바이오시스템공학 (*J. of Biosystems Eng.*)
Vol. 33, No. 5, pp. 296~302 (2008. 10)

# 유채 종자의 수분확산계수에 관한 연구

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# Estimation of Effective Moisture Diffusivity of Rapeseed (*Brassica napus* L.)

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## Abstract

The effective moisture diffusivity and its dependence on drying temperature during drying of rapeseed were experimentally investigated. The data were recorded from thin layer drying experiments at nine different combinations of drying air temperatures of 40, 50, and 60℃ and the relative humidities of 30, 45, and 60%.

The moisture diffusion equation was analyzed using stepwise multiple regression analysis. Effective moisture diffusivities were calculated based on the moisture diffusion equation for a spherical shape using Fick's second law. The effective diffusivities during the drying of rapeseed were $1.72\times10^{-11}$, $2.41\times10^{-11}$ and $3.31\times10^{-11}$ $m^2\cdot s^{-1}$ at 40, 50 and 60℃, respectively. The activation energy for moisture diffusion during drying was 28.47 $kJ\cdot mol^{-1}$. The dependence of moisture diffusivity on temperature was described by an Arrhenius-type equation. Drying occurred in the falling rate period and the internal moisture diffusion phenomenon is the governing physical mechanism of the moisture movement in the particles.

**Keywords** : Rapeseed, Moisture ratio, Diffusion coefficient, Diffusivity, Activation energy

## 1. INTRODUCTION

Rapeseed (*Brassica napus Linnaeus*) was cultivated in Korea for bio-diesel production. Rapeseed is usually harvested with a moisture content that is higher than what is safe for storage. Therefore, drying is an important post-harvest treatment prior to optimal storage. The drying process causes moisture to move from the depths of the grain to the exposed surface and then evaporate. A complete drying profile consists of two drying stages: a constant rate period and a falling rate period. However, not all grains follow this pattern. In most applications the falling rate period is dominant. In this case, the moisture flow within a grain kernel takes place by diffusion of liquid and/or vapor during drying (Brooker et al., 1974).

In spite of numerous experimental studies on the determination of drying profiles for various grain, only a small number of modeling studies have been carried out analyzing water diffusivity in grains during drying. In the analysis of falling rate drying period, a simple diffusion model based on Fick's second law of diffusion was considered for the evaluation of moisture transport. Diffusion of moisture is generally enhanced by the drying air temperature and has an exponential relationship (Arrhenius-type) with the inverse of the air temperature. However, the effect of relative humidity is not clearly established. Drying of many grain products such as rice, sorghum, corn kernels and sunflower (Danae et al., 2000), wheat (Debabandya and Srinivasa, 2004), green beans (Doymaz, 2005), peanuts (Palacios et al., 2004) have been successfully predicted using Fick's second law with an

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The article was submitted for publication on 2008-08-29, reviewed on 2008-09-22, and approved for publication by editorial board of KSAM on 2008-09-30. The authors are Le Anh Duc, Researcher, Sang Jin Hong, Researcher, Jae Woong Han, Research Professor, and Dong Hyuk Keum, Professor, Dept. of Bio-Mechatronic Engineering, SungKyunKwan University, Korea. Corresponding author: D. H. Keum, Professor, Dept. of Bio-Mechatronic Engineering, SungKyunKwan University, Suwon, 440-746, Korea; E-mail: <dhkeum@skku.ac.kr>.

Arrhenius-type temperature dependent diffusivity. However, no literature was found pertaining to drying profiles of rapeseed.

An effective diffusion coefficient, combining the vapor and bound water diffusion, is used to determine the rate of moisture movement. The prediction of moisture diffusion parameters of grains is important component of deep-bed drying models and is essential for an analysis of mass transfer processes in storage. Therefore, the objectives of this study were to analyze and estimate effective moisture diffusivity, activation energy for moisture diffusion of rapeseed and its dependence on temperature using Fick's second law of diffusion.

## 2. MATERIALS AND METHODS

### A. Sample Preparation and Experimental Procedures

After harvesting, all rapeseed samples were cleaned, sealed in double layers of polythene bags, and stored in a refrigerator at 4℃ (Cassells et al., 2003). Before starting the experiments, the samples were taken from the refrigerator and kept at room temperature for about 24 h, so that the samples had reached in thermal equilibrium (ANSI/ASAE S448.1, 2004). The moisture content of the samples was determined using the drying oven method: 10 g in a drying oven at 130℃ for 4 hours (ASAE S352.2).

The experiments for the thin layer drying were completely randomized. Nine different combinations of three temperature levels (40, 50, and 60℃) and three relative humidity levels (30, 45, and 60%) with three replicates for each of the nine test conditions were preformed for 36 tests in total.

Each experimental replication used a sample of about 200 g of rapeseed. The seed sample was distributed uniformly on the drying tray surface, with a thickness of approximately 0.5 cm, so as to fully expose it to the stream of drying air. The change in moisture content, relative to drying time, can be calculated based on the mass change. When the samples were reached at the predetermined moisture content, the experiment was stopped. We selected a final moisture content of 8% (d.b.) as being ideal for safe rapeseed storage. Thin layer apparatus and instruments were described in detail by Han et al. (2006).

### B. Moisture Diffusion Model

In general, drying of grains takes place in two periods, a constant rate and falling rate period. After a short heating period, a constant rate period was followed by a falling rate period, which is a dominating period during drying processes. The mechanism of moisture movement within a hygroscopic solid during the falling rate period could be represented by effective moisture diffusion phenomenon according to a diffusion model (Dincer and Dost, 1995).

The governing equation of axisymmetric diffusion equation in two-dimensions is given as follows (Crank, 1975):

$$D_{eff}\left(\frac{\partial^2 M}{\partial r^2}+\frac{\partial M}{r\partial r}+\frac{\partial^2 M}{\partial z^2}\right)=\frac{\partial M}{\partial t} \tag{1}$$

where: $D_{eff}$ : effective moisture diffusivity within particle ($m^2 \cdot s^{-1}$)

M : moisture content (%, dry basis)

r : radial coordinate (m)

z : axial coordinate (m)

t : time variable (s)

Analytical solution for simplified geometry: rapeseed is considered as a sphere (Duc et al., 2008). Therefore, the spatial component of the diffusion equation is assumed as one-dimensional in this study. The following assumptions were made for using Equation (1) with the spherical shaped bodies (Crank, 1975):

- Moisture is initially uniformly distributed throughout the mass of the sample
- Mass transfer is symmetric with respect to the center of the sphere.
- Surface moisture content of the sample instantaneously reaches equilibrium with the condition of surrounding air.
- Resistance to mass transfer at the surface is negligible compared to internal resistance of the sample.
- Mass transfer is by diffusion only.
- Diffusion coefficient is constant and shrinkage is negligible.

Therefore, the diffusion Equation (1) can be written as Equation (2):

$$D_{eff}\left(\frac{\partial^2 M}{\partial r^2}+\frac{2}{r}\frac{\partial M}{\partial r}\right)=\frac{\partial M}{\partial t} \tag{2}$$

Analytical solutions of Equation (2) for spherical bodies can be obtained directly by the following Equation (3) proposed by Crank (1975):

$$MR=\frac{M_t-M_e}{M_o-M_e}=\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2 D_{eff}\pi^2 t}{r^2}\right) \tag{3}$$

$$\ln(MR)=\ln\left(\frac{6}{\pi^2}\right)+\ln\left\{\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2 D_{eff}\pi^2 t}{r^2}\right)\right\} \tag{4}$$

Where, MR : moisture ratio (dimensionless)
$M_e$ : equilibrium moisture content (%, dry basis)
$M_o$ : initial moisture content (%, dry basis)
t : drying time (s or h)
n : number of terms of the infinite series
r : radius of seed (m)

### C. Statistical Analysis of Data

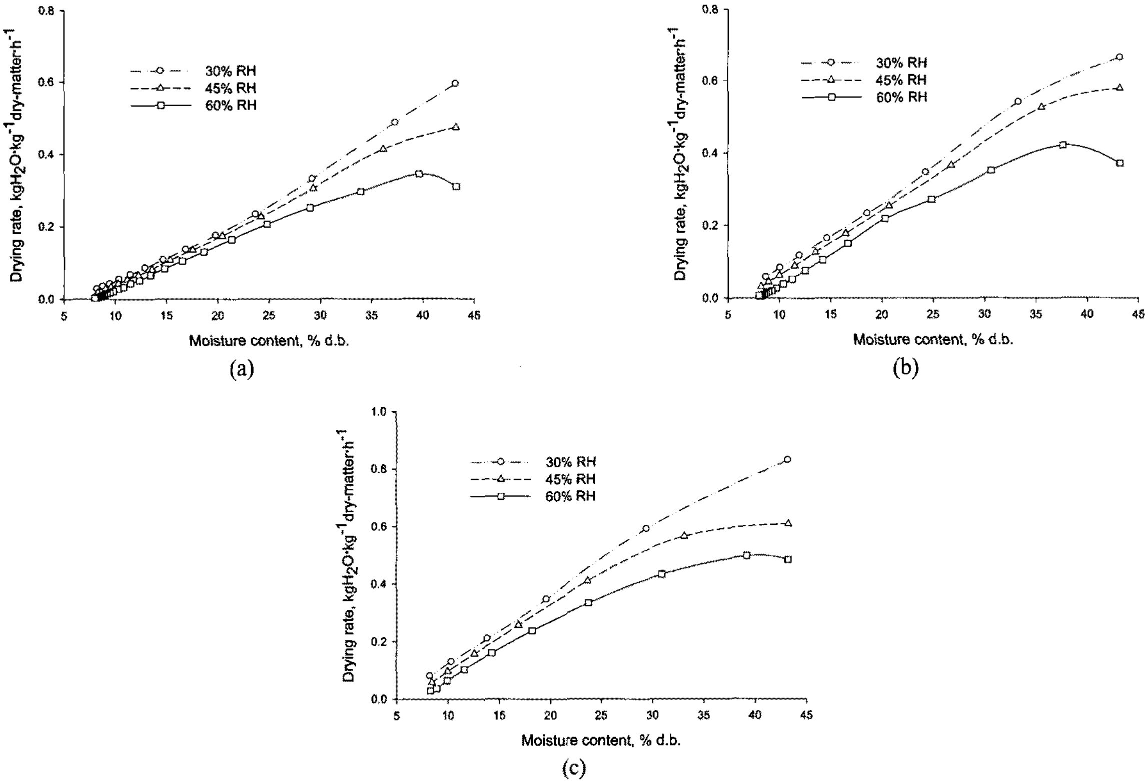
Effective moisture diffusivity was calculated based on the diffusion equation for a spherical shape using the Fick's second law. The effect of drying temperature on moisture diffusivity was determined by an Arrhenius-type equation using linear regression analysis. The models were analyzed by a stepwise multiple regression method, using the Statistical Analysis System (SAS ver. 9.1) program.

The observed and predicted values were compared and statistically analyzed for determining the fitted equation. The coefficient of determination ($R^2$) and the root mean square error (RMSE) were used as the criteria to determine the quality of the fit. The higher the $R^2$ value and the lower the RMSE value, the higher the model's accuracy.

## 3. RESULTS AND DISCUSSION

### A. The Characteristics of the Drying Process

The drying characteristics of rapeseed were determined by plotting the drying rate versus the moisture content under different drying conditions (Fig. 1). It showed that the drying process occurred in the falling rate period under all conditions except for the drying rate curves at 40, 50, and 60℃ with 60% relative humidity. These curves are indicated by the two distinct drying periods, namely an initial transitional



(a) (b) (c)

Fig. 1 Effect of drying conditions on drying rate at (a) 40℃; (b) 50℃; (c) 60℃.

warm-up period, at which a slight increase in drying rate takes place in a very short time, and a falling rate period, as shown by the rapid decrement of the drying rate. For the remaining curves, the falling rate period was only detected and no constant drying rate period was observed, which suggests that an internal moisture diffusion phenomenon is the governing physical mechanism of the moisture movement process (Vijayaraj et al., 2007).

The drying rate at the beginning of the process was higher because of initial water for evaporation exists on the surface and comes from regions near the surface of seed. Subsequently, the drying rate decreased with decreasing moisture content because water to be evaporated comes from parenchymal cells within the structure and must be moved to surface. Resistance to water movement may exist due to shrinkage at the surface of the seed, which reduces the drying rate considerably. Therefore, it can be considered that the rate of moisture removal is limited by diffusion of moisture from inside to the surface of the seed.

## B. Effective Moisture Diffusivity

As analyzed in the above section, the drying of rapeseed was found in the falling rate period. Therefore the value of the effective moisture diffusivities were calculated using a simple diffusion model based on Fick's second law.

The effective moisture diffusivities were determined by Equation (3) assuming that the radius is constant throughout the drying process. The value of the radius of rapeseed was determined in our previous study to be $r = 1.105 \times 10^{-3}$ m (Duc et al., 2008).

The values of effective moisture diffusivity were represented in Table 1. The diffusion coefficients for various values of temperature were shown in Fig. 2. They showed that effective moisture diffusivity increased with increasing drying air temperature and decreased with increasing relative humidity.

**Table 1** Effective moisture diffusivity under different drying conditions

| Temp. (℃) | RH (%) | $D_{eff} \times 10^{-11}$ ($m^2 \cdot s^{-1}$)*** |
|---|---|---|
| 40 | 30 | 2.1 |
| | 45 | 1.8 |
| | 60 | 1.2 |
| 50 | 30 | 3.0 |
| | 45 | 2.5 |
| | 60 | 1.8 |
| 60 | 30 | 4.2 |
| | 45 | 3.2 |
| | 60 | 2.5 |

****P-value* < 0.001

To estimate the effective moisture diffusivity of the seeds as a function of temperature and relative humidity, the following statistical model was fitted to the experimental data:

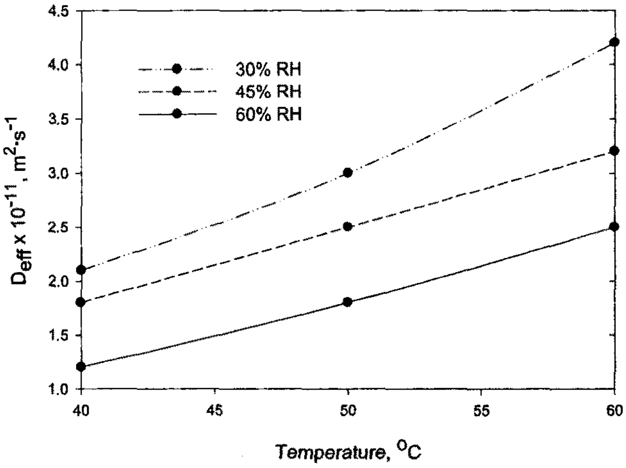


**Fig. 2** Diffusion coefficients for various values of temperature.

$$D_{eff} = a_0 + a_1 \times T + a_2 \times RH + a_3 \times T^2 + a_4 \times RH^2 + a_5 \times T \times RH \quad (5)$$

Where, T : drying air temperature (℃)

RH : relative humidity (%)

$a_0$, $a_1$, $a_2$, $a_3$, $a_4$, $a_5$: the regression constants.

Statistical analysis has shown that the effective moisture diffusivity of rapeseed was significantly affected by the drying conditions over the entire range of data (P-value < 0.001). The effective moisture diffusivity was estimated for each corresponding drying condition as a function of temperature and relative humidity were described by fitting Equation (5) with high $R^2$ and low RMSE as Equation (6).

$$D_{eff} = 1.366 \times 10^{-11} + 1.183 \times 10^{-14} \times T^2 - 8.558 \times 10^{-13} \times RH \times T \quad (6)$$

($R^2 = 0.989$; RMSE = 0.0036)

Generally, an effective diffusivity is used due to limited information on the mechanism of moisture movement during drying and complexity of the process (Kashaninejad et al., 2007). The logarithm of moisture ratio values ln (MR) was plotted against drying time (t) according to Equation (4) for different drying conditions is shown in Fig. 3. It is noted from the figure that the relationships were non-linear under all the drying conditions studied. This non-linearity in the relationship may be due to the reasons like shrinkage in the seed, variation in moisture diffusivity with moisture content and change in seed temperature during drying (Sharma and Prasad, 2004).

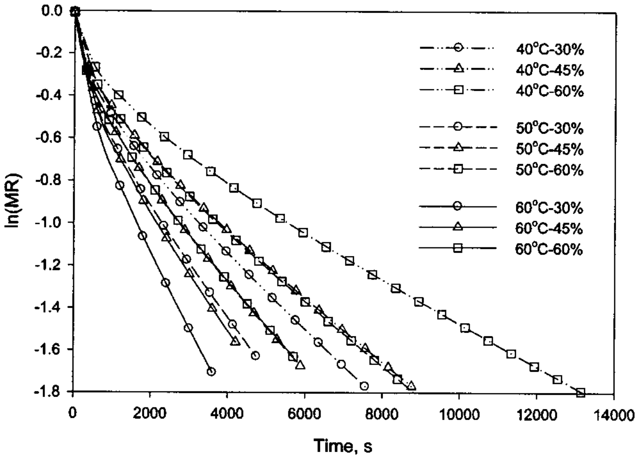


**Fig. 3** Logarithmic moisture ratio versus time at different drying conditions.

A second-order polynomial relationship between ln(MR) and drying time (t) was fitted well and was given below:

$$\ln(MR) = a_o + a_1 t + a_2 t^2 \tag{7}$$

Regression coefficients $a_o$, $a_1$ and $a_2$ and the coefficient of determination ($R^2$) and the root mean square error (RMSE) for different drying conditions are presented in Table 2. Almost the $R^2$ values are higher than 0.99, and RMSE values are lower than 0.05, this results indicated the goodness of fit of Equation (7).

## C. The Effect of Drying Temperature on Effective Moisture Diffusivity

The dependence of effective moisture diffusivity on the drying air temperature can be described by an Arrhenius-type equation to obtain a better agreement between the predicted values and the experimental data (Debabandya and Srinivasa, 2004; Dincer and Dost, 1995; Muir et al., 1991; Steffe and Singh, 1980). They reasoned that temperature is not a function of radial position in the seed under normal drying conditions and diffusivity varies mainly with temperature. The Arrhenius-type equation is written as:

$$D_{eff} = D_o \exp(-\frac{E_a}{R\,T_{abs}}) \tag{8}$$

Where, $D_o$ : diffusivity constant (equivalent to the diffusivity at infinitely high temperature)

$E_a$ : activation energy for moisture diffusion ($kJ \cdot mol^{-1}$)

R : universal gas constant, $R = 8.314 \times 10^{-3}\ kJ \cdot K^{-1} \cdot mol^{-1}$

$T_{abs}$: absolute temperature (K)

and can be linearized by applying logarithms as:

$$\ln(D_{eff}) = \ln(D_o) - \frac{E_a}{R\,T_{abs}} \tag{9}$$

Using the analytic method already described, the values of moisture diffusivity as a function of temperature were then fitted to the Arrhenius-type equation, producing:

$$D_{eff} = 9.598 \times 10^{-7} \exp(-\frac{3423.8}{T + 273.15}) \tag{10}$$

**Table 2** Regression coefficients, $R^2$ and RMSE for different drying conditions of Equation (7)

| Temp. (℃) | RH (%) | $a_o$ | $a_1$ | $a_2 \times 10^{-8}$ | $R^2$ | RMSE |
|---|---|---|---|---|---|---|
| 40 | 30 | -0.1334 | -0.0003 | 1.3172 | 0.9914 | 0.0479 |
| | 45 | -0.1399 | -0.0003 | 0.9597 | 0.9917 | 0.0462 |
| | 60 | -0.1955 | -0.0002 | 0.2286 | 0.9943 | 0.0448 |
| 50 | 30 | -0.0946 | -0.0005 | 3.5845 | 0.9899 | 0.0498 |
| | 45 | -0.1135 | -0.0004 | 2.2399 | 0.9901 | 0.0492 |
| | 60 | -0.1746 | -0.0002 | 0.5697 | 0.9931 | 0.0501 |
| 60 | 30 | -0.0714 | -0.0007 | 6.7348 | 0.9912 | 0.0509 |
| | 45 | -0.0790 | -0.0005 | 4.6366 | 0.9900 | 0.0482 |
| | 60 | -0.1143 | -0.0004 | 2.3248 | 0.9906 | 0.0479 |

**Table 3** Effective moisture diffusivity and activation energy for drying of various grains

| Grains | Drying Temp. (℃) | $D_{eff}$ ($m^2 \cdot s^{-1}$) | $E_a$ ($kJ \cdot mol^{-1}$) | References |
|---|---|---|---|---|
| Rapeseed | 40~60 | $1.72 \times 10^{-11} \sim 3.31 \times 10^{-11}$ | 28.47 | Present work. |
| Peanut | 20~40 | $1.89 \times 10^{-11} \sim 4.12 \times 10^{-11}$ | 27.22 | Palacios et al. (2004). |
| Rice | 30~50 | $0.4 \times 10^{-11} \sim 9.0 \times 10^{-11}$ | | Danae et al. (2000). |
| Corn kernel | 50~60 | $8.0 \times 10^{-11} \sim 1.0 \times 10^{-10}$ | | Danae et al. (2000). |
| Sunflower kernel | 40~50 | $7.0 \times 10^{-11} \sim 1.7 \times 10^{-10}$ | | Danae et al. (2000). |
| Sorghum | 20~50 | $0.9 \times 10^{-11} \sim 3.0 \times 10^{-11}$ | | Danae et al. (2000). |
| Green beans | 50~70 | $2.64 \times 10^{-9} \sim 5.71 \times 10^{-9}$ | 35.43 | Doymaz (2005). |
| Parboiled wheat | 40~60 | | 37.01 | Debabandya and Srinivasa (2004). |

The effective diffusivities during the drying of rapeseed were $1.72 \times 10^{-11}$, $2.41 \times 10^{-11}$ and $3.31 \times 10^{-11}$ $m^2 \cdot s^{-1}$ at 40, 50 and 60℃, respectively. The values of $D_{eff}$ increased progressively with increasing drying air temperature and this reduced drying time.

## D. Activation Energy

With fitting data for diffusivity to the Arrhenius-type equation based on drying air temperature, obtained activation energy for moisture diffusion ($E_a$) of rapeseed during drying was 28.47 $kJ \cdot mol^{-1}$. The value of activation energy of rapeseed is higher than peanut and lower than green bean and parboiled wheat. Effective moisture diffusivities found in this study were well within the range $10^{-9}$ to $10^{-11}$ $m^2 \cdot s^{-1}$ for drying of grain products (Debabandya and Srinivasa, 2004). The values of $D_{eff}$ and Ea lie within the general range as reported in the literature (Table 3). It can be seen that the values of $D_{eff}$ increased with increasing temperature, the higher drying temperature gave the higher $D_{eff}$ value for all kinds of grains.

# 4. CONCLUSIONS

The effective moisture diffusivity of rapeseed was determined experimentally. The analytic results illustrated that the drying of rapeseed occurred during the falling rate period and that no constant rate period was observed in this study. This indicated that a diffusion phenomenon was the governing physical mechanism of moisture movement in the rapeseed particles.

The moisture diffusion model was obtained. The influence of the drying temperature on the effective moisture diffusivity was satisfactorily described by an Arrhenius-type equation. The effective moisture diffusivity was also calculated to understand the mass transfer mechanism of rapeseed. The activation energy for moisture diffusion of rapeseed was calculated using exponential expression based on Arrhenius equation.

# REFERENCES

1. ASAE S352.2. 2004. Moisture measurement - Unground grain and seeds. ASAE standards 51st Edition 582-583.
2. ANSI/ASAE S448.1. 2004. Thin-layer drying of agricultural crops. ASAE standards 51st Edition 598-600.
3. Brooker, D. B., F. W. Bakker-Arkema and C. W. Hall. 1974. Drying Cereal Grains. The AVI Publishing Company Inc., Westport, Connecticut.
4. Cassells, J. A., L. P. Caddick, J. R. Green and R. Reuss. 2003. Isotherms for Australian canola varieties. Proceedings of the Australian Postharvest Technical Conference, pp. 59-63.
5. Crank, J. 1975. The Mathematics of Diffusion (Second edition). Oxford University Press, Ely House, London, W.I.
6. Danae, D., K. Tzia and V. Gekas. 2000. A knowledge base for the apparent mass diffusion coefficient ($D_{eff}$) of foods. International Journal of Food Properties 3(1):1-14.
7. Debabandya, M. and R. P. Srinivasa. 2004. A thin layer drying model of parboiled wheat. Journal of Food Engineering 66: 513-518.
8. Dincer, I. and S. Dost. 1995. An analytical model for moisture diffusion in solid objects during drying. Drying Technology 13(1&2):425-435.
9. Doymaz, I. 2005. Drying behaviour of green beans. Journal of Food Engineering 69:161-165.
10. Duc, L. A., J. W. Han, S. J. Hong, H. S. Choi, Y. H. Kim and D. H. Keum. 2008. Physical properties of rapeseed (I). Journal of Biosystems Engineering 33(2):101-105. (In Korean).
11. Han, J. W., D. H. Keum, H. Kim and S. E. Lee. 2006. Thin layer drying model of green rice. Journal of Biosystems Engi-

neering 31(5):410-415. (In Korean).

12. Kashaninejad, M., A. Mortazavi, A. Safekordi and L. G. Tabil. 2007. Thin-layer drying characteristics and modeling of pistachio nuts. Journal of Food Engineering 78:98-108.
13. Muir, W. E., R. N. Sinha, Q. Zhang and D. Tuma. 1991. Near-Ambient drying of canola. Transactions of the ASAE 34(5):2079-2084.
14. Palacios, T. R., L. B. Potes, R. A. Montenegro and S. A. Giner. 2004 Peanut drying kinetics: determination of the effective diffusivity for in-shell and shelled peanuts by applying a short-time analytical model to measured data. Proceedings of the 14th International Drying Symposium B:1448-1455.
15. Sharma, G. P. and S. Prasad. 2004. Effective moisture diffusivity of garlic cloves undergoing microwave-convective drying. Journal of Food Engineering 65:609-617.
16. Steffe, J. F. and R. P. Singh. 1980. Liquid diffusivity of rough rice components. Transactions of the ASAE 23(3):767-774, 782.
17. Vijayaraj, B., R. Saravanan and S. Renganarayanan. 2007. Studies on thin layer drying of bagasse. International Journal of Energy Research 31:422-437.