Mass Transfer and Solute Diffusion in Brined Cucumbers

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ABSTRACT: The exchange of malic acid, lactic acid, NaCl, and sugar between cucumber and cover brine was monitored over a course of 16 days for 5 sizes of cucumbers. Experimental results showed that sugar exchange between cucumbers and cover brine was the slowest. In comparison to Ficks diffusion equation, the exponential equation better described the movement of solutes during the brine fermentation of cucumbers. Diffusion coefficient of sugar was estimated to vary from 1.80 x 10-9 to 9.18 x 10-9 m2/s. Solute sorption rate from the exponential model varied from 0.0204 to 0.233 h-1 and decreased with increase in cucumber size and solute molecular weight.

Keywords: fermentation, diffusion, solute, cucumber, modeling

Introduction

BRINE FERMENTATION IS USED TO PRESERVE CUCUMBERS BEcause of sensory traits desired in some products, processing strategies, and for economic reasons (Fleming 1982; Fleming and Moore 1983). About 40% of the pickling cucumbers produced annually in the United States (590,000 tons) is preserved by brine fermentation (Fleming and others 1995).

In brine fermentation, fresh cucumbers are placed in NaCl solution, with the concentration of NaCl used being dependent on that required for microbial control and brinestock quality. The brined cucumbers undergo microbial fermentation involving lactic acid bacteria, yeast, and other microorganisms (Fleming and Moore 1983). During the fermentation process, the fermentable sugars are converted to acids (mostly lactic acid) and other end products (Fleming 1984).

Results from studies carried out in our laboratory indicate that fermentation occurs outside, as well as within, the brined cucumbers (Daeschel and Fleming 1981; Daeschel and others 1985). Lactic acid bacteria were found to be able to enter and multiply inside brined cucumbers. As part of the fermentation process, some lactic acid bacteria degrade malic acid into CO2 and lactic acid (Etchells and others 1968). This microbially produced CO2 is a major cause of bloater damage (hollow cucumbers) in fermented cucumbers (McFeeters and others 1982). If fermentation takes place inside the cucumbers as well as in the brine, solutes will have to diffuse out of (malic acid, fermentable sugars) and into the (NaCl, lactic acid) cucumber fruit.

Lumped or distributed models are used to describe the transfer of mass or heat in a biological material interacting with its environment (Incropera and DeWitt 1996). Lumped models ignore the internal resistances to heat or mass transfer, while distributed models take into account both the internal and external resistances. The lumped models are often exponential- or logarithmic-type equations (Eq. 1). In the distributed model approach, equations based on Ficks law (Eq. 2) are used because the mechanism of mass transfer is assumed to be controlled by diffusion phenomena (Crank 1975).

$$\frac{C - C_{eq}}{C_o - C_{eq}} = \exp(-kt) \tag{1}$$

$$\frac{\partial C}{\partial t} = div(D \nabla C) \tag{2}$$

(Symbols are defined in the Notation section).

Parti (1993) showed that distributed models are applicable to mass transfer processes when Bi (mass transfer Biot number), as defined in Eq. 3, is greater than 10. It is obvious from Eq. 3 that the diffusion coefficient (D) has to be determined before Bi can be calculated.

$$Bi = \frac{hL}{D} \tag{3}$$

Pflug and others (1967), and Bomben and others (1974), used Ficks second-order diffusion equation (Eq. 2) to estimate the diffusion coefficient of NaCl (D in Eq. 3) during the de-salting of fermented and cured cucumbers. The values of diffusion coefficients of solutes in already fermented cucumbers will be different from those of freshly brined ones because of differences in structure and physical characteristics. To our knowledge, no study has been carried out to determine the diffusion coefficient of solutes in freshly brined cucumber fruit.

The rate of attainment of solutes' equilibrium in brined pickling cucumbers was studied by Potts and others (1986). The authors assumed that the resistance to solute movement into and out of cucumbers is at the interface of fruit and brine (that is, internal resistance is neglected). Because of this assumption, a logarithmic equation (Eq. 1) was used to describe the movement of solutes in and out of the cucumber fruit. From the results obtained, Potts and others (1986) showed that lactic acid and reducing sugars, respectively, had the fastest and slowest rates to equilibrium. When Eq. 1 was applied to experimental data, the ratio of k values for malic acid, NaCl, and lactic acid to k values for reducing sugar was found to be 1.284, 3.505, and 4.170, respectively.

This study was carried out to determine the applicability of the lumped or distributed model to describe the movement of solutes in and out of freshly brined cucumbers.

Materials and Methods

Pickling cucumbers (Napoleon cultivar) were obtained from a local farmer. Only hand-washed cucumbers free of

Table 1—Physical characteristics of cucumbers used in the study

Size designation	Dia (mm)	Length (mm)	Weight (g)	Number of fruits per jar	Brine volume per fruit[a] (mm^3)
1A[a]	17.00 ± 0.69	67.03 ± 1.54	13.38 ± 1.29	142	1.33 x 104 ± 0.01 x 104
1B	22.67 ± 0.64	84.05 ± 2.11	29.60 ± 2.32	64	2.96 x 104 ± 0.03 x 104
2A	26.7 ± 1 .89	93.84 ± 4.55	44.37 ± 3.50	43	4.40 x 104 ± 0.02 x 104
2B	31.58 ± 1.30	105.84 ± 5.22	71.71 ± 5.45	27	7.01 x 104 ± 0.04 x 104
3A	46.10 ± 2.17	142.91 ± 8.95	200.05 ± 9.61	10	18.93 x 104 ± 0.04 x 104

[a]Based on average of 20 cucumber fruits

obvious physical damage and disease were used. Cucumbers were graded into the following sizes, based on cucumber diameter (maximum): 1A (17.0-mm dia); 1B (22.7-mm dia); 2A (26.7-mm dia); 2B (31.6-mm dia), and 3B (46.1-mm dia). It should be noted that this size range represents immature fruit, which is preferred by the pickle industry. Once the fruit starts to ripen, as evidenced by maturing of the seed area, the tissue in this region becomes unacceptable due to softening and ultimate liquefaction.

Twenty fruit were set aside from each size designation. The mass, diameter, and length of each fruit were measured. A digital Vernier caliper (Digimatic Solar Caliper, Mitutoyo Corp., Tokyo, Japan) was used to measure the diameter and length, while the fruit mass was obtained by means of a digital weighing scale (Model LC2200S, Sartorius Corp., Bohemia, N.Y., U.S.A.), which is accurate to 2 decimal places (see Table 1).

Cucumbers were brined in duplicate in 1-gal (3.8 L) glass jars containing 50% cucumbers and 50% brine by weight. Cover brines contained 10% NaCl and 0.8% lactic acid. Microbial growth was prevented by adding 1,000 ppm sodium benzoate and 300 ppm bisulfite to the cover brines. This allowed us to follow the changes in fermentable solutes due to diffusion until equilibrium between the cucumbers and the brine was reached. The rate of change of solutes in the brine solution was followed by taking 12 1.5-mL brine samples over a time duration of 16 d. The contents of each jar were mixed before sampling.

High-performance liquid chromatography (HPLC) analyses of acids and reducing sugars were carried out by the procedures of McFeeters (1993). An Aminex HPX-87H column was used, along with 3 mM of heptafluorobutyric acid (Aldrich Chemical Co., Inc., Milwaukee, Wis., U.S.A.), as the mobile phase. Organic acids (malic and lactic) were detected with a conductivity detector (Model CDM-2, Dionex Corp., Sunnyvale, Calif., U.S.A.), and sugars were detected by means of a refractive index detector (Model 410, Waters Associates Inc., Milford, Mass.). Data were collected and analyzed by using Chrom Perfect software (Justice Innovations, Inc., Mountain View, Calif., U.S.A.) on a 486 computer. NaCl was determined by titration with standard $AgNO3$, using dichlorofluorescein as an indicator (Fleming and others 1984).

Data analysis

The experimental data obtained were the concentrations of the solutes in the brine over the course of the experiment. The average concentrations of solutes in the cucumbers at any time (t) were obtained by carrying out mass balances as follows:

Mass balance equation for solute diffusing out of cucumber. Malic acid and sugar are the solutes diffusing out of the fruit.

$$\alpha_i C_{b,i}\{t\} + \sigma_i \sum_{j=1}^{n} C_{s,j} + \hat{C}_{c,i}\{t\} = C_{c,i,o} \quad (4)$$

Mass balance equation for solute diffusion into cucumber. Lactic acid and salt are the solutes diffusing into the fruit.

$$\alpha_i C_{b,i}\{t\} + \sigma_i \sum_{j-i}^{n} C_{s,j} + \hat{C}_{c,i}\{t\} = \alpha_i C_{b,i,o} \quad (5)$$

The second term on the left side of Eq. 4 and 5 compensates for the amount of fluid and solute removed during sampling. The calculated values of solute concentration in the cucumber fruit were then used in further analysis.

Results and Discussion

Physical dimensions

Table 1 shows the average values of diameter, length, and weight of cucumbers within each size designation, and the calculated volume of brine surrounding each fruit in the jar. As expected, brine volume per fruit increased, and the number of fruit per jar decreased with increase in fruit weight and size. The average length-to-diameter ratio varied from 3.94 for the 1A size cucumbers to 3.10 for 3B cucumbers.

Solute concentration in cucumber

The measured initial concentrations of solutes in the cover brine and in the cucumber are given in Table 2. Using ANOVA procedure (SAS 1996), statistical testing (at 95% confidence interval) showed that size had a significant effect on the initial reducing sugar concentration in cucumber. This is similar to the results reported by McCombs and others (1976) and Lu and others (2001). Size enlargement in cucumber is a maturation process, and the increase in sugar content is one of the biochemical and physiological changes that occurs in fruits during maturation (Wills and others 1989). Size did not significantly affect the initial malic acid concentration. In order to be able to compare results for the different sizes, solute concentrations within the cucumber (obtained from Eq. 4 and 5) were divided by their respective initial concentrations in the cover brine (or within the cucumber).

Figure 1 and 2 show the fractional change in concentrations of lactic acid, malic acid, reducing sugar, and NaCl for different sizes of cucumber. Generally, the rate of solute movement increased with cucumber size when solute was desorbed (reducing sugars and malic acid), but decreased with size when solute was absorbed (NaCl and lactic acid). This is an indication that cucumber structure may be playing a role in the diffusion of solutes in and out of cucumbers during brining. (Further explanation for this is given later).

Equilibration of solutes between brine and cucumbers was approached by 150 h of contact. The rate of sugar equilibration was the slowest. For lactic acid, malic acid, and NaCl, 95% of the diffusion that took place occurred within the first 70 h of fruit/brine interaction. It took about 100 h or more

Table 2—Measured initial concentration (kg/m³) of solutes in brine and cucumbers[a]

	NaCl	Reducing sugar	Malic acid	Lactic acid
Brine	9.92 ± 0.02	—	—	6.54 ± 0.003
Cucumber				
1A	—	12.79 ± 0.002	2.93 ± 0.005	—
1B	—	14.67 ± 0.005	3.13 ± 0.001	—
2A	—	16.52 ± 0.003	3.03 ± 0.003	—
2B	—	16.18 ± 0.004	2.79 ± 0.002	—
3B	—	16.95 ± 0.003	2.85 ± 0.002	—

[a]Reducing sugars and malic acid concentration values are based on average from 20 fruits. NaCl and lactic acid concentrations were based on two different readings.

Table 3—Estimated values of D_o and D_1 (Eq. 12)

Size[a]	D_o (m²/s)	D_1 (m⁵/(kg s))	Standard Error
1A (17.00 mm)	1.55e-09	5.05e-10	0.068
1B (22.67 mm)	2.05e-09	3.14e-10	0.054
2A (26.71 mm)	5.06e-09	4.64e-10	0.054
2B (31.58 mm)	4.45e-09	5.11e-10	0.059
3B (46.10 mm)	8.47e-09	1.41e-09	0.036

[a]Number in parentheses are the average of 20 fruits' dia in each size group.

for the reducing sugars to attain the 95% diffusion level (that is, when C/C_i is 0.525). In Eq. 1, the lower the value of diffusion coefficient, the higher the Biot number. Since the movement of sugar was the slowest among the solutes investigated in this study, the criteria for the use of lumped or distributed model (B_i >10) in describing the movement of solutes in freshly brined cucumbers were tested using the sugar data. The estimated values of diffusion equation parameters for reducing sugars are given in Table 3. The methodology used in the determination of diffusion coefficients is described in the Appendix.

Figure 3 shows a comparison of predicted and experimental data values for 1A, 2A, and 3B cucumbers eluting sugars into the surrounding brine. A similar fit was obtained for sizes 1B and 2B. The estimated values of Do and D1 and the associated standard error of estimate are given in Table 3 (see Appendix for the relationship between D_o, D_1, diffusion coefficient, and solute concentration). Statistical testing using GLM procedure in Statistical Analysis System (SAS 1996)

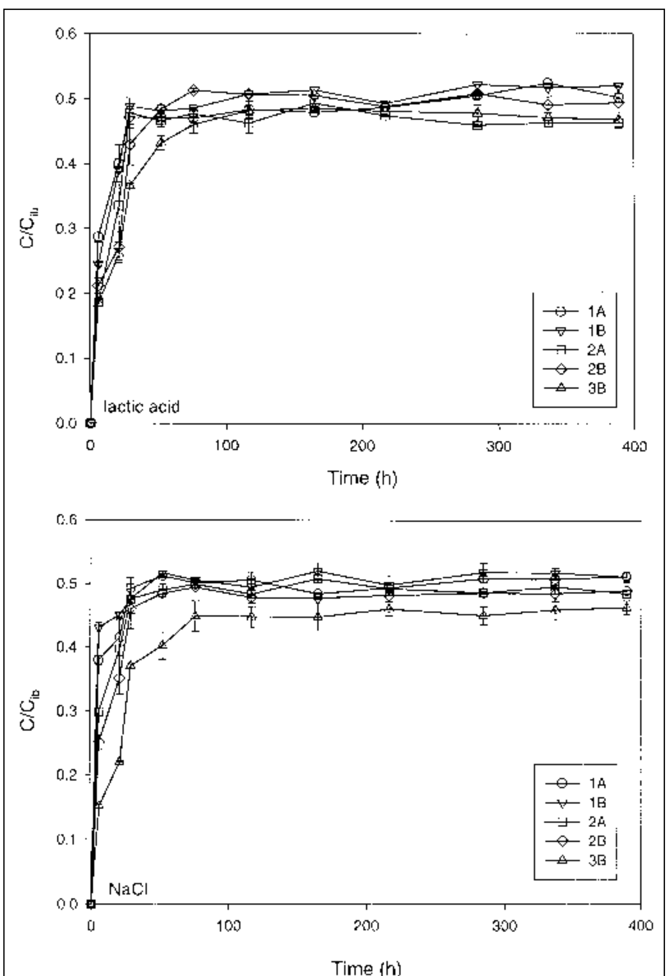

Figure 1—Experimental data showing the effect of size on absorption of lactic acid and NaCl by cucumbers. C_{ib} is the initial concentration of lactic acid or NaCl in the cover brine.

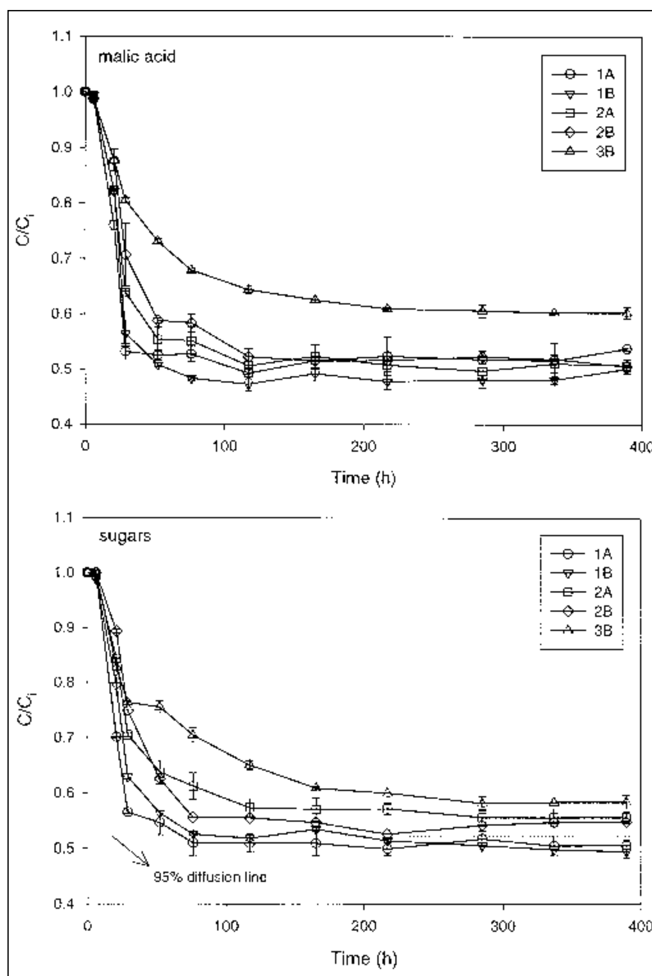

Figure 2—Experimental data showing the effect of size on diffusion of malic acid and sugars from cucumbers into cover brine. C_i is the initial concentration of malic acid or sugars in cucumbers.

showed that D_o significantly ($P < 0.05$) increased with increase in cucumber size. However, the value of D_1 was not significantly affected by size of cucumber. The equation below was therefore used to relate the diffusion coefficient to cucumber size.

$$D = 1.0x10^{-9}(-3.42 + 0.28d + 5.39C) \qquad R^2 = 0.93 \qquad (6)$$

Azedevo and others (1995) estimated mass transfer coefficient in acidified vegetables to be 1.0819 × 10^{-6} m/s. Using this value of mass transfer coefficient and calculated values of diffusion coefficient, the mass transfer Biot numbers were calculated to be 5.1, 5.5, 2.6, 3.6, and 2.7 for size 1A, 1B, 2A, 2B, and 3B cucumbers, respectively. These values are less than the critical value of 10 required for the use of distributed equations involving mass transfer diffusion studies (Parti 1993). This indicates that the lumped-type model (Eq. 1) is more applicable than the Ficks diffusion equation (Eq. 2) in describing the movement of sugars (and hence other solutes) in freshly brined cucumbers. This is further confirmed from simulation results (from Eq. 2) which showed that, at any time, there is no significant difference in sugar concentration between the surface and center of the fruit (Fig. 4).

The Nonlinear estimation procedure (NLIN) in the Statistical Analysis System package (SAS 1996) was used to estimate k and C_{eq} of Eq. 1. The estimates and the associated standard errors of estimate are listed in Table 4. Figure 5 shows comparison of the predicted and experimental data during the movement of malic acid and reducing sugars out of, and the uptake of lactic acid and NaCl, by brined cucumbers.

The estimated solute movement rate (k) for lactic acid, NaCl, and sugars significantly ($P < 0.05$) decreased with increase in cucumber size. Values of k for malic acid were not significantly affected by cucumber size. Sugars and NaCl had the highest and lowest values of k. The ratio of k values for malic acid, NaCl, and lactic acid to the k value for sugar (Table 4) decreased with increase in cucumber size. In addition, k values for solutes transported out of the cucumbers were lower than the corresponding values for solutes transported into the cucumbers. Similar relationship was obtained by Potts and others (1986). This is an indication that microstructure may play a role in the diffusion of solute in and out of cucumber fruit. Scanning electron microscopy (SEM) studies of the surface of fresh pickling cucumbers by Smith and others (1979) showed that stomatal frequency and pore area decrease with increase in fruit size. Stomata are natural openings in fruits and vegetables, and are important in regulating the exchange of gases between the fruit and the environment. Other factors, of which we are not currently aware, may also be contributing to solute movement between cov-

Table 4—Estimated parameters of exponential equation (Equation 1)

Size	Parameter	Lactic acid	Malic acid	NaCl	Sugars
1A	k (h^{-1})	0.127	0.0457	0.233	0.0452
	C_{eq}	0.486	0.509	0.494	0.502
	s.e.	0.0247	0.0550	0.0260	0.0442
	k/k_{su} [a]	2.81	1.01	5.14	1.00
1B	k (h^{-1})	0.0929	0.0261	0.174	0.0242
	C_{eq}	0.505	0.474	0.494	0.504
	s.e.	0.0121	0.0568	0.0377	0.021
	k/k_{su}	2.72	1.06	5.09	1.00
2A	k (h^{-1})	0.0788	0.0321	0.135	0.0285
	C_{eq}	0.473	0.502	0.487	0.559
	s.e.	0.0125	0.0404	0.030	0.023
	k/k_{su}	2.75	1.13	4.73	1.00
2B	k (h^{-1})	0.0561	0.0254	0.0922	0.0244
	C_{eq}	0.502	0.509	0.483	0.532
	s.e.	0.0346	0.0378	0.0255	0.0393
	k/k_{su}	2.31	1.04	3.78	1.00
3B	k (h^{-1})	0.0482	0.0208	0.0450	0.0204
	C_{eq}	0.476	0.604	0.456	0.592
	s.e.	0.0253	0.0139	0.0282	0.0267
	k/k_{su}	2.36	1.02	2.21	1.00

[a] k_{su} = solute sorption rate for sugars

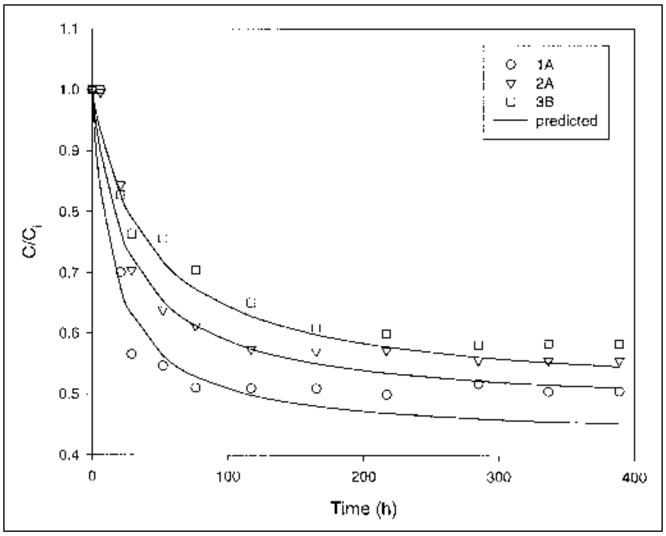

Figure 3—Fitted (Ficks diffusion equation, Eq. 2) and experimental data during sugar elution for three sizes of cucumber.

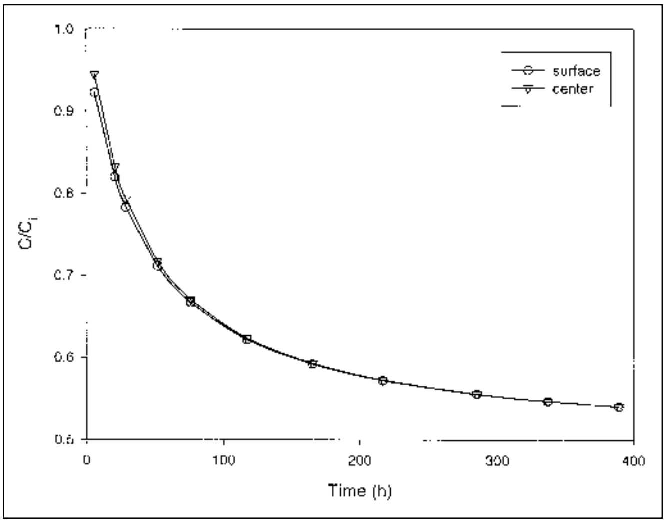

Figure 4—Predicted (Ficks diffusion equation) sugar concentration at the surface and center of size 3B cucumbers

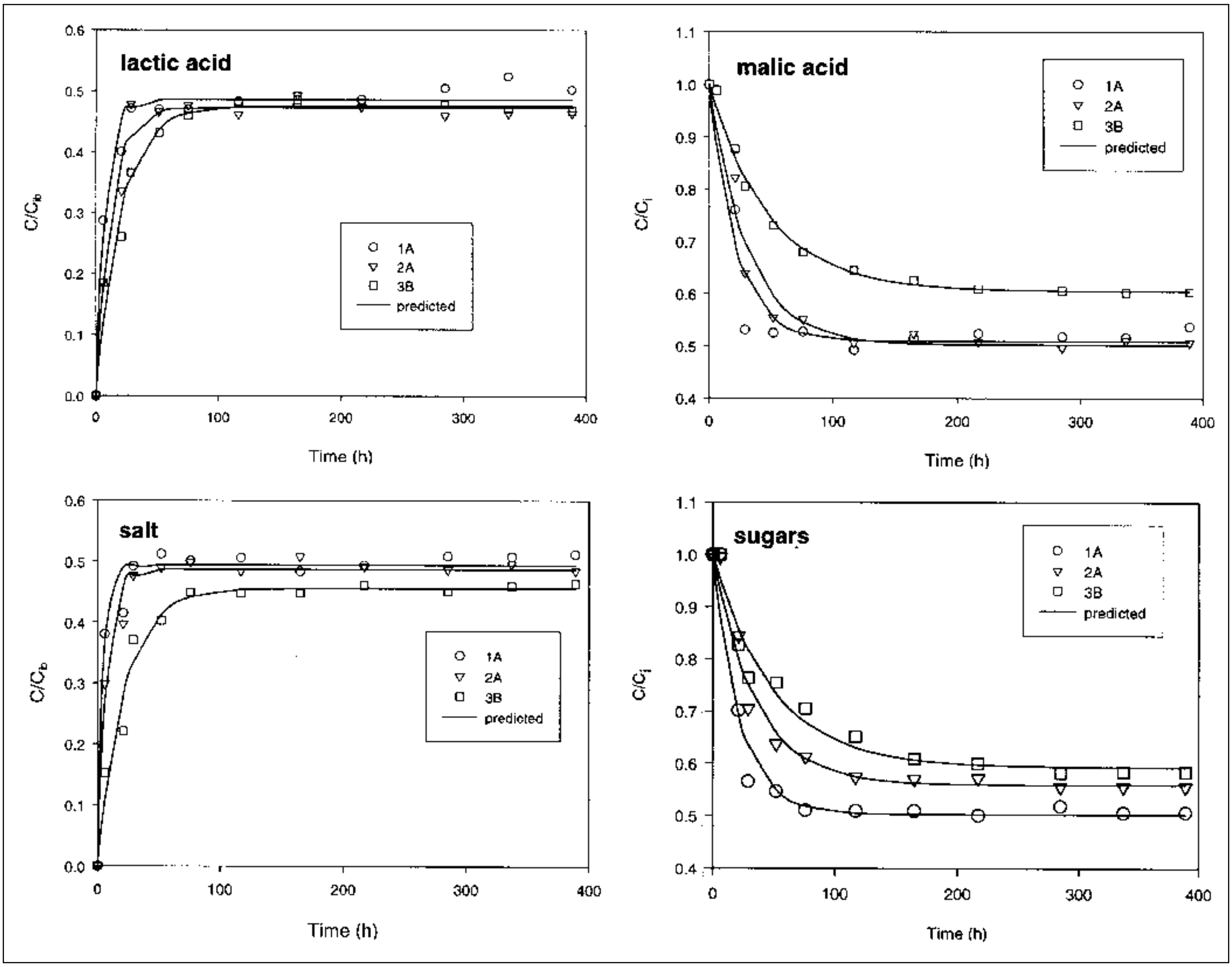

Figure 5—Predicted (Equation 1) and experimental data for malic acid, lactic acid, NaCl, and sugars in brined cucumbers for three cucumber sizes.

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ered brine and cucumber fruit. There was no definite trend between estimated equilibrium solute concentration and cucumber size.

Conclusion

THE FOLLOWING CONCLUSIONS CAN BE DRAWN FROM THIS study: (a) Initial concentration of sugars in cucumber was significantly dependent on fruit size. Initial concentration of malic acid in cucumber was not dependent on size. (b) About 95% of solute diffusion that took place during cucumber brining occurred within 1 5 h or less of contact between brine and cucumber. (c) The rate of solute exchange in brined cucumber is dependent on fruit size. For any particular size, the rate of diffusion is higher for solutes transported onto the cucumber than those of solutes transported out of the cucumber. (d) The movement of solutes in brined cucumbers is best described by exponential- or lumped-type model.

Notation

$\hat{C}$ volume averaged concentration (kg/m^3)
A_s surface area (m^2)
b estimate of the vector of parameters, $\beta_1, \beta_2, ..., \beta_n$
C concentration (kg/m^3)
$C_{b,i}$ initial concentration in brine (kg/m^3)
d diameter (mm)
D diffusion coefficient (m^2/s)
D_1 constant (m/s^2 per kg/m^3)
D_o constant (m/s^2)
h mass transfer coefficient (m/s)
k solute movement rate (h-1)
K_i partition coefficient
M molecular weight (kg)
n number of samples taken at time, t
P inverse vector of P^{-1}
P^{-1} calculated vector from equation
P_{jj} jth diagonal term in P
r radial dimension (m)
S error sum of squares
t time (s)
U inverse of the matrix of variance of measurements
v sampling volume (m^3)
V volume (m^3)
W inverse of matrix of variance of measurements
X matrix sensitivity coefficient of each dependent variable, derivatives of dependent variable with respect to the

parameter
Y vector of measured dependent variable
z scalar interpolation factor (this factor is iteration-dependent)

Greek Letters
δ change in parameter vector
ε initial random value vector of parameters to be estimated
ϕ iteration termination value
η vector of estimated dependent variable
$\beta_1, \beta_2, ..., \beta_n$ parameters to be estimated
σ_i parameter defined as v/VcKi
α_i parameter defined as Vb/Vc KI

Suffices
b brine
c cucumber
o initial
s sample

Appendix: Estimation of Diffusion Coefficient

The differential equation that describes the transient concentration change of a solute (reducing sugars) in a cylinder, assuming one-dimensional, is given by:

$$\frac{\partial C_c}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r} D(C) r \frac{\partial C_c}{\partial r} \tag{7}$$

For a cylinder that is placed in a well-stirred solution of finite volume, the boundary conditions to Eq. 6 are given by Crank (1995):

$$V_b \frac{\partial C_b}{\partial t} = K_i A_s D(C) \frac{\partial C_c}{\partial r} \qquad t > 0, r = R \tag{8}$$

$$\frac{\partial C}{\partial r} = 0 \qquad t > 0, r = 0 \tag{9}$$

The expression of Eq. 8 implies that the rate at which a solute leaves or enters the solution is always equal to that at which it enters the material, after adjusting for the fact that the concentration of solute just within the surface of the material is Ki times that in the solution (Crank 1979). The partition coefficient (Ki) for reducing sugars was obtained to be 0.88. Ki is the ratio of reducing sugar concentration in the crushed cucumber to that in the brine after equilibrium conditions were reached.

The initial conditions for the elution of reducing sugars from the cylindrical cucumbers to the surrounding brine is given by:

$$C_{c,o} = 1 \qquad t = 0, 0 < r < R \tag{10}$$

$$C_{b,o} = 0 \qquad t = 0, r > R \tag{11}$$

The values of sugar diffusion coefficient in Eq. 6 for the different cucumber sizes can be estimated from the rate of change of sugar concentration within the cucumber or in the solution. It is simpler from an experimental point of view to monitor the change of concentration in the solution and then to use mass balance equations to calculate the concentration of a solute in the material (cucumber) at any time, t (Eq. 4).

Diffusion coefficients are often a function of concentration (Fasina and Sokhansanj 1996; Crank 1995). For simplicity purposes, a linear relation between the diffusion coefficient and concentration was used.

$$D = D_o + D_1 C \tag{12}$$

Do and D1 are coefficients of Eq. 12. The derivation of expressions for the diffusion coefficient will therefore involve the estimation of these coefficients. This entails solving Equations 7 to 12 with a numerical technique (such as the finite element method or the finite difference method). The values of diffusion coefficient (or constants of Eq. 12) could be obtained by trial and error, or by a nonlinear estimation method. The trial and error method is known to be time-consuming, inefficient and impractical (Beck and Arnold 1977). A description of the method used in this study to estimate the diffusion coefficients is described below:

Estimation procedure

In situations where the constants (parameters) of an equation(s) describing a system (such as a solute diffusion system) are not known, discrete measurements of the dependent variable are made within the domain, as was done in this study. The measurements are then used to estimate values of the constants through an optimization technique. Concepts of probability and statistics are used to obtain estimates of the parameters due to errors that are inherently present in the measurements (Beck and Arnold 1977).

The inverse theory optimization method was used to estimate the diffusion coefficient in this study. This method determines the parameters of equations describing a system for which experimental data are available (Hensel 1991). The inverse theory method is particularly suitable for parameter estimation in nonlinear situations where: (a) the experimental data are uncertain; (b) parameters are sensitive to variability in the data; (c) the parameters are strong functions of the dependent variable; and (d) partial differential equations are used to describe the system. These situations are characteristics of parameter estimation involving the diffusion/elution of solutes in and out of cucumber during fermentation.

Beck and Arnold (1977) recommended the Modified Box-Kanemasu method for estimation of parameters in nonlinear systems. This method was used by Fasina and Sokhansanj (1996) to estimate the moisture diffusivity and thermal properties of alfalfa pellets during drying and cooling. The method optimizes the parameters of interest (such as diffusion coefficient) in an equation by minimizing the error sum of square function given by Eq. 10, while changing the direction and size of the corrections to the parameter vector.

$$S^{(j)} = [Y - \eta^{(j)}]^T W [Y - \eta^{(j)}] \tag{13}$$

The estimated parameter vector is given by:

$$b^{(j+1)} = b^{(j)} + z^{(j+1)} \delta^{(j)} \tag{14}$$

where

$$\delta^{(j)} = P^{(j)} [X^{T(j)} W (Y - \eta^{(j)}) + U(\varepsilon - b^{(j)})] \tag{15}$$

and

$$P^{-1(j)} = XT^{(j)}\, W\, X^{(j)} \tag{16}$$

X(j), the vector of sensitivity coefficient, is the first derivative of the dependent variable (concentration) with respect to the parameters to be evaluated and is given by:

$$X = \begin{vmatrix} X^{\,j}_{D_o} \\ X^{\,j}_{D_1} \end{vmatrix} = \begin{vmatrix} \partial C / \partial D_o \\ \partial C / \partial D_1 \end{vmatrix} \tag{17}$$

Apart from the use of the vector form of the sensitivity coefficient in computation, plots of scalar values of computed sensitivity coefficients against the dependent variable provide insight into the interdependency of estimated parameters (Beck and Arnold 1977).

To estimate the values of the constants in Eq. 12 and using the mass transfer set of equations (Eq. 7 to 11), initial values of Do and D1 were guessed from values given in the literature for solute diffusion in agricultural crops (Schwartzberg and Chao 1982). The estimated dependent variable (?) and the initial values of error sum of squares (Si) were calculated (Eq. 13). Using a z(j+1) (step size) of 1, new values of Do and D1 were then calculated according to Eq. 14. The new Do and D1 were used to compute new values of solute concentrations based on the time and duration of the collected experimental data. A new value of error sum of squares, S (Eq. 13), was calculated and compared with the previous value of S_i. If S is less than S_i, $z_{(j+1)}$ was calculated from Eq. 18. If S is greater than S_i, the step size was halved until $S < S_i$. The iteration was stopped when the value of ϕ was less than 0.01 (Beck and Arnold 1977).

$$z^{(j+1)} = G^{(j)}\, \phi 2\, [S^{(j)} - S^{i(j)} + 2\, G^{(j)}\, \phi] - 1 \tag{18}$$

where:

$$G = [\delta^{(j)}]T\, P^{-1(j)}\, \delta^{(j)} \tag{19}$$

Computation was achieved by writing the diffusion and the nonlinear estimation procedure equations in finite difference form in Fortran 90 on a personal computer. The details of numerical formulation are described in Fasina and Sokhansang (1996). The value of G calculated from Eq. 18 was used to check the validity of the systems of equations and the coding of the problem in a programming language. The value of G must be positive; otherwise, the solution is incorrect.

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