KINETIC MODELLING OF SUBLIMATION AND VAPORIZATION IN LOW-TEMPERATURE DEHYDRATION PROCESSES

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In this work a kinetic analysis has been carried out under two low-temperature dehydration techniques: freeze-drying and controlled low-temperature vacuum dehydration (CLTVD).

The CLTVD process is described as a uniformly retreating ice front (URIF) and a sublimation-vaporization model which considers an additional mechanism for the diffusion of liquid water.

A comparative analysis on the basis of mass transfer coefficients according to the proposed model is made. The kinetic parameters obtained were compared and studied in order to deduce conclusions about the convenience of both techniques and the possibilities of each model to describe the process kinetically.

Introduction

Freeze drying is a widely employed dehydration technique for obtaining high-quality dried products when deterioration risks because of temperature are important even at moderate levels.

Factors such as low-temperature operating conditions, preservation of flavor characteristics and inhibition of spoilage are important factors for obtaining low-density, easy-to-rehydrate products in which the original value is preserved if the frozen product is maintained. On the contrary several disadvantages deserves to be mentioned. Freeze drying is an expensive dehydration process because of the low drying rates, capital and energy costs due to refrigeration and vacuum units, which are directly dependent on the drying duration¹²⁾.

Research now in progress regarding freeze drying is moving in several directions: heat and mass transfer parameters and their dependence on process control variables²⁾, modelling, simulation and predicting searching for operating time reduction^{6, 10)}. Other studies are related to innovative processes by introducing modifications in the essential characteristics of conventional freeze drying: i.e. atmospheric pressure lyophilization^{16, 17)} and application of better and more efficient operating strategies using controlled low-temperature¹⁴⁾ techniques. This last approach tries to reduce dry cycles operating at temperatures within the melting interval of the product but avoiding serious alterations of the essential characteristics of freeze drying^{5, 9)}.

The most important design variables in freeze drying are⁴⁾: the minimum pressure attainable by the vacuum system, condenser temperature and heat flux. The necessary heat to remove water by sublimation or vaporization should be supplied by the heating plates. If not enough heat is received by the product, the frozen product temperature decreases to levels that could be

very similar to those of the condenser. In this case, the vapor pressure driving force is negligible and water removal will cease.

In freeze drying, heat and mass transfer phenomena come together to achieve a dried product. Sublimation of ice crystals gives rise to a porous zone that continuously advances inward from the surface. In many cases uniformly retreating front of ice is admitted which divides the product into a porous dried zone and a wet frozen zone. This progressively thicker dried layer is responsible for a lowering of drying rate as operation continues, since the resistances of heat and mass transfer increase. Controlled low-temperature vacuum dehydration (CLTVD), appears to be an interesting alternative to conventional freeze drying, making possible its application to other, non-high added value products, to which freeze drying was practically limited¹¹⁾. Temperatures within the melting interval of the product are characteristic of CLTVD¹⁴⁾, and a mechanism of liquid diffusion must be also considered. Operating conditions are between those of vacuum drying and lyophilization. Adequate consistency of product is achieved by avoiding excessive melting and consequent shrinking. Thus, a good control system to assure a semimelted state must be established.

Advantages of CLTVD with respect to conventional freeze drying include: i) lower resistance to mass transport due to the additional participation of liquid diffusion, and ii) Reduction of about 28% in the sublimation enthalpy of sublimation because of partial fusion of product. Operating costs of CLTVD are about 40 to 50% lower than those of lyophilization.

In this study, a differentiation between CLTVD and lyophilization is established through an adequate kinetic modelling. A kinetic model is proposed for each process, and this requires a knowledge of transport parameters experimentally deduced from heat flux and mass loss

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definition.

The quantitative analysis of lyophilization is not easy, due to its non-steady character and the multiple variables involved⁶⁾. Hence, this work aims at simple equations to predict kinetically drying processes either in the form of lyophilization or CLTVD, defining only characteristic product temperatures.

1. Analysis of Drying Processes

Apart from the previous freezing, two fundamental steps can be considered in freeze drying: i) primary drying or ice sublimation and ii) secondary drying or desorption down to equilibrium moisture content. The latter stage will not be considered here since the possibilities of modifying control variables to enhance drying rate are very limited. During secondary drying, pressure is kept as low as possible with product temperature close to its scorch point. Besides, the water amount involved in this period is hardly more than 5% for many products¹⁵⁾.

If hydrodynamic transport is neglected¹⁰⁾, water removal through a porous matrix depends on the effective $D_{w,e}$, influenced by the pressure, temperature, Knudsen diffusivity and dried product structure⁵⁾. Mass balance corresponding to water removal in the dried zone yields:

$$\frac{\rho_{II} - \rho_I}{\rho_{II}} \frac{\delta P_w}{\delta t} = -D_{w,e} \nabla^2 P_w \quad (1)$$

Under given conditions, the material can be partially melted so that a certain amount of water is removed as liquid according to:

$$\frac{\delta X_L}{\delta t} = -D_L \nabla^2 X_L \quad (2)$$

Simultaneous removal of water through the mechanisms indicated by the above equations gives rise to a reduction of moisture content of the product. Thus, the total water removed is due to the sum of vapor flux:

$$N_v = -D_{w,e} \nabla P_w / RT \quad (3)$$

and liquid flux

$$N_L = -\frac{P_s}{RT} D_L \nabla X_L \quad (4)$$

at the outer surface of the product, so that:

$$N_w = \frac{(\rho_{II} - \rho_I) L_o}{M_w} \frac{dX_{av}}{dt} = N_v + N_L \quad (5)$$

1.1 Freeze drying

In Fig. 1, a unidirectional system in which a dried (I) zone and a frozen zone (II), during freeze drying are shown. Vapor flows through the dried layer in the opposite direction to the heat flux⁷⁾. In a first simplification and for the considered geometry, freeze drying is described by a model based on the following assumptions. i) Vapor and heat fluxes go countercurrent to and perpendicularly to the sublimation front. ii) Sublimation

takes place at the interface parallel and distant by a length L from the surface, and its thickness is assumed to be negligible. iii) Vapor flows through the stagnant air inside the porous matrix are on thermal equilibrium with it. iv) Vapor pressure at the interface is that of the equilibrium at the ice-front temperature. v) The frozen zone is assumed to be homogeneous with uniform thermal conductivity, heat capacity and density. vi) The bottom and lateral walls of the recipient are perfectly insulated.

In freeze drying, there is no diffusion of moisture in liquid state. Consequently, if a pseudo-steady state is assumed for the considered geometry, Eq. (5) yields:

$$-\frac{(\rho_{II} - \rho_I) L_o}{M_w} \frac{dX_{av}}{dt} = \frac{D_{w,e}}{R T_1 L_o (1 - X_{av})} (P_{w,x=L} - P_{w,x=0}) \quad (6)$$

An external coefficient of mass transfer, through the vacuum chamber, from the product surface up to the condenser surface can be established and N_v can be written as:

$$N_v = -\frac{(P_{w,x=L} - P_c)}{\frac{R T_1 L}{D_{w,e}} + \frac{1}{k_g}} \quad (7)$$

From Eq. (7) and taking into account that $N_L = 0$ in freeze drying one reaches the characteristic equation of a uniformly retreating ice front (URIF):

$$1 - X_{av} = \frac{M_w (\rho_{II} - \rho_I) D_{w,e}}{\rho_{II}^2 R T_1 L_o^2} \frac{(P_f - P_c)}{(-dX_{av}/dt)} - \frac{(\rho_{II} - \rho_I) D_{w,e}}{\rho_{II} R T_1 L_o K_g} \quad (8)$$

Where P_f or $P_{w,x=L}$ is the vapor pressure of ice for the sublimation front temperature, T_f .

The theoretical location of the sublimation or dried thickness, L , is determined from a knowledge of the average residual moisture of product according to:

$$X_{av} = 1 - L/L_o = m/m_o \quad (9)$$

Integration of Eq. (8) makes it possible to obtain the evolution of the remaining mass of product during drying, assuming constant transport parameters and vapor pressure at the sublimation front.

1.2 Controlled low-temperature vacuum dehydration (CLTVD)

Temperatures close to the melting point or within the fusion interval are characteristic in CLTVD with variable amounts of moisture as liquid and ice. Moisture can migrate as liquid or vapor. Consequently, several assumptions made in freeze drying, fundamentally those regarding the interface, are very different from those indicated above.

In CLTVD, a hybrid sublimation-vaporization front is considered, due to the melting temperatures used, which present an undefined thickness, variable moisture contents and no distinction between frozen and dried zones (Fig. 1b). Nevertheless, here a virtual front is also considered according to Eq. (9) and moisture removal described by Eq. (5). In parallel, a global coefficient of mass transport, K_m , is considered by means of the equation:

Fig. 1 Sketches of product and moisture distribution during freeze-drying (a) and in CLTVD (b)

$$N_w = K_m \quad \Delta P_{w,t} = K_m (P_f - P_c) \quad (10)$$

Taking Eq. (5) and (10) and the definitions of N_y and N_L the following equation of dimensionless groups can be used to describe the process:

$$f \left\{ \frac{(\rho_{II} - \rho_I) L_o (-dX_{av}/dt)}{M_w K_m \Delta P_{w,t}}, \frac{D_{w,e} \nabla P_{w,in}}{K_m R T \Delta P_{w,t}}, \frac{D_L P_s X_L}{K_m R T \Delta P_{w,t}} \right\} = 0 \quad (11)$$

Many kinetic models calculate the drying rate as a function of the remaining moisture. Taking into account this consideration, the above equation can be written in the form:

$$-\frac{dX_{av}}{dt} = \frac{\Phi}{t^*} X_{av}^a \quad (12)$$

where Φ and t^* are defined respectively by:

$$\Phi = f \left(\frac{D_{w,e}}{R T_f K_m L_o}, \frac{D_L X_L}{L_o R T_{in} K_m}, \frac{P_{w,in} P_s}{\Delta P_{w,t}^2} \right) = f (Sh_L, Sh_v, \pi) \quad (13)$$

and

$$t^* = \frac{(\rho_{II} - \rho_I) L_o}{M_w K_m \Delta P_{w,t}} \quad (14)$$

2. Material and Method

2.1 Material

Food models consisting of a mixture of cellulose and hemicellulose commercially known as Tylose were used. This product, with a powdered white aspect, is frequently used as a model system. Mixed with water to give a 77% by weight water content, the Karlshue product is obtained¹³. For this case, to achieve a more fluid product, the Karlshue material is diluted by adding sodium sulphite to obtain a final 2.5% Na_2SO_3 and 3% Tylose water solution.

2.2 Method

Product was placed in cylindrical recipients 40 mm height and 75 mm diameter with five thermocouples to measure temperature at different depths and an electrical conductivity (EC) electrode at the bottom. The recipient

Fig. 2 Profiles of variables T_s , T_{in} and pressure in a freeze-drying process performed at -12°C T_{in} and 67°C $T_s - T_{in}$ increment

with the sample is placed on a METTLER, mod. BE-1200 balance, inside the vacuum chamber to measure mass loss.

Temperature recorded at 2 mm from the bottom or T_{in} was kept constant during an important period of drying at -12°C for freeze drying and 3, -2 and -1°C for CLTVD. The temperature increment between surface, T_s , and T_{in} was also measured and varied among values of about 17, 33 and 67°C in different experiments. Modification of heating temperatures between 20 and 120°C and pressure between 0.4 and 3 torr, ($53.32 - 399.87 \text{ N/m}^2$), must be adequately changed to try to keep T_{in} and the increment $T_s - T_{in}$ constant. The EC electrode located at the bottom of the recipient allows determination of local moisture, X_{loc} , according to data in a previous work⁸. Thus, moisture as liquid, X_L , in the lower position of product is obtained by:

$$x_L = x_{loc} (1 - f_i) \quad (15)$$

The ice fraction, f_i , was calculated using the equilibrium concentration of solution at temperature T_{in} , C_e , and the original concentration C_o , according to:

$$f_i = \frac{c_e(T_{in}) - c_o}{c_e(T_{in})} \quad (16)$$

3. Experimental Results

In all the experiments, temperature T_{in} , T_s , remaining mass and T_f were measured. Characteristic temperatures T_{in} and increment $T_s - T_{in}$ in each process are reached after a 2 h period and maintained thereafter, by adequately varying pressure, P , and heating plate temperature, T_p . Once prefixed values have been attained they are maintained to the end of the operation, in which T_{in} tends to increase to values close to T_s .

In Fig. 2 and 3, the profiles of some characteristic variables during freeze drying ($T_{in} = -12^\circ\text{C}$) and CLTVD ($T_{in} = -3^\circ\text{C}$), where the period in which the increment $T_s - T_{in}$ is maintained constant, is represented. Initially, a considerable increase in chamber pressure is performed to attain the T_{in} and $(T_s - T_{in})$ increment desired. How-

Fig. 3 Profiles of variables T_s , T_{in} and pressure in a CLTVD process performed at -3°C T_{in} and 51°C $T_s - T_{in}$ increment

Fig. 4 Calculated front temperatures T_f for CLTVD and freeze-drying experiments as a function of X_{av} ($T_s - T_{in} = 14^{\circ}\text{C}$)

ever, this high pressure favours heat transmission and therefore, as the process proceeds, maintain T_s and T_{in} on the desired levels it is necessary to progressively reduce the pressure.

In this work the operating conditions of pressure and heating have been combined to attain the prefixed temperature profiles following the strategy described in Figs 2 and 3. The aim of future investigations will be to obtain the most adequate combination of P and T_p so that the drying rate will be enhanced to achieve optimum control.

3.1 Drying kinetics from URIF and sublimation-vaporization models

The URIF and coupled sublimation-vaporization (CVS) models are proposed here to describe moisture evolution during lyophilization and CLTVD processes. Both models require a knowledge of ice or ice-liquid front temperature, T_f . This is determined on the basis of experimental temperatures, assuming linear gradients in the dried and frozen layers on the theoretical front position according to Eq. (9). In **Fig. 4**, the sequence of the evaluated T_f is shown as a function of X_{av} for both types of drying.

Taking the temperature T_f when X_{av} is 0.5 as constant through the process, the parameters $D_{w,e}$ and K_m are

Fig. 5 Mass loss evolution during freeze-drying ($T_{in} = -12^{\circ}\text{C}$) and 14°C $T_s - T_{in}$ increment

Fig. 6 Mass loss evolutions during CLTVD experiments ($T_{in} = -3$ and -1°C cases) and 14°C $T_s - T_{in}$ increment

calculated by fitting the experimental results of moisture loss according to Eq. (8). The evolution of m vs t is obtained by integration of Eq. (8) once the dependence of X_{av} on the moisture of product Eq. (9) is considered. In **Fig. 5** and **6**, calculated and experimental evolutions of mass loss are shown for freeze drying and CLTVD cases.

The transport parameters as well as the calculated and experimental duration of the process are indicated in **Table 1** for different experiments. $D_{w,e}$ seems low when the increment $T_s - T_{in}$ is increased because of the corresponding higher pressure employed in these cases. The behavior of K_g is similar, although more favorable temperature-driving forces are expected in high $T_s - T_{in}$ cases.

Although calculated and experimental mass loss evolutions do not exactly coincide, URIF yields good predictions of total drying time for freeze drying but shows considerable deviations for CLTVD.

A comparative analysis of experimental and calculated values of $(-dX_{av}/dt)$ was carried out, evaluating the maximum observed deviation for a 97% confidence factor, $E_{97}^{(1)}$. These values are in Table I, which shows that the greater discrepancies between θ_T and θ_T^* are those of CLTVD cases. It is necessary to indicate that the

Table 1. Characteristic parameters and results of freeze-drying and CLTVD experiments under consideration of the URIF model

T_{in} [°C]	$T_s - T_{in}$ [°C]	T_f [°C]	$D_w 10^4$ [m ² /s]	$K_g 10^5$ mol/Ns]	$E_{g7} 10^6$ [s-1]	θ_T [h]	θ_T^* [h]
-12	17	-17.8	30.52	18.05	1.01	16.3	13.2
	33	-16.8	25.56	34.67	3.94	10.5	8.2
	67	-15.0	29.72	35.81	4.64	6.7	5.5
-3	14	2.2	1.89	10.04	7.61	13.3	16.0
	33	6.5	1.58	6.54	12.35	11.0	12.5
	51	15.0	0.96	1.76	51.42	7.6	10.1
-1	9	2.0	3.06	2.70	6.37	15.3	13.2
	15	3.0	3.01	5.03	9.82	8.7	10.9
	56	16.0	0.26	0.29	54.46	7.6	9.7

Fig. 7 Influence of T_a and $T_s - T_{in}$ on terms Φ and t^*

URIF model is based on the linear relationship of $1 - X_{av}$ vs $(P_f - P_c)/(-dX_{av}/dt)$. In freeze drying, this behavior has been found to be fulfilled in an important period of the process. Moisture migration as liquid due to an intermediate melting state of CLTVD that is not considered in the URIF model seems to be responsible for the observed discrepancies.

The sublimation-vaporization model considers the possible migration of moisture as liquid through the parameter D_L . Experimental values of mass loss were correlated according to Eq. (12), obtaining a value of 0.533 for the exponential parameter a . Because of the semiempirical character of Eq. (12), the determination of transport parameters involved in the terms Φ and t^* has been avoided here. In a practical perspective, considering the dependence of both terms on T_{in} through T_s , dimensionless temperature T_a defined as:

Table 2. Characteristic parameters and results of the CLTVD experiments under consideration of CSV model

T_{in} [°C]	$T_s - T_{in}$ [°C]	T_f [°C]	t^* [s]	Φ	$E_{g7} 10^6$ [s-1]	θ_T [h]	θ_T^* [h]
-3	14	2.2	31264.44	1.37	2.73	13.3	13.20
	33	6.5	31264.44	1.74	7.44	11.0	10.7
	51	15.0	31264.44	2.57	7.94	7.6	7.9
-1	9	2.0	5493.17	0.15	2.47	15.3	14.8
	15	3.0	5493.17	0.24	3.57	8.7	9.4
	56	16.0	5493.17	0.38	3.03	7.6	7.7

Fig. 8 Mass loss evolutions during CLTVD experiments ($T_{in} = -3$ and -1 °C cases) and 14 °C $T_s - T_{in}$ increment

$$T_a = \frac{T_{in} - T_{m,s}}{T_{m,w} - T_{m,s}} \quad (17)$$

and increment $T_s - T_{in}$ were experimentally obtained. In **Fig. 7**, the dependence of Φ and t^* on T_a and $T_s - T_{in}$ are shown. While Φ is influenced by both temperatures, t^* appears to be independent of $T_s - T_{in}$.

In **Table 2**, maximum discrepancies between experimental and calculated data from Eq. (12) are indicated for CLTVD experiments. Terms Φ and t^* are indicated for each experiment and a better prediction of drying times θ_T^* is obtained, if compared with θ_T , than that obtained by the URIF model. However, we must mention that these results have been obtained for a given product thickness, $L_o = 10$ mm. It would be necessary to considerate this parameter influence upon Φ and t^* when using the sublimation-vaporization model with another thickness.

In **Fig. 8**, experimental and theoretical evolution of m vs. T are shown for all CLTVD experiments carried out at -1 °C and -3 °C T_{in} , and 14 °C $T_s - T_{in}$ temperature increments, obtained by integration of Eq. (12) with the parameters (Φ and t^*) indicated in Table 2.

Conclusions

On the basis of controlling a defined intermediate melting state, the CLTVD technique results in a reduction of about 20% in total drying time in comparable freeze drying conditions analysed. Nevertheless, to achieve important time reductions additional searching is required to find a better combination of vacuum and heating conditions. The CSV model has been found to be an easy and adequate model to describe CLTVD kinetically, giving better results than those obtained by URIF to describe lyophilization processes under conventional conditions.

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Nomenclature

c_e	= concentration from equilibrium freezing line of solution at solution at temperature T_m [% by weight]
c_o	= concentration of electrolyte solution [% by weight]
D_L	= diffusivity of liquid moisture [m^2/s]
$D_{w,e}$	= effective diffusivity of vapor through porous matrix [m^2/s]
f_i	= ice fraction [-]
K_g	= external coefficient of mass transfer (Eq. (7)) [$mol/Pa\ m^2\ s$]
K_m	= global coefficient of mass transfer (Eq.(10)) [$mol/Pa\ m^2\ s$]
L	= dried thickness of dried zone [m]
L_o	= initial thickness of product [m]
m	= remaining moisture of product [g]
m_o	= initial moisture of product [g]
M_w	= molecular weight of water [g/mol]
N_L	= molar flux of liquid moisture [mol/m^2s]
N_v	= molar flux of vapor [mol/m^2s]
N_w	= total water flux [mol/m^2s]
P_c	= vapor pressure at condenser surface [N/m^2]
P_f	= vapor pressure at front temperature [N/m^2]
P_s	= vapor pressure of saturation at temperature of medium [N/m^2]
P_w	= partial vapor pressure [N/m^2]
P	= chamber pressure [N/m^2]
R	= gas constant [$8.3114\ Kg\ m^2/mol\ s\ ^\circ C$]
Sh_L	= Sherwood of liquid diffusion [-]
Sh_v	= Sherwood of vapor diffusion [-]
t	= time [S]
t^*	= dimensional term (Eq. (14)) [S]
T_a	= dimensionless temperature, Eq. (16) [-]

T_f	= front temperature [$^\circ C$]
T_{in}	= temperature at bottom of recipient [$^\circ C$]
T_p	= temperature of heating plate [$^\circ C$]
T_s	= temperature at dried surface of product [$^\circ C$]
$T_{m,s}$	= melting point of solution [$^\circ C$]
$T_{m,w}$	= melting point of water [$^\circ C$]
X_{av}	= average moisture of product (Eq. (9)) [g water/g initial water]
x	= longitudinal coordinate [m]
X_L	= local moisture as liquid [g liquid water/g initial water]
X_{loc}	= total local moisture [g water/g initial water]
$\Delta P_{w,t}$	= total vapor pressure gradient (Eq.(10)) [N/m^2]
θ_T	= experimental duration of process [h]
θ_T^*	= predicted duration of process [h]
ρ_l	= density of dried zone [g/cm^3]
ρ_{II}	= density of frozen zone [g/cm^3]
Φ	= function given in Eq. (13)
π	= dimensionless group of pressure in Eq. (13) [-]

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