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Modeling the hydration step of the rice (*Oryza sativa*) parboiling process

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ABSTRACT

This work deals with the thermal, morphological, and kinetic characteristics of rice during hydration, as well as the modeling of the process. Rice grains were subjected to different hydrothermal conditions and showed no degradation, but presented an endothermic transition corresponding to gelatinization at 53.8 °C. During hydration, the water absorption rate increased with temperature and grain morphological changes were observed only after gelatinization. There was a good agreement between the predictions of the theoretical model based on Fick's second law and the experimental results (maximum error of 2.067%); the phenomenological model built numerically was able to represent (3D and 2D) moisture transfer into the grain with an error of 1.708%. The parameters adjusted to the different models confirmed the effect of temperature on the process, and the thermodynamic properties (enthalpy, entropy, and Gibbs free energy) determined showed that hydration happened with non-spontaneous exothermic transformations.

1. Introduction

Rice is considered one of the main cereals produced and consumed worldwide (Mir et al., 2016; IRRI, 2017a). It is estimated that everyday half of the world's population consumes rice (Oli et al., 2014; Hu et al., 2017), which makes this grain a powerful ally in the fight against hunger due to nutritional quality, since it is rich in carbohydrates, proteins, vitamins and minerals (Abbas et al., 2011; IRRI, 2017b). Due to the great economic and nutritional importance of rice, studies dedicated to its various forms of processing are of relevance for the development of the quality of the final product.

According to Paiva et al. (2016), among methods of processing the rice grain, parboilization has gained space in consumer and industry preference, mainly due to nutrition and physical characteristics. A number of studies confirm the beneficial changes that the grain undergoes when parboiled, such as texture (Buggenhout et al., 2013), color (Lamberts et al., 2006), nutritional content (Storck et al., 2005) and self-life (Paiva et al., 2016).

Although the physical and nutritional effects of the use of parboilization of the rice are well known, still has insufficiently disclosed information about the process, especially the hydration phase. The hydration, according to Thammapat et al. (2016), is the most important step of the process, since it is intended to provide the rice with the moisture necessary for gelatinization of the starch. The gelatinization causes a morphological phenomenon in the physical structure of the food that characterizes rice as parboiled (Sittipod and Shi, 2016).

In view of the importance of the hydration step for the rice parboilization, it is of interest to study thermodynamic properties, as well as kinetic parameters and morphological changes in rice during hydration. According to Montanuci et al. (2013), from the thermal properties of the food and the process, it is possible to improve and elaborate industrial projects, while the physical structure analysis provides information that make it possible to specify morphological changes in the grain and their impact in final quality (Witek et al., 2010; Mir et al., 2016).

Also, knowledge of the kinetics of water absorption over time, allows, through mathematical modeling, its optimization (Nicolin

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et al., 2017; Borges et al., 2017). With respect to the parboiling process, few studies approached the modeling, as Bakshi and Singh (1980) and Bakalis et al. (2009) assuming Fickian diffusion and Miah et al. (2002) and Sridhar and Manohar (2003), using exponential mathematical models and the model of Becker, respectively.

Though the hydration step has been modeled in previous studies, no work has focused on the simulation of the mechanism of incorporation of moisture over time. Thus, this study presents relevant and new information on the modeling of mass transfer that takes place inside the grain during hydration, taken from 3D images. Given the complexity of this proposed model, due to the differential equation, the solution, according to Perez et al. (2011) and Montanuci et al. (2014), requires the application of finite difference, finite volume or finite element methods through programming languages or simulation software, such as COMSOL Multiphysics®.

Among the various reported studies conducted with process of grain hydration (Jideani and Mpotokwana, 2009; Montanuci et al., 2013; Fracasso et al., 2014; Marques et al., 2014; Nicolin et al., 2015), only Perez et al. (2011), Montanuci et al. (2014) and Gulati and Datta (2016) employed computational tools. However, none of them dealt with rice hydration in the parboiling process. The main benefit of using these modeling software tools is that they greatly simplify the implementations, making it possible to simulate numerous process conditions quickly.

This work presents a pioneering study on the modeling of rice hydration during the parboiling process, using three-dimensional transient simulation with COMSOL Multiphysics software. In addition, experimental data were fitted to Peleg models and Fick's Second Law for different temperatures. Thermal properties of the rice and thermodynamics of the process were determined, as well as changes in the morphological structure of the cultivar.

2. Material and methods

2.1. Materials

Paddy rice cultivar BR-IRGA 409 (0.141 ± 0.002 g g^{-1} dry basis; 1.149 ± 0.051 mm radius and 7.782 ± 0.222 mm length) harvest of 2013/2014 was used. This hybrid rice results from the crossbreeding of IR930-2 and IR665-31-2-4. The cultivars were kindly donated by the company *Ivaiporã Alimentos LTDA* (Paraná, Brazil).

2.2. Rice thermal characterization

Thermal degradation of rice was determined using a thermobalance (TG/DTG Netzsch, TG209, Germany) in the temperature range 30–600 °C and a heating rate of 10 °C min^{-1}. A Perkin-Elmer ceramic crucible (N5200040) containing 10 mg of paddy rice was used in the analysis, which was carried out under nitrogen (grade 5.0, White Martins) at a flow rate of 20 mL min^{-1} to maintain an inert atmosphere.

The starch of gelatinization was characterized using a Differential Scanning Calorimetry (DSC 204F1, Netzsch, Germany); 10 mg of ground rice (with 30% of moisture attained by a saturated solution of magnesium chloride during 48 h–200 g of salt in 25 mL of water) was placed in a 50 µL aluminum sample pan (Perkin-Elmer 580-10437). The material was subjected to thermal treatment in the range of 30 °C–100 °C at a heating rate of 10 °C min^{-1}. The equipment was calibrated with Indium (99.99% purity, melting point 156.6 °C, $\Delta H = 28.56$ µg^{-1}), and an empty pan was used as reference. Nitrogen (grade 5.0, White Martins) at a flow rate of 20 mL min^{-1} was used to maintain an inert atmosphere. Initial, peak and final gelatinization temperatures (°C) were recorded, and enthalpy (µg^{-1}) was determined by the endothermic curve generated using the Proteus® software.

2.3. Hydration tests, moisture gain assessment, volume variation, and morphological changes

The hydration tests of paddy rice during the parboiling process were performed in triplicate at temperatures of 35, 45, 55 and 60 °C in a thermostatic water bath (SOLAB, SL-155/22, Brazil) at atmospheric pressure (1011 hPa). Rice grains were placed in non-stick aluminum pan sheets in a 1:4 mass ratio in distilled water (Tramontina, 20069030, Brasil). The samples were collected every 30 min for the first 3 h, and after that, they were collected every hour up to the total of 15 h of the hydration.

Moisture content (g g^{-1}, dry basis) was determined by measuring (Shimadzu balance AY220, Japan) the mass while wet and after drying at 105 °C for 24 h (Quimis oven Q.317B242, Brazil). Volume (cm^3) was determined by volumetric displacement (Glasslabor BV.10, Brazil) of 30 grains, according to the methodology adopted by Fracasso et al. (2014).

Morphological changes in the microstructure of the grains were observed using a Scanning Electron Microscope (SEM) (VEGA 3LMV, Tescan, Czech Republic) at magnification level of 1000× and an acceleration voltage of 5000 V. The rice samples were cut (Wilkinson Lamina, Sword, Brazil) and metalized (Bal-Tec, SCD 050, Liechtenstein) with gold for 15 s or until the obtainment of a superficial coating of 10 nm for the production of SEM micrographs.

2.4. Modeling of the hydration process

2.4.1. Peleg model

Data obtained by hydration kinetics were adjusted to the Peleg empirical model (1988) (Eq. (1)) where: U_t (g g^{-1}) is the moisture content as a function of time t (h); U_0 (g g^{-1}) is the grain initial moisture content; and the parameters C_1 (h g g^{-1}) and C_2 (g g^{-1}) are related to mass transfer and water absorption capacity, respectively. The constant C_1 (h g g^{-1}) and C_2 (g g^{-1}) were estimated by nonlinear regression using the Levenberg-Marquardt algorithm.

$$U_t = U_0 + \frac{t}{(C_1 + C_2 t)} \tag{1}$$

An Arrhenius-type equation was used to describe the influence of temperature on the parameter C_1 (h g g^{-1}) (Montanuci et al., 2013; Borges et al., 2017), Eq. (2), where: C_{ref} is the hydration reference constant at a reference temperature; E_a is the activation energy for the hydration process (kJ mol^{-1}); R is the universal gas constant (8.314 J mol^{-1} K^{-1}); and T and T_{ref} are hydration and reference temperatures (K), respectively. T_{ref} is the average of the temperatures employed (323.15 K).

$$\frac{1}{C_1} = C_{ref}\exp\left[\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \tag{2}$$

Substituting Eqs. (2) into (1), we obtain the generalization of the model (Eq. (3)), which is able to predict the amount of water absorbed at any temperature and time during the process. The parameter $\overline{C_2}$ (g g^{-1}) is the arithmetic mean of the values of the C_2 at different temperatures. The generalized equation was also solved using nonlinear regression.

$$U_t = U_0 + \frac{t}{\left\{\left(C_{ref}\exp\left[\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]\right)^{-1} + \overline{C_2}t\right\}} \tag{3}$$