

MATHEMATICAL MODELLING IN OSMOTIC DEHYDRATION

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Mass transfer parameters during osmotic dehydration of apple cv. Idared has been studied. The solution of Fick's law for unsteady state mass transfer in rectangular configuration has been used to calculate the apparent diffusion coefficient of fructo-oligosaccharides (FOS) - used as osmotic agent - and water. Apple cubes were blanched and osmotically treated (0-60 min) in 60 % FOS solution at 40 °C, sample-to-solution ratio was 1:10. Total solid (TS) content of the samples was determined by gravimetric method, total soluble solid (TSS) content was measured by refractometer and FOS content was measured by polarimeter. The apparent diffusion coefficient of FOS and water were found to be of the order of 10⁻⁹ m²/s. The model of the osmotic dehydration process is better for the water than for the FOS.

Keywords: mathematical modelling, osmotic dehydration, diffusion coefficient, apple

1. Introduction

Osmotic dehydration is a water removal process by immersing the fruit or vegetable in a hypertonic solution. Two simultaneous counter current flows take place because of the semipermeable property of the plant cell structure: a water flow from the tissues into the solution and a simultaneous transfer of solute from the solution into the food (Salvatori et al., 1999a,b). Since the membrane is not perfectly selective, other solutes (minerals, vitamins, and flavours) present in the food are also leached into the osmotic solution (Taiwo et al., 2002). The driving force of diffusion is the gradient of chemical potential.

In practice osmotic dehydration is used for partial dehydration of foods, especially fruits and vegetables as a pre-treatment step before different drying methods or freezing (Torreggiani, 1993).

The rate of mass transport depends upon many factors such as concentration, temperature and the kind of osmotic solution, time of treatment, level of agitation, sample-to-solution ratio, vacuum level and different pre-treatments if applied. Several studies in the literature describe the effect of these variables (Lerici et al., 1985; Beristain et al., 1990; Lazarides et al., 1997; Park et al., 2002). The conventional used osmotic agents are sucrose and sodium chloride.

The purpose of present work was to study mass transfer parameters during osmotic dehydration of

apple and to develop a model based on Fick's second law describing the transport phenomena in longitudinal direction.

2. Mathematical modelling

Most of the available models proposed are based on Fick's law of diffusion and use the particular solution given by Crank (1975) for one-dimensional unsteady state mass transport (Salvatori et al., 1999a):

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where C is the concentration of the diffusing component, D is the diffusion coefficient, t is the time coordinate, x is the space coordinate, the diffusion path.

The double mass transfer is reduced this way to only one transport process, either of water or solute. Lenart & Flink (1984) proposed a model that was able to predict osmotic mass transport data and water activity data for short, non equilibrium osmosis time. Solution of Fick's law for short contact time diffusion was used by Hawkes & Flink (1978) and Magee et al. (1983). Kaymak-Ertekin & Sultanoglu (2000) developed a model for OD of fruits with limited sample-to-solution ratio applying Fick's law. In order to analyse the data

and indicate the overall exchange of solutes and water between the apples and the osmotic solution, different parameters were determined for each sample, as water loss (WL), solid gain (SG), weight reduction (WR), soluble solid concentration (SSC). They investigated apple slices with thickness 5 mm. They used the following assumptions in the development:

1. Apple slices are infinite slabs of width = $2r$.
2. Initial water and SSC in the apple are uniform.
3. Apparent diffusion coefficient is constant ($D \neq f(c)$).
4. The process is isothermal.
5. Simultaneous counter-current flows; the diffusion of water from the apple and the diffusion of sugar into the apples are only considered.
6. A sugar solution film is thought to be at the surface of the apple as a boundary layer. Being a part of the apple, this film is assumed to the equilibrium concentration and the process is directly proceeded by diffusion.
7. Shrinkage is neglected.

In this model, using a mass balance on water movement inside the food, the rate of water loss was obtained as a function of time (Azuara et al., 1992):

$$WL = \frac{S_1 t (WL_\infty)}{1 + S_1 t} \quad (2)$$

where WL is the fraction of water loss at time t , WL_∞ the fraction of water loss at equilibrium, S_1 the model constant related to the rate of water loss and t is the time.

$$WL = \frac{M_0 X_0^w - M_t X_t^w}{M_0} 100 \quad (\text{g}/100\text{g fresh sample})$$

where M_0 is the initial mass of sample, M_t the mass of the sample at time t , X_0^w the initial water concentration of sample, X_t^w the water concentration of sample at time t .

Similarly for solid gain, it can be written as:

$$SG = \frac{S_2 t (SG_\infty)}{1 + S_2 t} \quad (3)$$

where SG is the fraction of solid gain at time t , SG_∞ the fraction of solid gain at equilibrium, S_2 the model constant related to the rate of SG.

$$SG = \frac{M_t X_t^{ts} - M_0 X_0^{ts}}{M_0} 100 \quad (\text{g}/100\text{g fresh sample})$$

where X_0^{ts} the initial total solids concentration of the sample and X_t^{ts} is the total solids concentration of the sample at time t .

Using WL and SG values calculated from the experimental data at different processing times, the WL_∞ , S_1 and SG_∞ , S_2 can be estimated from the slope and intercept of the plot t/WL or t/SG vs t of the linearized form of eq.(2) and eq.(3) respectively. Therefore the equilibrium solute concentration can be estimated from a mass balance equation derived as:

$$W_\infty^s = \frac{S_0 W_0^s - M_0 SG_\infty}{S_0 (1 - W_0^s) + M_0 WL_\infty} \quad (4)$$

where S_0 is the mass of the initial osmotic solution, W_0^s the initial SSC and W_∞^s is the SSC at equilibrium.

Solving eq.(1) numerically by the Crank-Nicholson method – at each time step the concentration profiles can be calculated numerically without considering the other component. Then concentration at each time step could be adjusted considering the other component changes in the same step calculated numerically from the eq.(1). If t and x are the subscripts indicating the time and position, at time t or at time $t+1$ the concentrations can be given as:

$$C_{t,x}^W = \frac{M_{t,x}^W}{M_{t,x}^W + M_{t,x}^S} \quad C_{t+1,x}^W = \frac{M_{t+1,x}^W}{M_{t+1,x}^W + M_{t+1,x}^S} \quad (5)$$

$$C_{t,x}^S = \frac{M_{t,x}^S}{M_{t,x}^W + M_{t,x}^S} \quad C_{t+1,x}^S = \frac{M_{t+1,x}^S}{M_{t+1,x}^W + M_{t+1,x}^S} \quad (6)$$

Since the concentrations can be calculated and the masses of water and soluble solids at each position are known, M values at time $t+1$ can be calculated from eqn.(5) and (6); total mass of water and soluble solids of fruit are estimated by sum of the masses at different positions. The WL and SG values were calculated from the experimental data. The concentration at time t is obtained from a mass balance equation derived as

$$X_t^{ts} = \frac{SG + X_0^{ts}}{1 - WL + SG} \quad (7)$$

where X_t^{ts} is the total solids concentration at time t and X_0^{ts} is the initial total solids concentration.

A model fitted to the experimental values and the apparent diffusivities of solute and water can be obtained by the trial and error method. Both diffusion coefficient representing water loss and solid gain are found to be in the range of $10^{-10} - 10^{-11} \text{ m}^2/\text{s}$.

Beristain et al. (1990) developed a model based on Crank's equation. They also used the solution of eqn.(1) gave by Crank (1975):

$$\frac{WL_t}{WL_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\left(\frac{-Dq_n^2 t}{l^2}\right) \quad (8)$$

where WL_t is the weight of water loss at time t , WL_∞ is the water loss at time ∞ ; α is the volumetric ratio of syrup to sample; q_n positive roots other than zero of equation: $\tan q_n = -\alpha q_n$.

The maximum fraction of water that a sample (pineapple ring) can lose, for given concentration of sucrose solution was determined; diffusion coefficients were calculated using Park's method (Crank, 1975).

The main limit of models based on Fick's law of diffusion is that the resulting diffusivities are a combination of the respective water and solute diffusivities and the probably interaction of the flows. Furthermore these methods neglect spatial distribution of the osmotic effect (Salvatori, 1999a). Salvatori developed a model in terms of the advancing rate of

disturbance front in the osmosed plant tissues. Diffusion coefficient was calculated by using a non simplified Fick's equation in terms of concentration profiles. They described the changes in plant tissues with the "advancing disturbance" front (ADF), later they (Salvatori et al., 1999b) developed generalised equations – on the base of the ADF – to describe the concentration profiles and the average concentration during OD process.

Regarding to the geometry of the food the mass transport phenomena occur during osmotic dehydration can be analysed in rectangular and in cylindrical configurations. Rastogi et al. (1997) studied the effect of temperature and concentration of the osmotic solution on the OD of banana, they determined the effective diffusion coefficient of water by the use of Fick's II law in terms of cylindrical coordinates (r, θ, z , Crank, 1975):

$$\frac{\partial C}{\partial t} = \frac{1}{r} \left\{ \frac{\partial}{\partial r} \left(rD \frac{\partial C}{\partial r} \right) + \frac{\partial}{\partial \theta} \left(\frac{D}{r} \frac{\partial C}{\partial \theta} \right) + \frac{\partial}{\partial z} \left(rD \frac{\partial C}{\partial z} \right) \right\} \quad (9)$$

For long cylinders ($\partial C/\partial z=0$), assuming the diffusion to be radial ($\partial C/\partial \theta=0$) and concentration (C) to be a function of radius (r) and time (t) only, eqn.(9) reduces to:

$$\frac{\partial C}{\partial t} = \frac{1}{r} \left\{ \frac{\partial}{\partial r} \left(rD \frac{\partial C}{\partial r} \right) \right\} \quad (10)$$

Considering boundary condition for $t>0$, $C=C_0$, at $r=a$ and initial condition for $t=0$, $C=C_1$, $0<r<a$, the solution of eqn.(10) can be written as (Crank, 1975):

$$\frac{C - C_1}{C_0 - C_1} = 1 - \frac{2}{a} \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t) J_0(r\alpha_n)}{\alpha_n J_1(a\alpha_n)} \quad (11)$$

where J_0 is the flux of diffusion (Fick I.), $a\alpha_n$ are the roots of the equation $J_0(a\alpha_n)=0$.

If M_t and M_∞ denote the amount of water diffused from banana at times $t=0$ and $t=\infty$ respectively, in the case of osmotic dehydration eqn.(11) can be rewritten for the diffused moisture ratio (M_t/M_∞) in terms of an effective diffusion coefficient (D_e), which accounts for the variation in diffusion coefficient (D) due to changes in the physical structure of the food, as:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n^2} \exp(-D_e \alpha_n^2 t) \quad (12)$$

If the Fourier number of diffusion (F_0) is given by the equation

$$F_0 = D_e t / a^2 \quad (13)$$

where D_e is the effective diffusion coefficient, eqn.(12) can be written as

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{(a\alpha_n)^2} \exp[-F_0 (a\alpha_n)^2] \quad (14)$$

In our earlier study the mass transport was investigated during osmotic dehydration of carrot

cylinders in longitudinal and also in radial direction (Matusek & Merész, 2002). In the case of radial diffusion the equation derived from Fick first law (eqn.15) and second law (eqn.16) in a cylindrical coordinate system was used to describe the diffusion coefficient ($D_{r,s}$):

$$J_r = -D_{r,s} \frac{\partial C(r)}{\partial r} \quad (15)$$

$$\frac{dC}{dt} = D_{r,s} \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) \quad (16)$$

where J_r is the flux density of soluble solid at radius r . If the diffusion was constant, eqn.(16) equal to zero. The equation is referred as:

$$\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} = 0 \quad (17)$$

if $\frac{\partial C}{\partial r} = z$, is substituted, than

$$\frac{\partial z}{\partial r} = -\frac{1}{r} z, \quad (18)$$

that can be transformed to eqn.:

$$\frac{\partial z}{z} = \frac{\partial r}{r} \quad (19)$$

solution is:

$$\ln(z) = K_1 - \ln(r) \quad (20)$$

back-substitution of z lead to the eqn.:

$$\frac{\partial C}{\partial r} = K_2 \frac{1}{r} \quad (21)$$

that gives a logarithmic solution for the distribution of the concentration in the media:

$$C - C_0 = K_2 \ln(r) \quad (22)$$

Solving the Fick's second law for stationary diffusion in Descartes system assuming finite diffusion, substituting in the eqn.(1) the expression: $C(t,x)=C_t(t)C_x(x)$, can be :

$$C_x \frac{dC_t}{dt} = DC_t \frac{d^2 C_x}{dx^2} \quad (23)$$

Solution of the eqn.(23) gives:

$$\frac{d \ln(C_t)}{dt} = D \frac{\frac{d^2 C_x}{dx^2}}{C_x} = \text{Konst.} = -\frac{D\pi^2}{4x_0^2} \quad (24)$$

substitution of C_x :

$$C_x := \cos\left(\frac{\pi x}{2 x_0}\right) \quad (25)$$

leads to the differential eqn.:

$$\frac{dC_x}{dx} = -\frac{\pi^2}{4x_0^2} C_x \quad (26)$$

than the changes of concentration distribution can be expressed as a function of time:

$$C_t = Konst. \exp\left(-\frac{D\pi^2 t}{4x_0^2}\right) \quad (27)$$

The eqn.(27) can be transformed to cylindrical coordinate system considering the Bessel function is the equivalent of the *cos* function in the cylindrical system:

$$e^{\frac{D_{r,s}t}{(R-R_b)^2}} I_0(r) = c(t, r) \quad (28)$$

where I_∞ is the abscissa value at first zero ordinate value of the zero order Bessel function ($I_\infty=2,4048$), $D_{r,s}$ is the radial diffusion coefficient of the solid, R is the radius of the cylindric sample, R_b is the radius of the plastic tube in the centre of the sample cylinder, $(R - R_b)$ difference is the geometric parameter, the diffusion distance.

The linearized distribution of concentration in the eqn.(28) and the slope of the linear function - presenting the concentration differences as a function of time - give the apparent diffusion coefficient:

$$S = -D_{r,s} \frac{I_\infty^2}{(R - R_b)^2} \quad (29)$$

where S is the slope of the linear function fit to observed data:

$$\ln\left(\frac{c_\infty - c_t}{c_\infty}\right) = S \cdot t \quad (30)$$

In this study we used the solution of Fick Law II. in a rectangular coordinate system eqn.(27) to determine the diffusion coefficient of FOS and water in the apple samples (Matusek & Merész, 2002):

$$S = -D_{l,s} \cdot \left(\frac{\pi^2}{4x_0^2}\right) \quad (31)$$

where S is the slope of the linear function fit to observed data eqn.(30), and $D_{l,s}$ is the longitudinal diffusion coefficient of the solved component, x_0 : is the geometric parameter: the diffusion distance. The apparent diffusion coefficients $D_{r,s}$ and $D_{l,s}$ can be calculated having known the other variables in the eqn.(29) and eqn.(31) in the case of radial or longitudinal diffusion respectively.

3. Materials and methods

Apples of the *Idared* variety (86% w/w moisture content, soluble solids content \cong 13 R%) were purchased from the local market and stored at 1-4 °C, 94-96 RH until use. Raftilose® P95, (ORAFTI) was used as osmotic agent. Raftilose® P95 is a fructo-oligosaccharide product from chicory inulin. The carbohydrate composition of the product is: oligofructose (degree of polymerisation: 2-8) \geq 93,2 %; glucose + fructose + sucrose \leq 6,8 %.

A few hours prior to use the apples were left to equilibrate at room temperature. They were peeled

manually and cut into 1x1x1 cm cubes after removing the pericarp. Apple cubes were immersed into a 1% citric-acid solution to inhibit enzymatic browning. Blanching was carried out under atmospheric conditions at 70 °C, for 5 minutes, the sample-to-solution ratio was 1:10. Continuous agitation was used ($v = 140$ 1/min). Osmotic dehydration was carried out also at atmospheric pressure at 40 °C, sample-to-solution ratio was 1:10, and the level of agitation was 140 1/min. Samples were taken out from the solution in every 5 minutes till 60 minutes. They were blotted on a filter paper and weighed.

Moisture content (MC) of the samples was measured gravimetrically, total soluble solid (TSS) content was determined by refractometer (Carl Zeiss, Jena) and FOS content was measured by polarimeter (Carl Zeiss, Jena). For the polarimetric method apple samples were rehydrated and homogenized with distilled water, Carrez I. and II. solutions and ethanol were add to precipitate the macromolecules. After 18 hours cooling the sample was filtrated under vacuum and the solution was measured by polarimeter.

4. Results and discussion

It was observed, that increased OD time result in increased TSS by logarithmic curve (Fig. 1), as well as FOS content and it decreased moisture content (Fig. 2). The apparent diffusion coefficient of FOS and water were found to be of the order of 10^{-9} m²/s (Table 1).

Table 1: Apparent diffusion coefficients

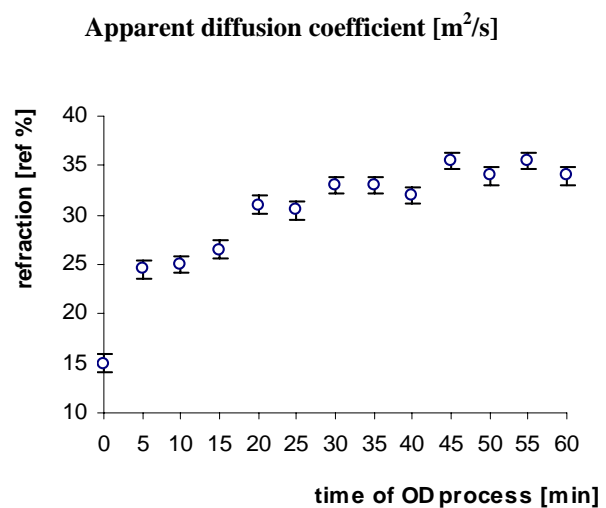


Figure 1. Effect of OD process time on TSS content

A correlation analysis for calculated (C-FOS) and measured (M-FOS) fructo-oligosaccharides content gives high correlation coefficient ($R^2 = 0,863$). The relationship for apple cubes (Fig. 3):

$$M-FOS = -0,4123 + 1,0151 (C-FOS) \quad (32)$$

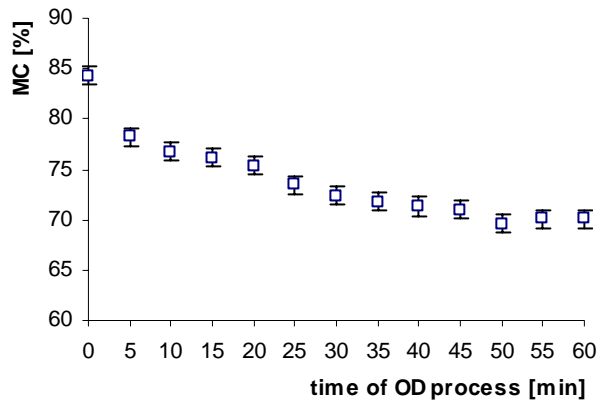


Figure 2. Effect of OD process time on moisture content

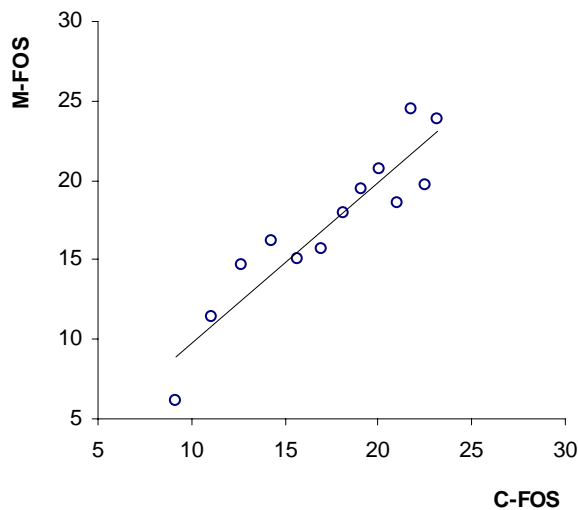


Figure 3: Relationship of measured (M-FOS) values and calculated (C-FOS) values

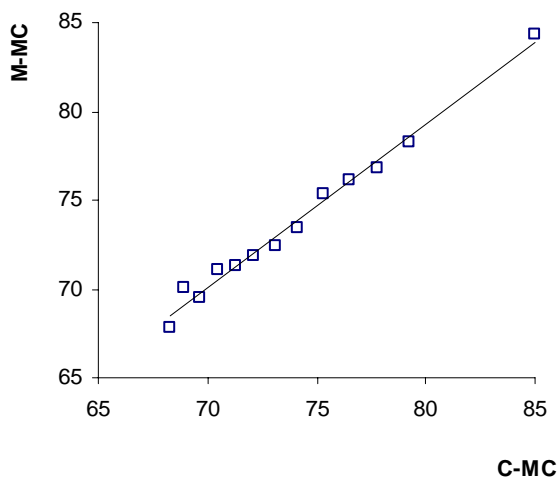


Figure 4: Relationship of measured experimental M-MC values and calculated C-MC values

The correlation analysis for calculated (C-MC) and measured (M-MC) moisture content gives high correlation coefficient ($R^2 = 0,988$). The relationship for apple cubes (Fig. 4):

$$M-MC = 5,5084 + 0,9218 (C-MC) \quad (33)$$

Conclusion

The model describes the osmotic dehydration process better in the case of FOS than in the case of water. The correlation analysis for measured and calculated values gives higher coefficient for water diffusion regarding to the better deviation attribute of the moisture determination, but the deviation attribute of the refraction is lower, as higher the standard error of prediction (SEP). The lower value of the FOS correlation coefficient appoints that the FOS intake is a complex phenomenon containing diffusion and other mechanisms too. The presumed hypothesis that the water leakage from the fruit tissue is characterised by diffusion mechanism based on Fick laws is verified by the relationship between the measured and calculated data. The slope of the relationship is very closed to the value 1 and the axis section is closed to zero that shows the better applicability of the model for the prediction of FOS diffusion than that of water.

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