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Hydration kinetics of transgenic soybeans

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ABSTRACT. The kinetic and experimental analyses of the hydration process of transgenic soybeans (BRS 225 RR) are provided. The importance of the hydration process consists of the grain texture modifications which favor grinding and extraction of soybeans. The soaking isotherms were obtained for four different temperatures. Results showed that temperature affected transgenic soybeans' hydration rate and time. Moisture content d.b. of the soybeans increased from 0.12 ± 0.01 kg kg⁻¹ to 1.45 ± 0.19 kg kg⁻¹ during 270 min. of process. Two models were used to fit the kinetic curves: an empirical model developed by Peleg (1988) and a phenomenological one, proposed by Omoto et al. (2009). The two models adequately represented the hydration kinetics. Peleg model was applied to the experimental data and the corresponding parameters were obtained and correlated to temperature. The model by Omoto et al. (2009) showed a better statistical fitting. Although K_s was affected by temperature ($K_s = 0.38079$ exp (-2289.3 T⁻¹)), the equilibrium concentration remained practically unchanged.

Keywords: hydration, kinetics, transgenic soybean, mass transfer.

Cinética de hidratação de soja transgênica

RESUMO. Este trabalho apresenta o estudo experimental e cinético do processo de hidratação de grãos de soja transgênica (BRS 225 RR). A importância da hidratação de grãos consiste na modificação da textura característica dos grãos, o que favorece a moagem e a subsequente etapa de extração. Foram obtidas curvas cinéticas de hidratação de soja para quatro níveis de temperatura. A análise destas curvas indicou que a temperatura exerce grande influência sobre a velocidade e o tempo de hidratação da soja transgênica. Durante 270 min. de processo, a umidade em base seca dos grãos aumentou de $0.12 \pm 0.01 \text{ kg kg}^{-1}$ até $1.45 \pm 0.19 \text{ kg kg}^{-1}$. Neste estudo foram empregados dois modelos para o ajuste dos dados experimentais de hidratação: o empírico desenvolvido por Peleg (1988) e o modelo fenomenológico de parâmetros concentrados, desenvolvido por Omoto et al. (2009). Verificou-se que os dois modelos representaram adequadamente o processo de hidratação. O modelo de Peleg foi aplicado aos dados experimentais e os parâmetros correspondentes foram obtidos e correlacionados com a temperatura. O modelo de Omoto et al. (2009) apresentou melhor ajuste estatístico, enquanto K_s sofreu influência da temperatura ($K_s = 0.38079 \text{ exp} (-2289.3 T^{-1})$), a concentração de equilíbrio praticamente não variou.

Palavras-chave: hidratação, grãos, soja transgênica, transferência de massa.

Introduction

Soybean is currently the most important oleaginous legume under extensive cultivation worldwide. Among the agricultural products used as food by humans, soybean plays an increasingly important role, coupled to an extraordinary expansion (MIYASAKA; MEDINA, 1981). In fact, it provides remarkable levels of high quality protein, polyunsaturated fatty acids and phytochemicals, such as isoflavones, saponins, phytates and others. In addition, soybeans are an excellent source of minerals, such as copper, iron, phosphorus, potassium, magnesium, manganese and B complex vitamins (EMBRAPA, 2012).

It is currently impossible to discuss soybean without mentioning its transgenic version. Genetic engineering deals with ADN manipulation and creates new features for the original living being, i.e., changing the original genes display or introducing a new gene to the ADN. The modified gene is called transgene, from which the terms transgenic and genetically modified are derived (LUNA et al., 2013).

Brazil is the second largest soybean producer in the world. Although there are no reports on the proportion between regular and transgenic soybeans cultivated, estimates suggest that the harvested area of transgenic soybean is roughly 50-58% of all 142 Fracasso et al.

harvested soybean. Approximately 31.1 million tons were of the transgenic kind for the 2008/2009 harvest (EMBRAPA, 2012).

Current study analyzes the hydration of transgenic soybeans. Hydration is a process similar to cooking and extraction of selected compounds. Soybean extract, soybean milk and tofu production also involve hydration (COUTINHO et al., 2007, 2009a). The substances involved in the hydration process are mainly proteins, but also include cellulose and pectic substances. When soaked in water these substances increase the size of the bean (BECKERT et al., 2000). Hydration is also an important step when studying the drying of cereals (COUTINHO et al., 2009a and b, 2010) and the capacity of grain germination as a function of their initial moisture content (BECKERT et al., 2000).

According to Coutinho et al. (2009a and b), hydration by immersion plays an important role during rice parboiling, sorghum flour preparation and the manufacture of canned grains (corn, peas, etc.). Further, the process of grain hydration reduces cooking time, minimizes losses and improves the quality of the final product. Water absorption by soybeans during hydration depends on the time and temperature of immersion during the process (COUTINHO et al., 2009a and b; OBEKPA, 1990; SOPADE; WANG et al., 1979).

Mathematical models for fitting grain hydration data have been developed to predict the time needed to reach the desired hydration rate at a given temperature and thus reflect the immersion process dynamic behavior. The models may be either empirical or phenomenological (COUTINHO et al., 2009a and b; MASKAN, 2002; RESIO et al., 2006). Empirical models are usually obtained from simple mathematical correlations between experimental data (PELEG, 1988; SINGH; KULSHRESTHA, 1987). Peleg (1988) proposed an empirical model to quantify water absorption by grains and cereals and his model has been successfully used by various researchers to this end (GOWEN et al., 2007; RESENDE; CORRÊA, 2007; TURHAN et al., 2002). On the other hand, the phenomenological models take into account mass transfer by diffusion and convection (COUTINHO et al., 2009a and b; HSU, 1983a and b). The phenomenological models may be either concentrated or distributed parameters models. Both are able to represent the main trends of the process even when outside the experimental conditions in which they were validated. Unlike the distributed parameters models, the concentrated parameters models do not represent the spatial changes in the system's physical properties. The two may be used to

simulate grain behavior during the hydration process (COUTINHO et al., 2007, 2009b).

In current assay, a phenomenological concentrated parameters model developed by Omoto et al. (2009) and Peleg (1988) empirical model were used to assess soybean hydration data. The models, applied in current analysis and validated with experimental data obtained at four different temperatures, 25, 35, 45 and 65°C, have been extensively used in the literature. However, the particularities of food products, whether raw or processed, provide a different behavior to each product submitted to the same process. The above is true even for different cultivars of the same product, especially in the case of genetically modified species. Moreover, the hydration of soybeans is an operation commonly employed in the industry prior to several processing technologies, such as in the manufacturing of soymilk and tofu. Therefore, it is important to validate models describing processes of hydration for different products and cultivars and thus foregrounding other assays that address the same type of product and process.

Material and methods

BRS 225 RR transgenic soybeans were obtained from EMBRAPA SOJA – Empresa Brasileira de Pesquisa Agropecuária (Londrina, Paraná State, Brazil) and analyses were performed at the Analytical Chemistry Laboratory of the Chemical Engineering Department, Federal University of Paraná, Curitiba, Paraná State, Brazil.

The centesimal composition of the soybeans with regard to water, ashes, proteins and fats was determined according to Instituto Adolfo Lutz (IAL, 1985). Carbohydrate contents were calculated by difference.

The main equipment used in this work was a Q226M2 hot water bath (Quimis, Diadema, São Paulo State, Brazil). Soybeans were hydrated at 25, 35, 45 and 65°C in 400 mL beakers with distilled water, placed in the hot water bath.

Soybean samples weighing 15 g were removed from the beakers at 0, 1, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 90, 100, 120, 150, 180 and 270 minutes. Samples were carefully rinsed with absorbent paper to remove the surface water and their weight, volume and moisture content were taken. The hydrated soybeans mass was measured in an analytical scale and volume was determined by placing the soybeans in a 50 mL measuring cylinder and computing the displaced water volume. The quantification of moisture content was carried out by drying about 6 g of hydrated soybeans at 105°C in

a convective oven until constant weight (IAL, 1985). Moisture content was calculated by Equation 1:

$$X_{bu} = \frac{100MU}{MS} \tag{1}$$

where:

MU is the initial mass (g);

MS is the dried sample mass (g);

 X_{bu} is the moisture content on a wet basis (%). The soybean's water mass concentration (ρ_A) was calculated by Equation 2:

$$\rho_{\rm A} = \frac{X_{\rm bu}\rho_{\rm s}}{100} \tag{2}$$

where ρ_s (1.18 \pm 0.02 kg/m³) is the soybean density.

Mathematical modeling

Current study comprised two mathematical models to fit the experimental data: the Peleg model (PELEG, 1988), shown in Equation 3, and the phenomenological model developed by Omoto et al. (2009), shown in Equation 4.

$$M(t) = M_0 + \frac{t}{(K_1 + K_2 t)}$$
 (3)

where:

M(t) is the moisture content on a dry basis at time $t (kg kg^{-1})$;

t is time (s);

 M_o is the initial moisture content on a dry basis (kg kg⁻¹);

 K_1 (min.⁻¹) and

K₂ (dimensionless) are the model's constants.

The model developed by Omoto et al. (2009) is based on a mass balance in transient state for the water contained in the soybean, as Equation 4 shows:

$$\frac{d(\rho_A v)}{dt} = -N_A A \tag{4}$$

where:

 $\rho_A v$ is the water mass variation in the soybean at time t (kg);

A is the external area of the soybean (m^2) ;

v is the soybean volume (m³);

 N_A is the water mass flux (kg m⁻²·s).

The following assumptions were made: constant soybean volume, spherical soybean geometry (with a r_o radius (0.00318 \pm 0.00003 m), and mass flow assumed to be $N_A = K_s.(\rho_{Aeq}-\rho_A)$, where K_s represents the apparent mass transfer coefficient (m s⁻¹); ρ_{Aeq} is the soybean water concentration at equilibrium (kg m⁻³);

 ρ_A is the soybean water concentration at time t (kg m⁻³). The model may be solved by assuming that the water concentration in the soybean at t = 0 is uniform and known, i.e., $\rho_A = \rho_{A0}$. Soybean water concentration at equilibrium may be estimated from experimental data, or rather, by measuring soybean moisture content when moisture does not vary anymore, i.e., at the end of the hydration process. Equation 5 shows the employed phenomenological model after the above mentioned assumptions were made:

$$\frac{d(\rho_A)}{dt} = \frac{3K_s}{r_0}(\rho_{Aeq} - \rho_A)$$
 (5)

By integrating Equation 5 and assuming that ρ_{Aeq} and K_s are constant for a given hydration temperature, Equation 6 is obtained:

$$\ln\theta = \ln\left(\frac{\rho_{\text{Aeq}} - \rho_{\text{A}}}{\rho_{\text{Aeq}} - \rho_{\text{A}0}}\right) = -\frac{3K_{\text{s}}}{r_0}t\tag{6}$$

The model parameters K_s and $\rho_{\Lambda eq}$ may be obtained by a linear regression and fit Equation 6 to the experimental data.

Results and discussion

According to Velasquez and Bhathena (2007), soybean may be considered a complete food source since the legume contains nearly all essential amino acids, nutritionally equivalent to animal protein. According to Garcia et al. (1997) and Grieshop et al. (2003), carbohydrates compose about 30% of the grains; specifically, 15% of soluble carbohydrates (sucrose, raffinose, stachyose) and 15% of insoluble carbohydrates (dietary fiber). Depending on the variety, soybean protein contents range between 36 and 46%. According to USDA (1979), soybean contains approximately 15% saturated fat, polyunsaturated fat and 24% monounsaturated fat in their lipid composition. In current study, the transgenic soybean cultivar showed difference when compared to conventional soybeans. Results for moisture w.b., ashes, proteins, fats and carbohydrates were 9.23, 4.23, 32.5, 24.98 and 29.02%, respectively. Seo et al. (2012) studied the chemical composition of transgenic soybeans and found rates 35, 18 and 10% for proteins, fats and moisture content w.b., respectively. According to Embrapa (2012), conventional soybean contains 5% minerals and 34% carbohydrates.

Figure 1 shows experimental results of soybeans hydration and demonstrates changes in the soybeans

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moisture content (on a dry basis) at specific times for the several studied temperatures. The average standard deviation of the experimental determinations is 11.38, 10.09, 14.46 and 11.04% for 25, 35, 45 and 65°C, respectively. At the beginning of the hydration process, the soybean's moisture content was approximately 10% w.b. (0.1 kg kg⁻¹). At nearly 150 minutes of hydration when the kinetics curve becomes roughly horizontal, equilibrium is reached (1.4605 kg kg⁻¹). Results showed that temperature affected the soybean's hydration kinetics. At 45 and 65°C, higher moisture contents were reached when compared to those at lower temperatures. Above results confirmed that the rate of the hydration process was positively affected by also temperature, reported by Tangratanavalee (2003), Chopra and Prasad (1994) and others.

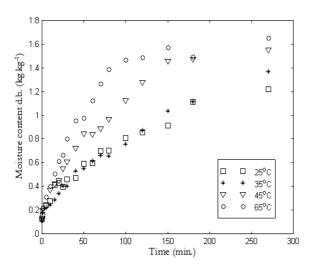


Figure 1. Experimental results for moisture content (d.b.) during soybean hydration.

Data fitting the concentrated parameters model

A linear regression was performed to fit the experimental data with the concentrated parameters model. Parameters K_s and ρ_{Aeq} were obtained for the different temperatures under analysis. Figure 2 shows the fitting of the model for the experimental data at 45°C and Table 1 shows the rates of the calculated parameters for all temperatures analyzed. A strong dependence of apparent mass transfer coefficient on temperature was observed (p < 0.05), as reported previously (COUTINHO et al., 2007, 2009b). Table 1 reveals a 142% increase in K_s rate when temperature rose from 25 to 65°C. On the other hand, although the mass transfer velocity increased with temperature, the soybean water concentration at equilibrium (ρ_{Aeq}) was not

significantly affected (p < 0.05). The high rates of determination coefficient (R²) demonstrated that the concentrated parameters model provided a good fitting to the experimental data for all temperatures under analysis. The deviation in R² rates may be accounted to the dispersion of the experimental data. The correlation coefficients obtained by Omoto (2009) for the hydration of pea grains at 30, 40 and 60°C were 0.97, 0.96 and 0.96, respectively, similar to rates in current study, or rather, 0.9644, 0.9620 and 0.9504, respectively.

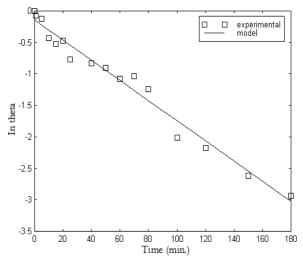


Figure 2. Concentrated parameters model for hydration at 45°C.

Table 1. Rates of parameters K_s and ρ_{eq} and the associated determination coefficient for temperatures under analysis.

T (°C)	K_s (m s ⁻¹)	ρ _{Aeq} (kg m ⁻³)	\mathbb{R}^2
25	0.001306	0.5830	0.9131
35	0.001458	0.6256	0.9644
45	0.001842	0.6377	0.9620
65	0.003162	0.6421	0.9504

Influence of temperature on the parameters of the concentrated parameters model

K_s increase by hydration temperature may be represented by a model similar to the one proposed by Arrhenius (Equation 7).

$$K_{s} = B.\exp\left(\frac{-E'}{T}\right) \tag{7}$$

The linear form of Equation 7 is shown below (Equation 8)

$$ln(K_s) = ln(B) - E' \cdot \frac{1}{T}$$
 (8)

Rates of parameters B (0.38079 m s⁻¹) and E' (2289.3 K⁻¹) were obtained by linear regression and the determination coefficient 0.9648 was reached for

this fitting (Figure 3). In their study on the hydration of pea grains, Omoto et al. (2009) obtained rates for the correlation coefficient (R2) similar to those in current assay, namely, 0.96. Jideani and Mpotokwana (2009) studied the hydration of varieties of Bambara and found correlation coefficients rates between 0.96 and 0.97. Abu-Ghannam and McKenna (1997) obtained R2 values from 0.902 to 0.989 for the hydration kinetics of red kidney beans. In their study on the hydration of paddy, brown rice and husk, Thakur and Gupta (2006) obtained determination coefficients 0.99, 0.95 and 0.84, respectively. Equation 9 presents the dependence of K_s parameter on temperature for the BRS 225 RR transgenic soybean.

$$K_s(T) = 0.3808.e^{\frac{-2289.3}{T}}$$
 (9)

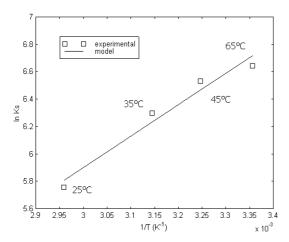


Figure 3. Arrhenius model for the effect of temperature on the parameters of the concentrated model.

Data fitting Peleg model

Peleg model has two parameters, K₁ and K₂, obtained through the linear form of Peleg Equation, represented by Equation 10. Figure 4 shows the fitting of the experimental data by linear Peleg model.

$$\frac{t}{M(t)-M_0} = K_1 + K_2 t \tag{10}$$

Table 2 presents the rates of parameters K_1 and K_2 and their respective determination coefficients (R^2) obtained for the four temperatures analyzed. In their study of soybean hydration at 25°C, Sopade and Obekpa (1990) found K_1 and K_2 rates at 0.01 and 0.006, respectively, which were close to those observed in current assay, or rather, 0.0094 and 0.0081, respectively.

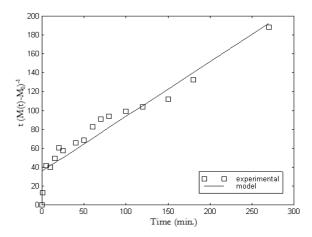


Figure 4. Peleg model for soybean hydration at 45°C.

The constant K₂ defines the equilibrium moisture content which is not temperature dependent. Knowledge on K2 might be important when studying the water absorption in food products. Rates of the determination coefficient (R²) shown in Table 2 suggested that the Peleg model provided a proper fitting for the experimental data. Deviation in R2 values might accounted to the dispersion of the experimental data since the average standard error was different for each set of experimental data. Parameter K₁ was temperature dependent, whereas K2 was temperature independent (p < 0.05). According to Resende and Corrêa (2007), parameter K2 from the Peleg model was related to maximum water absorption capacity of a system, or rather, the lower its value, the higher the system's water absorption.

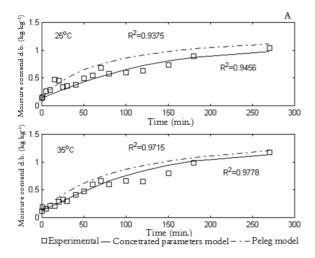
Table 2. Parameters K_1 and K_2 rates and the determination coefficient for all studied temperatures.

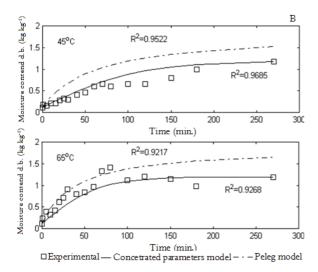
Temperature (°C)	K ₁	K_2	R^2
25	56.35	0.800	0.914
35	65.56	0.675	0.805
45	35.64	0.580	0.912
65	22.73	0.566	0.956

Figures 5A and B shows the experimental and predicted results for moisture content d.b. during soybean hydration. The two models yielded a high determination coefficient and were appropriate to represent the hydration process. In fact, the concentrated parameters model yielded a lower quadratic deviation and was rather more appropriate to represent the transgenic soybean hydration.

The concentrated parameters model proposed by Omoto et al. (2009) better represented the hydration experimental data with a quadratic 146 Fracasso et al.

deviation of 0.002709 ± 0.001679 , whereas the Peleg model yielded a quadratic deviation of 0.005199 ± 0.000734 .





Figures 5A and B. Comparison between experimental and predicted results for moisture content d.b. during soybean hydration at (a) 25°C; (b) 35°C; (c) 45°C; (d) 65°C.

Conclusion

In current study, two models were applied to represent the hydration kinetics of soybeans, namely, Peleg empirical model and a concentrated parameters model proposed by Omoto et al. (2009). The two models represented adequately the moisture content evolution during the process. Statistically, however, the concentrated parameters model provided a proper fitting to the experimental data in terms of quadratic deviation. Since apparent mass transfer coefficient (K_s) from the concentrated parameters model and parameter K₁ from the Peleg model increased with temperature, the hydration temperature and speed were directly proportional. In fact, a lower time for

reaching the equilibrium moisture content was observed for higher hydration temperatures. The average equilibrium moisture content for the BRS 225 RR transgenic soybean was 1.4605 kg kg⁻¹. As may be seen from K₂ results by the Peleg model, the above rate was not significantly affected by temperature.

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