the reaction time, indicating that the thermal decomposition reactions of corn and its derivatives follow the mechanism of the second order (Fig. 4).

The values of the rate constants presented an exponential behavior with temperature, permitting to estimate the rate constant at any temperature of interest. The apparent activation energy (E_a) and pre-exponential factor (A) for the thermal decomposition of corn and its derivatives were calculated from the Arrhenius equation (Table 1).

Conclusions

The isothermal thermogravimetric profile of corn and its derivatives presented similar characteristics, with the exception of some variations in relation to bran due to its heterogeneous composition. The results obtained from the method of Arrhenius law demonstrated that the thermal decomposition reactions of corn and its derivatives obey second order kinetics and the values of rate constants relate in a coherent form with temperature, allowing the calculation of apparent activation energy and pre-exponential factor. Their values were found to be in an agreement with the thermal decomposition reaction of corn and its derivatives. The study of the thermogravimetric profile was possible in a relatively short time through the isothermal thermogravimetric method, which requires only a small quantity of sample and permits the calculation of kinetic parameters. The method that utilizes the Arrhenius law of classical kinetics presented good results, suggesting its application for complex substances.

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