ANALYTICAL APPROACH FOR PREDICTING EFFECTIVE DIFFUSION COEFFICIENTS IN MULTIDIMENSIONAL SLAB GEOMETRY

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ABSTRACT

An analytical study is made to predict the effective diffusion coefficients from the experimental drying curves. A mathematical model based on three-dimensional Fick’s law in Cartesian coordinates was considered, with initial and boundary conditions according to the experimental procedure carried out in biological materials drying. Two methods i.e., the first-term approximation of the general series solution method, and the scale-up into an “equivalent 1-D diffusion” method were used in prediction of drying curves in 1-D and 3-D slab geometry. Geometry effect on the effective diffusivity estimation was numerically examined from the viewpoint of rapidity of convergence of the series.

Keywords: diffusion, analytical solution, multidimensional geometry, drying kinetics.

INTRODUCTION

The accurate modelling of processes of mass transfer inside particles of arbitrary shape is of concern in many engineering applications, such as leaching, wetting, and drying of biological raw materials. The most frequently used approach is to derive an effective diffusion coefficient indirectly from the macroscopic behaviour of the sample, e.g. from the kinetic curves (average concentration as a function of time). Diffusion limited kinetic models are used to describe the phenomenon of mass transfer, and thus the estimated values will be affected by the model hypothesis: geometry, boundary conditions, constant or variable physical and transport properties. In many cases, these processes have been interpreted on the basis of constant diffusion coefficients calculated through a series solution of the one-dimensional Fick’s law associated to simple geometries (infinite slabs, cylinders or spheres) which converges rapidly for large values of time [1-3].

In many practical situations, however, the solid particles have arbitrary shape (spheroids, hemi-spheres, ellipsoids, circular finite cylinders, cuboids, regular polyhedrons). For such cases, efficient numerical simulations to solve the Fick’s law transformed into an appropriate coordinate system have been presented in the literature [4]. In relation to the numerical methods used, the finite elements and control-volumes are the most often used formulations. Due to the complexity of these numerical solutions, the analytical models and approximate approaches to solve multidimensional problems that can be used during preliminary design are of particular interest [5].

The objective of the present study is to extend the one-dimensional (1-D) modelling approach to more general conditions involving multidimensional geometry. The methodology is developed using the available analytical solution of non-steady-state diffusion in three-dimensional (3-D) slab geometry. Special attention was paid to the effect of surface geometry. The applicability of the
MODELLING APPROACH

In particular we will concern with aspects of convective drying at low temperature when applied to high moisture content materials. To simplify the problem, the following hypotheses were made:

- The porous solid is homogeneous and isotropic.
- The mass transfer through the solid is controlled by liquid diffusion, and consequently, moisture evaporation occurs only at the external surface of the drying material.
- An isothermal process is considered taking into account that the heat transfer resistance in biological materials is negligible compared with the internal diffusion resistance.
- The drying occurs in the falling rate period; this behaviour is observed in many biological products with high initial moisture content (such as fruits and vegetables).
- Any effect likely to be caused by the shrinkage of the material is neglected.

The diffusion governing equation based on Fick’s second law in Cartesian coordinates is:

\[
\frac{\partial X}{\partial t} = \frac{\partial}{\partial x} \left( D_{eff} \frac{\partial X}{\partial x} \right) + \frac{\partial}{\partial y} \left( D_{eff} \frac{\partial X}{\partial y} \right) + \frac{\partial}{\partial z} \left( D_{eff} \frac{\partial X}{\partial z} \right)
\]  

where \( X \) is defined as moisture content on dry basis, kg/kg dry matter. The effective diffusion coefficient \( D_{eff} \) is assumed to be uniform though the sample due to the isotropy.

Uniform distribution in volume of the initial moisture content \( X_i \) is used as initial condition. The boundary conditions for the diffusion are given at the outside surfaces of the sample and on the planes defined by the axis at the centre of the sample.

It is assumed that the sample lies with the centre at \((0, 0, 0)\) and that the diffusion and distribution will be symmetrical. The boundary conditions reflect this by requiring there to be no moisture gradient across the centre of the sample:

\[
\begin{align*}
\frac{\partial X(0, y, z, t)}{\partial x} &= 0 \\
\frac{\partial X(x, 0, z, t)}{\partial y} &= 0 \\
\frac{\partial X(x, y, 0, t)}{\partial z} &= 0
\end{align*}
\]  

The boundary conditions on surfaces are modelled by assuming that there was no mass transfer resistance:

\[
\begin{align*}
X(x, y, z, t)|_{S_x} &= X_{eq} \\
X(x, y, z, t)|_{S_y} &= X_{eq} \\
X(x, y, z, t)|_{S_z} &= X_{eq}
\end{align*}
\]  

where \( S_x, S_y, S_z \) are the outside surface areas. This condition applies that the moisture content at the surface was always at its equilibrium \( X_{eq} \) at the corresponding operating conditions.

General series solution to the boundary conditions defined by Eqs.2 and 3 for constant diffusion coefficient is given by [5]:

\[
MR = \frac{X - X_{eq}}{X_{eq} - X_i} = \frac{512}{\pi^6} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[ -\frac{X}{X_{eq}} \frac{D_{eff}}{b^2} \right] \times \\
\sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[ -\frac{X}{X_{eq}} \frac{D_{eff}}{b^2} \right] \times \\
\sum_{p=0}^{\infty} \frac{1}{(2p+1)^2} \exp \left[ -\frac{X}{X_{eq}} \frac{D_{eff}}{c_p^2} \right]
\]  

where \( MR \) is the normalized moisture content, and \( X \) is the corresponding average moisture content at time \( t \); \( a_p, b, c_p \) denote the linear size along the \( x \), \( y \) and \( z \)-axes, and \( m, n \) and \( p \) are a positive integer. This general analytical solution is an appropriate equation to predict mass diffusion in 1-D, 2-D and 3-D rectangular systems, by making use of the superposition principle.

EXPERIMENTAL

Drying experiments were carried out in a laboratory convective dryer with a heated air under controlled temperature, 60°C with relative humidity at room temperature of 60% and 25°C, respectively. The kinet-
ics of the process was studied for two experimental systems:

- System I: spinach leaves (*Spinacia oleracea* L.), cut in slabs with a surface area 10x10 mm and a thickness of approximately 1 mm.

- System II: strawberry samples cut in the form of cubes 10x10x10 mm.

The changes in the samples masses were continuously measured and recorded every 2 minutes during the drying experiments (Kern MLS Moisture Analyzer, max 50 g, 10⁻³ g precision). The average moisture content $\overline{X}(t)$ and the drying rate $N(t)$ have been calculated for each weighing period using the following equations:

$$\overline{X}(t) = \left[\frac{(X_0 + 1)W(t)}{W_0} - 1\right]$$  \hspace{1cm} (5)

$$N(t) = \left(-\frac{d\overline{X}(t)}{dt}\right)_t = \frac{\overline{X}_{t+dt} - \overline{X}_t}{dt}$$  \hspace{1cm} (6)

where $W_0$ is the initial mass of the product to be dried and $W(t)$ - the mass at the time $t$.

Figs. 1 and 2 show the experimental drying rates as a function of time, and as a function of moisture content for the two case studies. The drying process took place predominantly in the falling rate period, depending on the structure of the material. This means that the internal diffusion is the dominant mechanism governing moisture movement in the material. The experimental drying rates are too noisy but the width of fluctuations remains very small compared to the duration of the entire drying process.

Faster drying rates were observed for System I, thus, the drying time needed to reach the final moisture content was decreased (100 minutes compared to 250 minutes of the System II).

The normalized drying curves were approximated using the exponential two-parameter function (model of Henderson and Pabis) [6]:

$$MR_{ex}(t) = B \exp^{-Ht}$$  \hspace{1cm} (7)

where the empirical constants $B$ and $H$ depend on the drying conditions. Values of $H$ and $B$ were determined by fitting the exponential function to the experimental data by means of a nonlinear least-squares algorithm (Table 1). The drying rate curve can be obtained from the time-derivative of Eq.7:

$$N_{ex} = \left(-\frac{dX}{dt}\right)_t = H \cdot MR_{ex}(t)$$  \hspace{1cm} (8)

![Fig. 1. Experimental drying rates as a function of time.](image)

![Fig. 2. Experimental drying rates as a function of moisture content.](image)

| Table 1. Data concerning the determination of effective diffusion coefficients. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Empirical model (Eq.6) | First-term approximation method (Eq.12) | Equivalent 1-D geometry method (Eq.13) |
| $B$ | $H, \text{s}^{-1}$ | $D_{eff, \text{m}^2\text{s}^{-1}}$ | $R^2$ | $D_{eff, \text{m}^2\text{s}^{-1}}$ | $R^2$ |
| System I | 1.108 | $7.267 \times 10^{-4}$ | $7.374 \times 10^{-10}$ | 0.9684 | - | - |
| System II | 1.091 | $2.562 \times 10^{-4}$ | $8.666 \times 10^{-10}$ | 0.7424 | 4.849 $\times 10^{-10}$ | 0.9352 |


RESULTS AND DISCUSSION

Geometry-dependent scale-up factor

The analytical solution is given by products of infinite-series and only approximations of Eq. 4 can be considered, which are carried out by cutting of a number of terms. Eq. 3 shows how the effect of its number considering $n = 1, 3, 5$ and 10 terms in the series solution for 1-D slab (a, $\infty$, $\infty$) and for 3-D cube ($a_r, a_s, a_t$). In the present case, the semi-logarithmic plots of the moisture content as function of Fourier number, $Fo = D_{eff} / (a/2)^2$, are given in the range $10^{-3} < Fo < 1$, for $a_p = 5 \times 10^{-3} \text{m}$ and $D_{eff} = 5 \times 10^{-10} \text{m}^2 \text{s}^{-1}$.

![Kinetic curves obtained with approximate and exact series solutions for each geometry and as calculated with “1-D slab equivalent” conversion.](image)

An analysis of the curves indicates considerable divergence in establishing the Regular regime where the first term of the series dominates. In 1-D slab geometry, the first five terms, while in 3-D geometry more than ten terms were included in the series to satisfy a convergence tolerance of $10^{-3}$ percent difference.

For all data set the Regular regime is attained for $Fo > 0.1$, the unaccomplished moisture content for slab is above 0.6, with in the cube being above 0.2.

The curves are displaced with respect to each other, but they have the same sigmoidal form. An equivalence of the characteristic length for mass transfer should be assumed to convert (scale-up) a particle of given geometry and size into a differently-shaped or sized particle with approximately the same diffusion characteristics. Using the square root of the dimensionless time, a scale-up factor is defined as follows:

$$f_{c,sl} = \left( \frac{F_{oc}}{F_{osl}} \right)^{1/2}$$

where the subscripts $c$ and $sl$ refer to cube and to reference 1-D slab geometry. Using the converged series solution, the values of $f_{c,sl}$ were derived empirically by comparing average moisture contents for both geometries. The scale-up factor was found to be a slowly decreasing function of $MR$, and ranged between $f_{c,sl} (0.8) = 0.353, f_{c,sl} (0.6) = 0.388, f_{c,sl} (0.5) = 0.409, f_{c,sl} (0.2) = 0.578$ and $f_{c,sl} (0.1) = 0.517$. The corresponding kinetic curve prediction for cube using “equivalent 1-D diffusion” is given in Fig. 3, when the averaged scale-up factor for the whole moisture content range was kept constant and equal to $f_{c,sl} = 0.433$. The use of the scale-up factor has the effect of shifting the horizontal axis for the 1-D slab such that the curves for the two geometries over loop. The scale-up approach slightly overestimates the exact solution and after that a slight underestimation is observed due to the dependence on the moisture content.

Estimation of the diffusion coefficients

For the kinetic study two approximate methods were used in prediction of the diffusion coefficients in multidimensional geometry:

a) by using a first-term approximation of a general series solution for the drying rate;

b) by using a scale-up into an “equivalent 1-D diffusion” problem.

The drying rates for 1-D slab and for 3-D cube for large values of time are obtained by the first-term approximation of Eq. 4:

$$N_{slab} = - \frac{dX}{dt}_{slab} = \left[ - \pi^2 \frac{D_{eff}}{a_p^2} \right] \frac{8}{\pi^2} \exp \left[ - \pi^2 \frac{D_{eff} t}{a_p^2} \right]$$

$$= \left[ - \pi^2 \frac{D_{eff}}{a_p^2} \right] \frac{X - X_{eq}}{X_0 - X_{eq}}$$

$$N_{cube} = - \frac{dX}{dt}_{cube} = \left[ - \pi^2 \frac{3D_{eff}}{a_p^2} \right] \frac{512}{\pi^6} \exp \left[ - \pi^2 \frac{3D_{eff} t}{R^2} \right]$$

$$= \left[ - \pi^2 \frac{3D_{eff}}{a_p^2} \right] \frac{X - X_{eq}}{X_0 - X_{eq}}$$
By matching Eqs. 10 and 11 with the drying rate constant $H_s$ in Eq. 8, a simple empirical correlation for calculation of $D_{st}$ is obtained:

$$H_{slab} = \frac{\pi^2 D_{eff}}{a^2_{p,slab}}$$

$$H_{cube} = \frac{3\pi^2 D_{eff}}{a^2_{p,cube}}$$

(12)

When the diffusion coefficient estimated with 1-D slab geometry is used to predict the drying curves for cube, the associated slab size was correlated through the scale-up factor:

$$H_{cube} = \frac{\pi^2 D_{eff}}{(f_{c,sl}a_{p,cube})^2}$$

(13)

So, the first method may be considered as an approximate case of the equivalence in characteristic length principle, when the asymptotic solution for the limiting cases of long values of time, namely $f_{c,sl}(0.2) = 0.578$ (i.e. $f_{c,sl}^2 = 0.333$) is incorporated as a quantitative criterion.

The calculated values of the diffusion coefficients using the both methods (Table 1) are similar to those reported for the varieties studied that values generally are in the range of $10^{-10}$ and $10^{-11}$ m$^2$ s$^{-1}$ [6,7]. Subsequently, these values are used to simulate the kinetic data during the entire drying process. The coefficients of determination ($R^2$) were used for comparing predicted and experimental data.

A good fitting was obtained by applying the first-term approximation for the 1-D slab geometry, as expected ($R^2 > 0.95$). In 3-D case, the considerable decay in starting the Regular regime ($MR < 0.2$) resulted an in underestimation of the predicted data at the early stages of drying. So, outside these conditions, the first-term approximation provided a satisfactory prediction of the long time behaviour and the drying times. The scale-up into an “equivalent 1-D diffusion” method, being derived from the converged series solution, indicated better correlation between the theoretical and experimental data, for the whole concentration range.

It is noted that there was a poor fit at the initial step of the drying, in all treatments. The model neglected the shrinkage to simplify the solution of the model equations. The drying experiments demonstrated a significant shrinkage of the material in all three directions. To reflect the reality, the model must incorporate linear dimensions, surfaces and volume reduction during the dehydration processes, especially in a complex situation, such as multidirectional deformations in materials with high initial moisture content.

**CONCLUSIONS**

The accuracy of approximate methods for predicting the effective diffusion coefficients in multidimensional slab geometry under constant drying conditions was studied. The applicability of the methods was strongly dependent on the rapidity of convergence of the series solution.

The computation in the 3-D diffusion problem required a larger number of terms using the series solution and resulted in loss of accuracy for the first-term approximation method in prediction of experimental data (difference>10%). The scale-up into an “equivalent 1-D diffusion” using the conversion from 3-D into equivalent 1-D slab geometry as an example, was found to be more accurate for the whole concentration range.

An advantage of the proposed analytical approach is that it can be extended effectively in multidimensional transport models with particles of different sizes and shapes.
REFERENCES