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Effect of environmental daily temperature fluctuations over one year storage on the prediction of non-enzymatic browning in reduced-moisture foods stored at "ambient" temperature

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Abstract

Non-enzymatic browning predictions in reduced-moisture foods stored over one year at "ambient" temperature, were made using, a) realistic environmental daily (and seasonal) temperature fluctuations, and b) a constant mean temperature. Daily temperature records taken every 6 hours from January 1st to December 31 (1460 temperature data) in four selected cities from Argentina, were used.

The predicted amount of browning over one year storage was different depending whether the annual mean temperature (T_{am}), the monthly mean temperature (T_{mm}) or the daily temperature fluctuations (T_{df}) were used for the predictions. Predicted browning over one year was generally higher when realistic storage conditions (i.e. daily/seasonal temperature fluctuations) rather than mean values (annual or monthly), were used instead.

Key words: Temperature; Fluctuations; Nonenzymatic browning; Storage; Shelf life; First order; Deteriorative

1. Introduction

The expected shelf life of a food product depends upon both the environmental conditions that the product will be exposed and how much of the initial quality (color, texture, nutritional value, etc) can be lost before the product should no longer be sold (Labuza & Schmidl, 1985). Temperature is the environmental condition which most affects the shelf life of packaged foods of reduced moisture; thus, quality of a product held in storage at ambient temperature will degrade over time, the rate of degradation being dependent on temperature. If the process associated with such degradation (i.e. non-enzymatic browning) is highly sensitive to temperature (reflecting high activation energy) the rate will increase substantially as the ambient temperature rises (Labuza & Riboh, 1982; Wrigth & Taub, 1998).

In order to determine ambient storage shelf life, studies are usually made at constant temperature (Labuza, 1982; Labuza & Riboh, 1982) and a point in time (at the selected constant temperature) is reached when the product quality degrades to a level taken as a cut off limit. That time corresponds to the product shelf life at that temperature. Typical dried foods (fruit and vegetables) have about 1 year shelf life at "ambient" temperature (Yang, 1998), and nonenzymatic browning is one important mode of deterioration (Labuza & Saltmarch, 1981) for these type of foods. However, for one year storage, the term "ambient" is a vaguely defined one since it is subjected to daily and seasonal fluctuations (Taub & Singh, 1998). Thus, the cut off quality may be reached in shorter or longer times that those calculated at a constant temperature. The modelling of the relationship between quality degradation and time when temperature is in nonsteady state storage conditions has been studied by other workers. These studies were mostly concerned with fluctuating conditions generated in selected laboratory conditions. Labuza and Saltmarch (1981) compared the amount of browning (and protein quality loss) during storage of whey powder under steady state conditions at 25, 35 and 45 ºC and a fluctuating temperature condition of 25/45 ºC with alternating 5 days periods at each temperature. They found that storage losses under fluctuating temperature condition were significantly greater that at the mean temperature of 35 ºC. Kamman and Labuza (1981) also found a faster rate for the simple loss of thiamine in pasta stored under a square wave condition.

It is the purpose of present study to compare predictions of the amount of browning over one year storage under realistic environmental daily (and seasonal) temperature fluctuations, and at a constant mean temperature. Literature data on the kinetics of nonenzymatic browning in some reduced-moisture foods held at various constant temperatures were used for the predictions. Daily temperature records taken every 6 hours each day from January 1st to December 31, in four selected cities from Argentina were used.

2. Methods

2.1. Analysis of data

2.1.1 Environmental temperatures

Daily temperature records taken every 6 hours (3 am, 9 am, 3 pm and 9 pm) from January 1st to December 31, 1990 in four selected cities from Argentina were utilized for present study. Data were obtained from the Argentinean Weather Bureau; conventional temperature monitor stations were used to measure the environmental temperature. **Table 1** shows the yearly (1990) mean environmental temperatures for the selected Argentine cities, namely Buenos Aires, Córdoba, Resistencia and Santiago del Estero, as well as its geographical location (latitude, longitude and altitude). The annual mean temperature of Resistencia and Santiago del Estero are higher than those of Buenos Aires and Córdoba.

Figure 1 shows the variation of the average monthly temperature along the year for the four selected cities; maximum values of monthly temperature occurred between December-February, while lowest temperatures in the months of June to August. Buenos Aires and Resistencia cities are close to large rivers, while Córdoba and Santiago del Estero are in continental locations of the country. In continental regions the difference between daily maximum and minimum temperatures are larger; as well as the difference between minimum and maximum annual values. This is best reflected in the value of temperature variability (σ) defined as,

$$\sigma = \sqrt{\frac{\sum (x - \bar{x})^2}{n-1}} \qquad (1)$$

where,

$x = T - T_{mm}$

T: actual temperature (ºC)

T_{mm}: average monthly temperature (ºC)

The temperature variability (σ) for Buenos Aires, Córdoba, Resistencia and Santiago del Estero was calculated to be, 4.0, 5.2, 4.9 and 5.7, respectively.

Figure 2 (a,b,c,d) shows daily temperatures (4 measurements each day) for selected cities throughout one complete year (1990), beginning on January 1st ; it is to be noted that 1460 temperature values are displayed for each location.

2. 1. 2 Kinetics of non-enzymatic browning reactions

Some low moisture foods may be stored at ambient temperature for over one year, and consequently are affected by the fluctuation of environmental temperature during storage. Sá and Sereno (1999) and Patel, Gandhi, Singh and Patil (1996) measured the kinetics of non-enzymatic browning of dried onion and strawberry (equilibrated to selected water activities (a_w), and sweetened condensed milk stored at constant temperatures. The amount of browning (B) was measured in terms of absorbance (A); a wavelength of 420 nm was used for onion and strawberry, and 450 nm for condensed milk. To obtain the kinetic parameters of the reactions, the systems were stored at different constant temperatures, and data was fitted using a zero-order reaction model:

$$B = A - A_0 = k.t \qquad (2)$$

where A_0 is the initial absorbance, k the reaction rate constant ($time^{-1}$) and t time. They analyzed the temperature dependence of rate constants using the Arrhenius model (Labuza, 1982), and obtained the kinetic parameters showed in **Table 2**. The expression of the rate constant using this model is

$$k = k_0 \exp(-E_a/RT) \qquad (3)$$

where E_a= activation energy (cal/mole), R= gas law constant= 1.987 cal/ K.mole, T= temperature (K) and k_0= pre-exponential constant ($time^{-1}$). The activation energies for the reactions ranged from 10.8 to 40.3 kcal/mol, as also shown in Table 2. These browning studies were performed in a temperature range of approximately 5 - 45 ºC, which encloses the range of environmental temperature data of the selected Argentine cities (as described above).

2. 1. 3 Calculation of amount of non-enzymatic browning at fluctuating temperatures

The amount of browning in the different food systems (Table 2) over one year storage and in selected Argentine cities (Buenos Aires, Córdoba, Resistencia and Santiago del Estero) was predicted using different approaches for the environmental (ambient) temperature. They are,

a) The annual mean environmental temperature (T_{am}) of each city (Table 1) was utilized to calculate kinetic constant *k* (Eqn. 2) and amount of browning predicted for a time interval of one year (365 days);

b) The average monthly environmental temperatures (T_{mm}) of each city (Figure 1) was utilized to calculate constant *k* ; the year was divided in 12 intervals of 1 month (taking the real days for each month) and *k* was calculated at the average monthly environmental temperature in each interval. The amount of browning for the whole year was obtained as the sum for the 12 intervals.

c)To evaluate the effect of daily ambient temperature fluctuations over one year storage, the amount of browning was calculated using the daily environmental temperatures (T_{df}) recorded every 6 hours for the different cities. Therefore, the amount of browning at the end of the year was obtained by accumulated sum of approximately 1460 intervals of 6 hours each. It is to be noted that for each 6 hours interval, constant *k* was evaluated (albeit arbitrarily) at the temperature recorded for the end of that interval.

3. Results and discussion

Figures 3 to 6 (a,b) show the predicted amount of browning over 1 year storage using either, the annual mean temperature (T_{am}), the monthly mean temperature (T_{mm}), or the daily temperature fluctuations (T_{df}), for the four locations considered (Buenos Aires, Córdoba, Resistencia and Santiago del Estero). The same browning scale (Y axis) was used for each product at the four different locations; this facilitates comparison of the effect of location temperature on amount of browning. Foods selected in this example, dried onion (a_w = 0.33) and sweetened condensed milk, have widely different activation energies, namely 40.3 kcal/mole and 10.8 kcal/mole, respectively. It can be seen that for dried onion (higher E_a) the estimated amount of browning over one year storage is clearly different depending whether the annual mean temperature, the monthly mean temperature or the daily temperature fluctuations were used for the predictions. The calculated amount of browning over one year storage (B) follows the order, $B(T_{df}) > B(T_{mm}) > B(T_{am})$. In other words, predicted browning over one year is higher when realistic storage conditions (daily temperature fluctuations, T_{df}) rather than mean values (T_{am} or T_{mm}) are used for the calculations. However, the differences were much smaller when the activation energy of the browning reaction is reduced, i.e. sweetened condensed milk (Ea = 10.8 kcal/mole).

The results for the system with higher activation energy (dried onion, a_w = 0.33) show that amount of browning calculated from the annual mean temperature follows the order, Córdoba ≈ Buenos Aires < Resistencia < Santiago del Estero, which agrees with the order of T_{am}, Córdoba ≈Buenos Aires < Resistencia < Santiago del Estero.
The use of monthly average temperatures (T_{mm}) or daily ambient temperature fluctuations in predictions, allows to observe that browning increases faster in the summer periods (1 to 90 days and 270 to 360 days). This effect is particularly noticeable in Resistencia and Santiago del Estero (Figs. 5 and 6) and is due to the high mean monthly temperatures in these locations (Fig. 1).

The results indicate that for zero order browning reactions having relatively high activation energies, predictions of amount of browning over one year storage should be done using the daily temperature fluctuations rather than mean values. However, this is not practical because it is somewhat difficult to get information of the daily fluctuations, since they comprise 1460 temperature values (four temperatures every day) for each location. For this reason an "effective temperature" (T_{eff}) was defined as a constant temperature value which over a year storage at "ambient" conditions will result in same amount of browning that the one calculated using the realistic daily and seasonal temperature fluctuations.

$$T_{eff} = \frac{-E_a}{R} / \ln\left(\frac{B_{(Tdf)}}{k_0 \cdot t}\right) \qquad (4)$$

Where, $B_{(Tdf)}$ is the amount of browning calculated over one year storage when daily/seasonal temperature fluctuations are used, and t = 365 days .

As observed on **Table 3** and for the selected geographical locations, the difference (ΔT) between the effective temperature (T_{eff}) and the annual mean temperature (T_{am}) is between 1 to 6 ºC, increasing when the activation energy of the browning reaction increases. The difference between T_{eff} and T_{am} (at same activation energy), also seems to depend on the geographical location, since it is somewhat higher for Cordoba and Santiago del Estero than for Buenos Aires and Resistencia. As noted before (Analysis of Data) in continental locations the difference between daily maximum and minimum temperatures are larger, as well as the difference between minimum and maximum annual values; and this is reflected in a higher value of temperature variability (σ, Eqn. 1). These results are of interest for shelf life studies in order to select the most appropriate constant temperature to reproduce storage under realistic environmental temperature conditions. For example, Buenos Aires has an annual mean temperature of 17.7 ºC . However, a food which deteriorates through nonenzymatic browning with an activation energy of 40.3 kcal/mole might be stored at 21.8 ºC instead of 17.7 ºC, to simulate the changes which would occur after one year of storage in Buenos Aires at "ambient" temperature.

Figure 7 shows a plot of (T_{eff}-T_{am}) versus the temperature variability of the geographical location, for activation energies from about 11 to 40 kcal/mole. It can be seen that larger values of temperature variability (i.e. a measure of temperature fluctuations in a region) produce an increase in the difference between (T_{eff}-T_{am}), and this is more noticeable for larger activation energies.

Conclusions

When realistic daily environmental temperature fluctuations or monthly mean temperatures were used for browning predictions in stored foods, the calculated amount of browning was greater than that predicted from steady state conditions at the calculated annual mean temperature. Differences increased with the value of activation energy of the browning reaction and also with the intensity of temperature fluctuations (typical of different geographical locations). However, browning predictions yielded similar values when the activation energy of the browning reaction was relatively small (i.e. 10.8 kcal/mole). These results are of interest for shelf life studies in order to select the most appropriate constant temperature to reproduce storage under realistic environmental temperature conditions.

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Figure Captions

Figure 1. Average* monthly environmental temperatures in selected Argentine cities (year 1990).

*average of daily temperatures recorded every 6 hours.

Figure 2. Daily environmental temperatures (recorded every 6 hours) in selected Argentine cities for whole year 1990. (Days from January 1st)

(a) Buenos Aires, (b) Córdoba, (c) Resistencia, (d) Santiago del Estero

Figure 3. Amount of non-enzymatic browning (B) for (a) dried onion and (b) sweetened condensed milk as predicted using:

——— annual mean environmental temperature

Δ – – - monthly average environmental temperatures

□ ········ daily environmental temperatures (recorded every 6 hours)

Location: Buenos Aires

*Absorbance defined as $A-A_0 = k.\ t$

Figure 4. Amount of non-enzymatic browning (B) for (a) dried onion and (b) sweetened condensed milk as predicted using:

——— annual mean environmental temperature

Δ – – - monthly average environmental temperatures

□ ········ daily environmental temperatures (recorded every 6 hours)

Location:Córdoba

*Absorbance defined as $A-A_0 = k.\ t$

Figure 5. Amount of non-enzymatic browning (B) for (a) dried onion and (b) sweetened condensed milk as predicted using:

——— annual mean environmental temperature

Δ – – - monthly average environmental temperatures

□ ·········· daily environmental temperatures (recorded every 6 hours)

Location: Resistencia

*Absorbance defined as $A-A_0 = k.\ t$

Figure 6. Amount of non-enzymatic browning (B) for (a) dried onion and (b) sweetened condensed milk as predicted using:

——— annual mean environmental temperature

Δ – – - monthly average environmental temperatures

□ ·········· daily environmental temperatures (recorded every 6 hours)

Location: Santiago del Estero

*Absorbance defined as $A-A_0 = k.\ t$

Figure 7. Effect of temperature variability (σ, eqn. 1) on the effective temperature for browning calculation over one year storage.