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The Kinetics of Forced Convective Air-drying of Papaya (*Carica papaya* L.) Slices Pretreated in Osmotic Solution

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Abstract

In this study, mathematical modeling of hot air-drying of thin-layer papaya (*Carica papaya* L.) slices with 5±1 mm thickness pretreated in osmotic solution (50% sucrose) was investigated. Thin-layer drying was conducted under three different drying temperatures of 40, 50 and 60 °C at a constant air velocity of 0.9±0.1 m/s and absolute humidity of 0.6 ± 0.02 g of water/kg of dry air. It was found that the drying process occurred in falling rate period over the drying time. The osmosis dehydration characteristics obtained by solid gain (SG), water loss (WL) and weight reduction (WR) parameters that increased with increasing immersion time. The effective diffusivity for papaya slices was within the range of 2.13×10^{-9} to 4.84×10^{-9} m^2/s over the temperature range. The activation energy was 38.63 kJ/mol indicated the effect of temperature on the diffusivity. Based on the statistical analysis using coefficient of determination (R^2) and root mean square error (RMSE), it was concluded that the best model in terms of fitting performance for hot air-drying of papaya pretreated in osmosis solution in all temperature range was Midilli *et al.* model.

Keywords: Papaya, Mathematical modeling, Osmotic solution, Cabinet drier, Thin-layer

Introduction

Papaya also called papaw or pawpaw is an edible melon-like fruit that is grown in the tropics and subtropics. It is juicy, sweet and tastes like cantaloupe (Morton, 1987). Due to its high content of the vitamin C, potassium, carotenoid and fiber content, papaya has been considered a top-ranking fruit (Yousefi *et al.*, 2012). It is widely produced in Brazil, Nigeria, India, Mexico and Indonesia. According to the Food and Agriculture Organization (FAO), about 6.5 million tons of papaya was produced in 2005 (Fernandes *et al.*, 2008). In Iran, papaya is grown in Bahu Kalat City, Baluchistan province. About 480 tons of papaya was produced in Iran in 2005 (Yousefi *et al.*, 2012). Drying is a technique of conservation that consists of the elimination of large amount of water from food materials applying heat under controlled conditions, to diminish the chemical, enzymatic and microbiological activities that are responsible for the deterioration of food (Barnabas *et al.*, 2010). Air-drying is one of the traditional methods, which used for food dehydration by means of some kinds of driers such as cabinet drier, fluidized-bed drier and so on. Recently, studies pointed out the efficiency in water removal when air-drying was combined with another dehydration method like osmosis or microwave (Momenzadeh *et al.*, 2011; Funebo and Ohlsson, 1998; Drouzas *et al.*, 1999). Many researchers recommended that osmotic dehydration could affect the final quality of dried products in terms of reducing of shrinkage as well as preventing oxidative browning and loosing of volatile flavoring components during convective hot air drying process (Mauro and Menegalli, 2003). To carry out osmotic dehydration, fruit pieces are immersed in a concentrated solution containing one or more solutes. The elimination of access water from food specimen tissue is completed by a counter-current diffusion of the osmotic agent (salt or sugar) from the solution toward the specimen tissue (Prothon and Ahrne, 2004; Petchi and Manivasagan, 2009). In the process, water usually transfers more than solute due to deferential permeability of cellular membranes (Mauro and Menegalli, 2003). The drying kinetics of food is a complex phenomenon and requires dependable models to predict drying behavior (Sharma *et al.*, 2003). There are three types of thin-layer drying models: theoretical, semi-theoretical and empirical (Midilli *et al.*, 2002; Demirats *et al.*, 1998). The theoretical model depends on the physical characteristics of grains. The empirical model presents a direct relationship between average moisture and drying time by means of regression analysis (Ozdemir and Devres, 1999). Semi-theoretical is a tradeoff between the theoretical and empirical models, and is derived from Fick's second law of diffusion. It is used in the form of the Page model, the Modified Page model, the

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Henderson model and other models. Kaymak-Ertekin and Sultanoglu (2000) investigated the osmotic dehydration of apple slices in different solution with different concentrations. They found that as temperature and concentration increased, water loss (WL) increased at a considerable level. Kingsly and Singh (2007) studied thin-layer drying of pomegranate arils in a cabinet drier at drying temperatures of 50, 55 and 60 °C. They reported that the Page model satisfactorily represented the drying characteristics of pomegranate arils than other models. Momenzadeh *et al.* (2011) studied drying characteristics of shelled corn (*Zea mays* L.*)* in a fluidized bed dryer assisted by microwave heating. Their results showed that increasing the drying air temperature resulted in up to 5% decrease in drying time, while in the microwave-assisted fluidized bed system, the drying time decreased dramatically up to 50% at a given and corresponding drying air temperature at each microwave energy level. Yousefi *et al.* (2012) compared two methods of mathematical and Artificial Neural Networks (ANN) modeling to estimate the moisture content of papaya fruit slices during hot air-drying. They found that estimation of the moisture content of papaya fruit could be better modelled by a neural network (R^2 = 0.9994 and RMSE= 0.0070) than by the mathematical models (R^2=0.9974 and RMSE=0.0123).

The purpose of this study was to model hot air-drying of papaya slices pretreated in osmotic solution as a new kind of combined drying method in different temperatures of 40, 50 and 60 °C. The moisture ratio (MR) at each drying temperature was obtained and eight well-known thin-layer drying models were used to describe the drying process. In addition, two drying parameters of effective moisture diffusivity and activation energy were calculated.

Materials and Methods

Sample preparation

Papaya fruits were purchased from a local market in the Bahu Kalat region and stored in a refrigerator at 4±1°C before they were subjected to the drying process. Then, they were allowed to reach to room temperature (24±1^{o}C) one hour before starting the experiments. For all experiments, papayas were peeled and sliced into 5±1mm thickness. The initial moisture content of papaya was 700±2 % dry basis (d.b.).

Preparation of osmotic solution

Osmotic solution was prepared with sucrose 50% (Merck Co., Germany). The product to solution ratio was 1:10 (weight basis) (Antonio *et al.*, 2004). Temperature controlled mixing tank was used for osmotic operation.

Cabinet dryer

A cabinet dryer (Model JE10 TECH, F-02G, South Korea) with controllable air flow, temperature and air humidity monitoring systems was used for the hot air drying process. The absolute humidity and the hot-air flow ratio for all drying temperatures were 0.6 ± 0.02 g/kg of dry air and 0.9 ± 0.1 m/s, respectively.

Microstructure analysis

SEM imaging of papaya carried out to exhibit the surface properties of the samples. The thin layers were prepared from the untreated and dried papaya and coated with gold using an ion sputter (Fisons

Nomenclature	Definition
M	Moisture content at any time of drying
M_e	Equilibrium moisture content
M_0	Initial moisture content
MR	Moisture ratio
$MR_{pre,i}$	I^{th} predicted MR
$MR_{\exp,i}$	I^{th} experimentally observed MR
N	Number of observations
R^2	Coefficient of determination
RMSE	Root of mean square error
ww_0	Weight of water in initial sample
ws_0	Weight of solids initially present in the fruit
ws_t	Weight of solids at the end of osmosis treatment
w_t	Weight of the fruit
D_{eff}	Effective diffusivity
D_0	pre-exponential factor of Arrhenius equation
E_a	Activation energy
n	Positive integer
R	Gas constant
T	Air temperature
t	Drying time

Instruments, UK). The coated samples were viewed and photographed using a scanning electron microscope (model 5526, Cambridge, UK) at 20 kV.

Experimental procedure

Osmosis treatment

Papaya slices were weighed and placed into the osmotic solution under dynamic condition provided by agitation (150 rpm) at room temperature (24±1^{o}C) for 4 h. The product to solution ratio was 1:10 (weight basis). The samples were removed from the solution in time intervals of 30 min and drained with a filter paper for 5 min in order to remove the excess solution at the surface and weighed (Antonio *et al.*, 2004). They also were weighed prior to placing in the cabinet drier.

For each treatment, water loss (WL), solid gain (SG) and weight reduction (WR) were evaluated based on the following equations (Eq. 1, 2 and 3) and the results were expressed in g/100g of initial fresh fruit weight:

$$WL = \frac{(ww_0) - (w_t - ws_t)}{(ws_0 + ww_0)} \tag{1}$$

$$SG = \frac{(ws_t - ws_0)}{(ws_0 + ww_0)} \tag{2}$$

$$WR = WL - SG \tag{3}$$

Where ww$_0$ is the weight of water in initial sample (g), ws$_0$ is the weight of solids initially present in the fruit (g); w$_t$ and ws$_t$ are the weight of the fruit (g) and the weight of solids at the end of treatment (g), respectively (Petchi and Manivasagan, 2009; Mujica-Paz *et al.,* 2003; Lazarides *et al.,* 1995). The changes in SG, WL and WR parameters were determined consecutively in time intervals of 30 min during the dehydration for 4 h.

Hot air-drying process

One layer of the sliced papaya samples after 4 h osmotic dehydration was placed in the cabinet dryer at three temperatures of 40, 50 and 60 °C for hot air-drying process and weight – time data were recorded until achieving to 20±1% (d.b.) moisture content from the initial moisture content of 700±2% (d.b.). The MR vs. drying time curve was obtained for each drying temperature.

Mathematical modeling

Eight well-known models of thin-layer drying described in Table 1 were investigated to find the most suitable drying model for the drying process of papaya. The MR was defined by:

$$MR = \frac{M - M_e}{M_0 - M_e} \tag{4}$$

Where, M and M$_0$ are the moisture content of the samples at any drying time and initial moisture content, respectively. The moisture ratio equation was simplified to M/M$_{\mathbf{0}}$ as the value of M$_e$ (equilibrium moisture content) is relatively small compare to M or M$_{\mathbf{0}}$ (Akgun and Doymaz, 2005; Doymaz, 2004).

In a general manner, the performance of a model is evaluated based on the comparison between the computed output (predicted) and input (experimental) data. The obtained predicted data for each model is evaluated using the coefficient of determination (R^2) and root mean square error (RMSE) (Eqs. 5 and 6).

A model with the maximum of R^2 and the minimum of RMSE shows the best performance (Kingsly and Singh, 2007):

$$R^2 = \frac{\sum_{i=1}^{N}(MR_{\exp,i} - \overline{MR}_{\exp})^2 (MR_{pre,i} - \overline{MR}_{pre})^2}{\sum_{i=1}^{N}(MR_{\exp,i} - \overline{MR}_{\exp})^2 \sum_{i=1}^{N}(MR_{pre,i} - \overline{MR}_{pre})^2} \tag{5}$$

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N}(MR_{\exp,i} - MR_{pre,i})^2\right]^{1/2} \tag{6}$$

Where, $MR_{exp.i}$ is the experimental moisture ratio at observation *i*, $MR_{pre,i}$ is the predicted moisture ratio at this observation, N is number of experimental data points, $\overline{MR}_{\exp}$ and $\overline{MR}_{pre}$ are the average of sum of the $MR_{exp.i}$ and $MR_{pre,i}$, respectively.

Table 1- Mathematical models for thin-layer drying

Model name	Model equation	References
Newton	$MR = \exp(-kt)$	Westerman and White, 1973
Page	$MR = \exp(-kt^n)$	Guarte, 1996
Modified Page	$MR = \exp(-kt)^n$	Yaldiz *et al.*, 2001
Henderson and Pabis	$MR = a\exp(-kt)$	Yagcioglu *et al.,* 1999
Logarithmic	$MR = a\exp(-kt) + c$	Yaldiz *et al,* 2001
Two-term	$MR = a\exp(-k_0t) + b\exp(-k_1t)$	Rahman, 1998
Wang and Sing	$MR = 1 + at + bt^2$	Ozdemir and Devres, 1999
Midilli et al.	$MR = a\exp(-kt^n) + bt$	Sacilik *et al.,* 2006

Results and Discussions

Osmotic treatment

The moisture content of the fresh papaya was 700± 2% (d.b.). The effect of osmotic treatment on dehydration of the samples pointed via the changes in parameters of the process (SG, WL and WR) during dehydration that is shown in Fig. 1. As the results show, the water loss, solid gain and weight reduction of the papaya slices increased with increasing immersion time. These results were in agreement with Petchi and Manivasagan (2009) and Heng *et al.,* (1990). In the most intense processing condition (after 4h immersion), water loss and weight loss attained to 33.64 and 22.19 g/100g of initial fresh fruit, respectively. According to Fig. 1, at the end of the osmotic treatment, especially at 210 and 240 min immersion times, the changes in SG, WL and WR were very slow because of decrease in osmotic pressure as driving force for dehydration (Levic *et al.,* 2008). Solid gain showed a tendency to increase with increasing the immersion time; also increasing the dehydration time caused greater loss of water from the papaya slices (Kaymak-Ertekin and Sultanoglu, 2000). The final moisture content of papaya slices after 4h immersion in the osmotic solution was 225.6 ± 0.4% (d.b.).

Hot air-drying

As expected, increasing air temperature reduced the drying time (Fig. 2). At higher temperature, due to the quick removal of moisture, the drying process occurred in a shorter period. The decrease in drying time with increase in drying temperature may be due to increase in water vapor pressure within the papaya slices, which increased the migration of moisture, especially when the drying occurs only in falling rate period. Similar observation was reported for apple purees (Vergara *et al.,* 1997). The moisture ratio of papaya reduced exponentially as the drying time increased. Continuous decrease in moisture ratio indicates that, diffusion governed the internal mass transfer (Haghi and Amanifard, 2008). As expected, higher drying air temperature decreased the moisture ratio faster. During hot air-drying, the moisture content of papaya slices at all the drying temperature was brought to 20 ± 0.1% (d.b.). It is found that there was no constant rate drying period in the drying kinetics of papaya slices, and all drying process occurred in the falling rate period (Fig. 3). This matter indicates that diffusion is the controlling physical mechanism regulating moisture transfer in the sample slices. The similar results were reported by Kaymak-Ertekin (2002) for green and red peppers, Sogi *et al.,* (2003) for tomato seeds and Doymaz (2007) for pumpkin.

Mathematical modeling

Fig. 2, shows the drying curves of hot air-drying of thin-layer papaya fruit slices pretreated in osmotic solution in which the effect of drying time on moisture ratio was exhibited. The MR values were fitted against the drying time at each temperature by applying the non-linear regression analysis technique. The best model for each treatment was obtained using comparison of statistical parameters of R^2 and RMSE. According to Table 2, Midilli *et al.* model was the best among the mathematical models in fitting the experimental data, which can be used to predict the drying behavior of papaya slices under the mentioned conditions. Fig. 4, shows the good coincidence between experimental and predicted MR obtained from the best model at each drying temperature, which banded around the straight line *(X=Y)*; that proved the feasibility of the selected model in describing the drying behavior of thin-layer papaya slices.

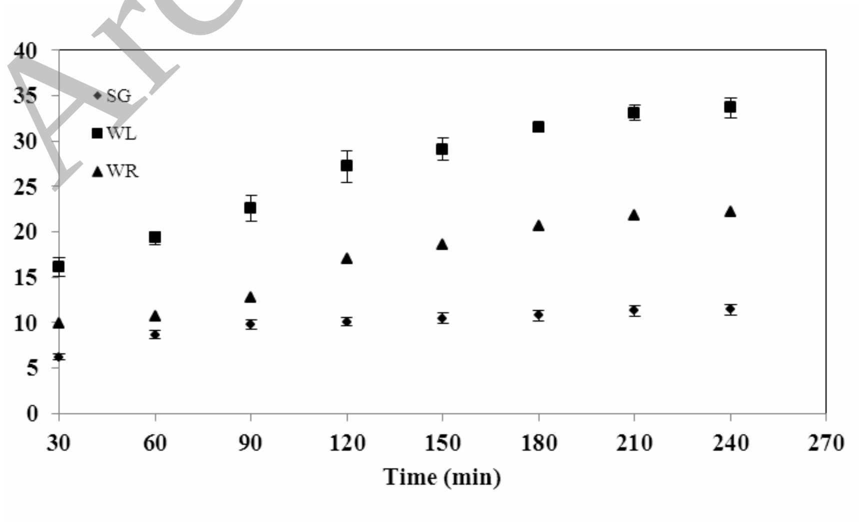

Fig. 1- The changes in SG, WL and WR during osmotic dehydration

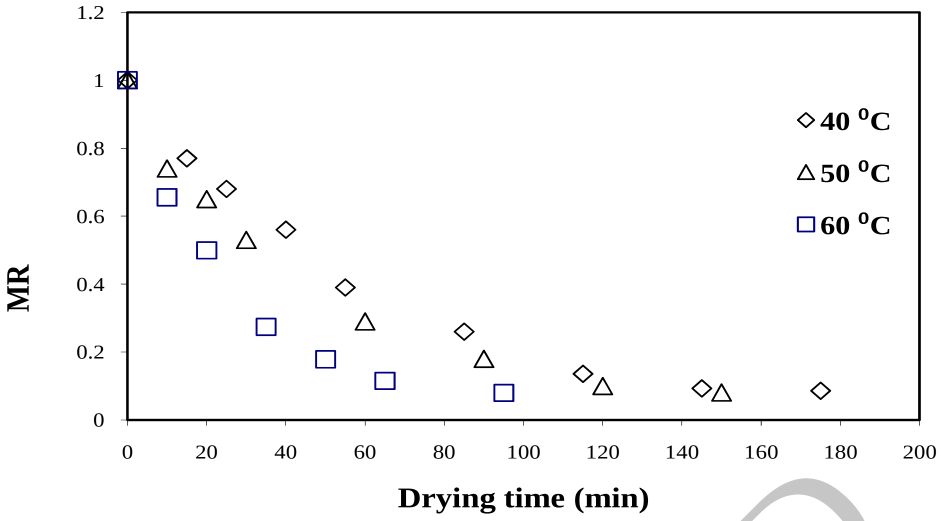

Fig. 2- Effect of drying temperature and drying time on moisture ratio

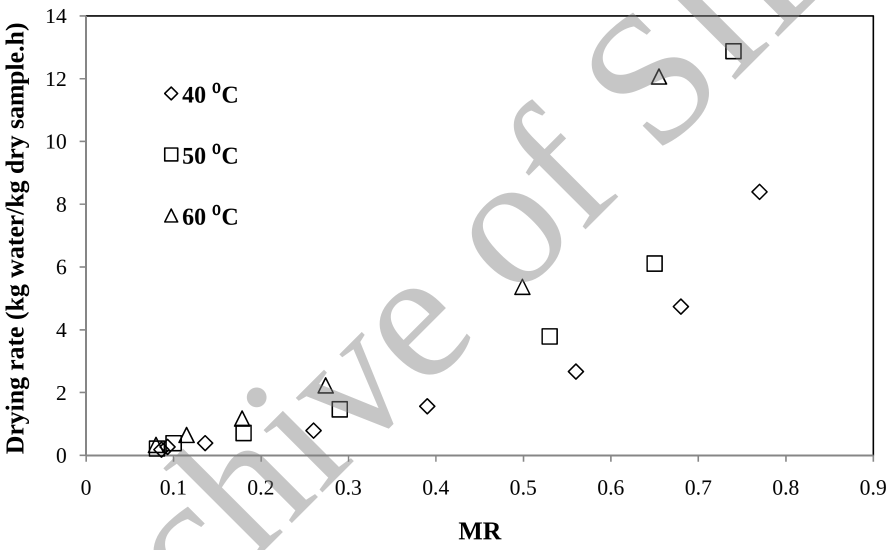

Fig. 3- Effect of drying temperature and MR on drying rate of papaya fruit slices

Yousefi *et al.*, (2012) reported that two-term model was the best mathematical model to describe thin-layer hot air-drying of papaya fruit without any pretreatments in a cabinet drier. Zomorodian and Moradi (2010) found that Midilli model had the closest results to the experimental data for forced convective indirect model type thin layer solar drying of *Cuminum cyminum* (R^2=0.994, RMSE=0.0225).

Calculation of effective diffusivity

From the experimental data, internal mass transfer resistance was observed because of falling rate drying period. Fick's diffusion equation analyzed the drying data in the falling rate period. Crank (1975) solved this equation and introduced the following equation which can be used for slab geometry with uniform initial moisture diffusion, constant diffusivity and insignificant shrinkage:

$$MR = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(-\frac{(2n+1)^2\pi^2 D_{eff}t}{4L^2}\right) \qquad (7)$$

where, D_{eff} is the effective diffusivity (m^2/s); *n* is positive integer, *t* is drying time, and *L* is the half thickness of the slab in samples (m). In practice, only the first term in Eq. (7) is used yielding:

$$MR = \frac{8}{\pi^2}\exp\left(-\frac{\pi^2 D_{eff}t}{4L^2}\right) \qquad (8)$$

As it is obvious, D_{eff} can be calculated from the slope of Eq. (8) using natural logarithm plot of MR versus drying time.

The calculated D_{eff} values for different drying temperatures are shown in Fig. 5. D_{eff} value for papaya slices increased with air temperature. This value was

2.13×10^{-9}, 2.75×10^{-9} and 4.84×10^{-9} m^2/s for 40, 50 and 60 °C drying temperatures, respectively. Madamba *et al.* (1996) reported that the D_{eff} value for food materials is within the range of 10^{-11} to 10^{-9}. The obtained results were in agreement with the results of Kaleemullah and Kailappan (2005), Sacilik *et al.*, (2006) and Doymaz (2007).

Calculation of activation energy

From the Arrhenius-type relationship, the dependence of D_{eff} can be explained (Simal *et al.*, 1996). This matter is shown in the following equation:

$$D_{eff} = D_0 \exp\left(-\frac{E_a}{R(T+273.15)}\right) \tag{9}$$

Where D_0 is the pre-exponential factor of Arrhenius equation (m^2/s), E_a is the activation energy (kJ/mol), T is the drying temperature (°C) and R is the gas constant (kJ/(mol.K)).

Table 2- Statistical results obtained from the selected models

Model name	Temperature (°C)	R^2	RMSE
Newton	40	0.9962	0.0189
	50	0.9950	0.0310
	60	0.9956	0.0261
Page	40	0.9964	0.0188
	50	0.9972	0.0166
	60	0.9970	0.0171
Modified Page	40	0.9962	0.0189
	50	0.9950	0.0310
	60	0.9956	0.0261
Henderson and Pabis	40	0.9963	0.191
	50	0.9938	0.0257
	60	0.9948	0.0246
Two- term	40	0.9962	0.0189
	50	0.9973	0.0164
	60	0.9969	0.0180
Logarithmic	40	0.9963	0.0189
	50	0.9957	0.0205
	60	0.9977	0.0149
Wang and Singh	40	0.994	0.0282
	50	0.981	0.0571
	60	0.9793	0.0545
Midilli *et al.*	40	0.9967	0.0177
	50	0.9983	0.0128
	60	0.9980	0.0139

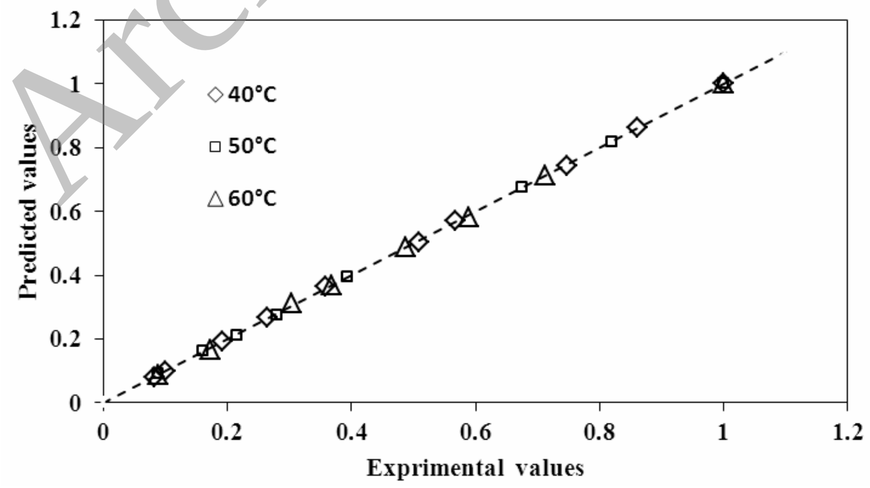

Fig. 4- Comparison of the experimental and predicted MR from Midilli et al. model

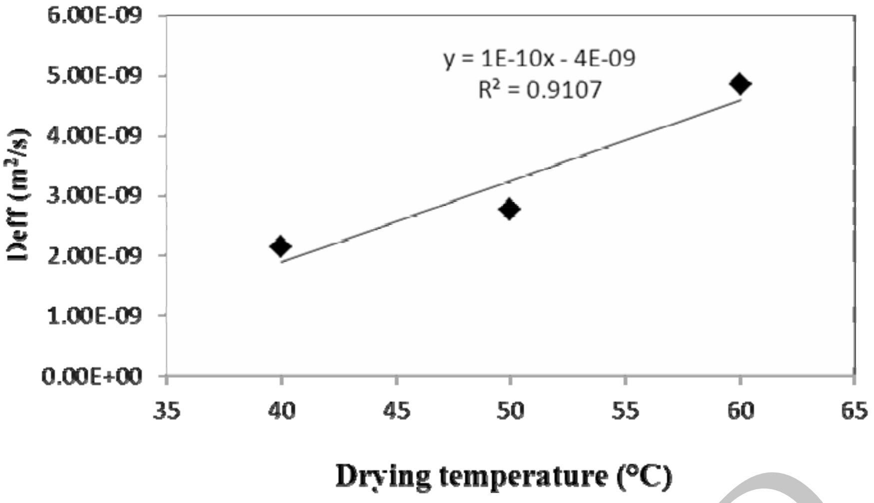

Fig. 5- Effect of drying temperature on the effective moisture diffusivity in papaya slices

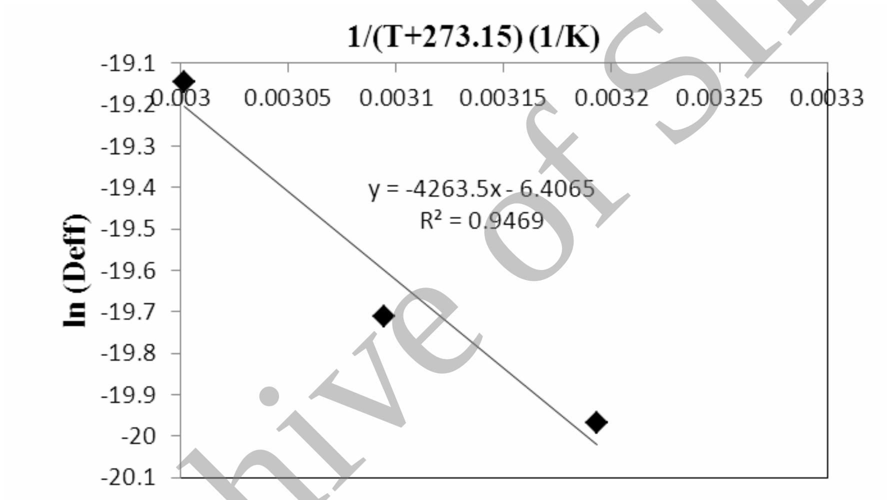

Fig. 6- Influence of drying temperature on the effective diffusivity

The E_a can be calculated from the slope of the plot on ln(*Deff*) vs. 1/(T+273.15) (Fig. 6). This value was 38.63 (kJ/mol) for papaya slices. This obtained value was lower than the E_a of green peppers drying (51.4 kJ/ mol) (Kaymak-Ertekin, 2002), mint drying (82.93 kJ/mol) (Park *et al.*, 2002) and higher than that of red chillies drying (24.47 kJ/ mol) (Kaleemullah and Kailappan, 2005).

Microstructure analysis

Fig. 7, shows the SEM images of fresh papaya, papaya at the end of osmotic dehydration (after 4h) and papaya sample at the end of hot air-drying process. Figs. 7b and 7c, clearly exhibited the existence of sucrose particles on samples surface. These particles were responsible for increasing the SG during 4h immersion in the 50% sucrose solution. Comparison of Figs. 7a and 7c obviously showed that the external porosity of the samples obtained from hot air-drying process was less than that of fresh sample. The similar results reported for garlic and carrot slices (Lozano *et al.*, 1980).

Conclusion

In this study, hot air-drying kinetics of papaya slices with 5±1 mm thickness pretreated in the osmotic solution at three levels of drying temperatures in a cabinet dryer were investigated. Like most of food materials, papaya slices had not constant drying rate and drying process entirely occurred in falling rate period. High value of R^2 in addition with low value for RMSE obtained for Midilli *et al.* mathematical model indicated the high performance of this model to determine MR during the drying process at all the drying temperatures. The obtained effective diffusivity was within the range of 2.13×10^{-9} to 4.84×10^{-9} m^2/s over the temperature range (40 to 60 ºC).

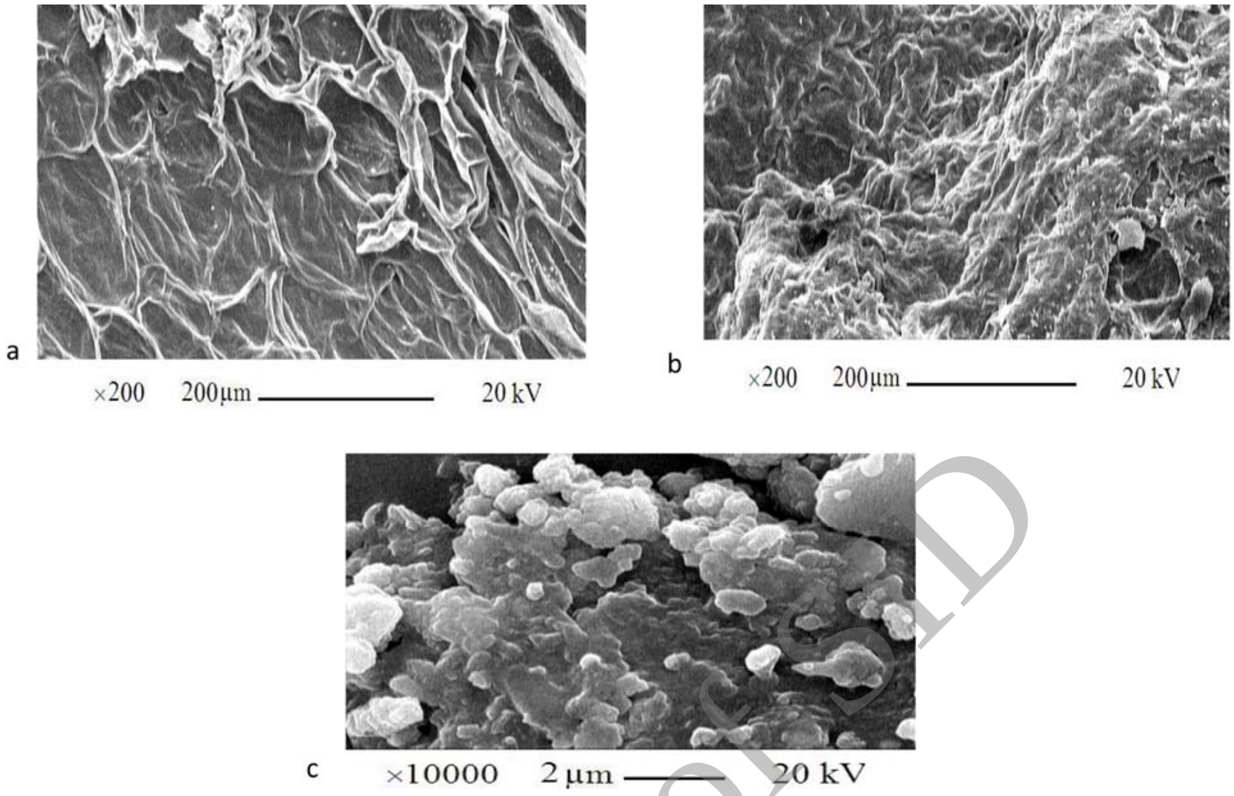

Fig. 7- SEM images of (a) fresh papaya (b) dried papaya after hot air-drying process (c) osmotic treated papaya for 4 h

It was found that, effective diffusivity increased with increasing drying temperature. The activation energy for papaya slices was found to be 38.63 kJ/mol using Arrhenius-type equation.

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