Drying Characteristics of Particles using Thermogravimetric Analyzer

**Yeong-Sung Park, Hyun Nam Shin, Dong Hyun Lee*,†, Duk Joon Kim*, Ji-Heung Kim*,
Young Kwan Lee*, Sang Jun Sim* and Kyong-Bin Choi****

Department of Environment Engineering, Daejeon University, Daejeon 300-716, Korea
*Department of Chemical Engineering, SungKyunKwan University, Suwon 440-746, Korea
**Industry Furnace Research Team, KIER, Daejeon 305-343, Korea

Abstract−The drying characteristics (critical moisture content, equilibrium moisture content, constant drying rate and effective diffusivity) of various particles (gypsum, millet, polyvinyl chloride and silica gel) using a thermogravimetric analyzer were measured. The experiments were performed in the gas temperature range of 40 to 100 °C under isothermal conditions. The drying rate curve was mainly dependent on the moisture content, particle size, gas temperature and the internal structure of the solid particles. The equilibrium moisture content of solid particles decreased with increasing gas temperature, while the critical moisture content and the effective dispersion coefficient increased with increasing gas temperature. The effective diffusion coefficients of both PVC and gypsum particles were not able to be determined by Fick's law since the experimental data were not well matched with the model predicted values, which consisted of the drying time in the falling-rate drying period.

Key words: Drying Characteristics, TGA, Gypsum, PVC, Millet, Silica Gel

INTRODUCTION

Drying is an important thermal process in the fine chemical, food, metallurgical, pharmaceutical and other industries [Zahed et al., 1995]. The analysis of the drying phenomenon is more complicated than that of heat or isothermal mass transfer alone [Lee and Kim, 1999; Choi et al., 2002]. Different mechanisms control the constant- and falling rate drying regimes that can be observed successively in the drying operation [Kunii and Levenspiel, 1991]. The constant-rate drying period has been associated with surface moisture on the particles and the falling-rate drying period is usually controlled by internal diffusion. The moisture content of the material in the course of drying and especially the final moisture content are very important parameters in drying technology. Under-drying may result in the formation of mildew, bacterial growth, agglomeration of particles and so on; over-drying may cause deterioration of product quality and wastage of energy [Strumillo and Kudra, 1986]. Ashworth and Carter [1980] invented a system that a null-deflection electronic analytical balance weighed continuously in a controlled air stream in a specially constructed wind-tunnel. This provided an accurate method for continuous measurement of solid-drying kinetics. They reported that no clear trend with temperature was apparent in the equilibrium moisture content of silica gel particles over the range of 20 to 70 °C. Arnaldos et al. [1998] reported results which were presented concerning the drying of two solids (millet and silica gel) in a vacuum fluidized bed. Their results revealed that the critical moisture content decreased with increasing temperature while conditions were below atmospheric pressure (0.2 bar). However, Kannan et al. [1994] observed that the critical moisture content increased with an increase in temperature. They have also reported

that the equilibrium moisture content decreased with increasing temperature at atmospheric pressure. Knowledge of drying kinetics is essential for the estimation of the drying time needed to reduce the moisture content to the desired level and for suggesting the optimal drying conditions. Therefore, the basic properties (equilibrium moisture content, critical moisture content and effective diffusion coefficient and so on) of the solid particles should be obtained accurately in the thermogravimetric analyzer.

In this paper we present the drying characteristics (critical moisture content, equilibrium moisture content, constant drying rate and effective diffusion coefficient) of various particles (gypsum, millet, polyvinyl chloride and silica gel) in the gas temperature range of 40 to 100 °C under isothermal conditions using the thermogravimetric analyzer.

THEORY

The moisture movement inside the spherical particle is defined by Fick's diffusion equation as follows [Crank, 1967]:

$$\frac{\partial C}{\partial t} = D_{eff}\left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right] \tag{1}$$

where C, D_{eff}, r and t are the moisture content, the effective diffusivity, the radius of the particle and time, respectively. The substitution parameter, u=rC is introduced, then the equation for u is

$$\frac{\partial u}{\partial t} = D_{eff}\frac{\partial^2 u}{\partial r^2} \tag{2}$$

The initial and boundary conditions are

$$u=0, r=0, t>0 \tag{3}$$

$$u = \frac{d_p}{2}C_0, \ r = \frac{d_p}{2}, \ t>0 \tag{4}$$

†To whom correspondence should be addressed.
E-mail: dhlee@skku.edu

$$u = rf(r), \ t = 0, \ 0 < r < \frac{d_p}{2} \quad (5)$$

where C_0 is the constant concentration at the surface of the sphere. If the sphere is initially at a uniform concentration, C_1 and the surface concentration is maintained constant at C_0, the solution becomes

$$\frac{C - C_1}{C_0 - C_1} = 1 + \frac{d_p}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin\left(\frac{2n\pi r}{d_p}\right) \exp\left[-\frac{4D_{eff} n^2 \pi^2 t}{d_p^2}\right] \quad (6)$$

The concentration at the center is given by the limit as $r \rightarrow 0$, that is by

$$\frac{C - C_1}{C_0 - C_1} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left[-\frac{4D_{eff} n^2 \pi^2 t}{d_p^2}\right] \quad (7)$$

The total amount of the diffusing substance leaving the sphere is given by

$$\frac{M_t}{M_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-\frac{4D_{eff} n^2 \pi^2 t}{d_p^2}\right] \quad (8)$$

where M_0 is the total amount of the unbounded moisture at constant temperature and M_t is the amount of the evaporated moisture during the elapsed time.

EXPERIMENTAL

Experiments were carried out in a thermogravimetric analyzer (TGA, Dupont 2050) as shown in Fig. 1. The experimental system consists of two sections: drying zone and weight detection zone. TGA was heated to the desired temperature under N_2 flow and a sample was placed in the sample basket suspended from an electronic balance. Sample masses varied between 35 and 50 mg case by case. The physical properties of the solid particles used in this work are given in Table 1. An electronic balance was used to monitor the weight variation of the sample with time. The signals from
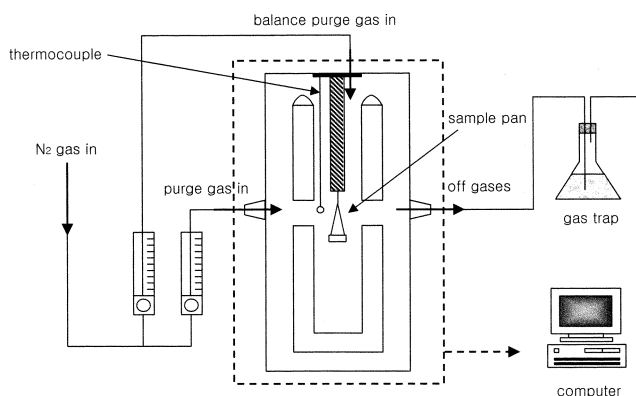
Fig. 1. Schematic diagram of thermogravimetric analyzer.

Table 1. Physical properties of various solid particles

Sample	Gypsum	Millet	PVC	Silica gel
Surface area, [m²/g]	8.83	0.26	2.53	260.5
Pore volume, [cc/g]	0.01	0.05	0.13	0.25
Mean particle diameter, [μm]	100	1,900	150	2,800
Particle density, [kg/m³]	2,300	1,340	1,400	1,650

Table 2. Experimental conditions of TGA drying test

Equipment	Dupont TGA 2050
Type of sample	Gypsum, Millet, PVC, Silica gel
Amount of sample, [mg]	30-50
Heating rate, [°C/min]	5-8
Carrier gas, [ml/min]	100 (purge/balance: 90/10)
Initial temp., [°C]	20-25
Applied temp. (isotherm), [°C]	40-100

(a) Millet (x 500) (b) Silica gel (x 500)

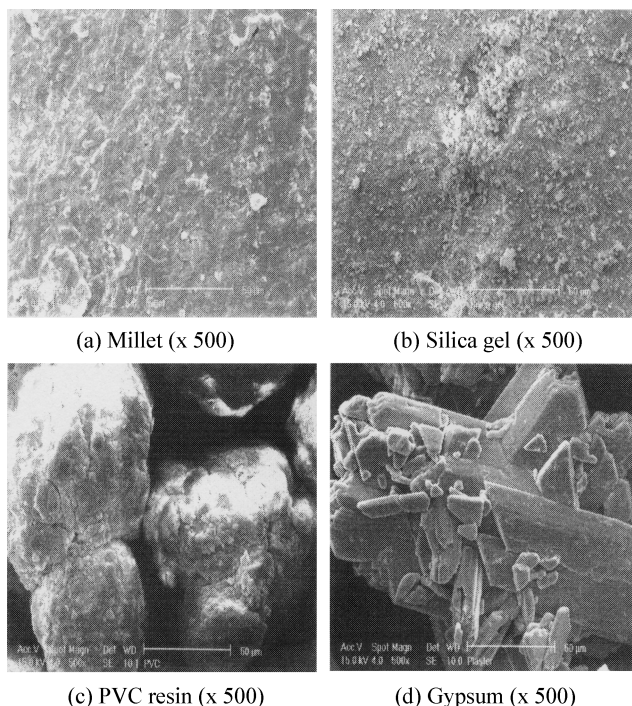(c) PVC resin (x 500) (d) Gypsum (x 500)

Fig. 2. SEM photographs of the various particles used.

the balance were recorded on a personal computer. The details of the experimental condition in TGA drying test are listed in Table 2. The SEM photographs of the various particles used are shown in Fig. 2.

RESULTS AND DISCUSSION

Drying kinetics are connected with the change of the material moisture content and the temperature with time, contrary to drying dynamics which describe changes in the temperature and moisture content profile throughout the drying body [Strumillo and Kudra, 1986]. The time profile of the moisture content of silica gel particles in the range of the constant chamber temperature (40-70 °C) is shown in Fig. 3. As can be seen, the moisture content decreases linearly with the elapsed time. Then the straight line becomes a curve which approaches the equilibrium moisture content asymptotically, C_{eq}. The first drying period is called the constant drying rate and the second, the falling drying rate period. In the constant drying rate period, the change in the moisture content of the silica gel particles with time is found from the energy where the heat loss by entering gas equals the heat transferred to the solid to vaporize the water in the silica gel particles. Furthermore, in the falling drying rate period,
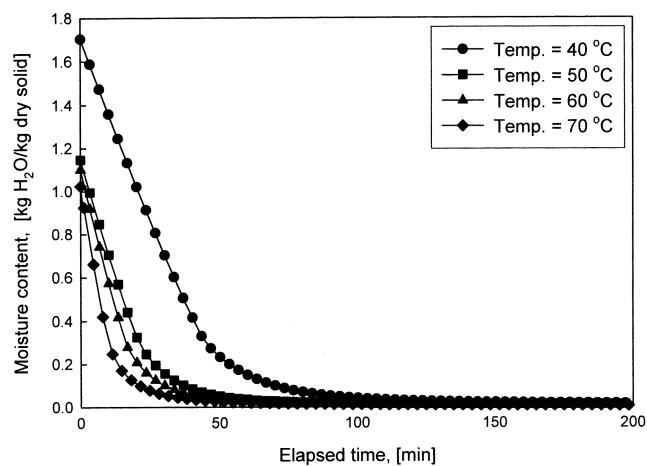
Fig. 3. Variation of moisture content of silica gel particles as a function of time elapsed.
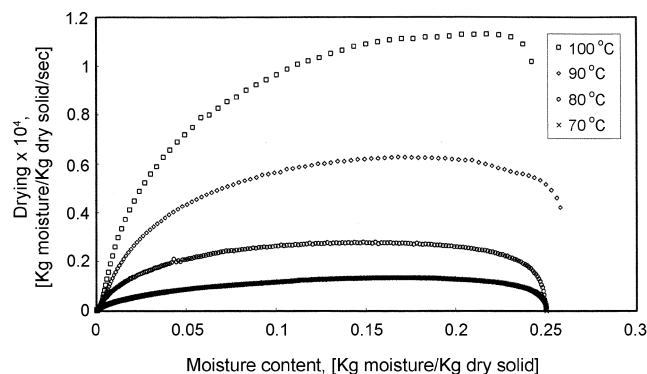

Fig. 4. Variation of drying rate as a function of the moisture content of gypsum particles.

this is a zone where the rate of water migration to the surface is limiting.

The variation of the drying rate of gypsum particles as a function of the moisture content is shown in Fig. 4. The drying rate is defined as the amount of moisture removed from the dried material in a unit time as follows [Strumillo and Kudra, 1986]:

$$R_d = \frac{dC}{dt} \qquad (9)$$

Moyers and King [1988] have pointed that the constant drying rate should only depend on velocity, humidity and temperature of the air and not on the nature of the particles. As can be seen, the constant drying rate of gypsum particles at 100 °C is higher than that of gypsum particles at 70 °C due to the entering energy. In the constant-rate period, the particle surface is sufficiently wet for the air layer adjacent to it to become saturated. During this period, the temperature of the particle surface remains nearly constant at the wet bulb temperature (T_{wb}) of air [Lee and Kim, 1993]. Constant-rate drying is usually associated with the removal of moisture from a saturated surface, and falling rate drying with internal diffusion in drying granules [Reay and Baker, 1985; Davidson et al., 2001].

The effect of the isothermal chamber temperature on the critical moisture content in the TGA is shown in Fig. 5. The critical mois-
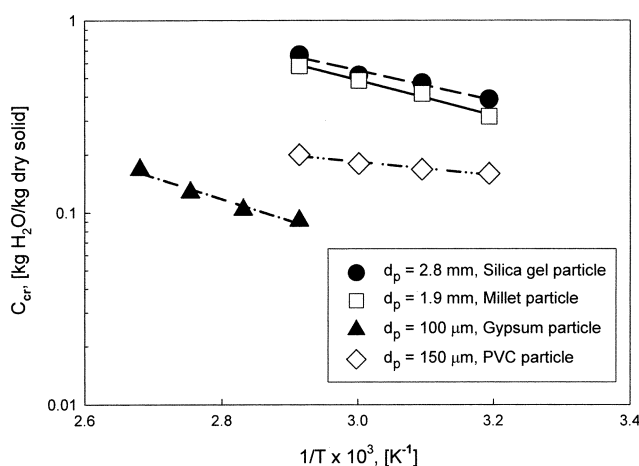

Fig. 5. Effect of the isothermal chamber temperature on the critical moisture content of the various particles in TGA.

ture content refers to the moisture content at the termination of the constant rate period and the beginning of the falling rate period. Kannan et al. [1994] observed that the critical moisture content increased with an increase in the temperature or the flow rate of the heating medium. The critical moisture content also increased with an increase in the initial moisture content of solids or a decrease in the solid holdups. Based on the experimental data, the critical moisture content on the various solid particles has been correlated with the system variables as follows:

$$\frac{C_{cr}}{C_i} = K d_p^{-0.26} U_g^{0.11} W_s^{-0.07} \exp\left[\frac{-1000}{T_{in}}\right] \qquad (10)$$

where K=11.5 for millet, 9.2 for ragi (Eleusine corocane), and 8.7 for poppy seeds. The parameter K differs with the type of materials since the critical moisture content is a function of the internal structure of particles (pore structure, surface area and so on) and the external heating conditions. Luikov [1968] mentioned that all wet materials were divided into three types, such as typical colloidal bodies, capillary-porous bodies and colloidal-capillary-porous bodies. The relative significance of the internal and external heat and mass transfer processes can be expressed by the Biot number, Bi_M, which is the ratio of external mass transfer to internal mass transfer. If $0.2 < Bi_M < 50$, both are important [Strumillo and Kudra, 1986]. As can be seen in Fig. 5, the critical moisture content increases with increasing the temperature due to increasing Bi_M.

The effect of the isothermal chamber temperature on the equilibrium moisture content of the various types of particles in the TGA is shown in Fig. 6. The equilibrium moisture content is the moisture of the solids which is in equilibrium with the vapor contained in the drying agent. This is the minimum moisture content to which a material can theoretically be dried in the given process condition [Strumillo and Kudra, 1986]. In Fig. 4, the equilibrium moisture content of solids is noted from the intersection of the drying rate curve with the abscissa. The equilibrium moisture content is a function of the temperature and humidity conditions [Mujumdar and Devahastin, 2003]. As can be seen in Fig. 6, the equilibrium moisture content of the solids decreases with increasing temperature. Also, Kannan et al. [1994] reported that the equilibrium moisture content was empirically related to the air temperature, as
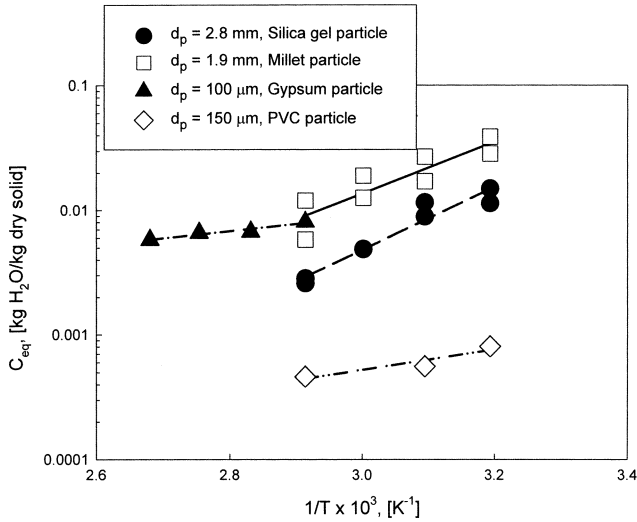
Fig. 6. Effect of the isothermal chamber temperature on the equilibrium moisture content of the various particles in TGA.

$$C_{eq} = K\exp\left[\frac{2000}{T_{in}}\right] \qquad (11)$$

Where $K=1.4\times10^{-4}$ for ragi, 3×10^{-4} for millet and 5×10^{-5} for puppy seeds. The relative humidity decreases with increasing temperature due to increasing the saturation vapor pressure. The equilibrium moisture content is proportional to the moisture content at a given relative humidity [Keey, 1978]:
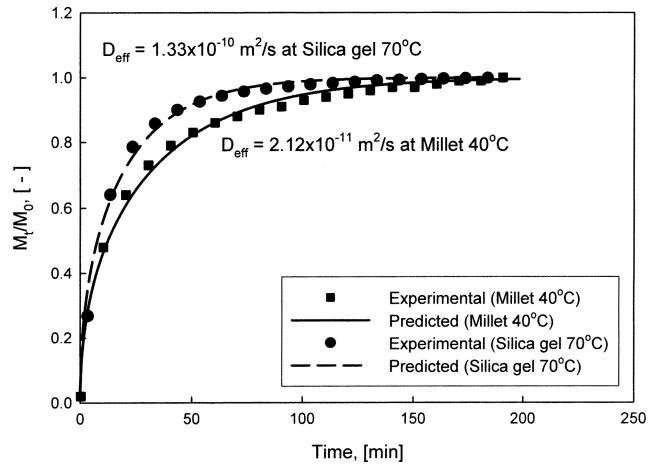

Fig. 7. Typical curve on the ratio of the total amount of the evaporated moisture, M_t/M_0 as a function of the time elapsed with the predicted value of Eq. (8).

$$\left(\frac{\partial C_{eq}}{\partial T}\right)_{\varphi} = -AC_{eq} \qquad (12)$$

The coefficient A lies between 0.005 and 0.01 K^{-1} for a relative humidity between 0.1 and 0.9 for materials such as natural and synthetic fibers, wood and potatoes. Therefore, the equilibrium moisture content of solids decreases with increasing temperature.

Fig. 7 shows a typical curve on the ratio of the total amount of the evaporated moisture, M_t/M_0 during the elapsed time with the
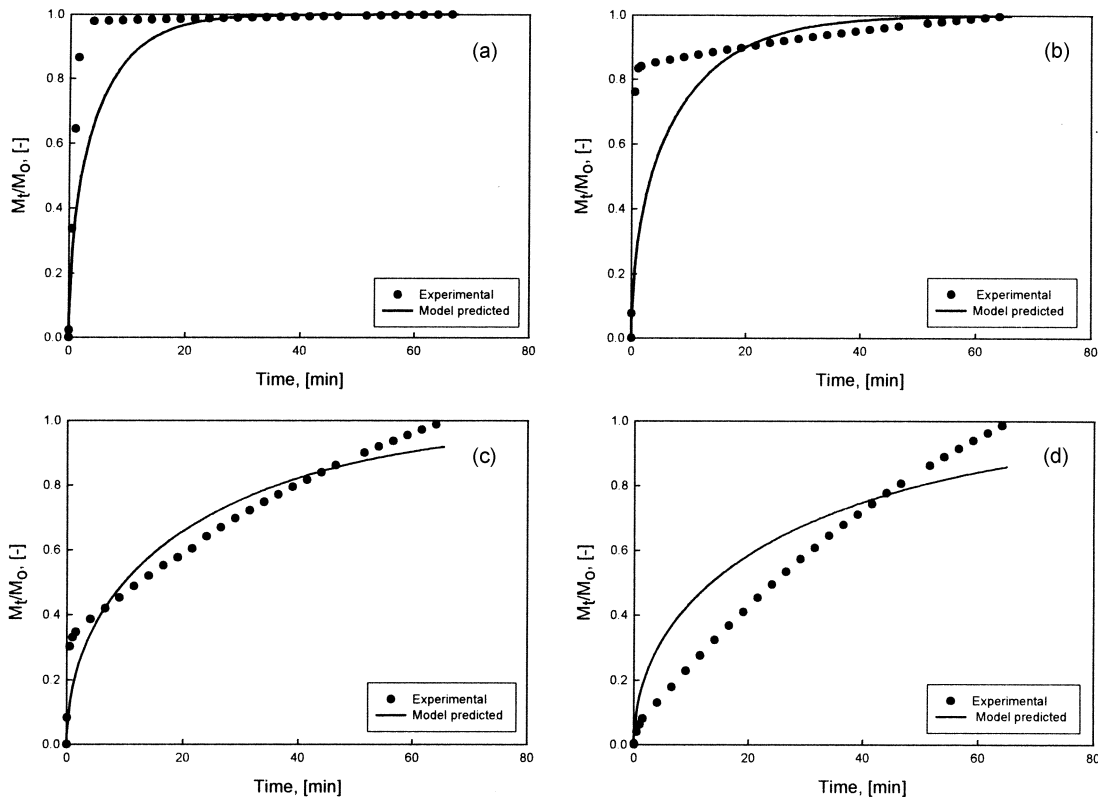

Fig. 8. Four time trials tested to optimize the effective diffusion coefficient of PVC particles at 70 °C.
(a) $C=C_{cr}=0.2$ kg H_2O/kg dry solid, (b) $C=0.1$ kg H_2O/kg dry solid, (c) $C=0.05$ kg H_2O/kg dry solid, (d) $C=0.03$ kg H_2O/kg dry solid

predicted values of Eq. (8). M_o is the total amount of the unbounded moisture at constant temperature and M_t is the amount of evaporated moisture during the elapsed time. As can be seen, the ratio of the total amount of the evaporated moisture increased with increasing the elapsed time and reached at 1.0. To predict the model parameter, D_{eff}, Eq. (8) was used by the Levenverg-Marquardt method. The predicted effective diffusion coefficients are 1.33×10^{-10} and 2.12×10^{-11} for silica gel at 70 °C and millet at 40 °C, respectively. As can be seen, the model predicted values are well matched with the experimental data. However, the model predicted values of PVC and gypsum particles are not well matched with the experimental data since the experimental value of M_t/M_0 increases sharply with the elapsed time. As can be seen in Fig. 8, four time trials are tested to optimize the effective diffusion coefficient of PVC particles at 70 °C. In Fig. 8(a), the initial moisture content is the critical moisture content, $C_{cr}=0.224$ kg water/kg dry solid. The initial moisture contents of Fig. 8(b), (c) and (d) are 0.118, 0.015, 0.004 kg water/kg dry solid, respectively. These values are lower than that of the critical moisture content of PVC particles at 70 °C. But all curves on M_t/M_o of PVC particles show severe deviation from the experimental data.

The effect of the temperature on the effective diffusion coefficient of the millet and silica gel particles is shown in Fig. 9. Kannan et al. [1995] have mentioned that the effective diffusion coefficients were found to depend on air temperature and the material itself. Moisture in a drying body can be transferred both in liquid and in gaseous phases. In general, the following main modes of moisture transport can be distinguished: transport by liquid diffusion, transport by vapor diffusion, transport by Knudsen type diffusion, transport by thermodiffusion, transport by capillary forces, transport by osmotic pressure and transport due to pressure gradient. However, transport by vapor diffusion is the main mechanism of vapor moisture transfer in the material. The qualitative effect of this transfer can be described by an equation of the Fick type, using instead of the kinematic diffusion coefficient, D_{AB}, the effective diffusion coefficient, D_{eff} in capillary-porous materials [Strumillo and Kudra, 1986].

$$D_{eff} = D_e D_{AB} \qquad (13)$$

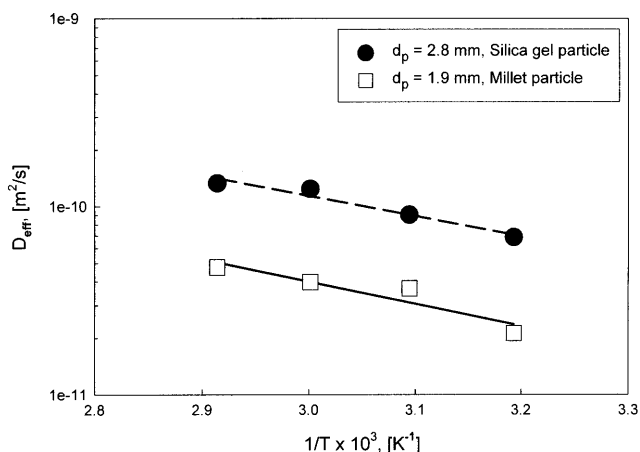where D_e is the equivalent coefficient of diffusion in a capillary-porous material. The most general relation for the determination of D_e was given by Van Brakel and Heertjes [1974]:

$$D_e = \frac{\varepsilon \delta}{\varepsilon_e} \qquad (14)$$

The value of D_e is present as a function of the structural parameters. The kinematic diffusion coefficient, D_{AB} is inversely proportional to the pressure, increases with increasing temperature, and is almost independent of the composition for a given gas-pair [Bird et al., 2002]. Therefore, the effective diffusion coefficient increases with increasing temperature and depends on the material structures.

CONCLUSION

The drying characteristics (critical moisture content, equilibrium moisture content, constant drying rate and effective diffusivity) of various particles (gypsum, millet, polyvinyl chloride and silica gel) were measured with a thermogravimetric analyzer. The equilibrium moisture content of solid particles decreased with increasing gas temperature, while the critical moisture content and the effective dispersion coefficient increased with increasing gas temperature. The effective diffusion coefficients of both PVC and gypsum particles were not able to be determined by Fick's law since the experimental data were not well matched with the model predicted values with drying time in the falling-rate drying period.

ACKNOWLEDGMENT

NOMENCLATURE

A   : coefficient in Eq. (12) [-]
Bi_M : Biot number of mass transfer [-]
C   : moisture content [kg H_2O/kg dry solid]
C_{cr} : critical moisture content [kg H_2O/kg dry solid]
C_{eq} : equilibrium moisture content [kg H_2O/kg dry solid]
C_i : initial solid moisture content [kg H_2O/kg dry solid]
D_{AB} : kinematic coefficient of diffusion [-]
D_e : equivalent diffusion coefficient [m/s²]
D_{eff} : effective diffusion coefficient [m/s²]
d_p : particle diameter [m]
K   : adjustable parameter [-]
M_t : total amount of unbounded moisture at constant temperature [kg H_2O]
M_0 : amount of the evaporated moisture during the elapsed time [kg H_2O]
r   : radius of particle [m]
R_d : drying rate [kg H_2O/kg dry solid/s]
T   : temperature [K]
t   : time [min]
T_{in} : inlet temperature [°C]
T_{wb} : wet bulb temperature [°C]

Fig. 9. Effect of the isothermal chamber temperature on the effective diffusion coefficient of millet and silica gel particles.

Plot legend:
● d_p = 2.8 mm, Silica gel particle
□ d_p = 1.9 mm, Millet particle

Y-axis: D_{eff}, [m²/s]
X-axis: 1/T × 10³, [K⁻¹]

u   : substitution parameter [-]
U_g : superficial gas velocity [m/s]
W_s : solid weight [kg dry solid]

Greek Letters

ε : internal void fraction [-]
ε_e : tortuosity factor [-]
φ : relative humidity [-]

REFERENCES

Ashworth, J. C. and Carter, J. W., "Examination of Drying Behaviour of Silica-Gel Granules by Continuous Weighing in an Airstream," Drying 1980, Vol. 1, Mujumdar, A. S., Ed., Hemisphere Publishing Corp., London (1980).

Arnaldos, J., Kozanoglu, B. and Casal, J., "Vacuum Fluidization: Application to Drying," Fluidization, IX, Fan, L. S. and Knowlton, T. M., Eds., New York, Engineering Foundation (1998).

Bird, R. B., Stewart, W. E. and Lightfoot, E. N., "Transport Phenomena," John Wiley, New York (2002).

Choi, K. B., Park, S. I., Park, Y. S., Sung, S. W. and Lee, D. H., "Drying Characteristics of Millet in a Continuous Multistage Fluidized Bed," *Korean J. Chem. Eng.*, **19**, 1106 (2002).

Crank, J., "The Mathematics of Diffusion," Oxford University Press, Oxford (1967).

Davidson, J. F., Thorpe, R. B., Al-Mansoori, O., Kwong, H., Peck, M. and Williamson, R., "Evaporation of Water from Air-Fluidized Porous Particles," *Chem Eng. Sci.*, **56**, 6089 (2001).

Kannan, C. S., Rao, S. S. and Verma, Y. B. G., "A Kinetic Model for Drying of Solids in Batch Fluidized Beds," *Ind. Eng. Chem. Res.*, **33**, 363 (1994).

Kannan, C. S., Thomas, P. P. and Verma, Y. B. G., "Drying of Solids in Fluidized Beds," *Ind. Eng. Chem. Res.*, **34**, 3068 (1995).

Keey, R. B., "Introduction to Drying Operations," Pergamon Press, Oxford (1978).

Kunii, D. and Levenspiel, O., "Fluidization Engineering," Butterworth-Heinemann Publication, Boston (1991).

Lee, D. H. and Kim, S. D., "Drying Characteristics of Starch in an Inert Medium Fluidized Bed," *Chem. Eng, Technol.*, **16**, 263 (1993).

Lee, D. H. and Kim, S. D., "Mathematical Model for Batch Drying in an Inert Medium Fluidized Bed," *Chem. Eng. Technol.*, **22**, 443 (1999).

Luikov, A. V., "Drying Technology," Energia, Moscow (1968).

Moyers, C. G. and King, C. J., "Drying-Relating Principles to Design," AIChE Continuing Education Series (1988).

Mujumdar, A. S. and Davahastin, S., "Applications for Fluidized Bed Drying," Handbook of Fluidization and Fluid-Particle Systems, Chap. 18, Eds. W. C. Yang, Marcel Dekker Inc., New York (2003).

Reay, D. and Baker, C. G., "Drying," Fluidization, Davidson, J. F., Clift, R. and Harrison, D., Eds., Academic Press (1985).

Strumillo, C. and Kudra, T., "Drying: Principles, Applications and Design," Gordon and Breach Science Publishers, New York (1986).

Van Brakel, J. and Heertjes, P. M., "Analysis of Diffusion in Macroporous Media in Terms of a Porosity, a Tortuosity and a Constrictivity Factor," *Int. J. Heat and Mass Transfer*, **17**, 1093 (1974).

Zahed, A. H., Zhu, J. X. and Grace, J. R., "Modeling and Simulation of Batch Fluidized Bed Dryers," *Drying Technology*, **13**, 1 (1995).