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Research paper

Experimental and numerical investigations on freeze-drying of porous media with prebuilt porosity

Wei Wang [a,*], Jing Yang [a], Dapeng Hu [a], Yanqiu Pan [b], Shihao Wang [a], Guohua Chen [c,*]

[a] School of Chemical Machinery and Safety, Dalian University of Technology, Dalian 116024, China
[b] School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China
[c] Department of Mechanical Engineering, The Hong Kong Polytechnic University, Hong Kong, China

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ABSTRACT

Freeze-drying of initially porous frozen material was investigated aimed at improving the process economics by reducing drying time and raising productivity. Experimental results showed that freeze-drying can be significantly enhanced by the frozen material with prebuilt porosity, and about 31% of drying time can be saved compared with the conventionally solid frozen material under the tested operating conditions. A multiphase transport model was formulated based on the local mass non-equilibrium assumption. Numerical results showed excellent agreements between measured and predicted drying curves. Analyses of saturation and temperature profiles displayed that volumetric sublimation-desorption can occur for the initially porous frozen material.

1. Introduction

Freeze-drying plays a unique role in the processing of delicate and heat-sensitive materials such as food, pharmaceuticals and biological products [1]. It has also found applications in the preparation of new materials [2–5]. However, it is the most sophisticated and expensive process of almost all drying techniques, both in capital investment and in operational expenses [6]. Reducing freeze-drying time in order to lower energy consumption and raise productivity therefore has been a worldwide challenge during the past decades [7,8].

Some efforts were made for minimizing freeze-drying time while maintaining an acceptable quality of dried products. Commonly used method is that freeze-drying should be carried out at the highest freezing temperature possible, i.e., *the eutectic temperature* or *the glass transition temperature* [9]. An important method is employed to improve the heating manner by means of dielectric energy. Microwave heating is recognized as an advanced heating mode, as opposed to the poor heat supply in conventional freeze-drying when a heated plate conducts and/or radiates from the exterior to the interior of material being dried. Microwave heating combined with freeze-drying has demonstrated its potential to enhance the internal heat transfer [10–13]. However, excessive microwave energy input could cause frozen materials to melt and collapse, leading to ruin the overall freeze-drying process [13].

Although modern industry has benefited from the existing knowledge of physical and chemical processes during freeze-drying, fundamental formulations in some areas are still incomplete. Understanding of different freeze-drying stages needs to be transferred into useful tools for the process enhancement. The heat transfer problem has been successfully settled using microwave freeze-drying while the mass transfer problem still remains unsolved. It is necessary to re-examine the freeze-drying process. There are generally three stages in freeze-drying: freezing, primary drying, and secondary drying. Freezing is the first stage and the overall process performance is closely related to this stage. The pore shape, distribution and connectivity of porous dried layer largely depend on the size of ice crystals during freezing [9,14]. This dependence is of extreme importance because the mass transfer rate is significantly affected by the porous structure of dried layer [15,16]. If ice crystals are small and discontinuous, the mass transfer rate could be limited. However, if large ice crystals are formed and homogeneous dispersion can be realized, the mass transfer rate could be higher and materials could be dried more quickly [17,18]. The prevailing transfer resistance of freeze-drying is from water vapor migration in the dried region, depending on the size of ice crystals formed during the freezing stage [19,20]. And mass transfer parameters during freeze-drying are strongly dependent of the textural and morphological parameters of the ice phase [21].

* Corresponding authors.
E-mail addresses: dwwang@dlut.edu.cn (W. Wang), guohua.chen@polyu.edu.hk (G. Chen).

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Nomenclature

Roman symbols

c	specific heat capacity (J kg^{-1} K^{-1})
D	diameter of frozen sample (mm)
D_K	Knudsen diffusion coefficient (m^2 s^{-1})
d	ice crystal size or equivalent capillary diameter (m)
e	emissivity
F	angle factor
H	height of frozen sample (mm)
ΔH	latent heat (J kg^{-1})
K	permeability (m^2)
k_c	mass non-equilibrium rate constant (s^{-1})
M_w	molecular weight of water (kg mol^{-1})
$\dot{m}$	mass source (kg m^{-3} s^{-1})
p	pressure (Pa)
R_v	gas constant of water vapor (J kg^{-1} K^{-1})
r	spatial coordinate in radial direction (m)
S	saturation of ice
T	temperature (K)
t	time (s)
u	Darcy velocity (m s^{-1})
z	spatial coordinate in axial direction (m)

Greek symbols

α	parameter of adsorption equilibrium relation
ε	intrinsic porosity
λ	thermal conductivity (J m^{-1} s^{-1} K^{-1})
μ	dynamic viscosity (kg m^{-1} s^{-1})
ρ	density (kg m^{-3})
σ	Stefan-Boltzmann constant (W m^{-2} K^{-4})
τ	tortuosity

Subscripts

0	initial value
amb	ambient value
cenl	central line of sample
i	ice
insf	inner surface of supporting pad
e	effective value
m	supporting pad
s	solid matrix
sfps	surface pore space
surf	end surface or side surface of sample
v	vapor

Superscripts

s	saturated value in phase equilibrium
eq	saturated value in adsorption-desorption equilibrium

Unlike fruits and vegetables with naturally formed pores that are partially filled with moisture, liquid materials are usually frozen into solid materials without initial pores. Such a freeze-drying operation is known to be lengthy and expensive. It was therefore hypothesized that if liquid materials were first frozen into porous materials with certain prebuilt porosity and then freeze-dried [22], the drying rate would be promoted due to the increased area of heat and mass transfer. Generally, such a frozen material is partially filled with ice crystals like ice-cream. The objectives of the present work are to perform experimental and numerical investigations to verify the proposed idea, and to draw comparisons between experimental measurements and model predictions in an attempt to attain good agreements. This freeze-drying method is expected to decrease mass transfer resistances and drying time, and raise energy utilization rate.

2. Experimental section

2.1. Materials and facilities

In the present experiments, mannitol (analytical grade, Aladdin, China) was selected as the solute in liquid material. It is an excellent pharmaceutical excipient in structure modifying [23]. Deionized water was used as the solvent that was made in Dalian University of Technology. Liquid nitrogen was purchased from Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Facilities employed here include an analytical balance (PL403, Mettler, Switzerland), a moisture analyzer (HR83-P, Mettler, Switzerland) and a scanning electronic microscope (Quanta450, FEI, USA).

2.2. Sample preparation

Aqueous solution of mannitol was prepared with 4.48 kg/kg of the initial dry-based moisture content, corresponding to 81.77 wt % on a wet basis. The solid frozen material without prebuilt porosity was prepared by pouring the solution into a cylindrical container of 14.8 mm in diameter with a supporting pad of Teflon at bottom, and placed into an ultralow temperature freezer (148 L, Aucma, China) to freeze for at least 4 h to reach −26 ℃. The porous frozen material with certain prebuilt porosity was prepared using the liquid nitrogen ice-cream making method. Detailed preparation procedures are described as follows.

The liquid nitrogen was added slowly into the solution in a heat insulated barrel while stirring at about 400 rpm. Gasification of the liquid nitrogen absorbed a large amount of heat resulting in quick freezing of the solution. At the same time, a certain amount of the nitrogen gas was incorporated into the solution through the rapid agitation. The solution being processed was thus expanded into the ice-cream-like material partially filled with ice crystals. Such a material was then molded in a container with a pad, and quickly placed into the freezer for further freezing and hardening until it reached the preset temperature.

Before freeze-drying, the molded material was first removed from the freezer temporarily in order to separate the sample from the container, and then replaced into the freezer to sit for at least 30 min to ensure a uniformly initial temperature. Thus the sample mold was well prepared as shown in Fig. 1 and ready to be freeze-dried. Three kinds of frozen samples, the solid one with 1.00 of initial saturation and the porous ones with 0.65 and 0.28 of initial saturations were prepared with the same sample mass of 1.8 g.

2.3. Experimental tests

Experiments were conducted using a lab-scale multifunctional freeze-drying apparatus. Detailed apparatus description and experimental procedures can be found elsewhere [24]. Typical operating conditions are listed in Table 1. Radiation heating mode was adopted in the experiments. In each experimental run, the apparatus would automatically record variations of the sample weight with time at given ambient temperature of T_{amb}, and chamber pressure of P_{amb}. When there was no any change in the sample weight, the test stopped. The dried product was removed out of the chamber to measure its residual moisture content. The real-time