Prediction of pH Change in Processed Acidified Turnips

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ABSTRACT
The acetic acid uptake by turnips was studied during an acidification process in containers. The process was successfully described by a Fickian diffusion, using a correlation for the buffer effect. Diffusion coefficients (0.629 to 3.99 × 10⁻³ m²/sec) and partition coefficients (0.8 to 1.1) were obtained by optimization of the fit between experimental and theoretical values, using the simplex method. The partition coefficient did not show an evident dependence on temperature, while diffusivity followed an Arrhenius type behavior. The relationship between acid concentration and pH was described using a cubic model with parameters independent of temperature. Results showed that the combination of these models describing the acid diffusion into the food and the buffering effects of the food allowed accurate prediction of pH evolution in the acidification process.

Key Words: turnips, acidification, pH change, acetic acid

INTRODUCTION
ACIDIFICATION of low acid vegetable products facilitates inactivation of spoilage microorganisms allowing processing below 100°C. Acidification to pH < 3 imparts a desirable sour flavor to some products (e.g. pickles and marinated products) and is usually sufficient for preservation. When pH near 4.5 is used a sour flavor is not as prominent, and a thermal process is required for preservation. The process may be however, less severe than for a nonacidified product, with correspondent benefits in quality. Section 21 CFR 114.80 of Good Manufacturing Practice (GMP; FDA, 1979) regulations stipulates that “A manufacturer must manufacture, process and pack acidified foods so that a finished equilibrium pH value of 4.6 or below is achieved and maintained in all finished foods.”

Many previous studies have focused on canned acidified food, e.g. tomato (Pray and Powers, 1966; Sapers et al., 1978), peppers, (Flora et al., 1978; Sapers et al., 1980; Daeschel et al., 1990), cucumbers (Poots et al., 1986), onions and mushrooms (Siroop et al., 1985) and carrot slices (Juliot et al., 1989). The acidification conditions were determined empirically. Omran et al. (1990) reported the acid uptake by cucumber tissue was a function of temperature, acid concentration, duration of heat treatment and size of cucumbers, but no mathematical model was used to describe the process. The mathematical models used in previous works considered the process as diffusion. Rodgers et al. (1984) measured the diffusion coefficient of acetic acid and salt into herring at different temperatures. McCarthy and Heil (1988) developed a technique using Fickian diffusion, using a correlation for the buffer effect. Diffusion coefficients (0.629 to 3.99 × 10⁻³ m²/sec) and partition coefficients (0.8 to 1.1) were obtained by optimization of the fit between experimental and theoretical values, using the simplex method. The partition coefficient did not show an evident dependence on temperature, while diffusivity followed an Arrhenius type behavior. The relationship between acid concentration and pH was described using a cubic model with parameters independent of temperature. Results showed that the combination of these models describing the acid diffusion into the food and the buffering effects of the food allowed accurate prediction of pH evolution in the acidification process.

MATERIALS & METHODS
Turnip samples
Turnips (cv. unknown) were obtained from a Department of the Ministry for Agriculture and Fisheries farm, located in the North of Portugal. All turnips were from the same harvest. On arrival at the laboratory they were characterized chemically (water, sugars, protein, fat, Vitamin C, pH and ash and fibbers content) and physically (weight, density, volume and surface area) and stored at 0°C and 95% RH, for up to 1 mo. Before each experiment the turnips were washed, hand peeled and cut in 2 cm cubes.

Acification experiments
Covered flasks were filled with 50 mL 0.2M acetic acid and immersed in a thermostatic shaking bath with reciprocating motion (Percistern S-14, Selecta), at a pre-set temperature from 20°C to 80°C. Acetic acid concentration was checked by titration with standard 0.2 M NaOH. After the acetic acid solution reached the bath temperature, one turnip cube was immersed in each flask and held there for given periods of time up to 4 hr. Usually 12 flasks were used for each experiment. After removal each cube was slightly rinsed with deionized water, wrapped in aluminum foil and stored at room temperature until used for pH measurement. The acid solution from that flask was titrated. The amount of acid uptake by each cube was calculated by a simple material balance, based on the initial and final acid concentrations in the solution.

Equilibrium data
Equilibrium values of acid uptake were determined at each temperature in acetic acid solutions with different initial concentrations. This method allowed determination of the partition coefficient as a
Function of both acid concentration and temperature. Equilibrium was assumed to occur when the acetic acid solution concentration in the flask remained constant with time (5 to 27 hr, depending on temperature).

**pH determination**

The turnip cubes were allowed to equilibrate overnight and the pH was measured by inserting a semi micro combination pH electrode (Xerolyt, Ingold) in the sample. The electrode and an automatic temperature compensator (PT100) were connected to a pH meter (Micro2001). This method provided fast results and was found experimentally to provide values consistent with those obtained with the FDA recommended method (measurement of pH after sample blending—Section 21 CFR 114.90).

**Mathematical considerations**

Considering diffusional behavior, acid intake by turnips can be described by the solution of Fick’s 2nd law. The boundary conditions for the diffusion of a solute from a well stirred limited volume of bath to an infinite slab are:

(1) initial condition \( t = 0 \) \( V_x = C = 0 \)

(2) symmetry condition \( t > 0 \) \( x = 0 \) \( \frac{\partial C}{\partial x} = 0 \)

(3) boundary condition \( t > 0 \) \( x = L \) \( -2AD \frac{\partial C}{\partial x} = \frac{V_b \partial C}{K_p} \)

Equation (3) assumes that equilibrium is instantaneously achieved at the surfaces \( x = \pm L \). At the surface the ratio of acid concentration in the slab to the acid concentration in the solution is given by the partition coefficient, \( K_p \). For these conditions the relation between the total amount of acid in the slab at a time \( t \), \( M_t \), and the corresponding amount after an infinite time, \( M_{\infty} \), is given by (Crank, 1979):

\[
\frac{M_t}{M_{\infty}} = 1 - \frac{\sum_{n=1}^{\infty} 2\alpha(1 + \alpha) x^n}{1 + \alpha + \alpha^2 x^2} \exp \left( -\frac{D_0 \alpha x^2}{L^2} \right)
\]

where \( q_n \) are the nonzero positive roots of

\[
\tan q_n = -\alpha q_n
\]

and \( \alpha \) is a measure of the fractional final uptake of acid, varying between 0 and infinite when the fractional uptake varies between 1 and 0, respectively.

The diffusion coefficient was calculated comparing experimental values at constant temperature as a function of time with Eq. (7). Several methods to perform this calculation have been described (Plug et al., 1967; Selman et al., 1983; Hendrickx et al., 1986; Oliveira, 1988). In our work the diffusivity was calculated using the simplex method of minimization. The objective function was the residual between experimental and theoretical points, expressed as:

\[
\text{RES} = \sqrt{\frac{\sum_{i=1}^{N} (M_i - M_{\text{exp}})^2}{N}}
\]

The partition coefficient was also considered as a parameter yielding an optimized value which was compared with the experimental data. This analysis was applied to each temperature. The overall diffusivity values were then correlated with temperature by an Arrhenius type equation, yielding the activation energy \( E_A \) and the pre-exponential factor \( D_0 \). The relationship between the \( \text{pH} \) of a sample and its acid content was obtained by fitting the experimental values to a cubic model.

**RESULTS & DISCUSSION**

**Diffusional process**

The use of Fick’s 2nd law to describe acid intake can be assessed by the analysis of the curves describing experimental and theoretical uptakes of acid at different constant temperatures. Figure 1 shows some of the results (the extremes and one intermediate curve). For all cases the process was adequately described by Fick’s 2nd law, on the range of temperatures tested (20–80°C). Values of the diffusion coefficient were in the range 0.629 to 3.99 \( \times 10^{-9} \) m²/sec and correlated well with an Arrhenius type equation, with an activation energy of 23.4 kJ/mol and a pre-exponential factor \( D_0 \). The relationship between the \( \text{pH} \) of a sample and its acid content was obtained by fitting the experimental values to a cubic model.
The relationship between pH and acid concentration

The relationship between acid concentration and turnip samples pH was successfully described by a cubic model for each temperature tested (Table 1). Hill et al. (1985) used the same model to describe the buffer behavior of cheese wheys. From the analysis of the polynomial coefficients we verified that they were not significantly dependent on temperature. This was analyzed by determining the standard deviation in relation to the mean of the pH values obtained at the different temperatures for a given concentration. Throughout the range the deviations were always smaller than 0.09 (less than 2%). A polynomial fit was then applied to all data, independently of temperature (Fig. 4):

\[ \text{pH} = 5.914 - 38.59 \times 10^{-1} + 189.8 \times 10^{-2} - 330.0 \times 10^{-3} \]

\[ \text{Acetic Acid Concentration (mol/dm}^3\text{)} \]

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>A1 (dm/mol)</th>
<th>A2 (dm/mol)²</th>
<th>A3 (dm/mol)³</th>
<th>A4 (dm/mol)⁴</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>5.847</td>
<td>-52.19</td>
<td>450.2</td>
<td>-1025</td>
<td>0.978</td>
</tr>
<tr>
<td>30</td>
<td>6.196</td>
<td>-40.74</td>
<td>169.8</td>
<td>-161.4</td>
<td>0.976</td>
</tr>
<tr>
<td>40</td>
<td>6.425</td>
<td>-69.23</td>
<td>603.1</td>
<td>-1861</td>
<td>0.991</td>
</tr>
<tr>
<td>50</td>
<td>6.688</td>
<td>-36.62</td>
<td>231.3</td>
<td>-666.5</td>
<td>0.989</td>
</tr>
<tr>
<td>60</td>
<td>6.984</td>
<td>-64.58</td>
<td>412.3</td>
<td>-1128</td>
<td>0.992</td>
</tr>
<tr>
<td>70</td>
<td>7.268</td>
<td>-32.77</td>
<td>138.0</td>
<td>-223.4</td>
<td>0.997</td>
</tr>
<tr>
<td>80</td>
<td>5.684</td>
<td>-32.66</td>
<td>176.8</td>
<td>-411.1</td>
<td>0.991</td>
</tr>
</tbody>
</table>

\[ \text{pH} = A_1 + A_2 \times C + A_3 \times C^2 + A_4 \times C^3 \ (C \text{ in mol/dm}^3) \]

\[ \text{Experimental pH} \]

\[ \text{Experimental Mt/M_{eq}} \]

\[ \text{Model} \]

\[ \text{Fig. 4} - \text{Relationship between turnips pH and its acetic acid concentration.} \]

\[ \text{Fig. 5} - \text{Prediction of acetic acid intake and pH at 40°C.} \]

a tortuosity value of about 2, a common value for foods (Oliveira, 1988).

Previous studies covering a wide range of temperatures indicated that the diffusional process showed a discontinuity around 50°C. At temperatures higher than that the mass transfer rate increased significantly. This is the result of cell membrane denaturation (Oliveira, 1988; Garrote et al., 1984). This change of behavior was not observed in our study. This may be due to differences both in the system and in the process. The studies cited were concerned with the diffusion of reducing sugars from food, while our study concerns the uptake of acid. Possible explanations are that acetic acid is a smaller molecule than sugars, electrostatic interactions may occur, and/or mass transfer from a food is frequently different than mass transfer to the same food. However, a final conclusion can not be drawn.

The influence of temperature on partition coefficients could be neglected (Fig. 3). Experimental values compared very well with those obtained by optimization, for all individual experiments. This indicated that the optimization procedure could be used instead of experimental determinations. The range of acid concentrations during the processes was 0.10 to 0.20M. The variation of the partition coefficient with concentration was negligible in that range.

For the mathematical model we assumed a constant Kp identical to the average of the optimized values, that is, 0.83 (Fig 3). This value is only a little below unity and had we considered a unit value for the partition coefficient, the final results in terms of modeling would be quite similar. This means that it would be reasonable to suppose that equilibrium was reached when the acid concentration of the food equalled the concentration of the acid solution. This has been the approach used by Rodgers et al. (1984) and by Potts et al. (1986), although they did not discuss or validate that assumption. The more usual approach however is to consider that equilibrium corresponds to an equality between the pH of the food and the pH of the acid solution. In our study we verified that at equilibrium the pH of the food was higher than the pH of the acid solution. This difference has been reported (Stroup et al., 1985; Flora et al., 1978) although it has been explained as a departure from equilibrium. Caution is recommended however because even if the difference of pH between the food and the solution at equilibrium is very small, the buffering effect of foods may lead to significant differences in concentration. Such differences can lead to important inaccuracies in the application of Fick's 2nd law.
where $C$ is the acid concentration (total acid intake/volume of the cube). This approach is empirical but results were satisfactory.

Prediction of pH change

The prediction of pH change was done by combining the diffusional and the buffer models in sequence. The amount of acetic acid was calculated with Eq. (5), (6), (7) and (8) using the diffusional parameters determined. The values obtained were transformed in pH with the buffering effect cubic equation. The accuracy of the model was checked by comparing predicted results with individual experimental data. Agreement was good (a typical result is shown in Fig. 5). In Fig. 6 the correlation between experimental and predicted data is shown for all experimental data. The procedure for pH prediction can be extended to different foodstuffs or acidification processes.

**NOMENCLATURE**

- $A$ - cross-sectional area of the cube (m$^2$)
- $A_1, A_2, A_3$ and $A_4$ - polynomial coefficients of the fit between pH and acid concentration
- $C$ - acetic acid concentration (mol/m$^3$) or (mol/dm$^3$)
- $C_0$ - initial concentration of acetic acid in the bath (mol/m$^3$)
- $D$ - Diffusivity (m$^2$/s)
- $D_0$ - Pre-exponential factor in the Arrhenius relationship between diffusivity and temperature (m$^2$/s)
- $E_a$ - Activation energy (kJ/mol)
- $L$ - semi-thickness of the cube (m)
- $M_t$ - Acid intake at time $t$ (mole)
- $M_a$ - Total acid intake at equilibrium (mole)
- $M_{aexp}$ - experimental total acid intake at time $t$ (mole)
- $N_P$ - number of experimental points
- $K_P$ - Partition coefficient (ratio between the acid concentration in the food and in the bath, at equilibrium)
- $q_n$ - non-zero positive roots of equation (5)
- $R$ - Ideal gas constant (8.314 J/mol.K)
- $t$ - time (seconds)
- $V_b$ - volume of the bath (m$^3$)
- $V_a$ - volume of the cubes (m$^3$)
- $x$ - position in the cube (m)
- $\alpha$ - fractional acid intake

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**REFERENCES**