

Modeling of Maltodextrin DE12 Drying Process in a Convection Oven

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Abstract

The drying kinetics of maltodextrin DE12 in a convection oven are modeled using Fick's second law of diffusion and following the WLF equation for the moisture and temperature dependence of the effective diffusivity. An experimental design with a temperature range from 70 [$^{\circ}C$] to 140 [$^{\circ}C$] and sample amount varying from 4 [ml] to 12 [ml] is used. The resulting diffusion equation describing the dynamics of moisture content is highly nonlinear and possesses Dirichlet and Neumann boundary conditions. Ordinary differential equations are added to take the time-dependent variation of temperature into account. The method of lines is applied to discretize the partial differential equation w.r.t. the space variable leading to a highly stiff and numerically unstable system of ordinary differential equations. The data fitting problem is formulated to estimate some unknown parameters for each of the 18 data sets under consideration. Moreover we show how a simultaneous fit of parameters that are independent from the actual experiment, is obtained over all data sets.

Nomenclature

$M_w(x, t)$	- moisture content [$g_w g_{MD12} sol^{-1}$]
$M_{w,eq}(t)$	- equilibrium moisture content [$g_w g_{MD12}^{-1}$]
$\overline{M}_w(t)$	- average moisture content [$g_w g_{MD12}^{-1}$]
$M_{w,0}$	- initial moisture content $t = 0$ [$g_w g_{MD12}^{-1}$]
$T(t)$	- temperature [$^{\circ}C$]
$T_g(t)$	- glass transition temperature [$^{\circ}C$]
T_0	- initial temperature [$^{\circ}C$]
$T_{db}(t)$	- dry bulb temperature [$^{\circ}C$]
T_r	- reference temperature [$^{\circ}C$]
T_{g_w}	- glass transition temperature of pure water [$^{\circ}C$]
$T_{g_{MD12}}$	- glass transition temperature of pure maltodextrin DE12 [$^{\circ}C$]
$X_w(t)$	- water mass fraction
X_{MD12}	- maltodextrin DE12 mass fraction
$D(M_w, T)$	- effective diffusivity [$m^2 s^{-1}$]
D_r	- diffusion coefficient [m^2/s]
x	- space or spatial variable [m]
L	- total thickness of the maltodextrin slab [m]
t	- time variable [sec]
C_1, C_2	- <i>WLF</i> model constants for diffusion parameter
C_{p_s}	- Maltodextrin specific heat [$J/(kgK)$]
C_{p_w}	- water specific heat [$J/(kgK)$]
k	- Gordon Taylor equation constant
a_w	- water activity
$\alpha(t)$	- heat conductivity [J/K]
$h_A(t)$	- heat transfer coefficient multiplied by the area [s^{-1}]
$\lambda_w(t)$	- Latent heat of vaporization of water [$kJ/mole$]
A_0	- drying area [m^2]
P_1	- eq. 9 parameter to estimate
m_s	- solid mass [kg]
E_a	- Activation energy [kJ/mol]
a_t	- relaxation factor
R	- universal gas constant [$8.314J/(moleK)$]

- C - GAB equation parameter
- K - GAB equation parameter
- W_m - GAB equation parameter
- n - number of experiments
- t_j - experimental time [sec]
- l - total number of experimental data

Subscripts

- r - reference value
- 0 - initial state at $t = 0$
- db - dry bulb
- w - water
- i - i -experiment
- j - j -time value

1 Introduction

Hot-air drying is a common food preservation process, characterized by the removal of water using air as heat delivering and water removal agent, see e.g. Hayashi [13] or Saravacos and Charm [32]. There exist several mathematical models published by Hayakawa and Furuta [12], Fortes [6], Husaim [14], and Mishkin et al. [24], applied to the drying of grains and other food materials. Thus the fundamentals that control the drying process are well defined. One of the key problems in this approach is that the moisture dependence of the diffusivity has been generally modeled using empirical functions of the moisture content. This procedure lacks essentially of generalisation power of the found dependency and usually leads the research to find moisture functions of the diffusivity that will dramatically change from one product to another despite of the possible common relationships that different biological materials could have. On the other way some studies [26, 30], have pointed up to the possibility of modeling this dependence using the concepts of the polymer science to model this dependence, considering the food matrix as a biopolymer and the water as the plastisizer of the system. The objective of this research work is to study this kind of approach to model the drying of a polymeric material, i.e., maltodextrin with a dextrose equivalent (DE) 12.

Fick's second law is used to model the water removal from a slab of maltodextrin DE 12. The parabolic equation is formulated in one space or spatial variable, respectively, and given in classical form

$$\frac{\partial}{\partial t}M_w = \frac{\partial}{\partial x} \left[D(M_w, T) \frac{\partial}{\partial x} M_w \right], \quad (1)$$

where M_w denotes the moisture content depending on the time variable t and the spatial variable x , and $D(M_w, T)$ the nonlinear diffusion coefficient depending on moisture M_w and temperature T . The dependency of the drying process from the temperature is modeled by an additional ordinary differential equation resulting from the energy balance.

Initial values are known from the experimental design. At the left boundary a homogeneous Neumann condition is given, whereas the right boundary is identified by a Dirichlet condition computed from the equilibrium condition of moisture.

The one-dimensional partial differential equation is discretized by the method of lines by defining a grid over the spatial interval under consideration. The state variable $M_w(x, t)$ at a grid point x_i is replaced by $M_w^i(t)$ for $i = 1, \dots, m$ leading to a system of m ordinary differential equations. The first and second spatial derivatives $\frac{\partial}{\partial x}M_w$ and $\frac{\partial^2}{\partial x \partial x}M_w$, respectively, are replaced by suitable approximations, e.g., difference formulae. For the right-most state variable $M_w^m(t)$ the Dirichlet boundary condition is inserted. The given Neumann boundary condition at the left-hand side is applied to approximate second derivatives. The coupled ordinary differential equation for temperature $T(t)$ is added to the discretized system without further manipulations.

The size of the resulting initial value problem depends on the number of lines used, i.e., of m . As a consequence of the discretization procedure, the ODE becomes stiff for increasing m and is also numerically unstable caused by the exponential term of the diffusion coefficient. Thus we have to apply an implicit ODE solver for integration and must scale the model equations carefully.

A set of 18 different experiments each consisting of about five measurements for moisture and temperature is given to estimate four unknown, i.e., non-measurable model parameters by a least squares fit. The resulting data fitting problems are solved by the Fortran code DN2GB of Dennis, Gay, and Welsch [4], a combination of a Gauss-Newton and Quasi-Newton method. First data fitting problems are formulated to estimate some unknown parameters for each of the 18 data sets under consideration. Moreover we show how a simultaneous fit of parameters that are independent from the actual experiment, is obtained over all data sets.

The mathematical model is motivated and outlined in Section 2 in detail. In Section 3 the parameter estimation model, the numerical algorithms, and the test environment are described. Section 4 summarizes the experimental design, especially the drying experiments. Some numerical results are presented and discussed in Section 5.

2 Mathematical Model

2.1 Mass and Heat Transfer Equations

In order to model the degradation kinetics during drying, the fundamental laws that govern the drying process itself were used, that is, Fick's second law of diffusion and the energy conservation laws. The model used in this study was first by Mishkin [24], and has been used in the past for the optimization of drying processes by Banga et al. [1], Mishkin et al. [22], Mishkin [24], Banga and Singh [2], and Mishkin et al. [21]. The moisture and temperature dependence of the diffusivity was modeled using the WLF/Gordon-Taylor equation, instead of choosing polynomial functions to describe it. Thus we expect more general results when considering a complex moisture dependence of a kinetic factor, if the food matrix can be considered to behave like a polymer, cf. Frias and Oliveira [9].

The most usual way to describe the water diffusion through a thin layer slab is the use of Fick's second law, i.e.

$$\frac{\partial}{\partial t} M_w(x, t) = \frac{\partial}{\partial x} \left[D(M_w(x, t), T(x, t)) \frac{\partial}{\partial x} M_w(x, t) \right] , \quad (2)$$

see also (1). The one-dimensional partial differential equation is defined for all x with $0 \leq x \leq L$ and $t \geq 0$, where the "effective" water diffusivity $D(M_w, T)$ is a function of temperature and moisture content. The thickness L depends on the actual experiment and is measured by the experiment.

The initial condition is

$$M_w(x, 0) = M_{w,0} , \quad (3)$$

$0 \leq x \leq L$, with an initial moisture content $M_{w,0}$. There exists a left Neumann boundary condition of the form

$$\frac{d}{dx} M_w(0, t) = 0 , \quad (4)$$

furthermore a right Dirichlet boundary condition of the form

$$M_w(L, t) = M_{w,eq}(t) , \quad (5)$$

$t \geq 0$.

The effective diffusivity $D(M_w(x, t), T(x, t))$ includes all known departures from pure diffusion ideality, e.g., moisture content and temperature dependence, and deviations from Fickian behavior, see Mishkin et al. [22, 23, 25, 20]. More details are given in Subsection (3.2).

A more theoretical approach to model the heat transfer during drying can involve the use of irreversible thermodynamics or Fourier law of heat transfer, and the coupling of the resulting partial differential equation with the mass transfer equation, see Fortes and Okos [8, 7] or Husaim et al. [15, 16]. However the same researchers came to the conclusion that in most cases in thin layer drying of food and biological materials, the assumption of a constant averaged temperature is a reasonable simplification, because the characteristic time for heat transfer is usually much lower than the mass transfer one in this kind of products. Thus the computational work involved in the drying model is facilitated and significant deviations from reality are not implied, cf. Husaim [14] or Fortes [6]. Therefore an energy balance to a drying slab is used to model the temperature during drying according to Mishkin [24], i.e.

$$\frac{d}{dt}T(t) = \frac{h_A(t)}{\alpha(t)}(T_{db}(t) - T(t)) + \frac{\lambda_w(t)m_s}{\alpha(t)}\frac{d}{dt}\overline{M}_w(t) \quad (6)$$

for $t > 0$ with initial condition

$$T(0) = T_0 , \quad (7)$$

where

$$\alpha(t) = m_s C_{p_s} + m_s \overline{M}_w(t) C_{p_w} , \quad (8)$$

$$h_A(t) = A_0 P_1 \overline{M}_w(t) , \quad (9)$$

$$\lambda_w(t) = 3114979.2 - 2248.3116 (T(t) + 273) . \quad (10)$$

P_1 is an unknown parameter we want to estimate. From the work of Meerdink [19] with maltodextrin we take $C_{p_s} = 1500$, $C_{p_w} = 4186.8$, and we define the average moisture content by

$$\overline{M}_w(t) = \frac{1}{L} \int_0^L M_w(\zeta, t) d\zeta . \quad (11)$$

The solid mass m_s and the initial temperature T_0 are measured at the beginning of the experimental procedure, and the dry bulb temperature $T_{db}(t)$ is continuously monitored for each experiment at intervals of 2 seconds. The raw temperature data is then smoothed using b-spline methods and the values for the sampling times are stored. Drying area A_0 is evaluated from the known diameter, i.e., $A_0 = \pi 0.0493^2/4$. Finally the moisture content at each of the sampling points is determined by weight difference from the initial state.

2.2 A Food Polymer Approach to Describe the Temperature-Moisture Dependence of the Diffusion Coefficient

Moisture diffusion in foods and pharmaceutical polymers is usually an internally controlled mechanism, see Shoeber [37], where the role of the wet matrix is very important. During the drying process the drying rate becomes increasingly controlled by the viscosity of the matrix until eventually driving forces equilibrium is reached.

Therefore the physical properties of the matrix during drying depend heavily on the drying history of polymeric materials, cf. Slade and Levine [39]. If one uses Fick's second law to model a drying process, usually the diffusion coefficient will be the parameter that will depend on the specific physical properties. In literature the diffusion dependence on the physical properties usually has been described by means of an Arrhenius temperature dependence and an empirical relationship on the water content of the Arrhenius pre-exponential factor and energy of activation, e.g.,

$$D(M_w, T) = D_r e^{\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_r} \right)}, \quad (12)$$

where the diffusion coefficient at the reference temperature D_r and the energy of activation of the diffusion process E_a are unknown functions of the water content that have to be determined. Several relationships and methods have been developed to estimate these functions, see Shoeber [38] or Karel [17].

Considering that moisture diffusion is a matrix controlled mechanism, where the water diffuses to the outer surface through a matrix that is increasing in viscosity, and considering the influence of this viscosity on the rate of diffusion, one could ideally apply the concepts of polymer science to the diffusion of water during drying as proposed by Slade and Levine [39].

If we suppose that viscosity of the food matrix is one of the main intrinsic properties that will affect the diffusion process and that viscosity is typically modeled in literature depending on moisture content and temperature, a more direct approach of modeling the diffusion coefficient dependence on moisture and temperature using this parallelism can be of interest, see Nelson [26].

The moisture-temperature dependence of polymer solutions viscosity is modeled using the William, Landel and Ferry [40] (WLF) equation, that relates the ratio of a mechanical or electrical relaxation a_t , which is directly proportional to the viscosity, to the temperature and the glass transition temperature of the system. This model is based on the Doolite [26] model, and considers a linear increase of the free volume in the matrix proportional to the temperature, assuming a linear chemical structure and that the polymer

is in the rubbery state, see Nelson [26] and William et al. [40].

The WLF model can also accommodate other mechanical or rate parameters as proposed by Peleg [28]. Thus we consider

$$\log \frac{D_g}{D} \propto \log a_t = \frac{-C_1(T - T_g)}{C_2 + T - T_g} \quad (13)$$

with $D = D(M_w, T)$. The glass transition temperature T_g is a smooth function of the moisture mass fraction and D_g the diffusion coefficient at glass transition temperature, see Maltini and Anese [18]. Then (13) defines a relation between D , T_g and T .

Equation (13) could be used to describe the temperature-glass transition temperature dependence of the diffusion coefficient. However, the original authors of the WLF model advised *against* the use of (13) because of the experimental problems in determining any property in the neighborhood of T_g , see Peleg [28] or Williams et al. [40]. In fact the high viscosity (around 10^{14} cP) at the glass transition temperature decreases the diffusion so much that rate measurement uncertainty is very high as reported by Nelson [26].

On the other hand if T_g is shifted to a reference temperature T_r in (13), where the diffusion rate is measurable, the model equation becomes

$$D(M_w, T) = D_r 10^{\frac{C'_1(T-T_r)}{C'_2+T-T_r}} . \quad (14)$$

C'_1 and C'_2 are functions of T_g as reported by Peleg [28] and Roos [30], i.e.,

$$C'_1 = \frac{C_1 C_2}{C_2 - (T_g - T_r)} , \quad (15)$$

$$C'_2 = C_2 - (T_g - T_r) , \quad (16)$$

yielding

$$D(M_w, T) = D_r 10^{\frac{C_1 C_2 (T - T_r)}{(C_2 - (T_g - T_r))(C_2 + (T - T_g))}} . \quad (17)$$

D_r is a constant, unknown parameter that is to be estimated by a least squares fit.

The Gordon-Taylor equation has been widely used to describe the moisture dependence of the glass transition temperature for a binary mixture of biopolymer and plastisizer, cf. Roos [30] or Nelson and Labuza [27],

$$T_g(t) = \frac{k X_w(t) T_{g_w} + T_{gMD12} (1 - X_w(t))}{k X_w(t) + (1 - X_w(t))} , \quad (18)$$

where the water-mass fraction $X_w(t)$ is defined by

$$X_w(t) = \frac{M_w(L, t)}{1 + M_w(L, t)}. \quad (19)$$

Using data from maltodextrins with DE ranging from 5 to 36, the glass transition temperature of maltodextrin DE 12 is interpolated and $k = 7.63$ and $T_{g_{MD12}} = 164$ are estimated from the data published by Roos and Karel [29]. The glass transition temperature of pure water T_{g_w} is assumed to be -135 .

In this way a relationship between the diffusion coefficient, the temperature, and the glass transition temperature can be postulated, using a theoretical basis that have already been used to describe the viscosity of materials, cf. Maltini and Anese [18].

It is clear that using $T_g(t)$ as the only explanation for the variation of the diffusion coefficient during the drying process is an not complete approximation that takes into account only the structure of the matrix. Any other influence is then neglected or dumped into the coefficients that characterise the model, which must be very carefully considered, once the physical state of the matrix is not the only factor influencing the diffusivity in a polymeric material, see Chirife and Buera [3] for a discussion in the sole use of polymer science to describe moisture content influence on kinetics. Development of porosity, shrinkage, structural changes, crust formation, chemical reactions may occur during the drying process, influencing the affinity of the biological matrix to the water and therefore its transport. Water transport in gas phase may be an important component of the whole water flux in the material at certain stages of the drying, masking the decrease of liquid water diffusivity with the decrease of water content.

Another important question is that glass transition may occur in certain locations (preferentially the surface) during the final stage of the drying process. At this stage the glassy material falls outside of the scope of the WLF equation, which was developed to describe rubbery materials. In any case the occurring drying rates at that state are very low in comparison with the ones at higher humidities and therefore the resulting errors will not be significant under normal drying conditions.

3 Numerical Implementation

3.1 The Parameter Estimation Model

Our goal is to estimate some unknown parameters of the moisture and temperature model simultaneously for a set of up to $n = 18$ experiments. Thus we have to solve a set of n partial differential equations

$$\frac{\partial}{\partial t} M_w^i(z, t) = \frac{1}{L^2} \frac{\partial}{\partial z} \left[D(M_w^i(z, t), T^i(z, t)) \frac{\partial}{\partial z} M_w^i(z, t) \right] \quad (20)$$

for $i = 1, \dots, n$, see (2), where the nonlinear diffusion coefficient is defined by (17),

$$D(M_w^i(z, t), T^i(t)) = D_r 10^{\frac{C_1 C_2 (T^i(t) - T_r)}{(C_2 - (T_g^i(t) - T_r))(C_2 + (T^i(t) - T_g^i(t)))}} . \quad (21)$$

In our case C_1 is fixed at the averaged value of 17.56, see [40], and the reference temperature T_r is set to $160^\circ C$. C_2 and the diffusion coefficient at the reference temperature D_r are considered as model parameters to be estimated from the moisture diffusion equation. They are independent from the underlying experiment. Glass transition temperature $T_g^i(t)$ is defined by (18) with

$$X_w^i(t) = \frac{M_w^i(1, t)}{1 + M_w^i(1, t)} \quad (22)$$

and $k = 7.63$, $T_{g_w} = 164$, and $T_{g_{MD12}} = -135$.

We have mixed boundary conditions of Dirichlet and Neumann type, i.e. $\frac{d}{dz} M_w^i(0, t) = 0$ and $M_w^i(1, t) = M_{w,eq}^i(t)$ with

$$M_{w,eq}^i(t) = \frac{C^i(t) K^i(t) W_m^i(t) a_w^i}{(1 - K^i(t) a_w^i) (1 - K^i(t) a_w^i + C^i(t) K^i(t) a_w^i)} , \quad (23)$$

$i = 1, \dots, n$, where the water activities a_w^i are measured for each experiment and the remaining data are taken from (28) to (30). The spatial variable z is dimensionless and replaces x , since the total thicknesses L^i of the maltodextrin slabs vary from one experiment to the other and need to be normalized. Initial values are $M_w^i(z, 0) = M_{w,0}^i/L^i$, $i = 1 \dots, n$.

For the same reason we get now n coupled ordinary differential equations of the form

$$\frac{d}{dt} T^i(t) = \frac{h_A^i(t)}{\alpha^i(t)} (T_{db}^i(t) - T^i(t)) + \frac{\lambda_w^i(t) m_s}{\alpha^i(t)} \frac{d}{dt} \overline{M}_w^i(t) \quad (24)$$

with measured initial temperature values $T^i(0) = T_0^i$, $i = 1, \dots, n$. The remaining terms $h_A^i(t)$, $\alpha^i(t)$, and $\lambda_w^i(t)$ are defined analogously to equations (8), (9), and (10). The coefficient P_1 from eq. 9 is to be unknown and independent of the experimental setup. Instead of using $\frac{d}{dt} \overline{M}_w^i(t)$ we insert (20) and $\frac{d}{dz} M_w^i(0, t) = 0$ to obtain

$$\frac{d}{dt} \overline{M}_w^i(t) = \frac{1}{L^2} D(M_w^i(1, t), T^i(1, t)) \frac{\partial}{\partial z} M_w^i(1, t) . \quad (25)$$

This equation completes the description of the dynamical model.

To formulate the parameter estimation problem, we proceed from $l = 71$ different experimental time values t_j , $j = 1, \dots, l$, and n sets of measured moisture content $M_w^{i,j}$ and temperature $T^{i,j}$ values, and corresponding weights w_M^{ij} and w_T^{ij} , respectively, where $j = 1, \dots, l$, $i = 1, \dots, n$. Fitting criteria are $L^i \overline{M}_w^i(t)$ and $T^i(t)$, which depend on the unknown parameters D_r , C_2 , P_1 , and $M_{w,0}^i$. The initial moisture content is considered for each experiment individually as an unknown parameter to be estimated, since the measured initial values are subject to errors. However most of the weights are zero since measured data are available only for certain subsets of $\{1, \dots, l\}$ consisting of about 6 individual measurements at different experimental times. Since measurements are obtained for moisture and temperature, the total number of experimental data is 197 samples where moisture and temperature are measured.

In a formal way we need to minimize

$$\sum_{i=1}^n \sum_{j=1}^l \left(w_M^{ij} (L^i \overline{M}_w^i(t_j) - M_w^{i,j})^2 + w_T^{ij} (T^i(t_j) - T^{i,j})^2 \right) \quad (26)$$

where non-zero weights serve to select the experiments for which measurements are available, and for scaling the measurement sets, i.e., they are defined by the inverse sum of squared measurement values for each data set.

The least squares problem consists of minimizing (26) w.r.t. unknown model parameters D_r , C_2 , P_1 , and $M_{w,0}^i$ for $i = 1, \dots, n$. The diffusion coefficient D_r is scaled by the factor 1.0E-8, once most of the diffusion coefficient found in literature are well below this value.

3.2 Mathematical Algorithms and Test Environment

Numerical simulation and parameter estimation results are obtained by the interactive software system EASY-FIT of Schittkowski [35], that allows to identify parameters in dynamic systems, especially in systems of one-dimensional, time-dependent partial differential equations with coupled ordinary differential equations. Starting from given experimental data, i.e. moisture and temperature values for given observation times, the minimum least squares distances of measured values from fitting criteria are computed, in our case $L^i \overline{M}_w^i(t)$, cf. (11), and $T^i(t)$, by adapting the unknown model parameters. For the numerical integration and parameter identification, the Fortran code PDEFIT is executed by the user interface, see Schittkowski [36, 34].

The underlying idea is to transform the set of partial differential equations into a system of ordinary differential equations by discretizing the model functions with respect

to the spatial variable z . This approach is known as the method of lines, see Schiesser [33]. Coupled ordinary differential equations are added without any further manipulations. The integration interval is divided into m equidistant grid points and first and second partial derivatives of $M_w^i(z, t)$ w.r.t. the spatial variable z are approximated by a 3rd-order difference formula, which is adapted in a straightforward way at the boundaries.

For our numerical tests we proceeded 11 lines motivated by some initial simulation runs yielding sufficiently accurate results. The total number of stiff and extremely unstable ordinary differential equations is $(m + 1)n$, i.e., 216, and 22 parameters are to be fitted. Numerical instabilities occur because of the exponential terms for the evaluation of the diffusion coefficient.

The derivatives of the flux function w.r.t. z are evaluated by the automatic differentiation tool PCOMP, see Dobmann, Liepelt, and Schittkowski [5], i.e., without any numerical approximation errors, and the derivatives of the fitting criteria w.r.t. model parameters by forward numerical differences. To compute the total moisture amount $\overline{M}_w^i(t)$, the integral is approximated by Simpson's rule.

The resulting large system of ordinary differential equations is then solved by the implicit Runge-Kutta method RADAU5 of Hairer and Wanner [11] of order 5, since these equations tend to become stiff with increasing discretization accuracy. Relative and absolute error tolerances were set to 1.0E-5 and 1.0E-6, respectively.

The resulting nonlinear least squares problem is solved by the code DN2GB of Dennis, Gay, and Welsh [4], a combination of Gauss-Newton and quasi-Newton method for constrained problems. Since each iteration requires at least one objective function evaluation and one evaluation the derivatives w.r.t. all unknown model parameters, one has to integrate the system of 216 stiff differential equations at least 23 times within each iteration step. Stopping tolerance of DN2GB was set to 1.0E-5.

Numerical experiments are conducted on a PC with a Pentium P2 processor running with 450 MHz under Windows 95.

4 Experimental Design

4.1 Maltodextrin DE 12 Desorption Isotherm

In order to determine the desorption isotherm, desorption isotherms at four different temperatures (4 [°C], 25 [°C], 37 [°C] and 50 [°C]) are performed. One milliliter of maltodextrin solution (400 [g/l] Glucidex 12, Roquette, France) is placed in chromatography vials (Cat no. 10201, Chrompack International, BV The Netherlands) and placed in sat-

urated binary salt solutions environment of known relative humidity, see Greenspan [10], until equilibration following the methodology of the COST 90 project [31]. The equilibrium moisture content is determined by weight difference from the initial state and from the known initial moisture content. In order to model the temperature dependence of the maltodextrin, a modified GAB model equation was used

$$M_{w,eq}(t) = \frac{C(t)K(t)W_m(t)a_w}{(1 - K(t)a_w)(1 - K(t)a_w + C(t)K(t)a_w)}, \quad (27)$$

where a_w denotes the water activity. The model parameters $C(t)$, $K(t)$ and $W_m(t)$ are fitted to an Arrhenius temperature dependence as in Mishkin [24], and the data are fitted in a single least squares regression yielding the following parameters:

$$C(t) = 0.04e^{\frac{1257.14}{T(t)+273}}, \quad (28)$$

$$K(t) = 0.65e^{\frac{144.57}{T(t)+273}}, \quad (29)$$

$$W_m(t) = 0.05e^{\frac{-99.27}{T(t)+273}}. \quad (30)$$

By using equations (28) to (30), $M_{w,eq}(t)$ is computed and inserted into the drying model, i.e., in (5).

4.2 Drying experiments

In order to model the drying kinetics of maltodextrin DE 12 in a broad range of temperatures, drying experiments are conducted using a non-centered 3x3 factorial design with the volume of maltodextrin and temperature as design factors. The variable ranges vary from 70 [°C] to 140 [°C] for the drying temperature and 4 [ml] to 12 [ml] for the volume. Experiments are conducted over up to 27.000 seconds.

At each experiment 12 petri dishes of 0.05 [m] of diameter with a fixed amount of a 400 [g/l] maltodextrin DE 12 (Glucidex 12, Roquette, France) solution in distilled water are placed in an isolating pad and dried using a cabinet convection drying oven (Convection Oven MOV-212F Sanyo Electric Co., Ltd. Japan) . At predetermined times 2 samples are taken and the moisture content is determined by gravimetry.

Three thermocouples monitor the dry bulb temperature and six the sample temperature. The factorial design was replicated, in order to see the variation of an experiment with the variation of laboratory environmental conditions, e.g., change in relative humidity of the air, that influence the equilibrium moisture content.

j	t_j	$T_{db}(t_j)$	$M_w^{1,j}$	$T^{1,j}$
1	0.0	42.11	-	-
2	2900.0	71.69	1.117	45.57
3	4500.0	70.06	0.799	50.87
4	7000.0	70.69	0.461	66.17
5	9500.0	71.13	0.243	69.28
6	12800.0	72.35	0.188	72.30

Table 1: Measured Dry Bulb Temperatures, Average Moisture Contents, and Temperatures

To give an impression on the typical order of magnitude of experimental data, we select one experiment arbitrarily. The measured maltodextrin slab thickness for the first experiment is $L = 0.0020954$, water activity is $a_w = 0.621$, solid mass is $m_s = 0.00152$, and initial temperature is $T_0 = 42.11$. Corresponding dry bulb temperatures are listed in Table 1. Measured data for moisture content and temperature at different time values are also shown in Table 1, again only for the first experiment. These data are to be fitted by adapting the model parameters D_r , P_1 , T_r , and $M_{w,0}$.

5 Results and Discussion

The iterative least squares algorithm DN2GB is always started from $D_r = 80$, $P_1 = 1$, $C_2 = ???$ and $M_{w,0}^i = 2$ for $i = 1, \dots, n$, where $n = 18$ experimental data sets are taken into account. Table 2 contains numerical results for individual fits of each experiment, i.e., the obtained parameter values, the final residual scaled by sum of squared measurement values res , and the number of iterations n_{it} . The column headed by $M_{w,0}^i$ contains the estimated initial moisture values that are treated separately for the simultaneous fit over all measurement sets. In one case the upper bound 50.0 is reached. This is due to the experimental error of the setup.

Obviously the parameter values differ drastically, since we have to expect approximation of local solutions or terminations because of a very flat objective function values, making it impossible to find a profitable new iterate. Also, due to the exponential term in the dependence of the diffusivity, statistical correlation of D_r and C_2 was expected, making possible that local minima could be found if the experimental set was not able to

i	D_r	P_1	T_r	$M_{w,0}$	$M_{w,0}^i$	res	n_{it}
1	181.0	0.79	188.9	2.23	13.31	0.0143	42
2	26.8	281.81	172.1	0.44	50.00	0.0016	54
3	534.0	1.41	189.8	2.48	3.38	0.0063	16
4	185.3	1.48	120.7	2.99	2.14	0.0113	7
5	146.9	1.14	133.7	2.93	2.43	0.0045	15
6	383.2	1.45	155.3	2.78	2.29	0.0165	17
7	656.3	1.59	202.6	3.53	7.57	0.0393	41
8	191.6	2.74	169.2	3.30	6.29	0.0065	13
9	295.5	2.09	154.9	3.10	2.78	0.0024	20
10	87.6	1.52	119.0	3.08	2.67	0.0060	6
11	148.9	1.74	126.4	2.31	1.79	0.0031	11
12	275.6	1.68	138.7	2.94	2.01	0.0027	32
13	159.9	2.67	117.4	54.81	4.29	0.0108	28
14	117.8	2.01	78.2	4.21	4.46	0.0114	39
15	2.7	3.58	30.7	3.31	1.00	0.0059	80
16	38.4	2.75	82.3	4.95	2.11	0.0042	36
17	68.6	3.93	81.2	5.86	0.94	0.0087	59
18	241.6	2.86	114.7	4.18	1.40	0.0024	22
$\frac{1}{n} \sum$	222.2	2.05	130.4	3.39	-	0.0082	28
<i>all</i>	67.7	2.07	117.9	-	-	1.19	18

Table 2: Numerical Results

describe precisely the behaviour. Thus the simultaneous fit over all data sets is necessary to get interpretable results. The final results are also presented in the last row of Table 2 to be compared with arithmetic mean values of the individual fits. For computing the mean values the experimental data sets no. 2 and 13 are ignored because of obvious wrong convergence. In particular the diffusion coefficient D_r gets different values in both cases, whereas the other two parameters P_1 and T_r are comparable.

The corresponding measurement values, model function curves, and moisture content profile over time and space for the first measurement set are displayed in Figures 1 to 3, to give an example on the quality of the achieved results.

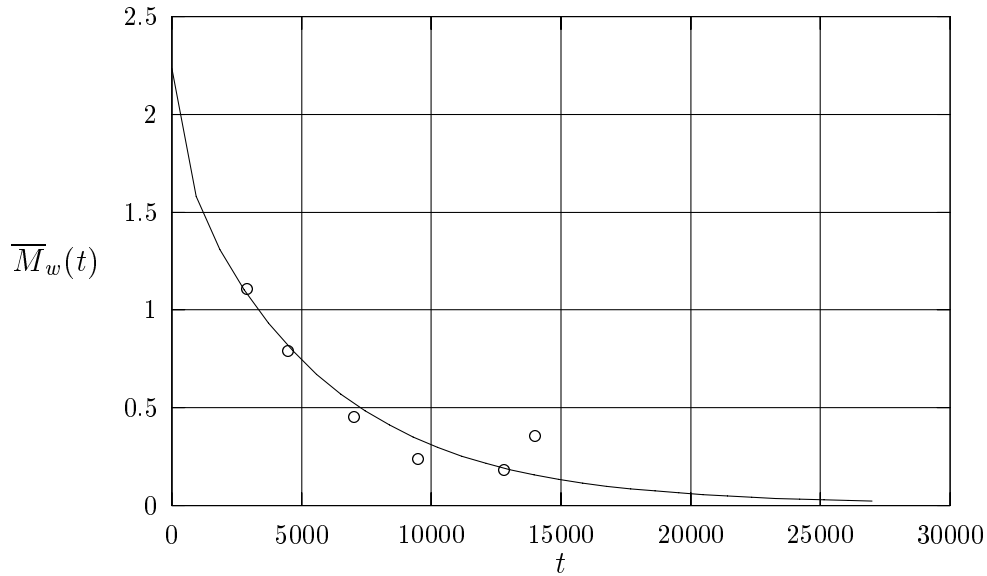


Figure 1: Measured Average Moisture Contents and Fitting Criterion for First Data Set

6 Conclusions

We introduced a mathematical model that describes the drying kinetics of maltodextrin DE 12 in a convection oven. The WLF and Gordon-Taylor equation are used for the moisture and temperature dependence of the effective diffusivity. The resulting diffusion equation describing the dynamics of moisture content is highly nonlinear and possesses Dirichlet and Neumann boundary conditions. Ordinary differential equations are added to take the time-dependent variation of temperature into account. The model provided the possibility of fitting a wide range of drying process with a little number of parameters to describe the effective diffusivity and may be used in other processes that involve the thin layer drying of biopolymers. This model has the characteristic of having more fundamentally based effective diffusivity function than empirical modelling with the moisture content, although it cannot be considered a complete description of the moisture dependence of the diffusivity.

An experimental setup to cover a range of initial drying volume (4mL to 12ml) and drying oven temperature (from $70^{\circ}C$ to $140^{\circ}C$) was performed to try to demonstrate the validity of the assumptions over the moisture and temperature dependence of the effective diffusivity. No control over the relative humidity was made. Because of the high drying

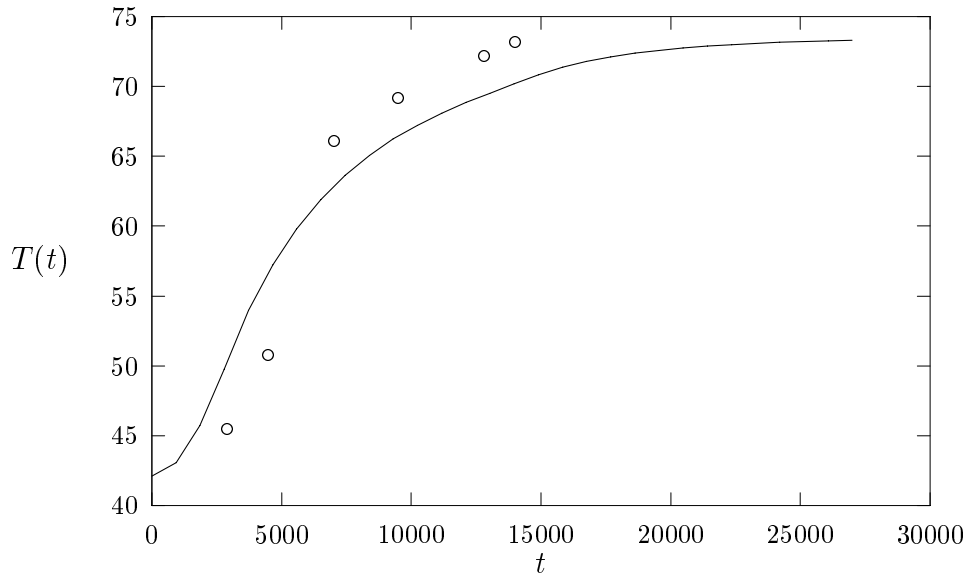


Figure 2: Measured Average Moisture Contents and Fitting Criterion for First Data Set

temperatures and big variation in the drying course of each individual sample to be dried in the oven, a big error in the sample moisture content determination was observed.

The method of lines is applied to discretize the second-order partial differential equation w.r.t. the space variable. For the very crude accuracy used, i.e., only 11 lines, we get a system of 216 highly stiff and numerically unstable ordinary differential equations. The data fitting problem is formulated to estimate 22 unknown parameters over 18 measurement sets under consideration. 71 time values and 197 measured data are given by the experimental design, and are incorporated in the least squares fit. It is shown that the achieved results are more stable than those obtained by individual fits.

The noisy experimental data was fitted to the model yielding significant parameters that were inside the normal literature values. The global fitting could predict the moisture and temperature of the drying process adequately independently the temperature range and the big variation of the diffusion thickness, that greatly influenced the process course.

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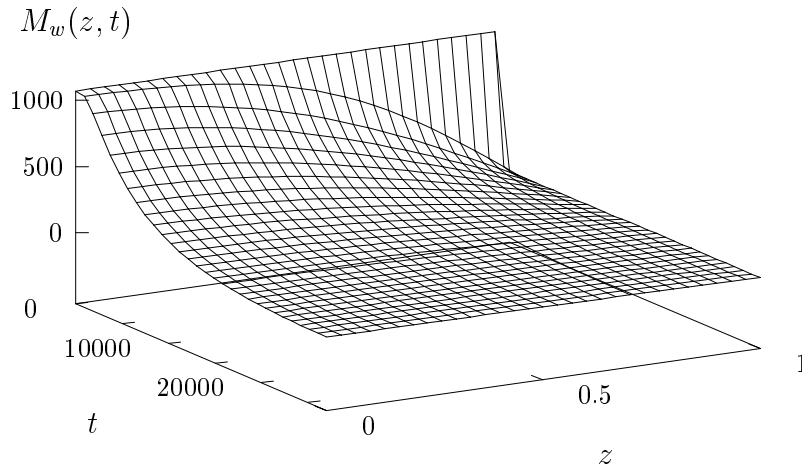


Figure 3: Moisture Contents for First Data Set

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