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Viscoamylographic Studies on *Zea Mays* [Mexican White Tuxpeño Maize] Partial Gelatinization with Calcium Hydroxide

Mexicans staple food is maize “tortilla”, prepared by thermal-alkaline processes. The sensory properties of “masa” and “tortilla” depend on the reactions occurring between lime and chemical compounds in maize. In the present study, the effect of different calcium hydroxide, Ca(OH)₂, concentrations (0.0, 0.10, 0.30, 0.50 %, dry basis, d.b.) on the apparent viscosity and maximum gelatinization temperature of a cornstarch water slurry was assessed. This Mexican traditional thermal-alkaline gelatinization reaction (TAGR) was evaluated in a Brabender Viscoamylograph. This small well-mixed reactor was homogeneously heated, and apparent viscosity data from corn starch were recorded in Brabender Units BU). It was found that an increase in Ca(OH)₂ concentrations considerably increases the apparent viscosity, thus reducing the time needed to reach the maximum gelatinization temperature. A mathematical model that represents the phenomena, that occur in the Viscoamylograph, was developed. In the model the Viscoamylograph was considered as a batch reactor and the apparent kinetic coefficients for the TAGR were obtained, including mass balances and thermal-alkaline gelatinization rates, considering a spherical cornstarch granule formed by a starchy matrix. Activation energy found for this reaction was 1241 kJ.

Keywords: Viscoamylographic studies; *Zea mays* cornstarch; Thermo-alkaline corn starch; Gelatinization; Calcium hydroxide

1 Introduction

In Mexico and Central America, maize (*Zea mays*) is a staple food (per capita consumption 300 kg per year). For maize preparation, a process known as traditional “nixtamalization” is carried out. Nixtamalization is a Nahuatl derived word, that means lime-cooked corn (*nextli*, lime ashes, and *tamalli*, cooked corn). Traditionally, whole maize grains are boiled or cooked for 45 to 60 min with water and lime, at a mass ratio corn/water of around 1:2–1:3, and 0.5 to 2% calcium hydroxide, Ca(OH)₂. The resulting broth and corn are steeped, usually overnight (8 to 14 h). Then, the cooked corn is washed with fresh water to eliminate excess lime and grains pericarp to ease the milling. This process produces a deformable solid named “masa”, widely used for the preparation of different food products for human consumption, such as “tortillas”, “tamales”, and suspensions named “atoles” [1–3]. Little

research exists pertaining to the reaction between the maize starch with water and calcium hydroxide; maize meal industries are still very empiric. The understanding of the thermal-alkaline gelatinization reaction is, thus, a very important issue for the application of a cleaner alternative technology, known as thermal-alkaline extrusion, a process that only uses the stoichiometric amount of water and calcium hydroxide (using 0.01 to 0.2%, d.b.) [4–8]. In developed countries, where maize is used with the objective of producing grits, dextrinized products, fructose syrups, and animal feedstuffs, most authors have described maize starch gelatinization by the traditional way considering moisture and temperature changes as the variables, that affect mass and heat transfer phenomena of leaching out. These phenomena are indicated by the loss of the amylose fraction from the granule, swelling, retrogradation and disruption of granules and begin with loss of birefringence. Salts and sugars could affect any one of the last steps by a competitive or non-competitive effect [7–19]. Traditional models of starch gelatinization consider actions of water, temperature, salts and sugars. However, these models are not sufficient to explain phenomena when calcium hydroxide is used, because it has the effect of a moderate alkali producing a relative small degree of hydrolysis of starch chains to malto-oligosaccharides or to produce low mo-

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lecular mass products (soluble in aqueous ethanol fractions). On the other hand Ca^{2+} ions could compete with the water molecules, affecting molecular and structural polymeric properties of maize starch indicated by the glass transition and melt temperatures, T_g and T_m , respectively. Rheological properties as the apparent viscosity or modulus of elasticity could also be influenced because calcium may act as a ligand with starch and protein matrices. All this could change the traditional kinetic models that have been proposed to explain the reactions. It has been shown that the starch fraction has the most significant effects on the final characteristics of cooked cereals [20–24]. Research carried out in Mexico gave a chemical explanation regarding the “nixtamalization” reactions after studying dough “masas” with differential scanning calorimetric methods. As a result a model was proposed, in which lime and water form van der Waals and hydrogen bonds. Results derived from the comparison of sodium hydroxide, potassium hydroxide, and lime showing that lime was the only alkali that was adequate for rendering the final textural quality desired in the corn products. Other researchers have studied diffusion phenomena to explain gelatinization in boiling corn, finding that diffusivity was the limiting factor in the gelatinization of corn starch [25–31]. Some kinetic models have been proposed for thermal-alkaline gelatinization during “nixtamalization” in which the corn whole grain is regarded as a “black box” without considering diffusion through the different walls, starting with the cellulosic wrapping or “pericarp” and the protein aleurone; this models are not practical for the application to the maize industries [32–34]. In the present study, carried out in a Brabender Viscoamylograph, the concentrations of calcium hydroxide have been varied to relate the conversion of non-gelatinized starch into gelatinized starch with the change in apparent viscosity. Effects of variation of calcium hydroxide concentration keeping water, starch contents, and rotational speed (rpm) constant were monitored. This arrangement gave the possibility to use the shell and core model and the Arrhenius law to determine the dependence between temperature, cooking time, and calcium hydroxide concentrations in the thermal history and cooking time.

2 Materials and Methods

2.1 Materials

“Tuxpeño” corn starch was collected from 100 samples of 10 kg each one by “Military Standard Method” from the warehouses of the biggest producer company in Mexico City. Bromatological analyses following the AACC [35] and AOAC [36] methods were performed in the final per-

fectly mixed sample. Lime slurry was prepared using $\text{Ca}(\text{OH})_2$ (Sigma, St. Louis, MO, USA) at 98.5% purity and demineralized water to avoid the influence of other salts dissolved in water in the experiments.

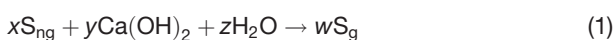
2.2 Methods

Maize starch samples of 45 g each were mixed with different concentrations of calcium hydroxide (0.0, 0.10, 0.30, 0.50% d.b.). Samples were suspended in 500 mL demineralized water. A Viscoamylograph (Brabender OHG, Duisburg, Germany) was used as the batch reactor to observe and follow the thermal-alkaline gelatinization and the pasting properties recorded in Brabender Units (BU). The Viscoamylograph can be considered as a cylindrical uniformly stirred and electrically heated reactor, with a defined reactor volume (RV) and a defined fluid volume (FV), where FV is a fraction of RV. The rotational speed of the reactor stirrer was 45 rpm, and rate of heating was 1.5°C/min. The graphic records indicated that the maximum pasting viscosity is obtained before retrogradation phenomena occur and the final temperature of thermal-alkaline gelatinization is reached.

2.3 Theoretical considerations

General mass balance

It was assumed that the limiting reagent is the non-gelatinized starch during the reactions occurring between starch and water and calcium hydroxide. A mathematical model to explain the “disappearance” of starch as a function of the appearance of thermal-alkaline gelatinized starch in a batch reactor, may be written according to the mass balances as follows:



Where S_{ng} and S_g denote non-gelatinized and gelatinized starch during the thermal-alkaline reactions and w , x , y , z , are the respective molar coefficients and can be expressed as n [mol]:

$$n = \text{mass [g]/molecular mass [g/mol]} \quad (2)$$

and:

$$\begin{array}{l} \text{Mass} \\ \text{entrance} \end{array} = \begin{array}{l} \text{Mass} \\ \text{exit} \end{array} + \begin{array}{l} \text{Disappearance of} \\ \text{non-gelatinized} \\ \text{starch during the} \\ \text{thermalalkaline} \\ \text{reactions} \end{array} + \begin{array}{l} \text{Formation of} \\ \text{gelatinized starch} \\ \text{during the thermal-} \\ \text{alkaline reactions} \end{array} \quad (3)$$

3 Results and Discussion

The bromatological analyses of the cornstarch yielded 96.2% of starch, 0.08% of protein, 0.35% of ashes, 0.0% fat, with the rest as moisture. The starch could be analyzed without interference from protein or fiber.

Viscosity values were obtained from the typical Brabender Viscoamylograms (see Fig. 1). Two distinct stages can be recognized: The first one yields a straight line in which no changes in the viscosity is observed. Here, the diffusion phenomena last between 30 and 34 min. The chemical changes occur in the second stage and are explained with apparent viscosity (A. V.) data that last between 5 and 14 min. It is interesting to mention that for higher calcium hydroxide concentrations, even before starting measurements there is already a change in initial viscosity (1,260 BU).

Fig. 2 shows that the apparent viscosity (between 600 and 1000 BU) increases when $\text{Ca}(\text{OH})_2$ concentrations (d.b.) increase. The average data show a good correlation ($R^2 = 0.928$), when adjusted to a polynomial line.

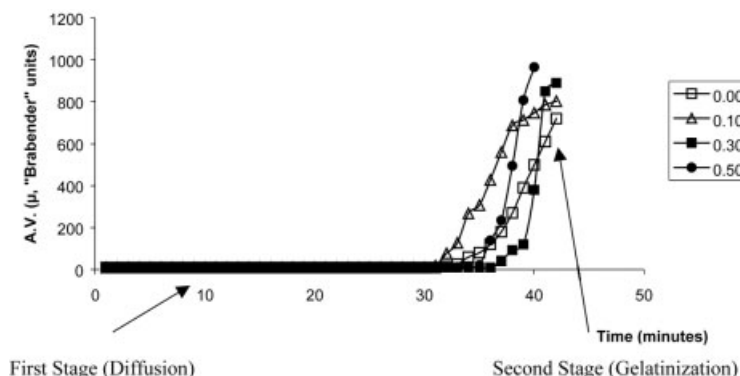


Fig. 1. Typical cornstarch viscoamylograms (first stage as a horizontal straight line, second one as a typical slope line) using different initial $\text{Ca}(\text{OH})_2$ concentrations.

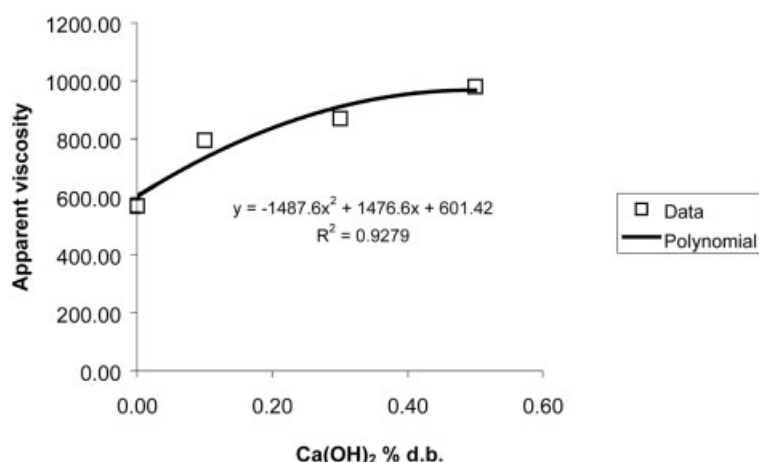


Fig. 2. Apparent viscosity (BU) vs. $\text{Ca}(\text{OH})_2$ % d.b.

In Fig. 3 it can be seen that the maximum gelatinization temperatures tend to decrease when there is an increase in the initial amount of $\text{Ca}(\text{OH})_2$. Using a polynomial equation for the average data, the correlation is $R^2 = 0.995$. As shown in Fig. 4, the time to reach maximum gelatinization tends to decrease when the $\text{Ca}(\text{OH})_2$ concentration increases. Again, using a polynomial equation, the correlation is 0.980.

These two stages can be described as follows:

First stage (heating without changes in apparent viscosity)

This stage can be explained by the diffusion theory: When the Ca^{2+} and OH^- ions diffuse competitively through a spherical starch granule migrating to the center, movement becomes increasingly more difficult as the ions come closer to the center (Fig. 5). According to Fick's law, diffusion rate of component n , G_n may be described by [22, 28]

$$\frac{G_n}{\left[\frac{4}{3}\right] \pi \cdot R^3} = \frac{D_n \cdot dC_n}{dR} \quad (4)$$

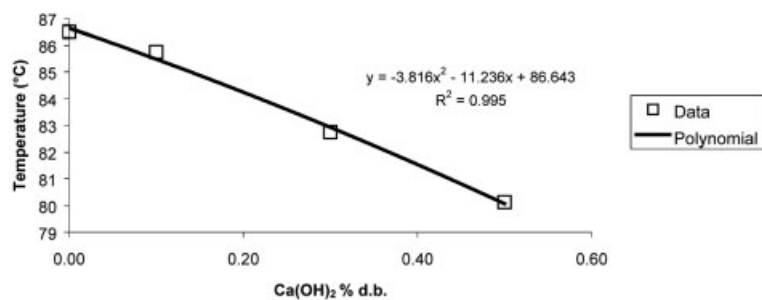


Fig. 3. Maximum gelatinization temperature vs. Ca(OH)₂% d.b.

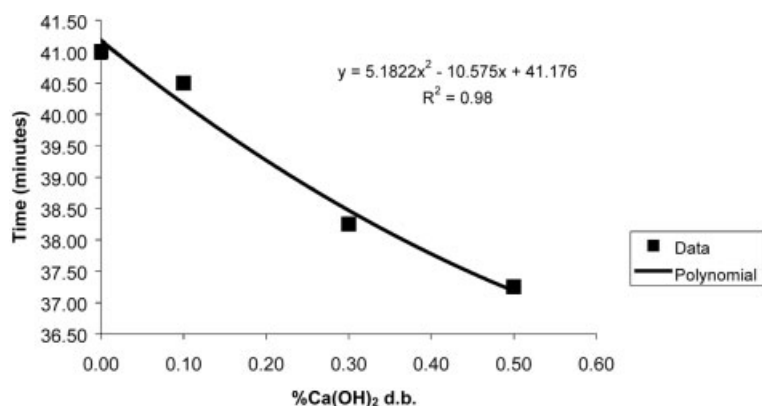


Fig. 4. Maximum gelatinization time vs. Ca(OH)₂% d.b.

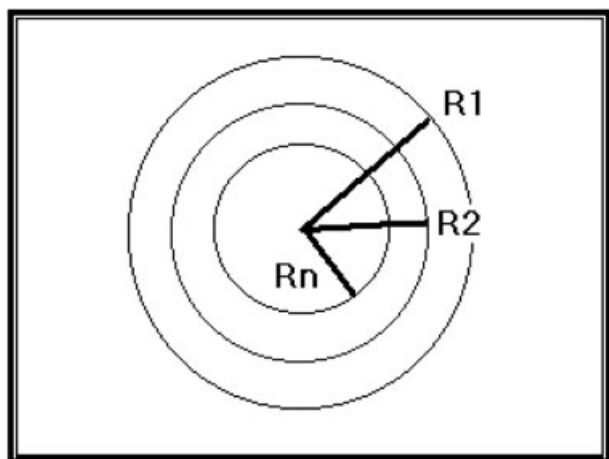


Fig. 5. Ratio between non-gelatinized and gelatinized layers in a corn starch granule during “nixtamalization” process.

where G_n is the diffusion rate of component n [mol/unit time], R, R_1, R_2 are the starch granule radii [μm], D_n is the diffusivity or diffusion coefficient for component n [m^2/s], and C_n is the concentration of component n [mol/reactor volume]. Rearranging and applying the defined integral:

$$\frac{3}{4} G_n * \int_{R_1}^{R_2} \frac{dR}{\pi \cdot R^3} = -D_n \int_{C_n}^{C_{n2}} dC_n \quad (5)$$

Then

$$\frac{3 * G_n}{8\pi} * \left[\frac{1}{R_2^2} - \frac{1}{R_1^2} \right] = D_n * (C_{n2} - C_{n1}) \quad (6)$$

In order to obtain the diffusivity with these equations, further experiments should be carried out for obtaining the concentrations of any of the diffusing ions ($\text{Ca}^{2+}, \text{OH}^-$), and research is currently ongoing to obtain the appropriate diffusivities. Diffusion of these ions is a very important phenomenon, and it ceases at the instant when the chemical reaction begins.

Second stage (heating with changes in apparent viscosity)

This stage could be explained by kinetic theory:

$$\begin{array}{l} \text{Disappearance of starch} \\ \text{[mol/time]} \end{array} = -r_s * VF \quad \begin{array}{l} = \text{Formation thermal-alkaline} \\ \text{gelatinized starch,} \\ \text{[mol time}^{-1} \text{ fluid} \\ \text{volume}^{-1}] \end{array} * \text{Fluid volume} \quad (7)$$

where $-r_s$ is the starch gelatinization rate [$\text{mol L}^{-1} \text{min}^{-1}$] = $k C_a^a C_b^b \dots C_n^n$, within the volume of fluid, VF [L], and the accumulation of thermal-alkaline gelatinized starch at any time is given by:

$$S_g(\text{mol}/\text{time}) = \frac{dNa}{dt} = \frac{d[N_{ao} \cdot (1 - X_a)]}{dt} = -N_{ao} \frac{dX_a}{dt} \quad (8)$$

where S_g is the thermal-alkaline gelatinized starch mass, N_{ao} is the initial number of moles of starch, N_a is the number of moles at a defined time t , and X_a are the moles converted during time t .

Therefore, X_a = Gelatinized starch moles converted during time t , $(N_{ao} - N_a)/N_{ao}$,

$$X_a = \frac{N_{ao} - N_a}{N_{ao}} \quad (9)$$

$$-r_S * VF = N_{ao} * \frac{dX_a}{dt} \quad (10)$$

$$dt = \frac{N_{ao} * dX_a}{-r_S * VF} \quad (11)$$

and, applying a defined integral method:

$$-r_S * VF \int_{t=0}^t dt = N_{ao} \int_{X_{ao}}^{X_a} dX_a \quad (12)$$

the resulting equation is

$$-r_S * VF * (t - t_o) = N_{ao}(X_a - X_{ao}) \quad (13)$$

In this model reactor, the reactor volume may be determined by geometric measurements, and the initial concentration of non-gelatinized starch may be calculated by analytical methods (colorimetric measurement of non-reacted starch). The molar conversions and the thermal-alkaline gelatinization rates are difficult to measure:

$$N_{ao} = \frac{(\text{Starch.mass.feed})}{(\text{Starch.molecular.mass})} \quad (14)$$

To solve the model equation, there are some assumptions, that have to be considered:

The conversion during the gelatinization period ($X_a - X_{ao}$) is directly proportional to the viscosity increase μ (in Brabender units),

$$X_a - X_{ao} = g\mu \quad (15)$$

where g [BU^{-1}] is a dimensional proportionality factor.

Substituting Equation (15) into (13):

$$-r_S * VF * (t - t_o) = N_{ao} * g * \mu \quad (16)$$

The viscosity is, then

$$\frac{-r_S * VF * (t - t_o)}{N_{ao} * g} = \mu \quad (17)$$

If $t_o = 0$

$$\frac{r_S * VF * t}{N_{ao} * g} = \mu \quad (18)$$

If a “lumped” group “a” is considered:

$$\frac{r_S * VF}{N_{ao} * g} = a$$

Then

$$\frac{-r_S * VF * t}{N_{ao} * g} = at = \mu \quad (19)$$

Equation (19) represents an ideal case where a straight line slope is the kinetic coefficient with the slopes values. Fig. 6 shows the adjustment of real data obtained in the Viscoamylograph in the gelatinization stage. In the same graph, it could be observed that these lines do not converge in the origin as they should, due to the computer program adjustment to a linear correlation. Tab. 1 shows the calculations for obtaining the gelatinization rates considering the proportionality factor g . The ratio between time [min] and gelatinization rates (and the “constant” g), $-r_S/g$, (in $\text{mol min}^{-1} \text{L}^{-1} \text{BU}$), presented in Fig. 7 shows a good correlation (with $R^2 = 0.9621$). Fig. 8 shows that the ratio between the concentrations of $\text{Ca}(\text{OH})_2$ in percent (d.b.), and the gelatinization rate (and g), $-r_S/g$, is a straight line with $R^2 = 0.9876$.

Kinetic theory establishes that the rate of reaction of different species a, b, \dots, n , can be written as:

$$-r_S = k C_a^a C_b^b \dots C_n^n \quad (20)$$

where a, b, \dots, n are the molecularity exponents for each species, k is the kinetic constant, and C is the concentration of each species. Rewriting Equation (20) and substituting Equation (15), the conversion of starch granules as a function of concentration is:

$$-r_S = k (X_a - X_{ao}) = k g \mu \quad (21)$$

$$\text{and } (-r_S/g) = k \mu \quad (22)$$

where k is the rate constant ($-r_S/g \mu$, $\text{mol L}^{-1} \text{min}^{-1}$)

Figs. 9 and 10 show the calculation of the rate constant, k , as the slope of the straight lines drawn (Tab. 2). For the concentrations 0.1% $\text{Ca}(\text{OH})_2$ and 0.3% $\text{Ca}(\text{OH})_2$, the lines result in similar k values (0.00008504 and 0.00009098 $\text{mol min}^{-1} \text{L}^{-1}$), whereas 0.5% $\text{Ca}(\text{OH})_2$ gives a straight line with a k of 0.00012308 $\text{mol min}^{-1} \text{L}^{-1}$, slightly higher than the other two concentrations, and for the control with no $\text{Ca}(\text{OH})_2$, k is 0.00004605 $\text{mol min}^{-1} \text{L}^{-1}$ (about one half of the rate constants with lime). A possible explanation is that when the first stage ends, and

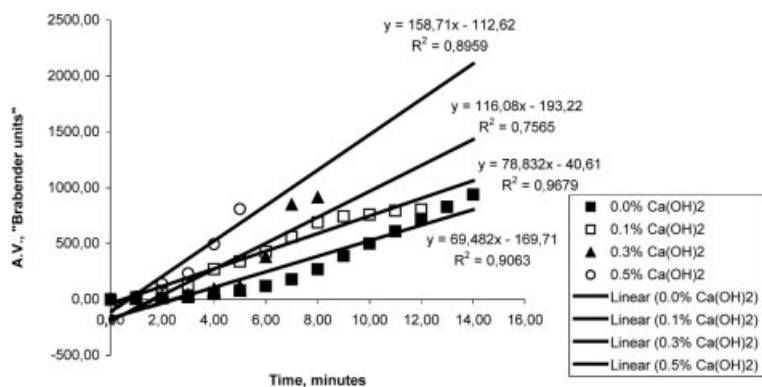


Fig. 6. Apparent viscosity, A.V. (BU) vs. time (min).

Tab. 1. Calculations of gelatinization rates versus lumped group “a” from Equation (19) (N_{ao} = 0.000333 mol).

	% Ca(OH) ₂	a [BU (min) ⁻¹]	-rA/g [mol L ⁻¹ min ⁻¹ BU]	VF [L]	t [min]
Control	0.0	69.48	0.00356308	0.5	13
M1	0.1	78.50	0.00523333	0.5	10
M2	0.3	116.08	0.01289778	0.5	6
M3	0.5	158.71	0.02116133	0.5	5

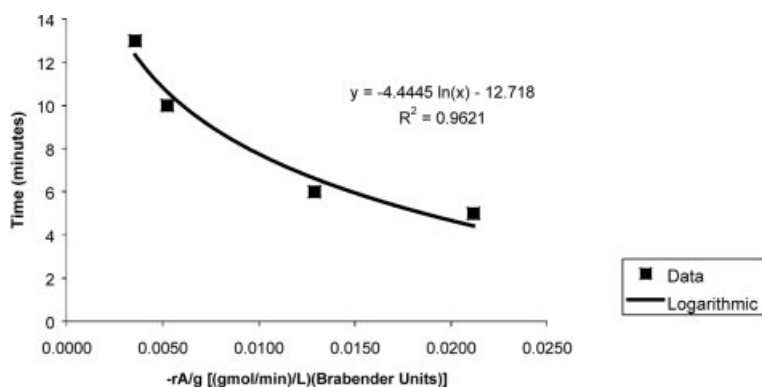


Fig. 7. Time (min) vs. gelatinization rate -rA divided by dimensional constant g (mol L⁻¹ min⁻¹ BU).

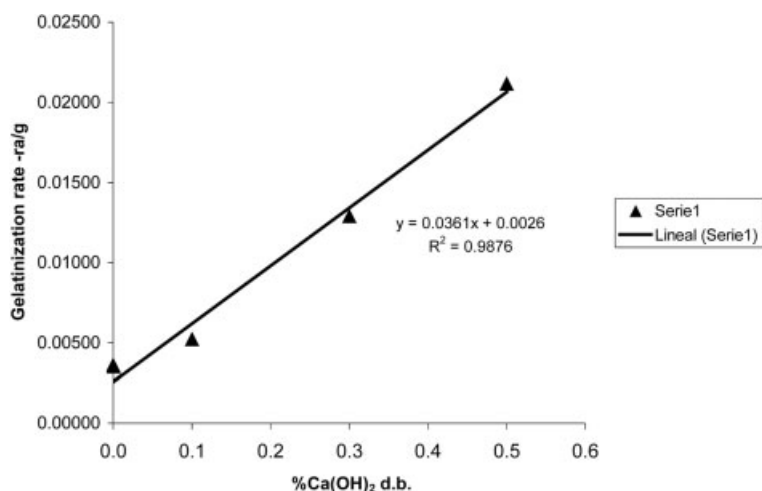


Fig. 8. Effect of calcium hydroxide on the gelatinization rate -rA divided by dimensional constant g.

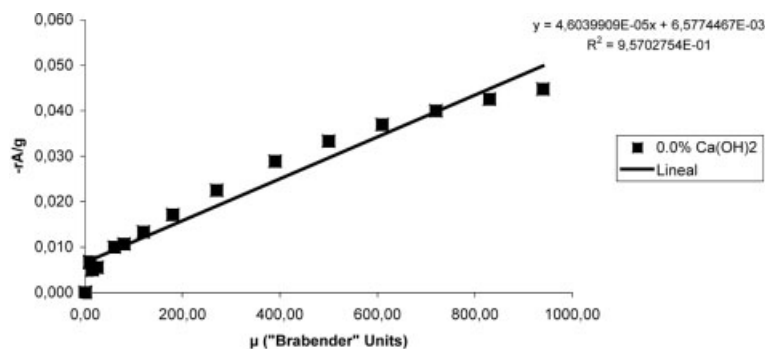


Fig. 9. Data of apparent viscosity of cornstarch control at zero percent Ca(OH)_2 d.b. vs. gelatinization rate $-rA$ divided by dimensional constant g ($\text{mol L}^{-1} \text{min}^{-1} \text{BU}$).

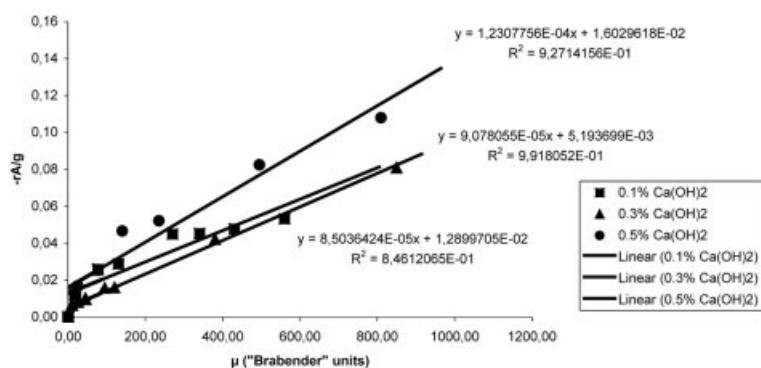


Fig. 10. Data of apparent viscosity of cornstarch doughs with three different concentrations of Ca(OH)_2 d.b. vs. gelatinization rate $-rA$ divided by dimensional constant g ($\text{mol L}^{-1} \text{min}^{-1} \text{BU}$).

Tab. 2. Calculations of the rate constants versus apparent viscosity.

	% Ca(OH)_2	$-rA/g$ [$\text{mol L}^{-1} \text{min}^{-1} \text{BU}$]	$k E+5$ [$\text{mol L}^{-1} \text{min}^{-1}$]	T [K]
Control	0.0	0.00356308	4.604	359.65
M1	0.1	0.00523333	8.504	358.90
M2	0.3	0.01289778	9.078	355.90
M3	0.5	0.02116133	12.308	353.28

swelling of starch granules begins, the OH^- ions from Ca(OH)_2 could produce hydrolysis, and the Ca^{2+} ions insert into the starch molecule. Then, leaching of amylose fractions starts from the granules. The starch chains that have been liberated to the alkaline aqueous medium immediately react with water, Ca^{2+} , and OH^- , probably forming coordination complexes that tend to increase the global viscosity of the starchy suspension. Each of these phenomena must be studied to decide which one is the limiting step of the hydrolysis reactions. Another explanation could be given that becomes the hypothesis of this research: The rate of thermal-alkaline gelatinization depends on the diffusion rate of Ca^{2+} and OH^- ions, as well as on the water diffusion through the initial gelatinized outer layer that is produced immediately by the

contact between the starch granule surface and the alkaline aqueous media. Fig. 5 shows a "spherical" starch granule where a hard wall that presents a certain resistance to diffusion (of a thickness $E = R_1 - R_2$), considering the outer and inner radii. At the same time, ions continue migrating through the starchy matrix increasing the thickness of this hard wall. Immediately, chemical reactions start increasing the granule density and the resistance to diffusion reaching a gelatinization maximum at radius R_n . This phenomenon may hinder the gelatinization towards the center of the granule. Corn starch gelatinization using non-alkaline extrusion has been already studied but so far, the effect of lime from the chemical point of view has not yet been thoroughly assessed.

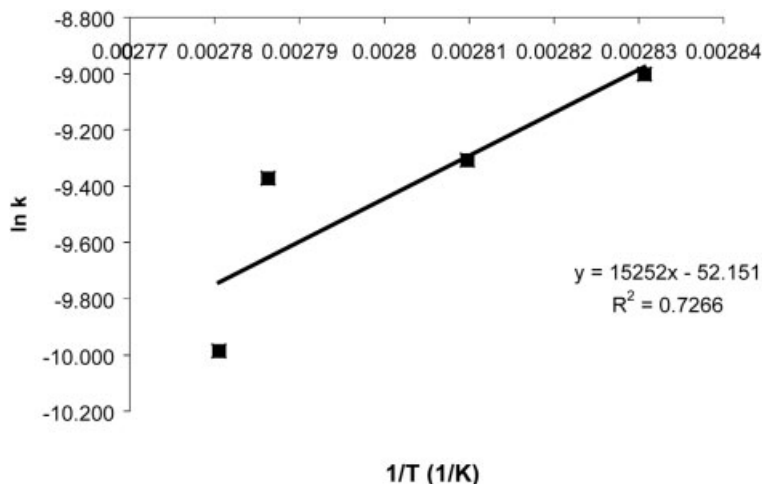


Fig. 11. Arrhenius relationship to obtain the activation energy for the gelatinization reaction.

By using the data obtained from Fig. 11, following the Arrhenius analysis, the activation energy required by the gelatinization reaction is calculated as: $E_a/R = 15,252$ and for $R = 0.0081341 \text{ kJ mol}^{-1}\text{K}^{-1}$, the activation energy $E_a = 1,240.61 \text{ kJ/mol}$.

4 Conclusions

Results corroborate previous experiments indicating that calcium hydroxide exerts an important influence on the hydrolysis phenomena that produce a particular effect in the gelatinization of corn [28]. The model presented is based on the assumptions given in the theoretical considerations discussed above. If Ca^{2+} acts as a “ligand”, it modifies the spaces between the starch chains. If this phenomenon increases or reduces the swelling has not yet been defined, but the interaction with the starch within the granule as well as in the outer region is clear because of the increase in the viscosity and the reduction in the time needed to reach peak viscosity. This perspective opens new research possibilities to corroborate the use of calcium hydroxide for the thermal-alkaline cornstarch gelatinization, a pre-Columbian technique. In fact, it seems fundamentally different from the traditional concepts for this phenomenon when no calcium is added.

A continuing line of research may be the study of possible competition between the Ca^{2+} and OH^- ions for the water molecules during the alkaline reactions. This will depend on the initial concentrations of the ions and on the fact that the gelatinization phenomenon behaves as a pseudo-first order reaction. This behavior should be taken cautiously, since it should be remembered that starch granules show a heterogeneous population within the

starch (particle diameters from 10 to 54 μm), and they will gelatinize at different velocities (depending upon their surface area). These experiments are only measuring the average behavior of gelatinization as a “bulk” process.

Finally, in the conventional gelatinization of wheat or potato starch and even cornstarch, when only hot water is used, most of granules reach the stage at which they collapse after maximum viscosity is reached, with a final viscosity decrease or setback. When thermal-alkaline gelatinization occurs, this setback is considerably reduced and the viscosity tends to be increased as alkali concentration increases.

It can also be said that a relationship exists between thermal-alkaline conditions (i.e., lime concentration) and the changes in the starch granules. In order to find the best operating conditions to reduce gelatinization time and consumption of energy to obtain optimum gelatinization properties for preparing corn doughs and “tortillas” in industrial processes, further experiments are being carried out considering the full grain to obtain the chemical, molecular, and structural effects on the process. These data will be published in the near future.

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