Study of the rehydration kinetics of nixtamalized corn by using two nixtamalization methods

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Abstract*–The present work aimed to study the rehydration kinetics of previously nixtamalized and dried corn. Nixtamalization was carried out by two methods: using wood ash (classical method) and using calcium hydroxide ($Ca(OH)_2$) (traditional method), after the samples were sun-dried. The rehydration kinetics was described using six mathematical models (Fick, Peleg, Weibull, Page, Ibarz et al. and first-order model) in which the possible interpretation of its parameters and the goodness of fit was evaluated. As results, it was obtained that the nixtamalization with wood ash obtained better rehydration properties. The kinetic parameters values of all the used models showed that the rehydration in this treatment was the fastest. In addition, this treatment also reached a high moisture content (49.22 ± 2.10% w.b.) compared to other treatments (Control and $Ca(OH)_2$). The evaluation of the models fit suggests that the first-order model is not adequate to describe the rehydration in any treatment here evaluated, while Fick is suitable to describe the rehydration of Control samples (without treatment), and the models such as Page, Peleg or Weibull are suitable for describing rehydration in samples processed by nixtamalization, especially with ash.

***Keywords*—nixtamalization, corn, mass transfer, mathematical modeling, rehydration.**

I. INTRODUCTION

Nixtamalization is a widely used process in American societies (principally in central and south countries, such as in Mexico, Guatemala, Peru, Colombia) to produce nixtamalized grains. Different grains could be processed through nixtamalization such as wheat, corn, or beans, of which the most consumed is the nixtamalized corn. It could be directly consumed in the cooked form (mote) or as a principal ingredient of different traditional products such as tortilla, tamal, atole, totopos, among other chips and snacks [1, 2]. Due to its commercial importance, this study has been focused on nixtamalized corn.

Nixtamalization consists in cooking grains in dispersions of water and wood ashes (classic method) or by using alkaline compounds (traditional method), of which ashes were historically the first calcium source used for nixtamalization [3]. Nowadays, both classic and traditional are still used, classic nixtamalization presents nutritional advantages containing highest functional components. However, the removal of the pericarp is more delayed compared to traditional ones [1]. Therefore, to reduce processing time ashes have been largely replaced by lime ($Ca(OH)_2$) or other alkaline agents in industrial production [1, 3].

It is important to mention that nixtamalized corn and its derivatives are not only consumed in the producing countries but that the international market in North America, Europe, Asia is increasing [1]. The commercialization of nixtamalized corn is normally done in dry form, which at the time of being processed or transformed into by-products needs to be rehydrated. To date, only the hydration kinetics of corn has been studied during the nixtamalization process. For example, the authors Fernandez-Muñoz, et al. [4], Peña-Reyes, et al. [5], Ruiz-Gutiérrez, et al. [6] evaluated different cooking temperatures, different types and concentrations of alkaline compounds. However, to our knowledge, there are no studies that have investigated the rehydration kinetics of nixtamalized corn. This being a particularly important process to be described and controlled since during nixtamalization changes in structure and composition occur, the main ones being: removal of the pericarp [7], partial gelatinization of starch [8, 9], and calcium uptake [10, 11]. These modifications will impact the rehydration kinetics.

Rehydration properties of dried products in one of the most important properties in this type of products. In this process, it is expected that the dry product will hydrate quickly to the desired moisture level and that the water will remain inside after the process. In nixtamalized corn, rehydration would be important since, for example, nixtamalized corn before grinding needs to have a moisture level of around 50% to produce a good quality of dough [5]. The description of the rehydration process is carried out by evaluating the kinetics, where the process can be explained through the parameters obtained from mathematical models. Currently, in addition to traditional models such as the first-order kinetics equation [12] or the phenomenological Fick´s diffusion model [13], other empirical models are being studied to describe rehydration and other mass transfer operations. The motivation of the researchers for using other mathematical models is that the rehydration of dry products cannot only be explained by a purely diffusive mechanism, but other phenomena such as imbibition, swelling, capillarity, structural changes, among others, in addition to the inherent properties of the product and fluid are important [14-

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16]. In general, the use of one or another model in rehydration will depend on the type of behavior observed in the experimental data, for example, if it is a sigmoidal or concave downward behavior [17]. On the other hand, in addition to the quality of fit of the model to the experimental data, the choice of a model depends on the interpretation of its parameters and explanation of process mechanisms.

In this study, the nixtamalized process has been carried out in corn using two methods (classic and traditional), after drying the nixtamalized grains, the rehydration has been evaluated. The rehydration kinetics have been evaluated using six mathematical models, where their parameters, as well as their quality of fit, have been described and interpreted.

II. MATERIAL AND METHODS

A. *Raw material*

White maize grains (*Zea mays* var. Capia) were obtained from the fields of cultivation in Otuzco, La Libertad (Peru). The corn kernels with a firm texture, without mechanical damage, and a characteristic creamy white color were selected.

B. *Nixtamalization process*

Two methods of nixtamalization without steeping stage was performed, one by using wood ash and another by using calcium hydroxide both classified as classic and traditional methods respectively by Escalante-Aburto, et al. [1].

1) Nixtamalization with ash: The ash was obtained from artisan kitchens which use wood as fuel, leaving the ash as waste. To prepare the nixtamalization medium, 3.5 kg of ash dispersed in 6 L of water was used. The ash dispersion was heated until reaching 105 °C, then 2 kg of corn were added at 1:3 corn/water ratio according to the reported by Ruiz-Gutiérrez, et al. [6]. After 35 min the process was finished, and the corn was washed and rinsed to remove the husk completely and to eliminate residues. Subsequently, the nixtamalized corn was placed to dry in the sun for 24 h.

2) Nixtamalization with $Ca(OH)_2$: For this process, accelerated nixtamalization of corn kernels was performed. For this, 700 g of calcium hydroxide and 7.5 L of water were used to prepare the nixtamalization medium. The preparation was heated until reaching 100 °C, then 2 kg of corn were added, after 20 min of cooking the process was finished. Finally, the corn was washed and rinsed to remove the husk completely and to eliminate $Ca(OH)_2$ residues. Subsequently, the nixtamalized corn was placed to dry in the sun for 24 h.

C. *Rehydration process*

The rehydration process was carried out at atmospheric pressure and 25 °C after dying in samples of corn without processing (Control), nixtamalized corn with ash (Ash) and nixtamalized corn with calcium hydroxide ($Ca(OH)_2$).

The samples were separated into portions which were rehydrated for different periods. The first four points were registered every 5 min, the next five points every 20 min, the next four points every 30 min, the next 5 five points every 1 hour and finally the last point was determined 24 h after starting the process. For each rehydration period, approximately 4 g of sample placed in 100 mL of water was used. Throughout the process, the moisture before and after each period was determined, with these data the rehydration curves of each treatment were constructed.

D. *Rehydration kinetics description*

The rehydration curves of corn samples showed a concave downward behavior. Therefore, the mathematical models used were those that are typically used to describe this behavior of the hydration kinetics of grains [17] and other foods [14].

1) Fick´s diffusion model: This model based in Fick's second law [13] allows obtaining the moisture effective diffusivity (D_{eff}). This parameter is a lumped constant that represent the global transport phenomena; it includes mechanisms such as molecular diffusion, liquid diffusion through the solid pores, vapor diffusion, capillarity and all other mechanisms that affect mass transport [18]. For modelling purposes, it was assumed a uniform temperature and initial moisture content inside the sample, as well as negligible deformation during the process. The moisture effective diffusivity (D_{eff}) was considered constant over the process and across the sample, where moisture movement regulates rehydration process.

Corn kernels are considered with spherical geometry [19]. Therefore, the analytical solution integrated for a spherical body is showed in (1), which is the result of this purely diffusive model controlled by internal resistances [20].

$$\frac{M_t - M_\infty}{M_0 - M_\infty} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-\left(\frac{n\pi}{R_{eq}}\right)^2 D_{eff} \cdot t\right] \quad (1)$$

Where D_{eff} is the effective moisture diffusivity (m^2/s), M_t is moisture content on a dry basis (g water/g dry matter (d.b.)) at time *t* (s), M_0 is the initial moisture, M_∞ is the equilibrium moisture content, which expresses the water concentration at saturation estimated from the last point of rehydration, R_{eq} is the equivalent radius (6.35×10^{-3} m), i.e. the radius of the sphere having the same volume as the corn kernel. For resolution, 50 terms of the summation were considered.

2) Peleg model: An empirical equation widely used to describe the rehydration of various foods due to its goodness of fit and interpretation of its parameters is the equation known as Peleg model, given by (2)[21].

$$M_t = M_0 + \frac{t}{k_1 + t k_2} \quad (2)$$

Where, M_t is moisture content on a dry basis (g water/g dry matter (d.b.)) at time t (s), M_0 is the initial moisture, M_∞ is the equilibrium moisture content, which was estimated from the last point of rehydration, k_1 is the rate constant ($min \cdot d.b^{-1}$) and

k_2 is the constant of the asymptotic level (d.b^{-1}). The reciprocal of k_1 represents the water absorption rate and the reciprocal of k_2 represents the water retention capacity.

3) Weibull distribution function: It describes the process as a sequence of probabilistic events [22]. Among the empirical models, the Weibull distribution function was frequently utilized for describing the hydration process of a variety of dried foods [14, 23], (3).

$$\frac{M_t-M_\infty}{M_0-M_\infty}=1-\exp\left[-\left(\frac{t}{\propto}\right)^\beta\right] \tag{3}$$

The scale parameter α is related to the reciprocal of the process rate constant, and the shape parameter, β. The scale parameter defines the rate and represents the time needed to accomplish approximately 63% of the process. Different values of β lead to different shape of curves, when β=1, the Weibull distribution reduces to first-order kinetics (6).

4) Page model: Page empirical model [24] was also used to describe the process (4), which has been successfully applied to describe processes of drying and hydration of different food products. Where, k_3 is the hydration rate constant (min^{-n}), while n is the dimensionless drying constant.

$$M_t=M_\infty+(M_0-M_\infty)\cdot\exp[-k_3(t^n)] \tag{4}$$

5) Ibarz et al. model: Ibarz, et al. [25] proposed that the mechanism of water adsorption occurs in two steps. A first step is assumed in which the samples retain the water according to zero-order kinetics. In a second step, the retained water can be released according to first-order kinetics. The equation proposed by the authors after integration is showed in (5), where k_4 and k_5 are the zero-order and first-order kinetics constants, respectively. For large times $M_\infty=\frac{k_4}{k_5}$, consequently $k_4=M_\infty\cdot k_5$, which indicates the velocity of retention and liberation of water are equalized.

$$M_t=\left(\frac{k_4}{k_5}\right)-\left(\frac{k_4}{k_5}-M_0\right)\cdot\exp[-k_5\cdot t] \tag{5}$$

6) First-order model: First-order kinetics is one of the most used model describing the moisture transfer during hydration [26], and is based on an empirical approach that the rate of hydration is proportional to a temporary driving force (6) [12].

$$M_t=M_\infty+(M_0-M_\infty)\cdot\exp[-k_6\cdot t] \tag{6}$$

Where k_4 is the hydration rate, and t is the time of hydration.

Equations 1-6 were fitted to experimental data by identifying their parameter values that minimize the sum of squared errors (SSE, (7)) between the experimental and the predicted values. The Generalized Reduced Gradient method implemented in the 'Solver' tool of software Excel 2016 (Microsoft, USA) was used for this purpose.

$$\mathrm{SSE}=\sum_{\mathrm{i=1}}^{\mathrm{x}}((\mathrm{predicted})-(\mathrm{experimental}))_{\mathrm{i}}^2 \tag{7}$$

To report the fit criteria of the models were considered the errors distribution, the coefficient of determination (R^2), and the normalized root-mean-square deviation values ($NRMSD$, (8)).

$$NRMSD=\frac{RMSD}{ymax-ymin} \tag{8}$$

E. Statistical analysis

A completely randomized design (CRD) was used, all processes and analyses were performed at least 3 times. The one-way ANOVA was carried out with a significance level of 5%. To determine statistical differences among means of treatments, the Tukey test was used. Statistical analyses were determined using the IBM SPSS Statistics 23 software (IBM SPSS, USA).

III. RESULTS AND DISCUSSION

After the nixtamalization and drying treatments, the corn samples were rehydrated, and the proposed mathematical models were fitted to experimental rehydration data. For better visualization, Fig. 1 shows the individual adjustment of each model after 9 h of hydration. Rehydration curves are characterized by a higher rate of water uptake at the beginning of the process, which decreases along the processing time until moisture saturation. For comparison, all the models were included in Fig. 2, where the maximum rehydration point after 24 h is also evidenced. At this time, the moisture reached by Control was 0.63 ± 0.03 (g of water/g of dry matter), 0.97 ± 0.02 (g of water/ g of dry matter) for samples treated with ash and 0.80 ± 0.04 (g of water/g of dry matter) for samples treated with $Ca(OH)_2$.

In the rehydration processes during the cooking and steeping processes, saturation moisture from 40% to 50% (g water/100g of sample) has been reported [4, 5], referring to the fact that quality doughs are produced at this level of moisture. It should be mentioned that in the authors' studies the samples were directly processed without going through a drying process. Considering this purpose (producing dough), in the present study, according to the moisture level reached during rehydration, it is observed that in both treatments the samples reached the necessary moisture (49.22 ± 2.10% for samples treated with ash and 44.37 ± 3.64% for samples treated with $Ca(OH)_2$) to produce good quality dough.

Graphically (Figures 1 and 2), the treatment with ash can be easily differentiated, which was the one that rehydrated the fastest and reached the highest equilibrium moisture. In the next section, a description of the resulting parameters (Table I) for each mathematical model used will be made, focusing on the interpretation and relationship with the possible changes resulting from the nixtamalized treatments.

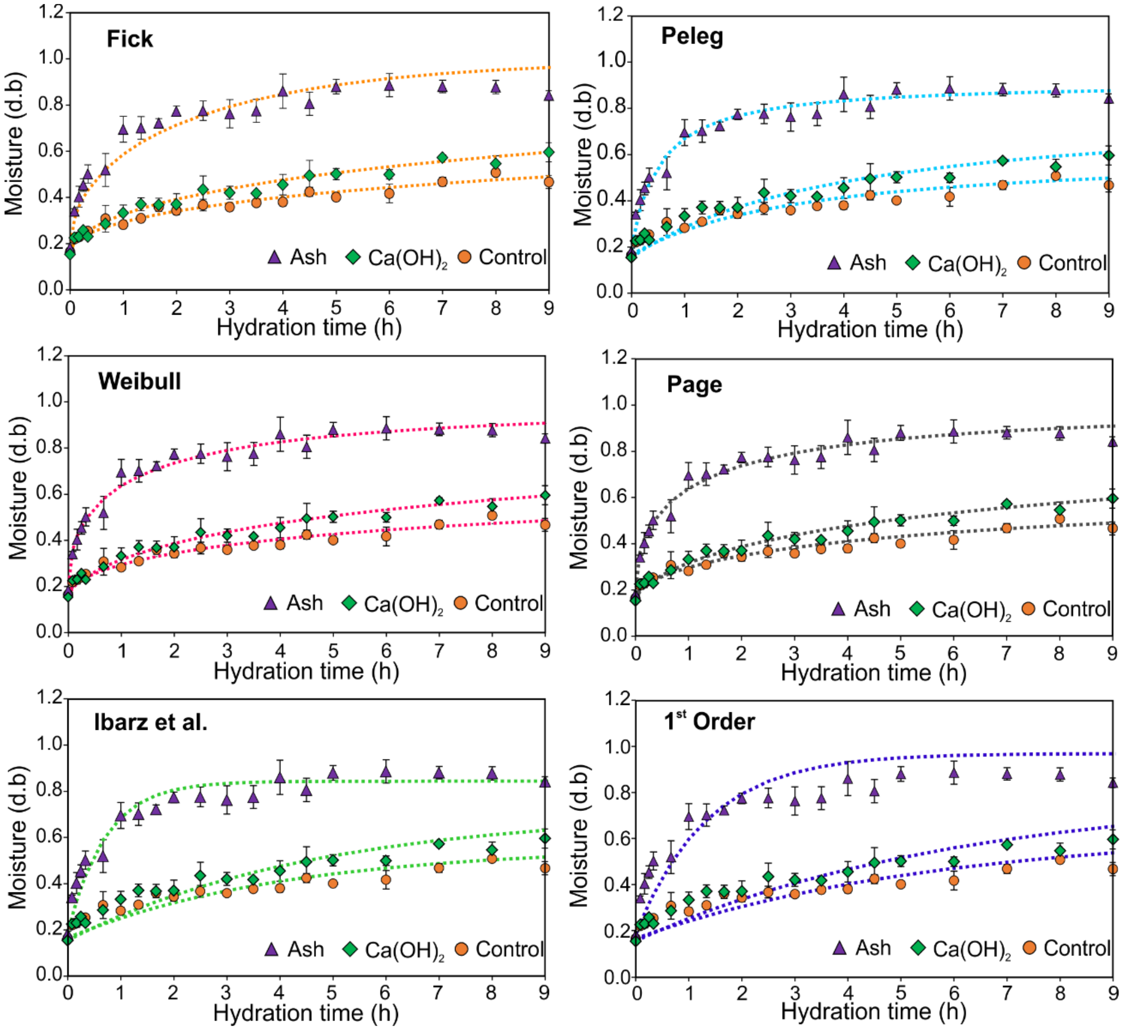

Fig. 1 Mathematical models fitted to rehydration experimental data (9h) of Control and nixtamalized corn with ash and $Ca(OH)_2$

A. Rehydration kinetics description trough mathematical model parameters

1) Fick diffusion model: From Fick diffusion model, the moisture effective diffusivity (D_{eff}) was estimated. The Control samples showed a D_{eff} value of $0.091 \times 10^{-9} \pm 0.016 \times 10^{-9}$ m^2/s. The obtained results were higher than reported by Martínez-Garza, et al. [27] for white corn with D_{eff} of 0.019×10^{-9} m^2/s, it is possible because of the different maize variety. Compared to control, the D_{eff} value was significantly ($p > 0.05$) higher for ash treatment, it increased the D_{eff} in about 354% (Table I).

Among the factors that affect the water diffusion are the pericarp permeability, grain physical characteristics and nixtamalization conditions. The pericarp is the external layer of grain structure, this layer is firstly modified during nixtamalization where occurs the hydrolysis and solubilization of its structural components [3, 7]. By considering that pericarp is a barrier to water entry, in fact, it presents the lowest diffusion coefficient compared to other parts of corn kernel [28], it is expected that its hydrolysis enhances the rehydration process as is observed in nixtamalized samples with Ash treatment. The same behavior would be expected for the nixtamalized samples with $Ca(OH)_2$, however, the diffusion coefficient was similar to that of the Control samples. This can be explained by the different composition, concentration of compounds between both treatments and the temperature reached during the nixtamalization process, which could have produced different modifications in the structure resulting in different rehydration behaviors. This will be better explained in section 3.3.

2) Peleg model: Regarding the rate constant (k_1, min·d.b^{-1}) of Peleg model, it was lower for the treatment with ash when compared to Control and $Ca(OH)_2$ treatments. By considering that the reciprocal of k_1 is related to the rehydration rate, the lower k_1 value, the higher the rehydration rate. It means that the samples processed with ash ($k_1 = 41.551 \pm 3.913$ min·d.b^{-1}) presented the highest rehydration rate. In addition, Fernandez-Muñoz, et al. [4] compared the Michaelis–Menten equation with the Peleg equation making equivalences of constants between them, where $v_{max} = 1/k_1$ when $t \rightarrow 0$. Therefore, the maximum rehydration rate (increase in moisture content per minute) was ~ 0.024 d.b ·min $^{-1}$ for Ash treated samples, ~ 0.0027 d.b ·min $^{-1}$ for $Ca(OH)_2$ treated samples and ~ 0.0023 d.b ·min $^{-1}$ for Control samples.

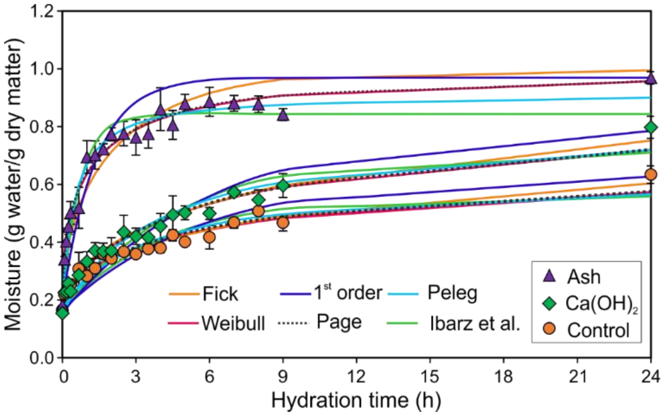

Fig. 2 Comparison among mathematical models fitting to experimental rehydration data after 24h.

On the other hand, by analyzing the constant of the asymptotic level (k_2, d.b^{-1}), which reciprocal of k_2 represents the water retention capacity. That is, the lower the value of k_2, the less moisture retained at the end of the process. Therefore, the ash and $Ca(OH)_2$ treated samples were those that showed a higher amount of retained water than the Control ones. According to Fernandez-Muñoz, et al. [4], $k_2 = \frac{1}{A}$, where A represents the moisture content increment at the end of the rehydration process and is equal to $(M_\infty - M_0)$. In other words, $M_\infty = M_0 + \frac{1}{k_2}$. Considering the above, the results showed in Table I suggests that, at the end of the process, the samples treated with ash reached a moisture increase of ~ 0.732 d.b, the $Ca(OH)_2$ treated samples an increase of ~ 0.661 d.b and finally an increase of ~ 0.456 d.b for the Control samples. On the other hand, if the initial moisture of the samples is considered, which was similar for all the treatments, the equilibrium moisture will be proportional to the moisture increase at the end of the process $(\frac{1}{k_2})$.

TABLE I
MODEL PARAMETERS OBTAINED FROM REHYDRATION KINETICS OF CONTROL, ASH AND $CA(OH)_2$ TREATMENTS. DIFFERENT SUPERSCRIPT LETTERS MEAN SIGNIFICANT DIFFERENCES ($P < 0.05$) AMONG TREATMENTS.

Model parameters		Treatment		
		Control	Ash	$Ca(OH)_2$
Fick (1)	D_{eff} [x10^{-9} m^2/s]	0.091 ± 0.016^{a}	0.413 ± 0.051^{b}	0.083 ± 0.005^{a}
Peleg (2)	k_1 [min·d.b^{-1}]	436.693 ± 43.156^{a}	41.551 ± 3.913^{b}	369.782 ± 21.233^{a}
	k_2 [d.b^{-1}]	2.194 ± 0.122^{a}	1.366 ± 0.036^{b}	1.512 ± 0.111^{b}
Weibull (3)	β [-]	0.578 ± 0.049^{ab}	0.495 ± 0.027^{b}	0.625 ± 0.015^{a}
	$\propto$ [min]	428.661 ± 103.857^{a}	81.708 ± 12.251^{b}	436.581 ± 52.144^{a}
Page (4)	k_3 [min^{-n}]	0.031 ± 0.006^{b}	0.114 ± 0.011^{a}	0.023 ± 0.002^{b}
	n [-]	0.578 ± 0.049^{ab}	0.495 ± 0.027^{b}	0.625 ± 0.015^{a}
Ibarz et.al (5)	k_4 [min^{-1}]	0.002 ± 0.000^{b}	0.020 ± 0.003^{a}	0.003 ± 0.000^{b}
	k_5 [min^{-1}]	0.004 ± 0.001^{b}	0.024 ± 0.003^{a}	0.004 ± 0.000^{b}
1st Order (6)	k_6 [min^{-1}]	0.003 ± 0.000^{b}	0.012 ± 0.002^{a}	0.003 ± 0.000^{b}

3) Weibull distribution model: Regarding the shape parameter β, the samples treated with ash showed a lower value compared to those treated with $Ca(OH)_2$, but both were similar to Control. As was stated, when β=1, the Weibull distribution reduces to 1st order kinetics [14, 23], therefore all treatments show a rehydration behavior far from first-order kinetics. For other maize cultivars, higher values of shape parameter were reported during rehydration [29]. Therefore, different shape parameter values are expected for different material structure, composition and processing conditions. According to Marabi, et al. [23], Cunha, et al. [30] the shape parameter values are specific depending on geometry (spheres, cylinders and slabs) and mechanism type that controls the rehydration process which includes internal diffusion, external convection and relaxation. For example, in samples with sphere geometry, if the process is controlled by internal resistance, the shape parameter β was in the range of 0.6-0.7. However, these values were determined using mostly simulated data, only with two products: carrot and apple. Therefore, it is still difficult to attribute an isolated explanation to the obtained β values since many factors are influencing at the same time. In general, in this study, a possible explanation is that the low value obtained in samples treated with ash (β = 0.495 ± 0.027) is related to a reduction in water uptake resistances for this treatment which depends on modification in structure and composition caused during processing.

On the other hand, the lower value of the scale parameter $\propto$ indicated a faster rate of water absorption, which represent the time needed to accomplish approximately 63% of the process [23]. Therefore, the treatment that needs significantly lower time was the Ash treatment, while there were no differences between Control and treatment with $Ca(OH)_2$.

4) Page model: Page model parameter k_3 indicate that the treatment with ash showed a higher rehydration rate than the other two treatments (Control and $Ca(OH)_2$), which showed k_3 values without significant difference. Regarding the n parameter, the value was higher for $Ca(OH)_2$ treatment being significantly different from Ash treatment but similar to Control. For a better interpretation of these values, it is necessary to know the explanation given by some authors to the parameters of the Page equation as shown below.

Simpson, et al. [31] demonstrated that Page equation and Fick's second law are particular cases of the anomalous diffusion model based on fractional calculus approach [32], being possible to attribute phenomenological interpretations to its parameters. If $n = 1$, the fractional equation transforms into Fick's second law model (evaluated only with the first term of summation) for long processing time. According to these authors, k_3 is related to the diffusion coefficient and sample geometry; n is related to sample microstructure and "type of diffusion". Therefore, $n = 1$ for a purely diffusive mechanism of water transfer. On the contrary, if n is different from 1, this parameter could be related to domains of anomalous diffusion: sub-diffusion if $0 < n < 1$ or super-diffusion if $n > 1$.

According to what is observed in Table I, all values of n are less than 1, indicating a sub-diffusive behavior of water transfer during rehydration. Furthermore, the different values among treatments could indicate that there were differences in the microstructure. On the other hand, it was stated that k_3 could be related to the diffusion coefficient [31]. However, by considering that in this work, the value of n has not been 1, it cannot be related to the purely diffusive coefficient D_{eff} (m^2/s) obtained by Fick's second law. The difference is that the "diffusive coefficient" related to k_3 would have the dimension (m^2/s^n).

Finally, it is important to note that the n values of the Page model were equal to β values obtained for Weibull model fitting. This makes sense due to the similar structure of the of both model's equations, where the following equivalences could be made: $n = \beta$ and $k_3 = \frac{1}{\propto\beta}$.

5. *Ibarz et al. model:* According to Ibarz, et al. [25] k_4 and k_5 are the zero-order and first-order kinetics constants, which indicates the rate of retention and liberation of the retained water respectively. As shown in Table I, both k_4 and k_5 values were higher for samples treated with ash. It means that these samples showed higher water absorption rate and higher amount of water release than the other two treatments. For large times $M_\infty = \frac{k_4}{k_5}$, resulting in calculated M_∞ of 0.5 (d.b) for Control; 0.75 (d.b) for $Ca(OH)_2$ treatment and 0.83 (d.b) for ash treatment, these values are according the experimental M_∞ values observed in Fig. 2 for each treatment. In addition, the water absorption rate (k_4) were lower than k_5 constant in all cases especially in Control samples, which means that in these samples the rate of liberation of absorbed water is higher explaining their low M_∞.

6. *First-order:* The kinetic parameter of first-order model (k_6) indicates the rate of rehydration, which is proportional to a temporary driving force. The k_6 values for Control samples (0.003 min^{-1}) were between the values reported by Martínez-Garza, et al. [27] for white corn (0.0024 min^{-1}) or for yellow corn (0.0046 min^{-1}) reported by Miano, et al. [33]. Compared to Control, only the k_6 value for ash treatment was significantly different and was the highest, indicating higher rehydration rate in these samples.

B. *Mathematical models fitting description*

There are models in which a lack of fit can be seen graphically in some regions of the curves (Fig. 1), where the most remarkable is the Fick model, followed by Peleg, Ibarz et al. and first-order models. Regarding the first-order model, Ibarz et al. and Peleg model, there is a lack of fit in the initial rehydration step (constant rate stage), similar behavior was reported by Miano, et al. [33] where these models do not explain the first step in rehydration process of corn. At the transition stage, from constant rehydration rate stage to lower rate stage, the lack of fit was evidenced mainly for the Ibarz et al. and first-order models where moisture values were overestimated. In addition, in Fig. 2 is observed that first-order and Peleg models underestimated the equilibrium moisture value for all treatments. Considering the experimental data in Fig. 2, the adjustment criteria were shown in Table II and Fig. 3.

TABLE II.
MODEL FITTING CRITERIA OBTAINED FROM REHYDRATION KINETICS DATA FOR EACH USED MATHEMATICAL MODEL.

Fitting criteria		Treatment		
		Control	Ash	$Ca(OH)_2$
Fick (1)	NRMSD	0.735 ± 0.283	2.068 ± 0.285	0.848 ± 0.054
	R^2	≥ 0.900	≥ 0.925	≥ 0.947
Peleg (2)	NRMSD	1.436 ± 0.745	1.454 ± 0.777	1.552 ± 0.162
	R^2	≥ 0.829	≥ 0.918	≥ 0.921
Weibull (3)	NRMSD	0.774 ± 0.428	1.219 ± 0.363	0.947 ± 0.091
	R^2	≥ 0.884	≥ 0.937	≥ 0.938
Page (4)	NRMSD	0.774 ± 0.428	1.219 ± 0.363	0.947 ± 0.091
	R^2	≥ 0.884	≥ 0.937	≥ 0.938
Ibarz et.al (5)	NRMSD	2.025 ± 0.887	2.573 ± 1.104	2.210 ± 0.179
	R^2	≥ 0.821	≥ 0.886	≥ 0.904
1st Order (6)	NRMSD	2.203 ± 0.874	5.684 ± 1.173	2.373 ± 0.171
	R2	≥ 0.857	≥ 0.902	≥ 0.924

Fig. 3 shows the errors (between experimental and calculated data) distribution along the rehydration process. A good fit means that the error distribution should be random and as close to zero as possible. Errors were randomly distributed and close to zero when the Weibull and Page models were used, for all treatments but especially for Ash treatment data compared to other ones. Regarding Fick diffusion model, showed good error distribution only for Control and $Ca(OH)_2$ treatments. Peleg and Ibarz et al. show a non-randomized distribution of errors, but rather follow a pattern especially for Control and $Ca(OH)_2$ treatments. Finally, the first-order model showed high error values with a non-random distribution for all treatments.

By evaluating the NRMSD (Table II), which allow comparisons among treatments and models. For Control and $Ca(OH)_2$ treatment, the Fick diffusion model and first-order model showed the lower and higher value of NRMSD, respectively. For Ash treatment, both Weibull and Page model showed the lower values while the first-order showed the highest NRMSD values. By considering that the lower the value (the closer to 0), the better the fit, all treatments show a rehydration behavior far from first-order kinetics. In addition, the ash treated samples showed non-Fickian rehydration behavior. Regarding R^2, the closer to 1, the better the fit. The observed values of R^2 coincide inversely with what was observed for the NRMSD values in each treatment, that is, in the models where lower NRMSD values were obtained, the highest R^2 values were obtained.

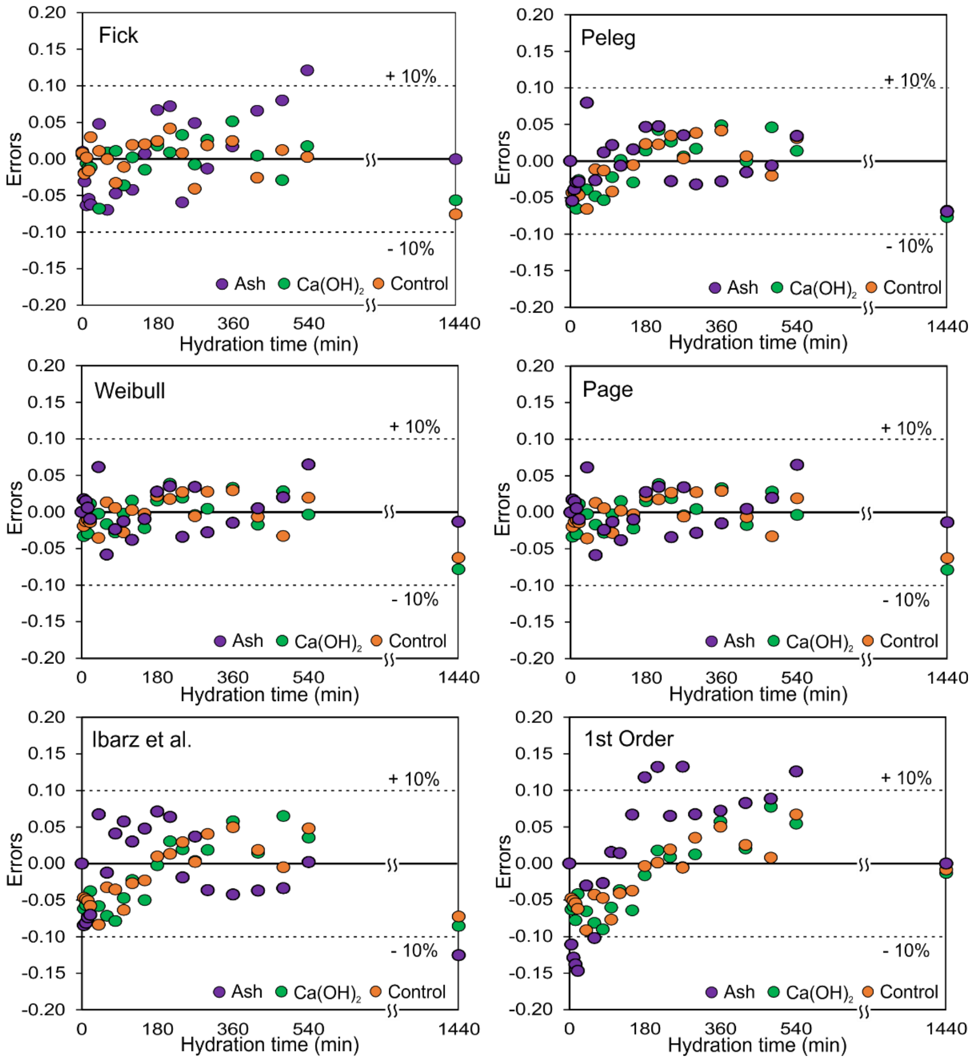

Fig. 3 Errors distribution for each mathematical model used to describe rehydration kinetics of Control, Ash and $Ca(OH)_2$ treatments. For comparison, dotted horizontal lines indicate ± 10% interval for error values.

C. General discussion

The rehydration kinetics of nixtamalized corn was evaluated. The observed rehydration data (Figures 1 and 2) suggested that the Ash treatment rehydrated faster and reach high moisture equilibrium values. It was demonstrated through the highest D_{eff} value from Fick diffusion model (1), lower k_1

and k_2 values of Peleg model (2), highest $\propto$, k_3, k_4 and k_5 values from Weibull (3), Page (4), Ibarz et al. (5) and first-order (6) models respectively. Regarding $Ca(OH)_2$ treatment rehydration properties, it remained similar to Control.

The observed differences among treatments could be explained by the different used alkaline compound, concentration and nixtamalization effects in structure, principally in the pericarp. Ash is mainly composed of $CaCO_3$ with traces of CaO and Ca(OH) [3], in addition, ash is rich in K while lime is rich in Ca [34], since the composition and concentration of each compound in the ash is different, probably the intensity of modification in the external structure of corn was not the same as when $Ca(OH)_2$ was used. In addition, the time of processing could also influence, in the case of treatment the cooking time was lower than when ash was used. According to Gutiérrez-Cortez, et al. [11] calcium requires a longer time to degrade all layers of the pericarp. Another important aspect is that during the nixtamalization process, partial gelatinization of corn starch has been reported (which occurs at > 70 °C) in the external layers of the endosperm. Starch in raw corn exhibited X-ray diffraction pattern type A, and after nixtamalization, it changed to V-type reflecting changes in their structure [9]. Gelatinization is influenced by temperature but also in the dissociation level of each compound used during nixtamalization [3, 8]. Therefore, due to the temperatures used during the nixtamalization process (100 °C with $Ca(OH)_2$ and 105 °C with ash), the level of gelatinization achieved in the samples with ash could be higher, also influencing the differences observed during rehydration.

Regarding model fit criteria, the previous description (section 3.3) reinforces the idea that changes in the structure and processing conditions (nixtamalization) influence and rehydration is not only a purely diffusive mechanism.

IV. CONCLUSION

The nixtamalization process was carried out in corn using ash and calcium hydroxide. Considering its commercialization, the nixtamalized corn was dried, then rehydration was evaluated as an important process before any possible use of the nixtamalized corn. The rehydration kinetics show that the ash treatment confers the best rehydration properties: higher rate and higher amount of moisture at the end of the process. The description of the rehydration behavior in the treatments was carried out using six mathematical models, the parameters of which were explained. However, not all models proved to be appropriate for describing rehydration kinetics. The Fick model is adequate only to describe the hydration behavior of the control samples, which suggests that the main hydration mechanism in these samples is diffusive. On the contrary, due to changes in the structure such as the removal of the pericarp during nixtamalization, the hydration mechanism is not purely diffusive, and the description is more appropriate using other models such as Page.

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