Mathematical model of vacuum freeze-drying in the secondary drying

Hua Li*, Lihua Li, Xingli Jiao, Xueli Qin
School of Chemical and Energy Engineering, Zhengzhou University, Zhengzhou 450001, China,
Email: lihua@zzu.edu.cn
School of Chemical and Energy Engineering, Zhengzhou University, Zhengzhou 450001, China,
Email: hua_iou@126.com
School of Chemical and Energy Engineering, Zhengzhou University, Zhengzhou 450001, China,
Email: jiaoxingli123@163.com
School of Chemical and Energy Engineering, Zhengzhou University, Zhengzhou 450001, China,
Email: 943167120@qq.com

Abstract:
The freeze-drying process is a complex heat and mass transfer process virtually. The drying process of freeze-drying is not only the key stage which decides the success of freeze-drying, but also the most difficult stage to control. There are lots of papers about heat and mass transfer in vacuum freeze drying at home and abroad. The present status of research on heat and mass transfer during vacuum freeze drying in the secondary drying is summed up and analyzed, and the trend of research in this field is discussed in this paper.

Keywords: vacuum freeze-drying; heat and mass transfer; mathematical model; the secondary drying
1. Introduction

The secondary drying is the last stage of the freeze-drying process which is a desorption step where the residual moisture is reduced to a low level ensuring long-term product preservation at room temperature. At the condition of vacuum, materials which are heated to sublimation during primary drying are heated up again during the secondary drying. And the water taken away is mainly combined water in materials, and the energy is mainly used for desorption and sublimation of combined water. However, after primary drying, there is a little of frozen water in materials that is sublimated and taken away during the secondary drying process\(^1\). The secondary drying is usually carried out at high vacuum and moderate temperature\(^2\).

2. Mathematical model of the secondary drying

2.1 The energy equation and mass equations of the secondary drying

After the primary drying is finished, the process passes into the secondary drying and the temperature is higher. There is no frozen layer in the material at the moment, so the whole material can be taken into consideration uniformly.

Then, there are some assumed conditions as followings.

(1) The heating mode of materials is mixing heating.

(2) The heat transfer process is unidimensional.

The energy equation of the secondary drying process can be shown as follows\(^3\).

\[
\frac{\partial T_d}{\partial t} = \alpha_{de} \frac{\partial^2 T_d}{\partial x^2} - \frac{C_{pg}}{\rho_{de} C_{pde}} \frac{\partial (G_t T_d)}{\partial x} + \frac{\Delta H_v}{\rho_{de} C_{pde}} \frac{\partial m_{sw}}{\partial t}, \quad t > t_{x_{min}}, 0 \leq x \leq X
\]  

\(T_d\) - temperature of dried layer;

\(t\) - time;

\(\alpha_{de}\) - effective thermal diffusivity of dried layer;

\(k_{de}\) - effective thermal conductivity in material;

\(C_{pg}\) - thermal capacity of gas in material;

\(\rho_{de}\) - density of material;

\(C_{pde}\) - effective thermal capacity of material;

\(\Delta H_v\) - heat of desorption of combined water;

\(G_t = G_w + G_i\) - total flow rate of the gas extracted from the material;

\(G_w\) - flow rate of water vapor;

\(G_i\) - flow rate of non-condensable gas;

\(\rho_{de}\) - density of dried layer during the secondary drying.
\( m_{sw} \) - ratio of desorbed combined water.

In the equation above, the last term represents the desorption during the secondary drying, which not only can’t be ignored, but also is the most important term. \( m_{sw} \) means the ratio of solid combined water, while \( m_{sw}^* \) means the ratio of solid combined water when the pressure of water vapor \( p_{sw} \) is at equilibrium state. The principle that \( m_{sw} \) varies over time can be shown: \( \frac{\partial m_{sw}}{\partial t} = f_s (m_{sw}^* - m_{sw}) \) or \( \frac{\partial m_{sw}}{\partial t} = -f_d m_{sw} \). The \( m_{sw}^* \) can be calculated approximately with the equation: \( m_{sw}^* = \exp \{2.3[1.36 - 0.036(T - T^0)]\} / 100, \text{kg_water/kg_dry} \). \( T^0 \) means the initial temperature. And \( f_s \) and \( f_d \) can be calculated by fitting experimental values and theoretical calculations.

The mass equation of water vapor of the secondary drying is:

\[
\frac{1}{R} \frac{\partial}{\partial t} \left( \frac{p_{sw}}{T_d} \right) = -\frac{1}{M_w \varepsilon} \frac{\partial G_w}{\partial x}, t > t_{x=L}; 0 \leq x \leq X
\]  

(2)

The mass equation of non-condensable gas of the secondary drying is:

\[
\frac{1}{R} \frac{\partial}{\partial t} \left( \frac{p_{sw}}{T_d} \right) = -\frac{1}{M_w \varepsilon} \frac{\partial G_{in}}{\partial x}, t > t_{x=L}; 0 \leq x \leq X
\]  

(3)

\( p_{sw} \) - pressure of water vapor in dried layer;

\( M_w \) - molecular weight of water;

\( \varepsilon \) - porosity;

\( R = 8.314 \text{KJ/(kmol} \cdot \text{K)} \);

\( p_{sw} \) - pressure of non-condensable gas in material;

In the equations above, \( G_w \) and \( G_{in} \) are closely related to the structure of in material. Based on the dusty-gas model \[^7\], \( G_w \) and \( G_{in} \) can be expressed as follows \[^7\].

\[
G_w = -\frac{M_w}{RT_d} \left[ K_1 \frac{\partial p_w}{\partial x} + K_2 p_w \left( \frac{\partial p_w}{\partial x} + \frac{\partial p_{in}}{\partial x} \right) \right]
\]  

(4)

\[
G_{in} = -\frac{M_w}{RT_d} \left[ K_3 \frac{\partial p_{in}}{\partial x} + K_4 p_{in} \left( \frac{\partial p_w}{\partial x} + \frac{\partial p_{in}}{\partial x} \right) \right]
\]  

(5)

So we can find the complex effects of structure and other factors by \( K_1, K_2, K_3 \) and \( K_4 \)[^7]. And the mass balance partial differential equations about \( p_w \) and \( p_{in} \) are shown as follows.

\[
\varepsilon \frac{\partial}{\partial t} \left( \frac{p_w}{T_d} \right) = \frac{\partial}{\partial x} \left[ \frac{1}{T_d} \left( K_1 \frac{\partial p_w}{\partial x} + K_2 p_w \left( \frac{\partial p_w}{\partial x} + \frac{\partial p_{in}}{\partial x} \right) \right) \right], t > t_{x=L}; 0 \leq x \leq L
\]  

(6)
2.2 Simplification of energy equation and mass equation of the secondary drying

In the secondary drying process, if diffusion is the only mass transfer way in porous dried layer, and the thermal physics of materials is constant, the equation (1) can be simplified as follows.

\[
\frac{\partial T_d}{\partial t} = a_d \frac{\partial^2 T_d}{\partial x^2} + \frac{\Delta H_r \rho_d}{\rho_b C_{p,b}} \frac{\partial m_w}{\partial t}, \quad t > t_{x=L} ; 0 \leq x \leq X
\]

(8)

And if the ratio of mass of removed water vapor in materials and increased temperature is constant, the following equation is true [8].

\[
- \frac{\partial W_d}{\partial T} = \frac{W_H}{T_u - T_i} = \text{constant}
\]

Then, the equation (1) can be shown as follows.

\[
\frac{\partial T_d}{\partial t} = a_d \frac{\partial^2 T_d}{\partial x^2} + \frac{\Delta H_r \rho_d}{\rho_b C_{p,b}} \frac{\partial T_d}{\partial t}, \quad t > t_{x=L} ; 0 \leq x \leq X
\]

(9)

Or

\[
(1 + \frac{\Delta H_r \rho_d}{\rho_b C_{p,b}}) \frac{\partial T_d}{\partial t} = a_d \frac{\partial^2 T_d}{\partial x^2}, \quad t > t_{x=L} ; 0 \leq x \leq X
\]

(10)

3. Conclusion

The process of figuring out parameters in the secondary drying is comparatively hard. So the simplified equations are used widely in fact. The process of simplifying equations in the secondary drying are summarized and introduced in this paper. Combined with actual circumstance and relevant boundary conditions, the parameters in the secondary drying can be easily obtained.

Reference


