

## 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  $3.99 \times 10^{-9}$  m<sup>2</sup>/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 (Stroup 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 diffusional. 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 for measuring acid diffusion and determined diffusion coefficients based on Fick's second law.

The change in pH of a foodstuff in an acidification process is directly related to the acid uptake but is modified by the buffering effect of the food. Therefore acidification can not be described unless both rate of acid intake and relation between pH and acid concentration are considered. Omran et al. (1990) reported pH changes in acidified cucumbers under different conditions but no models or correlations were proposed. Divito et al. (1982) used a quadratic model for relating a fixed pH of

4.4 to the amount of acid in the containers rather than the acid content in the food. The parameters obtained were a function of the type of food. This model could be used to predict acid requirements but does not provide any information on the process kinetics. Flora and Heaton (1979) related the change in pH of pimientos to the acid concentration in the solution. The model used was a multi-linear equation. This was a purely empirical correlation valid only for the food and operating conditions used.

The development of adequate theoretical models depends both on the correct prediction of acid intake (process rate and equilibrium) and on the modelling of the buffering effect. Thus the objective of our work was to provide experimental evidence to test the ability to describe the process by using independent models for acid diffusion and for the buffering effect. The first one can be theoretically well described by Fick's second law. The buffering behaviour of foods is a very complex phenomenon that has been rarely studied and therefore data was fit with an empirical correlation. The shape of buffer curves is typical of third order polynomials. Turnips were chosen for the study. Specific objectives were: (1) to assess whether Fick's 2nd law is an adequate model for acetic acid intake by turnip cubes acidified in container and to determine the diffusional parameters (activation energy,  $E_a$ , pre-exponential factor,  $D_0$  and partition coefficient,  $K_p$ ) for a wide range of temperatures; (2) to relate the concentration of acid in the turnips with its pH using a third order polynomial; and (3) to verify the procedure suggested by correlating experimental test data with results obtained by using the two models in sequence.

### 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 fibers 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.

#### Acidification experiments

Covered flasks were filled with 50 mL 0.2M acetic acid and immersed in a thermostatic shaking bath with reciprocating motion (Precisterm 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 de-ionized 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

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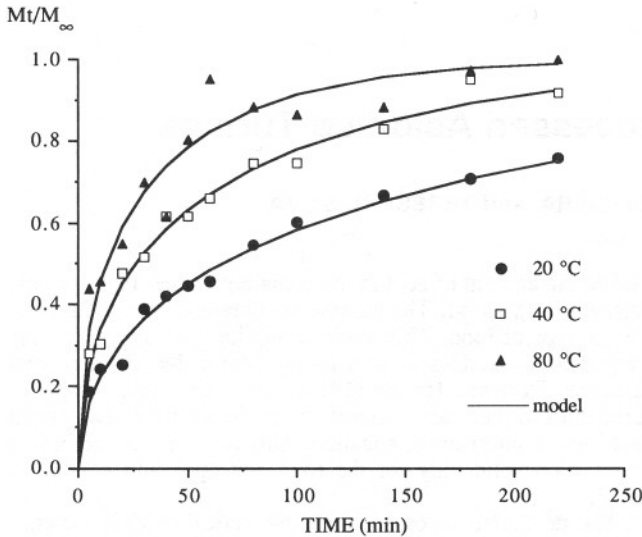


Fig. 1—Acetic acid uptake by turnip cubes at 20,40 and 80°C.

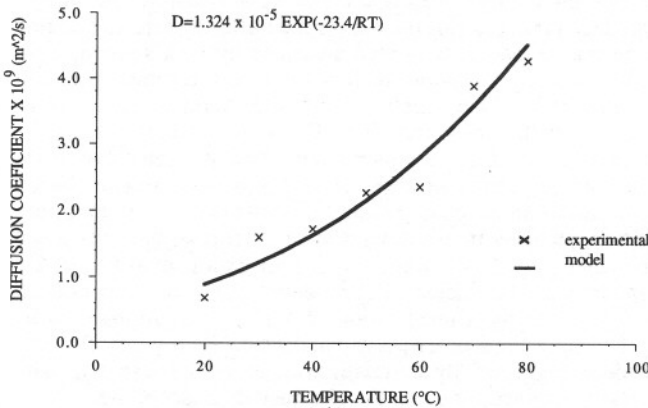


Fig. 2—Variation of the diffusion coefficient with temperature.

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, Inglood) in the sample. The electrode and an automatic temperature compensator (PT100) were connected to a pH meter (Micro2001 RS, Crison). 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:

$$\text{(initial condition)} \quad t = 0 \quad \forall x \quad C = 0 \quad (1)$$

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

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

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):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2q_n^2} \text{EXP}\left(-\frac{Dq_n^2t}{L^2}\right) \quad (4)$$

where  $q_n$  are the nonzero positive roots of

$$\tan q_n = -\alpha q_n, \quad (5)$$

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,

$$\alpha = \frac{V_b}{V_p K_p} \quad (6)$$

The total amount of solute in a cube at time  $t$  is given by:

$$\frac{M_t}{M_\infty} = 1 - \left( \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2q_n^2} \text{EXP}\left(-\frac{Dq_n^2t}{L^2}\right) \right)^3 \quad (7)$$

This equation results from the application of Newman's Rule (Crank, 1979). The application of this method was ensured by checking that the solution verified the three-dimensional differential equation and its boundary conditions. This is the best procedure to assess the validity of this solution, as suggested by Kreyzig (1979).

The acid content at equilibrium is given by a simple mass balance:

$$M_\infty = \frac{V_b C_0}{(1+\alpha)} \quad (8)$$

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:

$$\text{RES} = \frac{\sqrt{\sum_{i=1}^{NP} (M_i - M_i^{\text{exp}})^2}}{NP} \quad (9)$$

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 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  $3.99 \times 10^{-9}$  m<sup>2</sup>/sec and correlated well with an Arrhenius type equation, with an activation energy of 23.4 kJ/mol and a pre-exponential factor of  $1.324 \times 10^{-5}$  m<sup>2</sup>/sec (Fig. 2). The order of magnitude of these values is the same as usually published for such situations (Rodgers et al., 1984; McCarthy and Heil, 1988). The values are smaller than diffusivities of acetic acid in water solutions as expected. Assuming that the porosity of the turnips could be described in terms of its water content (Califano and Calvelo, 1983; Alzamora et al., 1985), the relationship between diffusivity in turnips and diffusivity in water solutions leads to

pH CHANGE IN ACIDIFIED TURNIPS. . .

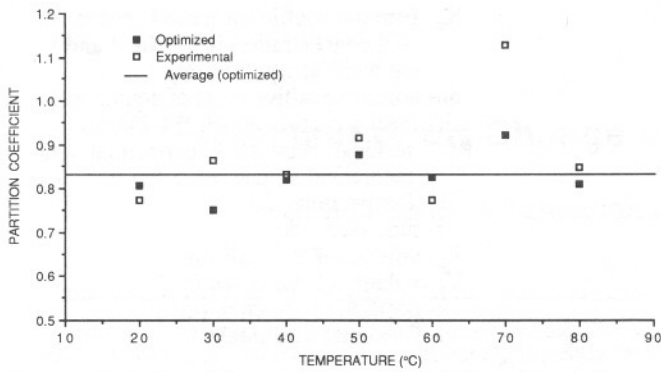


Fig. 3—Variation of the partition coefficient (experimental and optimized) with temperature.

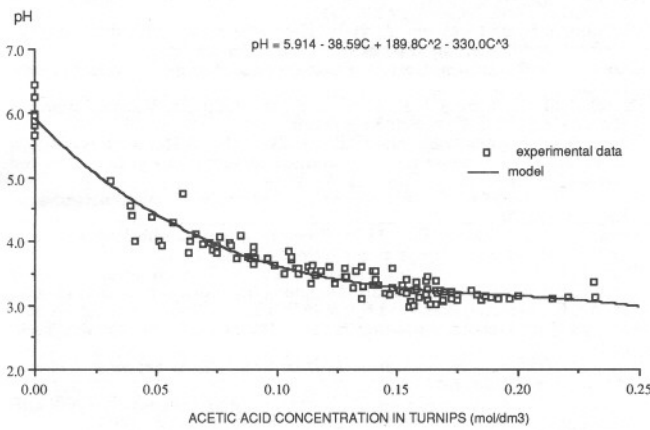


Fig. 4—Relationship between turnips pH and its acetic acid concentration.

Table 1—Polynomial coefficients of the cubic model relating pH with acid concentration<sup>a</sup>

Temperature (°C)	Polynomial coefficients				Correlation coefficient
	A1	A2 dm <sup>3</sup> /mol	A3 (dm <sup>3</sup> /mol) <sup>2</sup>	A4 (dm <sup>3</sup> /mol) <sup>3</sup>	
20	5.847	-52.19	460.2	-1625	0.978
30	6.196	-40.74	169.8	-161.4	0.975
40	6.425	-69.23	603.1	-1851	0.991
50	5.868	-38.62	231.3	-556.5	0.990
60	5.964	-54.55	412.3	-1126	0.992
70	5.958	-32.77	138.0	-223.4	0.997
80	5.664	-32.66	176.8	-411.1	0.991

<sup>a</sup> pH = A1 + A2 × C + A3 × C<sup>2</sup> + A4 × C<sup>3</sup> (C in mole/dm<sup>3</sup>).

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 work. 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 exper-

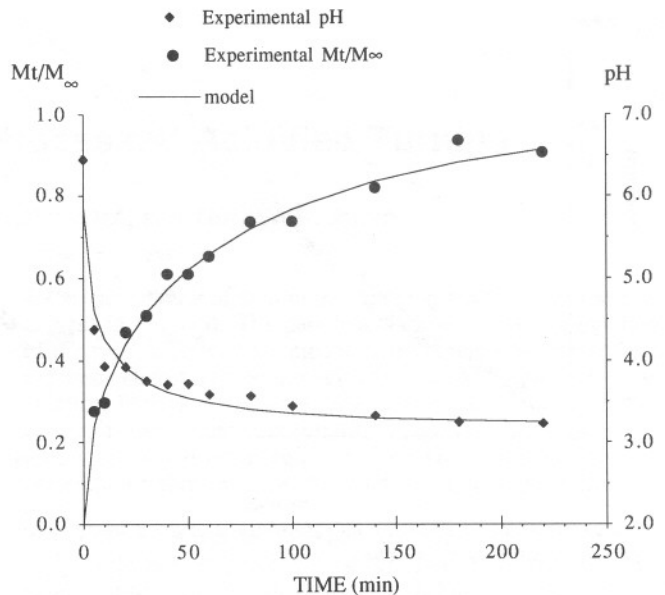


Fig. 5—Prediction of acetic acid intake and pH at 40°C.

iments. 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  $K_p$  identical to the average of the optimized values, that is, 0.830 (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.

**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) had 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):

$$pH = 5.914 - 38.59 C + 189.8 C^2 - 330.0 C^3$$



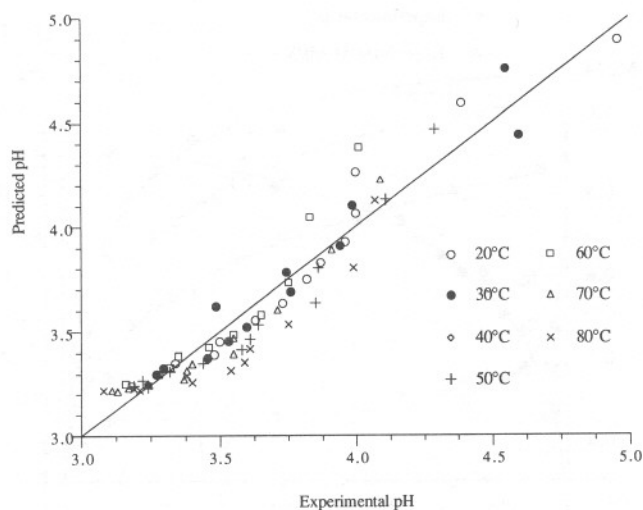


Fig. 6—Correlation between experimental and predicted pH values for all experimental data

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 ( $m^2$ )
- A1,A2,A3 and A4 - polynomial coefficients of the fit between pH and acid concentration
- C - acetic acid concentration ( $mol/m^3$ ) or ( $mol/dm^3$ )
- Co- initial concentration of acetic acid in the bath ( $mol/m^3$ )
- D - Diffusivity ( $m^2/s$ )
- Do- 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)
- Mt - Acid intake at time t (mole)
- $M_\infty$  - Total acid intake at equilibrium (mole)
- $Mt^{exp}$  - experimental total acid intake at time t (mole)
- NP- number of experimental points

- $K_p$  - Partition coefficient (ratio between the acid concentration in the food and in the bath, at equilibrium)
- qn- nonzero positive roots of equation (5)
- R- Ideal gas constant ( $8.314 J/mol.K$ )
- Res- residual between experimental and theoretical values (equation 9)
- T- Temperature (K)
- t- time (seconds)
- $V_b$ - volume of the bath ( $m^3$ )
- $V_p$  - volume of the cubes ( $m^3$ )
- x- position in the cube (m)
- $\alpha$ - fractional acid intake

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