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Kinetics of water diffusion in corn grain during the alkaline cooking at different temperatures and calcium hydroxide concentration

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ABSTRACT

The kinetics of corn grains hydration during the nixtamalization process is described for different temperatures, cooking times and $Ca(OH)_2$ concentrations. Samples were prepared using different cooking times from 0 to 120 min; cooking temperatures of 62, 72, 82, and 92 °C, and $Ca(OH)_2$ concentrations of 0.0%, 0.8%, 1.0%, and 2.0% related to the mass of corn grains. The fitting of the experimental data to the empirical Michaelis–Menten equation gives a good approach of the hydration process. From the first derivate of the Michaelis–Menten equation the rate of the corn grain hydration can be obtained. This mathematical model predicts the hydration and hydration rate of the corn grains during the cooking time of the nixtamalization process. Furthermore, with this proposed model, we can predict that for short times the rate reaches its maximum, and tends to zero for long times as the saturation of the grain is reached. It is concluded that hydration and hydration rate of white corn grains depends significantly on the temperature and cooking water lime concentration ($P < 0.005$).

1. Introduction

Hydration of the corn grains during the alkaline cooking process is important because it is the means through which calcium ions penetrate into the corn grain during the cooking and steeping in the nixtamalization process. In the phases of cooking and steeping, hydration and partial gelling of the corn grain starches occur simultaneously, along with the diffusion of calcium ions, which determine the physicochemical and sensorial properties of the final product. The hydration process of corn grains has been investigated by several authors; Trejo-González et al. (1982) calculated the hydration of Toluca-style popcorn grains with a heating period of 13 min at 92 °C. In this work, they showed that hydration as a function of time, follows a non-linear pattern as the steeping time increases. Ramos et al. (2004) concluded that hydration experiments without $Ca(OH)_2$ depend on the grain size, percentage of broken grains, variety and cooking temperature. They mentioned that hydration of corn grain during cooking and steeping process occurs first in the tip (tip–cap) of the grain for short time periods. They also studied the hydration kinetics of different types of corn kernel with and without mechanical damage, in order to obtain the water diffusion coefficients as a function of the temperature and the activation energies from the Arrhenius plots. On the other hand, Laria et al. (2005) found that the hydration kinetics were governed by the physiochemical changes in the components of the corn grain and the concentration of $Ca(OH)_2$ during the nixtamalization process.

Noorbakhsh et al. (2006) analyzed and fitted the experimental data of yellow corn grain hydration using a mathematical model. They concluded that the grain hydration depends on the velocity and the degree of gelling during the nixtamalization process.

There are different manners to fit any experimental data: by using empirical models or by using mathematical models based in the physics of the system. In the case of the study of hydration curves for corn kernels, it is necessary to take into account that this is a multivariable and non-uniform system (Valderrama-Bravo et al., 2010), it means that the used of empirical model could help to understand these behaviors. Peleg (1988) proposes the use of empirical model to fit some already publish sorption curves, because the model predict or estimate the long rate moisture grains from experimental data for relative short duration, but one problem associate with the model depend of the number of data; if the number of data increase the precision would improve. One of these empirical models that follow the same form that the hydration curves of corn kernel during the cooking steep was proposed by Michaelis–Menten in 1913, to describe the enzyme substrate consumption (Holmberg, 1982).

The aim of the present research is to study the effect of the cooking water temperature and $Ca(OH)_2$ concentration on the

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hydration and hydration rate as a function of the time only for the cooking steep. As well as establishing a mathematical model for short and long hydration times, and hydration rate, through the Michaels–Menten equation.

2. Materials and methods

2.1. Sample preparation

The hydration process during nixtamalization was made with a water proportion of 3:1 in relation to the corn grain weight. Puma hybrid without any mechanical damage, from Monsanto (Semillas y Agroinsumos, México) was used. The width, length, thickness, and weight as well as the thickness of the pericarp of the corn grains were measured. Each corn sample was cooked at different temperatures: 62, 72, 82, and 92 °C using different $Ca(OH)_2$ (Calcium Hydroxide, reagent powder, Fermont, Monterrey, NL, México) concentrations: 0.0%, 0.8%, 1.0%, and 2.0% in relation to the corn weight and different cooking times: 60, 80, 100, and 120 min. Then, the samples were drained and dehydrated at 100 °C for 24 h. The hydration is measured by employing a Mettler Toledo HR83 balance and taking $\{[M(t) - M_0]\}/M_0\} \times 100\%$ as representative values for water uptake. Here $M(t)$ is the weight of grain at time t, M_0 is the weight at $t = 0$. Every experiment was repeated three times.

2.2. Chemical composition analysis

Puma corn grains were studied, the crude protein (N 6.25) was measured by the micro-Kjeldahl (Method 46-13, AACC, 2000), moisture (Method 925.10, AOAC, 2000), total ether extract (Method 30-25, AACC, 2000) and ashes (Method 08-01, AACC, 2000), total dietary fiber, (Method 992.16, AOAC, 2000). All the measurements were carried out three times.

2.3. Mathematical model

(a) *Hydration process. Eq. (1)* proposed by Michaelis–Menten (MM), can be used to describe the changes in moisture content as a function of the time. It describes the enzyme substrate consumption (Holmberg, 1982).

$$V_0 = \frac{V_{\max}[S]}{K_M + [S]} \tag{1}$$

where S is the substrate concentration, V_0 is the rate at which the enzyme consumes the substrate for any S, K_M is the Michaelis–Menten constant and V_{max} is the maximum rate at which has to high substrate concentration. This model can be used to describe the changes in moisture content as a function of the time because they follow the same shape curve. It can be done by changing the parameters of Eq. (1) as follow: S for t, where t is the time of hydration, V_{max} for A and K_m for B. A has units of hydration percentage and B has units of time. It is formed the following expression: the empiric equation of Michaelis–Menten, transformed for the purposes of this investigation it is proposed to predict the hydration process of the corn grain like a function of cooking time. Changing the parameters, the equation is as follows:

$$M(t) - M_0 = \frac{A * t}{B + t} \tag{2}$$

In Eq. (2) $M(t)$ (%) is the corn hydration percentage at a time t, M_0 is endogenous humidity of grain (%), t is the hydration time (min), A and B are constants. Using the MM model and by direct comparison it is possible to establish that A represent the increases of the moisture content at the end of the process, B represent the time in which the process reach a moisture value corresponding to the half of the total change (A).The follow two boundary conditions have to be satisfied:

$$M(t) = \begin{cases} M_0 \Longleftrightarrow t \to 0 \\ M_E \Longleftrightarrow t \to \infty \end{cases} \tag{3}$$

These boundary conditions were determined with base to that observed experimentally, where: $M(t) = M_0$ means that it is only endogenous humidity is present in the grain, that means that the grain has not begun to be hydrated; $M(t) = M_E$ is the humidity that would have the grain if it was hydrated to infinite time, M_E is the saturation humidity where the grain does not have changes significantly in the hydration as the time of hydration passes. Evaluating the initial conditions in Eq. (2), it was obtained:

$$\lim_{t\to\infty}(M(t)) = \lim_{t\to\infty}\left[M_0 + \frac{A * t}{B + t}\right] = M_0 + A = M_E \tag{4}$$

Eq. (2) takes the following form:

$$M(t) = M_0 + \frac{(M_E - M_0) * t}{B + t} \tag{5}$$

(b) The hydration process rate. To determine the hydration rate of the corn grain it is obtained deriving Eq. (5) and as a result we obtain:

$$V = \frac{dM(t)}{dt} = \frac{(M_E - M_0)B}{(B + t)^2} \tag{6}$$

Boundary conditions that should complete are:

$$V = \frac{dM}{dt} = \begin{cases} V_{\max} \Longleftrightarrow t \to 0 \\ 0 \Longleftrightarrow t \to \infty \end{cases} \tag{7}$$

The hydration rate V (%/min) is higher at short cooking times, because the capacity of absorption is higher into the available spaces inside the grain, and for $t \to \infty$, the receiving spaces of water tend to diminish and as a consequence the rate tends to zero. We have found the maximum rate when $t \to 0$ and its value is $V_{max} = (M_E - M_0)/B$. Also with Eqs. (2) and (6) it is possible to predict the hydration and hydration rate of the corn samples appropriately for all time. Now we compared the Michaelis–Menten equation with the Peleg equation: Table 1 shows both model and the equivalence of constants between them.

2.4. Statistical analysis

All the treatments were made in a random way, and the hydration and hydration rate data were statistically analyzed using the SAS Systems for Windows Software, 6.12 TS020 versions (SAS, Statistical Analysis System, Institute Inc., Cary, NC, 1996). Variation analysis and F-tests were used to determine the differences between the thermal treatments, with $P \leqslant 0.05$. Multiple comparisons of means were made using the LSD.

3. Results and discussion

The average obtained values for the physical dimension of the corn kernel were: 8.19 ± 0.4 mm width, 11.80 ± 0.12 mm long, 3.9 ± 0.09 mm thick, 355 ± 32 mg of weight, and 165 ± 12 μm the thickness of the pericarp. The protein content was 8.36 ± 0.20%, fat 4.92 ± 0.56%, total fiber 3.59 ± 0.50%, ash 1.16 ± 0.06%, and moisture content 8.93 ± 0.18%.

Figs. 1 and 2 show the corn grains hydration profiles as function of the cooking time, at different temperatures (62, 72, 82 and 92 °C), and different $Ca(OH)_2$ concentrations (0.0%, 0.80%, 1.0%, and 2.0%). The continues lines correspond to the best fitting of the experimental data using the Michealis–Menten model as func-

Table 1
Different models used to establish the hydration of corn kernels during the cooking steep.

Michaelis–Menten model (Holmberg, 1982)	Peleg model (1988)	Constants relationship
$M(t) - M_0 = \frac{(M_E - M_0) * t}{B + t}$	$M(t) - M_0 = \frac{t}{K_1 + K_2 t}$	$K_1 = \frac{B}{(M_E - M_0)}$; $K_2 = \frac{1}{(M_E - M_0)}$
$\lim_{t\to\infty}(M(t)) = M_E$	$\lim_{t\to\infty} M(t) = M_E = M_0 + \frac{1}{K_2}$	$M_E = M_0 + \frac{1}{K_2}$
$V = \frac{dM}{dt} = \frac{(M_E - M_0)B}{(B+t)^2}$	$V = \frac{dM}{dt} = \frac{K_1}{(K_1 + K_2 t)^2}$	$\lim_{t\to 0} V = \frac{(M_E - M_0)}{B} = \frac{1}{K_1} = V_{max}$

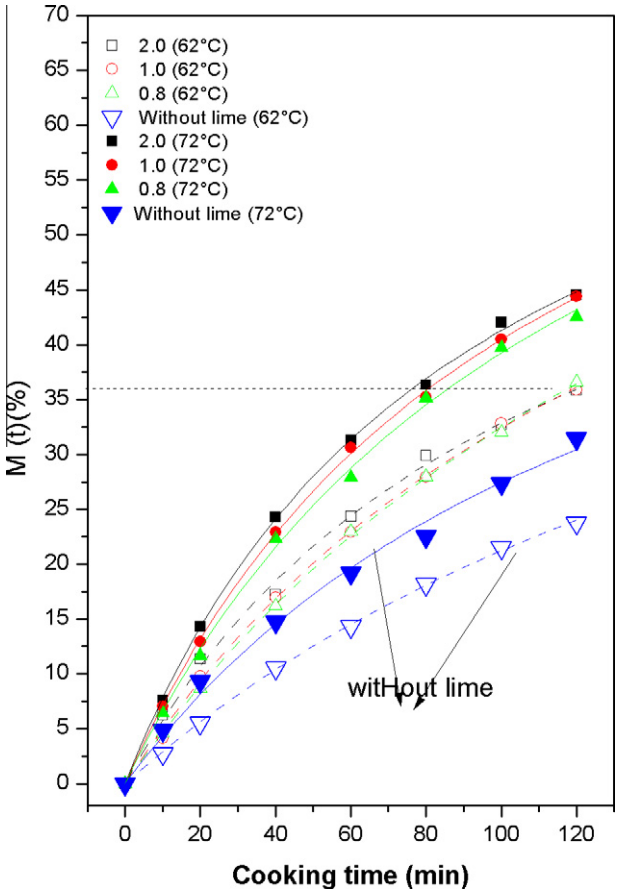

Fig. 1. Corn grains hydration profiles to different temperatures (62 and 72 °C) and different Ca(OH)2 concentration (0.0, 0.8, 1.0, and 2.0 %) as a function of the cooking time.

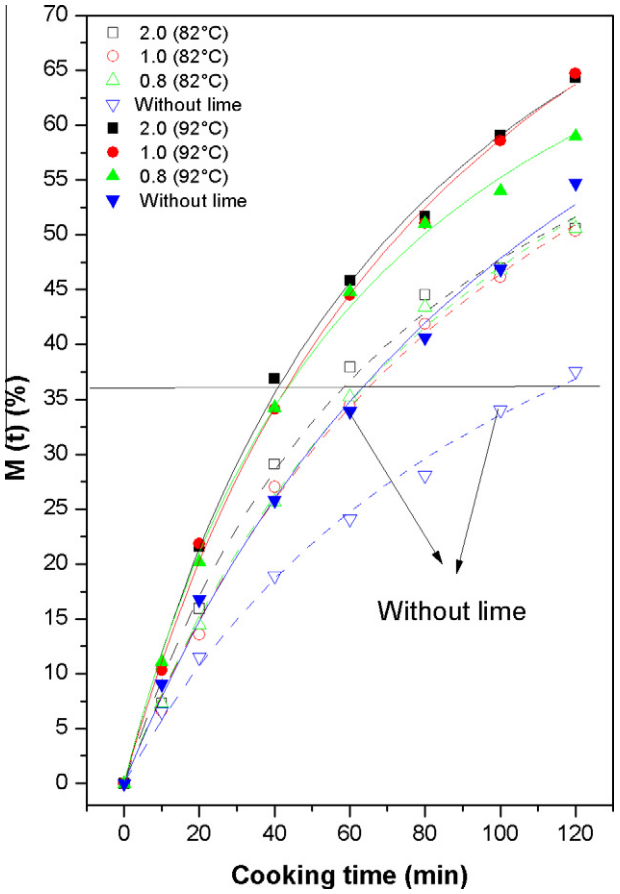

Fig. 2. Corn grains hydration profiles to different temperatures (82 and 92 °C) and different Ca(OH)2 concentration (0.0, 0.8, 1.0, and 2.0 %) as a function of the cooking time.

tion of the cooking time, and the horizontal dash line corresponds to the hydration at the end of the cooking time for a nixtamalization process that is around 36% according to Gutiérrez et al. (2007) and Rojas-Molina et al. (2007). It means that this model is suitable to predict the kinetic of the corn grain hydration during alkaline cooking steep. The adjustment to the experimental data is very satisfactory as the R^2 determination coefficients were from 0.9954 to 0.9999 for a $P \leqslant 0.05$.

It could be observed that the addition of $Ca(OH)_2$, in the cooking water, a significantly higher hydration of the corn grain is produced compared to sample without $Ca(OH)_2$. The hydration curves at 62, 72, 82, and 92 °C show typical corn grain hydration behavior according to Gutiérrez et al. (2007) and Fan et al. (1963). On the other hand, the loss of dry mass does not have a significant influence on the corn grains hydration profiles during the cooking process according to Resio et al. (2006). These results agree with that previously published by Trejo-González et al. (1982) who demonstrated that hydration during the nixtamalization process follows a non-linear process with increasing steeping time. Noorbakhsh et al. (2006), demonstrated that corn grain hydration depends on

the cooking time and temperature, as indicated in the work of Gutiérrez et al. (2007) where they demonstrated that hydration reaches 36% in the cooking phase. Therefore, we can say that the saturation point of the corn grain during the nixtamalization process will depend on the: time, the cooking temperature and the $Ca(OH)_2$ concentration. These results are confirmed by Fernández-Muñoz et al. (2002). By direct inspection of Figs. 1 and 2 it is possible to establish the end of the cooking time for different temperatures using 36 ± 1% of hydration as criteria. The hydration percentage reached by the corn grain during the alkaline cooking process with 2% of $Ca(OH)_2$ is 119 min at 62 °C, the cooking time at 72 °C is 79 min, around 62 min for cooking at 82 °C, and 43 min for samples cooked at 92 °C. These results are in agreement with those published by Rojas-Molina et al. (2007) and Martinez-Herrera and Lanchance (1979). They reported that when the $Ca(OH)_2$ concentration in They reported that when the $Ca(OH)_2$ concentration in the cooking water diminishes, the cooking time increases. Figs. 3 and 4 show the corn grains hydration rate for 62 and 72 °C, and 82 and 92 °C respectively as a function of the cooking time for samples without lime, 0.8%, 1.0%, and 2.0% of $Ca(OH)_2$, using the fitting data of $M(t)$ from Figs. 1 and 2.

The hydration rate increases as the cooking temperature and $Ca(OH)_2$ concentration rise, observing higher rate for short times and reaching a minimal rate for long times (saturation). Such behavior can be modeled by differentiating the Michaelis–Menten equation with respect to time. The high values of hydration rate for short times are due to the nature of the capillarity present on the corn grain surface. When those capillarities are exposed to water, the suction function of the capillary zones is activated originating the hydration gradient and causing a fast hydration of the corn

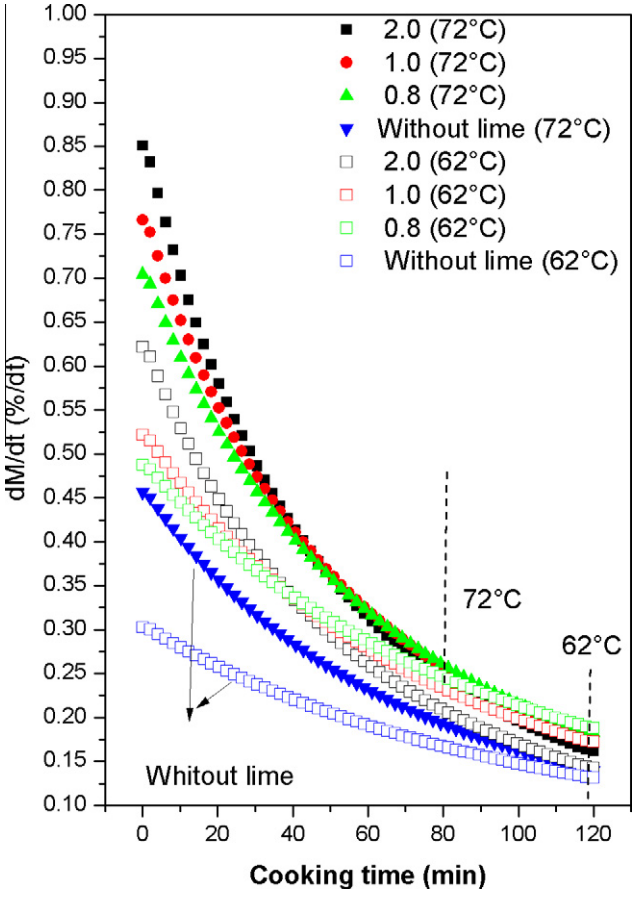

Fig. 3. Corn grains hydration rate profiles at different cooking temperatures (62 and 72 °C) and different Ca(OH)2 concentration (0.0, 0.8, 1.0, and 2.0 %) as a function of the cooking time.

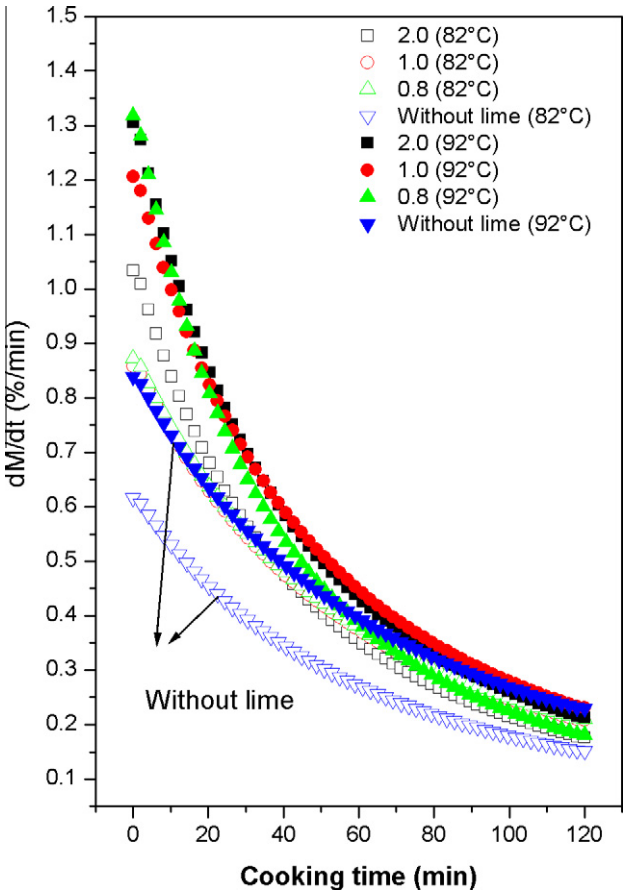

Fig. 4. Corn grains hydration rate profiles at different cooking temperatures (82 and 92 °C) and different Ca(OH)2 concentration (0.0, 0.8, 1.0, and 2.0 %) as a function of the cooking time.

grains according to Noorbakhsh et al. (2006).The hydration rate values depend on time, cooking temperature, and $Ca(OH)_2$ concentration.

If the complete set of data of Figs. 1 and 2 is fitted from $t = 0$ to $t = 120$, water absorption does not fit with the relationship $M(t) = Dt^{1/2}$. It is due to the end of the cooking steep depended on the temperature, as was mentioned before by choosing the end of this steep, when the moisture content is around 36%.

Fig. 5 shows $M(t)$ values (ln scale) as a function of the inverse of absolute temperature for $t = 60$ min taken from Figs. 1 and 2. Here, the effect of lime on water absorption is more evident than in Figs. 1 and 2 In this figure, it is clear that systems up to 36% correspond to steeping process and under this value is still under cooking process. The main effect of the cooking process is the solubilization of the pericarp that allows it to be removed from the corn kernel. From a physicochemical point of view the removal of the pericarp can be influenced by the temperature as well as the lime content. According to the methodology proposed by Ramos et al. (2004) after the determination of the diffusion coefficient it is possible to obtain the activation energy. In our case the $M(t)$ value is close related to the diffusion coefficient including only the geometrical parameter of the corn kernels. It means that the $M(t)$ values also follow the Arrhenius equation. Larger slope in Arrhenius curves indicates larger activation energy.

The activation energy, during the cooking steep is then related to the excess of energy during the process, which is necessary to remove the pericarp, and to allow the free entrance of water and calcium into the most internal layers of the corn kernel (endosperm). According to this figure and for $M(t)$ less than 36%, for

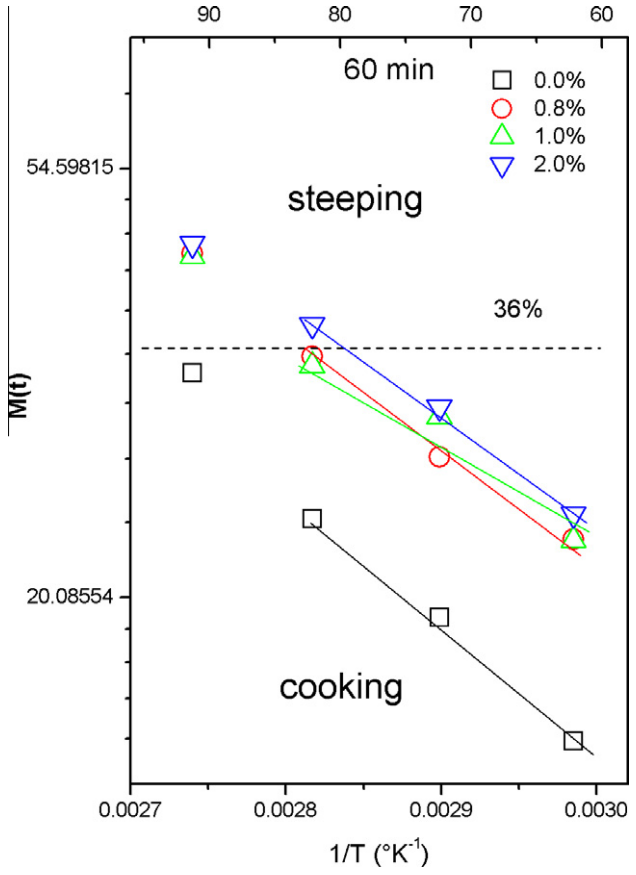

Fig. 5. Shows the hydration percent of corn grains as an inverse function of cooked temperature at 60 min of time cooked.

0%, 0.8%, 1.0% and 2.0% of $Ca(OH)_2$ it is not possible to establish differences between the processes. It could means that the activation energy to remove the pericarp is independent of the process.

It can be seen a change in significance in the percentage of moisture $M(t)$ for temperatures > 80 °C this is because during the gelatinization temperature of starch granules exuded amylose and amylopectin. The exudation process increases the number of hydroxyl groups that are available from amylose and amylopectin, which can bind to water molecules. All this is reflected in the increased hydration of the corn kernels. The above is related to Aytunga Arik Kibar et al. (2010), where they found the diffusion water into starch granules depended on temperature and solubility of polysaccharides, amylose an amylopectin leaching.

4. Conclusions

The behavior of the hydration of the corn grains during the nixtamalization process can be modeled by the phenomenological Michaelis–Menten equation. Examining the kinetics of the hydration for different temperatures and $Ca(OH)_2$ concentrations as a function of time, the Michaelis–Menten equation shows good behavior for short and long times; and also for the hydration rate. A synergistic effect is also observed between the cooking temperature and the $Ca(OH)_2$ concentration, and at higher values of these two factors the hydration is increased as well as the hydration rate. But, by direct inspection of Fig. 5, it can be establish that the activation energy for the pericarp removal does not depend on the temperature and lime content and also it is not necessary to obtain the diffusion coefficient. The used of MM model instead of the Peleg model is because in the first case the A and B constant are independent. According to this result, and in terms of industrial applications, the moisture content increases when the temperature and $Ca(OH)_2$ concentration increase.

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