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Water desorption of cassava starch granules: A study based on thermogravimetric analysis of aqueous suspensions and humid powders

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ABSTRACT

This work reports on water desorption from cassava starch in relation with the structure and conditioning of granules in suspensions or after equilibration in desiccators. The experimental work is performed by thermogravimetric analysis with isothermal and non-isothermal protocols and interpreted to derive the activation energies and desorption frequencies according to the humidity range with no adjustable parameter. The analysis points out the different types of water interacting with the starch granules and relates the drying coefficients to their microscopic structure. The work helps clarifying contradictory and partial results from the literature.

1. Introduction

Water removal from granular biological systems is a well-developed method for improving physicochemical stabilization of raw materials and/or products before storage (Aguerre & Suarez, 2004; Babalis & Belessiotis, 2004; Moreira et al., 1993). Moreover it is also a widespread method in many other industries (food, pharmaceuticals, paper, ceramics, textile...). There exist many types of industrial dryers according to the purpose and to the product (Mujumdar, 2007 (Chapter 1)). For each method, the processing conditions (temperature, pressure, air velocity, relative humidity, time) have to be determined according to the material properties and to the objectives. Drying is considered as one of the most complex processes related to the material properties, to physical or chemical transformations and to difficulties of mathematical descriptions and is mostly investigated with engineering objectives. Drying involves large energy consumption and consequently, with aim of seeking conditions for optimization, it is important to better understand the relation between water desorption and physicochemical characteristics of the granular materials.

In granular biological materials, isothermal treatments are the most utilized methods (Babalis & Belessiotis, 2004; Doymaz, 2011; Ogawa, Kobayashi, & Adachi, 2012), but some recent work reports on non-isothermal treatments in corn, wheat and rice straw and corn stalk. Correlations expressing the drying constants and effective moisture diffusivity were reported (Cai & Chen, 2008; Chen, Zhang, & Zhu, 2012).

Reviewing the literature recently, Erbay and Icier (2009) report on a large discrepancy of "effective moisture diffusivities" determined in vegetables, fruits, plants and others, between 10^{-12} and 10^{-6} m^2/s! The authors suggest that the drying temperature is critical, but results depend also on the method for a given material. The measured activation energies also vary considerably between 12 and 82 kJ/mol. Despite the large number of investigations in the context of drying, there is no clear evidence of what parameters precisely describe the water diffusion in materials exhibiting complex structures. In the course of drying, the change from the constant to the falling rate period is of major economic importance, since a large quantity of water can be removed during the constant and high drying rate periods. It is important to define the limiting conditions when the falling rate periods would start. It is important to reveal the influence of the matrix structure upon the diffusivity of water molecules. For instance, Ogawa et al. (2012) listed up to fourteen types of empirical and semiemprical equations on decreasing rate periods in a food material.

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This work aims to study dewatering and drying process of cassava starch granules after conditioning under different environments, which do not involve their gelatinization. Cassava starch was selected because it is a natural biopolymer with granular shape and with numerous industrial and pharmaceutical applications (Cornell, 2004 (Chapter 7); Odeku, 2013). Cassava starch granules after extraction can be dispersed in water or only hydrated under controlled atmospheres depending on application (Coativy, Chevigny, & Sabaté, 2015; Liu, Xie, Yu, Chen, & Li, 2009). Hence, in order to optimize the industrial processes it is necessary to closely associate desorption and/or drying properties of granules to the binding state of water and to the different processing.

Our experiments aim to analyze the starch-water interactions: in first part, cassava starch granules were dispersed in distilled water at room temperature for various periods of time and later were isothermally dried. Mass loss measurements were performed by means of thermogravimetric analysis (TGA) under controlled gas flow (nitrogen). In the second part, cassava starch granules were conditioned under different relative humidities (RHs) at room temperature and were investigated by TGA using isothermal and non-isothermal treatments. We demonstrate that these experiments are able to identify the different populations of water molecules according to their desorption energy and diffusion times. Our experimental approach and modelling can be applied to any type of biological or inorganic granular materials or suspensions where dehydration is necessary for production or storage. The characterization of the drying steps allows to better control and design different processing and to clarify the influence of the matrix on water diffusion.

2. Materials and methods

2.1. Materials and characterizations

Cassava starch with an initial water content of $w_{init} = 0.12 \pm 0.1$ g water/g dry starch (AOAC, 1990) was purchased from Yoki Food Industry (São Paulo, Brazil). Physicochemical characterizations show that cassava starch granules are uniformly smooth, without scratches and with a truncated form (Fig. 1a). The granules have monomodal distribution, with particle size varying between 10 and 53 μm, and mean size of 22 μm (Fig. 1b). Cassava starch exhibits a diffraction pattern of A-type crystal (Fig. 1c) with relative crystallinity of 24.10%. Differential scanning calorimetry of granules dispersed in water show that the gelatinization transition has an onset temperature 50 °C, a peak temperature 62 °C and transition enthalpy ΔH of 13.58 J/g dry starch (Fig. 1d). Our scanning electron microscopy images, particle size distribution, XR diffractograms and differential scanning calorimetry results are in agreement with those reported by Garcia, Colonna, Bouchet, and Gallant (1997), Lindeboom, Chang, and Tyler (2004) and Chen, Huang, Tang, Chen, and Zhang (2011) for cassava starch powder. All methodologies for physicochemical characterizations of cassava starch are reported as supplementary material.

2.2. Sample preparation and thermogravimetric analysis (TGA)

We investigated drying of cassava starch both from suspensions and from powders. Cassava starch granules were dispersed in deionized water (from Milli® Q system with a resistivity of 18 MΩcm) at room temperature and suspensions were kept for different times before investigation: 5 min, 15 min, 1 h, 18 h, 26 h and 76 h. A fixed volume of the suspension was deposited with a pipette in an open Pt pan. Sedimentation of granules takes place rapidly. By TGA we analyzed the weight loss of suspensions under isothermal conditions at 40 °C, 45 °C and 50 °C during 180 min. Before thermal analysis, we measured the pH of samples, the pH in all suspensions remained constant and it was equal to 6.8 ± 0.2. Such pH values suggest that during the different dispersion times at room temperature, no hydrolysis of cassava starch was induced as a consequence of fermentation process.

Cassava starch granules were also conditioned under different relative humidities (RHs) before investigation. Cassava starch initially stored at room conditions (T = 23 °C and 52% RH) was placed in desiccators either with silica gels, for RH values of 0.1% and 3%, or with different saturated salt solutions imposing 31%, 45%, 71%, 89% and 94% RHs. Preliminary results showed that samples were stabilized after 4 days under each RH and reach a constant weight. We analyzed the drying rates of the granules with various quantities of adsorbed water using two different protocols: isothermal drying kinetics at 35 °C and 45 °C during 100 min and constant heating rate measurements, of +1 °C/min, from 20 °C to 150 °C. In the first protocol we analyzed the rate of weight loss (mg/min) and in the second protocol we analyzed the temperature derivative of the weight, in mg/°C, during the thermal ramp.

The thermogravimetric balance is TGA Q500 (TA Instruments, USA) with a precision of 0.1 μg operating with a constant nitrogen gas flow rate of 25 mL/min and using an open Pt pan with 10 mm diameter and 2 mm height (Agaciak, Yahiaoui, Djabourov, & Lasuye, 2015).

Isothermal and non-isothermal experiments were repeated at least two times for each sample and show a very good reproducibility.

The decanting process of cassava starch in water allowed evaluating the water retention under gravity and the interstitial water content. For this purpose, 2 g of cassava starch granules were dispersed in 15 mL deionized water inside tubes of 20 mL volume capacity, equipped with a 10 μm mesh filter at room temperature without exerting any external force. Weight fraction of water in saturated state $w_{saturation}$ was determined by Eq. (1):

$$w_{saturation} = \frac{m_{DS} - m_{\text{dry starch}}}{m_{\text{dry starch}}} \quad (1)$$

where m_{DS} is the mass of the wet paste (decanted starch) and $m_{\text{dry starch}}$ is the mass of starch calculated after correction for initial humidity by AOAC method. We found after repeated measurements an average $w_{saturation} = 0.89 \pm 0.01$ g water/g dry starch representing water between granules and initially present in granules.

3. Results and discussions

3.1. Thermogravimetric analysis of cassava starch suspensions in water

The aim of this investigation is to show the effect of imbibition time on starch granules kept in water at room temperature, in absence of gelatinization. We were interested to see changes during imbibition of the granules that could affect drying rates and eventually affect the gelatinization process. The impregnation times varied between 5 min and 76 h (Fig. 2a). The drying rates were measured in isothermal mode at 40 °C. TGA experiments are shown in Fig. 2. The curves (Fig. 2a) show four distinct periods of the drying rates: firstly, it is observed a Rising Rate Period (RRP) when the evaporation rate increases following the raise of the temperature (from 23 °C to 40 °C). The preheating period lasts in these experiments for 5 min. After temperature stabilization, free water or water in excess, on the top of the granules, evaporates at almost constant rate of 1.05 mg/min at T = 40 °C (2d period). Independently, we measured the drying rate for pure water, with the same experimental protocol, 1.06 mg/min. Thus, the first plateau corresponds to free water evaporation. The effect of temperature is shown in Fig. 2b, after a constant imbibition time. The overall profiles are