DETERMINATION OF EFFECTIVE MOISTURE DIFFUSIVITY AND ACTIVATION ENERGY FOR DRYING OF POWDERED PEANUT SHELL UNDER ISOTHERMAL CONDITIONS

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In this study, the effect of drying temperature, from 50 °C to 90 °C, on the drying characteristics of powdered peanut shell was investigated, and an isothermal procedure was used to determine the moisture diffusivity and the activation energy. All the experiments were performed using a thermogravimetric analyzer (TGA) for rapidly achieving the isothermal condition and accurately recording the mass loss of the sample. With increasing drying temperature, the drying rate increased and the drying time decreased. A short rising rate period was found in all drying processes due to increasing temperature of the sample in the beginning of drying. The predicted values by the diffusion model based on Fick's second law were in good agreement with the experimental data obtained from the falling rate period. The values of effective moisture diffusivity ranged from 9.60×10^{-9} to 2.26×10^{-8} m^2/s, and the activation energy was determined to be 21.2 kJ/mol.

Keywords: Effective moisture diffusivity; Drying activation energy; Isothermal condition; Peanut shell, TGA

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INTRODUCTION

Biomass powder is widely used in thermochemical conversion technologies aimed at production of gas, liquid, and char. In preparation for such conversion it is essential to dry the biomass to a low moisture content level, as the materials often contain considerable water (Dobele *et al.* 2007). The effective moisture diffusivity (D_{eff}) and the activation energy (E_a) are the important drying parameters for describing the diffusion mechanism and designing a new dryer (Albitar *et al.* 2011; Chen *et al.* 2011). In the literature, the drying parameters are generally determined under isothermal conditions by a two-step method (Elenga *et al.* 2011; Li and Kobayashi 2005). First, effective moisture diffusivity is calculated from the drying curves by Fick's second law for each of several drying temperatures. Then, the well-known Arrhenius-type equation is used to correlate the set values of effective moisture diffusivity as a function of temperature, from which the activation energy and the pre-exponential factor (D_0) are obtained.

In recent years, the two-step method has been widely used, and the drying parameters values have been obtained for numerous materials, such as fruits (Minaei *et al.* 2012), food (Doymaz and Kocayigit, 2011), fiber (Elenga *et al.* 2011), vegetables (Wu *et al.* 2007), sawdust (Chen *et al.* 2012), and leaves (Kaya and Aydin 2009). However, few drying studies have been carried out for biomass powder, and the drying parameters of agricultural residues such as peanut shell are unknown.

In addition, the isothermal condition has a significant influence on the accurate determination of the effective moisture diffusivity. However, drying experiments are usually not performed isothermally in practical processes due to thermal lag. A relatively large error can result when a temperature gradient exists within the sample (Srikiatden and Roberts 2006).

The thermogravimetric analyzer (TGA) is an outstanding instrument with advantages of minimal sample requirement, online recording of weight loss, and ease of operation. Most importantly, it has precise control capability that can rapidly heat the sample to the required temperature. In recent years, the TGA has been applied in biomass drying by different researchers (Cai and Chen 2008; Hu *et al.* 2012).

Therefore, the objectives of this work were to study experimentally the drying characteristics of powdery peanut shell under isothermal conditions, and to determine the effective moisture diffusivity and the activation energy by thermogravimetric analysis.

EXPERIMENTAL

Materials

Peanut shell was crushed into small particles using a high-speed rotary grinder. The particles of 0.125 to 0.3 mm size were selected for the experiments. Sample size was generally consistent with previous studies on dry biomass (Cai and Chen 2008; Chen *et al.* 2012). To make moisture distribute evenly, the sample was kept for 96 hours in a sealed vitreous container. The moisture content of peanut shell was determined by using the oven method at 105 ºC for 6 hours. As an average of the results of such measurements, it was found to be 0.079 g water/ g dry matter.

Drying Experiments

The drying experiments were performed at five temperatures (50, 60, 70, 80, and 90 °C) using a thermogravimetric analyzer (TGA, Q5000IR, TA Instruments, USA). The specification of the sample pan (Platinum) was 100 μL with a height of 1 mm. The material was distributed uniformly in the sample pan. Thus the thickness of the material was nominally 1 mm, and the sample weight stabilized at 9 mg for each experiment. The air flow rate was kept at 100 mL/min with a velocity of 0.01 m/s for all experiments. The relative humidity of air was 20%. More information about the experimental procedure can be obtained from the literature (Li and Kobayashi 2005).

A computer connected to the TGA automatically recorded the changes in weight and temperature. Each drying experiment was repeated twice, and the average values were used for drawing the drying curves. Sample shrinkage can be negligible in the tested temperature range, and moisture was distributed evenly inside the sample. These selected conditions were in agreement with other drying studies by TGA (Chen *et al.* 2012; Hu *et al.* 2012).

Data Analysis

The moisture ratio (MR) of peanut shell was calculated by the following equation,

$$MR = \frac{M - M_e}{M_0 - M_e} \quad (1)$$

where M is the moisture content at any time (g water/g dry matter), M_0 is the initial moisture content (g water/g dry matter), and M_e is the equilibrium moisture content (g water/g dry matter). The value of M_e was determined as the moisture content at the end of drying when the sample ceased to lose mass.

Effective Moisture Diffusivity and Activation Energy

There are many methods to determine drying parameters, of which the most common is the Fick's second law of diffusion, as shown in Eq. (2).

$$\frac{\partial MR}{\partial t} = \nabla[D_{\text{eff}}(\nabla MR)] \quad (2)$$

The solution of Eq. (2), as shown in Eq. (3), has been widely used to describe the drying process. Assumptions inherent in the use of these equations include that the process took place under isothermal conditions, that moisture transport was dominated by internal diffusion, that there was a uniform initial moisture distribution, and that there was negligible shrinkage.

$$MR = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(-\frac{(2n+1)^2\pi^2 D_{\text{eff}}t}{4L^2}\right) \quad (3)$$

In Eq. 3, t is the drying time (min), L is the half thickness of the sample (m), and n is a positive integer. In this study, D_{eff} was determined by non-linear regression based on the simplex method. These calculations were performed by mathematical software (Origin 8.0). The maximum value of n was set to 1000.

Temperature dependence of the effective diffusivity has been shown to follow an Arrhenius relationship,

$$D_{\text{eff}} = D_0 \exp\left(-\frac{E_a}{R(T + 273.15)}\right) \quad (4)$$

where E_a is the drying activation energy (kJ/mol), D_0 is the pre-exponential factor (m^2/s), T is the drying temperature (°C), and R is the ideal gas constant (J/mol K). The drying activation energy can be calculated by plotting ln(D_{eff}) versus 1/(T+273.15).

RESULTS AND DISCUSSION

Evaluation of the Isothermal Condition

During the drying process, an ideal isothermal condition means that the temperature gradient can be negligible in the sample and that the temperature remains constant throughout the drying. The material's surface can easily reach the desired temperature, while the interior usually cannot, especially in large particles. The temperature gradient has a significant effect on the determination of the effective moisture diffusivity (Srikiatden and Roberts 2006). On the other hand, the sample's temperature often varies with drying time. This phenomenon is relatively common in high moisture content material (Rovedo *et al.* 1995). Moreover, the sample's temperature may exceed the drying temperature because too much energy is supplied at high heating rate by TGA (Li and Kobayashi 2005). Thus, the temperature overshoot should be avoided.

In this study, temperature data of the sample were recorded online by TGA. The results of the temperature profiles are shown in Fig. 1. It can be observed that there was no indication of a temperature overshoot, although the material was heated quickly to the drying temperature. A short time of within 50 seconds was needed to heat the material to the drying temperatures (50, 60, 70, 80, and 90 °C), and then the material's temperature remained constant over a long period of time. Owing to minimal material used in the experiment and low heat capacity of the samples, as well as precise temperature control capability of TGA, the temperature gradient in the sample can be negligible. Therefore, the important assumption of isothermal drying condition was generally met for proper determination of the drying parameters.

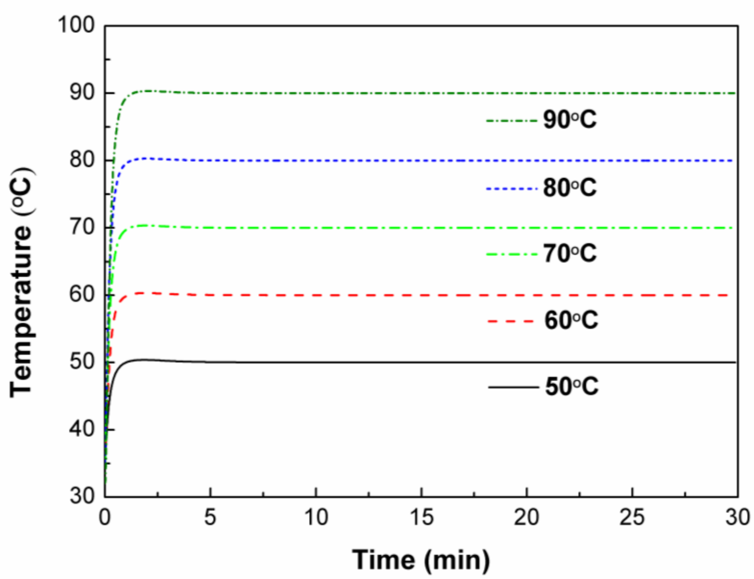

Fig. 1. Temperature profiles of peanut shell under isothermal drying conditions

Evaluation of the Internal Diffusion

The effect of drying temperature on the moisture ratio is shown in Fig. 2, and the drying rate curves are shown in Fig. 3. It can be seen that temperature significantly affected the drying process. With increasing drying temperature, the drying rate loss was increased, and the time needed to achieve specific moisture content was reduced notably. Similar results have been reported for cotton straw (Hu *et al.* 2012) and pine forest residues (Phanphanich and Mani 2010).

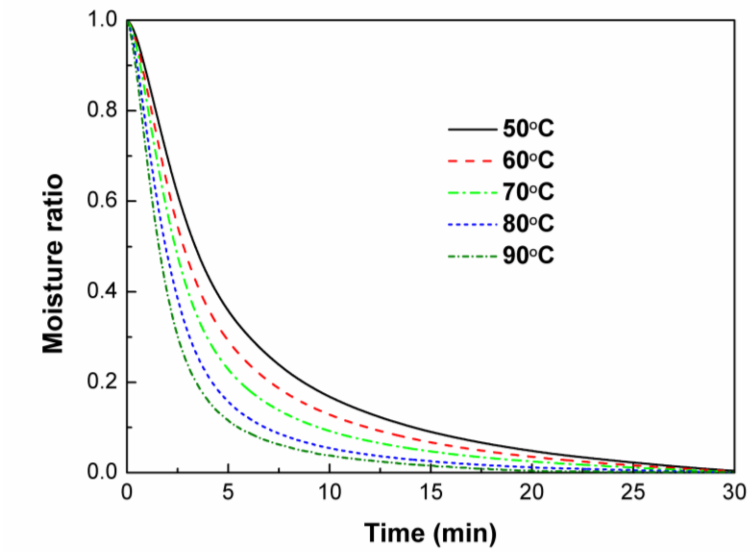

Fig. 2. The moisture ratio of peanut shell at different drying temperatures

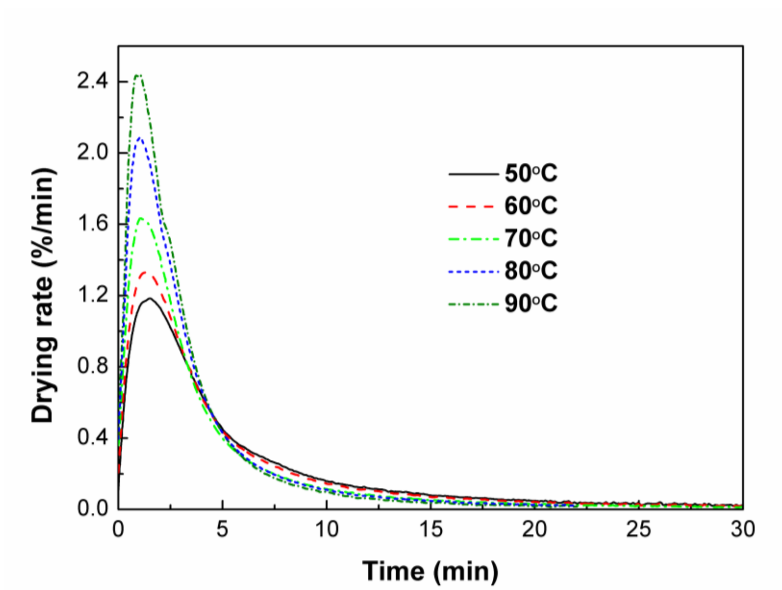

Fig. 3. Drying rates of peanut shell at different drying temperatures

As seen from Fig. 3, there was no constant rate period, but a long falling rate period was found in all drying processes. A short rising rate period appeared in the beginning of each drying process, lasting about 60 seconds. In particular, biomass heating to the drying temperature also occurred in this period (see Fig. 1). According to previous studies, the rising drying rate could be attributed to increased moisture evaporation on the surface of biomass due to increasing temperature in the beginning of drying (Kaya and

Aydin, 2009; Minaei *et al.* 2012; Shi *et al.* 2008). Figure 3 clearly indicates that the short rising rate period was not a diffusion process. In order to obtain accurate results, this period should be excluded from the determination of the drying parameters. Thus, it is very important to reduce the thermal lag.

Afterwards, with less free water available on the surface, the drying rate started to decrease. The drying process occurred mainly in the falling rate period, during which most of the water was removed. Similar results were obtained for blueberries (Shi *et al.* 2008) and poplar sawdust (Chen *et al.* 2012). It should be noted that the evidence presented here is not sufficient to demonstrate a diffusion mechanism in this study, because a similar falling rate period can exist without being a diffusion process at low air flow speed. In the range of flow speed that can be controlled, the drying curve was almost the same. The flow speed cannot increase so high as to verify the diffusion mechanism for the limit of TGA. Nevertheless, it can be first assumed that the falling rate period was dominated by internal diffusion. The diffusion model based on Fick's second law was then used to predict dry curves in order to verify the reasonableness of the assumption. Therefore, the falling rate period was modeled as process diffusion. Equation (1) was replaced by $MR = (M\text{-}M_e)/(M_{to}\text{-}M_e)$ before using Eq. (2) to calculate the drying parameters, where t_o is the initial time point of the falling rate period.

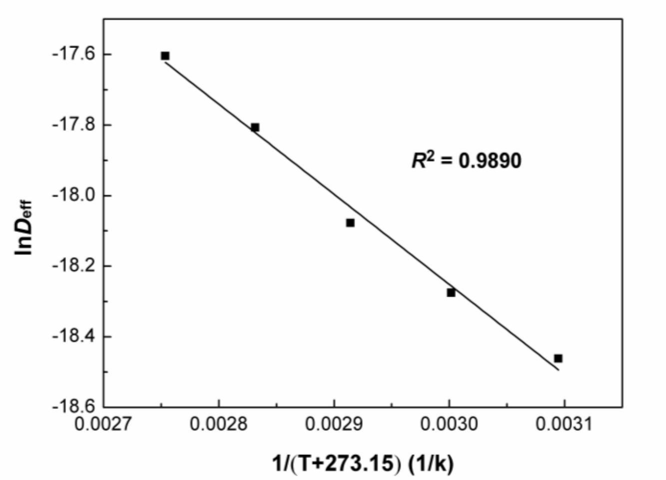

Fig. 4. The relationship between ln(D_{eff}) and 1/(T+273.15)

Determination of Drying Parameters

Equation (3) was used for determining the D_{eff} during the falling rate period. The initial values of D_0 and E_a were set rationally according to the previous studies in the literature (Chen *et al.* 2012). The calculated values of D_{eff} were 9.60×10^{-9}, 1.16×10^{-8}, 1.41×10^{-8}, 1.85×10^{-8}, and 2.26×10^{-8} m^2/s at 50, 60, 70, 80, and 90 °C, respectively. D_{eff} increased with increasing drying temperature. The high moisture diffusivity could be due to more energy being provided at high drying temperature, which increased the activity of water molecules and increased the drying rate. The difference between predicted values and experiments data was evaluated by the coefficient of determination (R^2). The R^2 values were 0.9850, 0.9831, 0.9783, 0.9789, and 0.9789 for drying at 50, 60, 70, 80, and 90 °C, respectively. The predicted values by the diffusion model based on Fick's second law were in good agreement with the experimental data obtained from the falling rate period. Therefore, the drying process of peanut shell in this study was mainly controlled by diffusion mechanisms. The activation energy was determined using Eq. (4). A linear relationship between $\ln(D_{eff})$ and $(1/(T+273.15))$ was found in Fig. 4. The activation energy was determined as 21.2 kJ/mol by means of the slope of the line.

Evaluation of the Determination Results

The determined values of peanut shell have a certain reliability and comparability compared with the results of other biomass. Table 1 shows the effective moisture diffusivity of the present study as well as information available in the literature. It can be seen that the values obtained for peanut shell in the present study were within the general range of 10^{-10} to 10^{-8} m^2/s for forestry and agricultural residues, as reported in the literature (Erbay and Icier 2010). The activation energy of peanut shell was also similar to some agricultural residues. Table 2 shows the activation energy values of different biomass. The activation energy of peanut shell in the present study was close to that of mung beans but higher than wheat straw, olive-waste cake, and cotton stalk.

It should be noted that the results are limited to the TGA used in this study, because many factors, such as drying apparatus, moisture content, material type, and temperature range have an influence on the experimental results. However, the present study demonstrates the methodology and provides guidance for isothermal procedure by TGA as an effective and alternative way for determining the drying parameters.

Table 1. Comparison of the D_{eff} for Peanut Shell and Other Biomass

Biomass	D_{eff} (m^2/s)	Temperature (°C)	References
Rice husk	8.42×10^{-9} to 1.69×10^{-8}	30–60	(Thakur and Gupta, 2006)
Mint leaves	1.97×10^{-9} to 6.17×10^{-9}	35–55	(Kaya and Aydin, 2009)
Coconut husk	1×10^{-8} to 6×10^{-8}	30–70	(Tirawanichakul, 2008)
Poplar sawdust	9.38×10^{-10} to 1.38×10^{-9}	60–90	(Chen *et al.* 2012)
Peanut shell	9.60×10^{-9} to 2.26×10^{-8}	50–90	Present study

Table 2. Comparison of the E_a for Peanut Shell and Other Biomass

Biomass	E_a (kJ/mol)	References
Mung beans	23.28	(Li and Kobayashi, 2005)
Wheat straw	14.1	(Cai and Chen, 2008)
Olive-waste cake	12.34	(Vega-Gálvez *et al.* 2010)
Cotton stalk	15.1	(Chen *et al.* 2011)
Peanut shell	21.2	Present study

CONCLUSIONS

1. Increasing drying temperature increased the drying rate and decreased the drying time. A short rising rate period appeared in all drying curves due to increasing temperature of the sample in the beginning period of drying. The drying process mainly was accomplished during the falling rate period. It is very important to reduce the thermal lag for accurately determining the drying parameters by the isothermal procedure.
2. The predicted values by the diffusion model based on Fick's second law were in good agreement with the experimental data obtained from the falling rate period. Therefore, the drying process of the falling rate period was mainly controlled by diffusion mechanisms. The effective diffusivity values changed from 6.96×10^{-9} to 2.26×10^{-8} m^2/s within the given temperature range, and the activation energy was calculated to be 21.2 kJ/mol.

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REFERENCES CITED

Albitar, N., Mounir, S., Besombes, C., and Allaf, K. (2011). "Improving the drying of onion using the instant controlled pressure drop technology," *Drying Technol.* 29(9), 993-1001.

Cai, J. M., and Chen, S. Y. (2008). "Determination of drying kinetics for biomass by thermogravimetric analysis under nonisothermal condition," *Drying Technol.* 26(12), 1464-1468.

Chen, D. Y., Zhang, D., and Zhu, X. F. (2011). "Heat/mass transfer characteristics and nonisothermal drying kinetics at the first stage of biomass pyrolysis," *J. Therm. Anal. Calorim.*, DOI: 10.1007/s10973-011-1790-4.

Chen, D. Y., Zheng, Y., and Zhu, X. F. (2012). "Determination of effective moisture diffusivity and drying kinetics for poplar sawdust by thermogravimetric analysis under isothermal condition," *Bioresour. Technol.* 107, 451-455.

Dobele, G., Urbanovich, I., Volpert, A., Kampars, V., and Samulis, E. (2007). "Fast pyrolysis - Effect of wood drying on the yield and properties of bio-oil," *BioResources* 2(4), 699-706.

Doymaz, İ., and Kocayigit, F. (2011). "Drying and rehydration behaviors of convection drying of green peas," *Drying Technol.* 29(11), 1273-1282.

Elenga, R. G., Dirras, G. F., Maniongui, J. G., and Mabiala, B. (2011). "Thin-layer drying of raffia textilis fiber," *BioResources* 6(4), 4135-4144.

Erbay, Z., and Icier, F. (2010). "A review of thin layer drying of foods: Theory modeling, and experimental results," *Crit. Rev. Food Sci. Nutr.* 50(5), 441-464.
Hu, J., Shen, S., Lei, T., Huang, H., and Zhang, Q. (2012). "Research on constant-temperature drying test of cotton straw and regression analysis of drying rate," *Adv. Mater. Res.* 472-475, 1645-1651.
Kaya, A., and Aydin, O. (2009). "An experimental study on drying kinetics of some herbal leaves," *Energy Convers. Manage.* 50(1), 118-124.
Li, Z., and Kobayashi, N. (2005). "Determination of moisture diffusivity by thermo-gravimetric analysis under non-Isothermal condition," *Drying Technol.* 23(6), 1331-1342.
Minaei, S., Motevali, A., Ahmadi, E., and Azizi, M. H. (2012). "Mathematical models of drying pomegranate arils in vacuum," *J. Agr. Sci. Tech.* 14(2), 311-325.
Phanphanich, M., and Mani, S. (2010). "Drying characteristics of pine forest residues," *BioResources* 5(1), 108-120.
Rovedo, C. O., Suarez, C., and Viollaz, P. E. (1995). "Drying of foods: Evaluation of a drying model," *J. Food Technol.* 26, 1-12.
Shi, J. L., Pan, Z. L., McHugh, T. H., Wood, D., Hirschberg, E., and Olson, D. (2008). "Drying and quality characteristics of fresh and sugar-infused blueberries dried with infrared radiation heating," *LWT Food Sci. Technol.* 41(10), 1962-1972.
Srikiatden, J., and Roberts, J. (2006). "Measuring moisture diffusivity of potato and carrot (core and cortex) during convective hot air and isothermal drying," *J. Food Eng.* 74(1), 143-152.
Thakur, A. K., and Gupta, A. K. (2006). "Water absorption characteristics of paddy, brown rice and husk during soaking," *J. Food Eng.* 75(2), 252-257.
Tirawanichakul, S. (2008). "Paddy dehydration by adsorption: Thermo-physical properties and diffusion model of agriculture residues," *Biosystems Eng.* 99(2), 249-255.
Vega-Gálvez, A., Miranda, M., Díaz, L. P., Lopez, L., Rodriguez, K., and Di Scala, K. (2010). "Effective moisture diffusivity determination and mathematical modelling of the drying curves of the olive-waste cake," *Bioresour. Technol.* 101(19), 7265-7270.
Wu, L., Orikasa, T., Ogawa, Y., and Tagawa, A. (2007). "Vacuum drying characteristics of eggplants," *J. Food Eng.* 83(3), 422-429.

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