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Freeze drying of quince (Cydonia oblonga): Modelling of drying kinetics and characteristics

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Abstract−Drying kinetics of quince (Cydonia oblonga) in mashed form was investigated in a pilot scale freeze dryer. Experiments were conducted in various operating conditions, and the effects of initial moisture content, heat load power and the initiation time of heat application were investigated on drying rate and performance of the dryer. The experimental data of the moisture changes were correlated through non-linear regression and an appropriate mathematical model was obtained. The drying kinetics of the sample was determined on the basis of the pre-identified mathematical models as a function of operating parameters. The obtained values of mean relative percent deviation for the kinetics models of the primary and secondary drying stages are 7.47% and 5.94%, respectively. It is revealed that by applying a high heat load power at the beginning of the process the drying time is reduced significantly.

Key words: Freeze Drying, Lyophilisation, Quince, Cydonia oblonga, Kinetics Model

INTRODUCTION

Freeze drying or lyophilization is a dehydration process widely used to remove water from heat-sensitive products, including foodstuffs, biological materials, and pharmaceuticals for the purpose of increasing their stability at room temperature [1]. The process consists of three stages: freezing, primary drying and secondary drying.

During freeze drying, no liquid water exists and the product is at a low temperature; most of the microbiological reactions and deterioration will be stopped, and therefore final products with excellent quality are obtained. Many of food products such as natural orange juice [2], paneer and mango [3], strawberry [4], acerola [5] are dried by means of freeze drying. Despite its advantages, freeze-drying is the most expensive method for producing dehydrated product; hence, improving and optimizing the drying operation is an essential need.

The drying kinetics of various materials in freeze drying process is essentially different. Thus, development of conceptual-based mathematical expressions for drying kinetics is useful for the design and optimization of dryers. Mathematical expressions of drying kinetics seek a proper estimation of the drying time involved as well as the related behavior of all corresponding operational factors playing an important role in the design and optimization of dryers [6].

There are a few reports involving drying kinetics in freeze dryers. Pikal et al. [7] studied the effects of temperature and chamber pressure on the drying kinetics of a crystalline solute and two amorphous solutes for secondary drying stage. The temperature profile of the sample during freeze-drying is the key parameter for design of the optimal control policies, and keeping it in the range of respective constraints is a challenge in producing products of the highest quality [8]. As an important operating point, the temperature of the frozen layer must not exceed the melting point, and the temperature of the dried layer must not exceed the scorch point. Hottot et al. [9] determined the drying kinetics of pharmaceutical protein formulation only for primary drying stage. Although these authors investigated the influence of chamber pressure and temperature on drying rate, they have not presented an empirical equation for dehydration kinetics.

Shishehgarha et al. [10] investigated the drying kinetic, as well as color and volume variation, of whole and sliced strawberries after freeze drying under various temperatures. They found that the dehydration time increased proportionally to the thickness of the product and heating plate temperature reduced it significantly. Marques and Freire [11] investigated drying kinetics for pineapple, guava, and mango pulps using five empirical equations commonly applied for convective drying of foodstuffs. The best fittings for the drying kinetics of all the materials were obtained using the Page and Chen and Douglas equations. Kirmaci et al. [12] investigated the freeze-drying behavior and the drying kinetics of 5- and 7-mm thick sliced strawberry samples. They deduced that the Page model could sufficiently describe the drying behavior of strawberry samples. Daoussi et al. [13] investigated the effects of different freeze-drying parameters on the rate of sublimation and on sublimation end-point by using a microbalance placed inside the product chamber. Chakraborty et al. [14] studied the infrared assisted freeze-drying of Aloe-vera (Aloe barbadensis). They employed a three-parameter three-level face centered central composite design (FCCD) to develop multivariate regression models in order to evaluate the influence of process parameters on the quality of the freeze-dried aloe-vera powder.

The purpose of this study is to investigate the influence of the applied heat load at the bottom of the container on the drying kinetics of quince in a lab-scale freeze dryer. As the drying rate is highly affected by the operating conditions, the performance of the freeze dryer is investigated at various operating parameters. Moreover, attempts are made in order to present a suitable drying kinetics model as a function of operating conditions.

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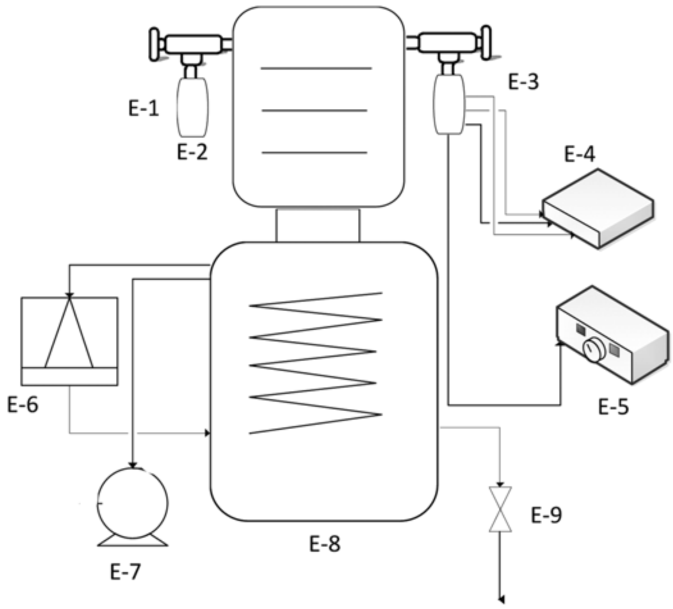

Equipment list	
Displayed text	Description
E-1	PTFE container
E-2	Heating plate
E-3	RTD sensor
E-4	Data acquisition system
E-5	Power supply
E-6	Refrigeration system
E-7	Vacuum pump
E-8	Condenser
E-9	Drain valve

Fig. 1. Schematic diagram of the experimental apparatus.

MATERIALS AND METHODS

1. Materials

In this study, the test material is fresh quince (Cydonia oblonga). Quinces have been long used as an herbal medicine and they are a good source of A, C and B_2 vitamins. The quince tree is native to Iran. To investigate the influence of initial moisture on drying rate, two different quince samples with initial moisture content of 2.7 and 6.2 kg/kg (dry basis) were chosen as the drying material. The chopped quince was charged in the container up to 1.5 cm of the bottom in a manner that one thermocouple was completely located inside the material.

2. Drying Apparatus

A schematic diagram of the experimental apparatus is shown in Fig. 1. Experiments were carried out in a laboratory freeze dryer (Operon, Model FDU100). Typically, the manufacturer of this type of freeze dryer fabricates the sample containers from glass. Thus, applying heat to the bottom of sample container was not possible. For these reasons and to prevent heat loss from the side walls of vials, hand-made PTFE containers with metal bottom for heating purpose were prepared and used instead of the general vials of the apparatus.

The variation of the sample temperature as a function of drying time was measured by a temperature measurement system including three RTD sensors, located at the distances of 0.5, 2, and 4 cm from the bottom of the vials. The openings around the thermocouple wires were sealed carefully to prevent the air leakage into the container.

In food freeze driers, heating the product is the rate-controlling variable when it is applied to the inner core of ice crystals through an outer layer of dry product. If heat is applied directly through the ice layer by conduction, the vapor diffusion will be the rate-controlling variable. Food freeze driers usually apply heat by radiation to the product surface which proceeds by conduction through the dry layer. However, the dry product layer insulates the product and limits the radiated heat supply [15].

In this study the heat is directly applied to the bottom of the containers. The heat transfer from the shelf to the product was found to be an important parameter on reducing the dehydration rate [16]. Here, the direct contact between warm plate and the samples effectively reduces this resistance.

The bottom of the container was warmed by using a heating system and with different heat loads from 13 to 266 W. The temperature recording system and heating system were designed, constructed, fabricated and calibrated by ourselves.

Through the tests, the connection valve between the container and the vacuum chamber was closed at specified time intervals and the container was removed and weighed with a digital balance (SETA, Model: Mark 205A). To ensure the accuracy of the results, the weighing procedure took no more than 10 s. The initial moisture content of the samples was determined by drying the sample in an electrical oven at 110 °C for 24 h. Since the quality of the dried product was not of major concern in this study, no procedure was considered for enzymatic oxidation of the samples, and also the characteristics of the dehydrated product (color, texture, etc.) were not measured.

3. Data Analysis

The effective parameters on drying of quince in a freeze dryer are the initial moisture content (X_0), the imposed heat load (q), the heating initiation time (t_s). To investigate the effect of various parameters on drying of quince and obtaining the desired correlations, several sets of experiments were designed as follows:

a) Experiments at constant t_s and X_0 with five different levels for q

b) Experiments at constant q and X_0 with three different levels for t_s

c) Experiments at constant q and t_s with two different levels for X_0

Here the dimensionless moisture is defined and applied as the ratio of measured moisture content to the initial moisture content of the sample. The measured dimensionless moisture content as a function of time is used to obtain the experimental drying rate data. In general, the differential method is used for this aim. In this study,

Table 1. Fitting parameters of Eq. (1)

Exp.#	Heat load imposed (W/kg)	Heating initiation time (min)	The end point of the primary drying stage	X_0	a	b	c	d	e	R^2
Q1	40	0	0.14	6.14	−0.00760	−0.28595	0.034246	−0.00499	0.00018	0.9997
Q2	66	0	0.13	6.14	−0.00045	−0.19693	−0.00638	−0.00024	−0.00001	0.9999
Q3	93	0	0.135	6.14	−0.00166	−0.33031	0.06427	−0.01456	0.00119	0.9999
Q4	133	0	0.11	6.14	0.000745	0.23987	−0.00002	0.005226	0.000585	0.9998
Q5	0	–	0.25	6.14	−0.00689	−0.15320	−0.00168	0.00013	0.00001	0.9998
Q6	40	30	0.23	6.14	−0.00123	−0.14911	−0.01111	0.00100	−0.00005	0.9995
Q7	66	30	0.22	6.14	−0.00363	−0.16450	−0.01951	0.00230	−0.00013	0.9998
Q8	133	30	0.19	6.14	−0.00184	−0.16821	−0.02882	0.00148	−0.00001	0.9998
Q10	0	–	0.22	2.7	−0.00635	−0.19023	0.00218	−0.00078	0.0000	0.9998
Q11	66.7	30	0.18	2.7	−0.00612	−0.19973	−0.00740	−0.00144	0.00008	0.9997
Q12	133	30	0.16	2.7	−0.00542	−0.21012	−0.01325	−0.00583	0.00097	0.9995
Q13	66	90	0.26	6.14	0.01320	−0.00822	−0.14172	−0.01207	0.00096	0.9996

for increasing the accuracy of this method, each set of the experimental dimensionless moisture is first correlated by the nonlinear regression method and an appropriate mathematical equation is obtained. The regression coefficient (R^2) is used as a statistical criterion for selecting the most suitable equation. The best-fit equation selected is in the following general form:

$$\ln\left(\frac{X}{X_0}\right)=a+bt+ct^2+dt^3+et^4 \tag{1}$$

where, X is the moisture content at time t, X_0 is the initial moisture of sample and a, b, c, d, and e are the fitting parameters.

The experimental drying rate equation is then obtained by derivation of Eq. (1). The following general equation is obtained:

$$\frac{d\left(\frac{X}{X_0}\right)}{dt}=(b+2ct+3dt^2+4et^3)\exp(a+bt+ct^2+dt^3+et^4) \tag{2}$$

The results of non-linear estimation as well as the corresponding values of the statistical criteria adopted to evaluate the goodness of fit of Eq. (1) are listed in Table 1. The results show that all R^2 values are equal or higher than 0.999; therefore, Eq. (1) could be selected for a good representation of the experimental data. This indicates that the obtained functions in this section could be properly used for obtaining the experimental drying rate.

4. Proposed Models for Drying Kinetics

A drying kinetics equation describes the mechanisms of heat and mass transfer, and it is necessary to study the impact of some specific process variables on moisture removal procedures.

In this study, for the first time, two new different models are introduced and used for fitting the observed drying rates for both primary and secondary drying stages. These mathematical forms are proposed on the basis of conceptual understanding of drying process in a freeze dryer and the effect of operating parameters on its performance. The model proposed for drying kinetics of primary drying stage is expressed as follows:

$$\frac{dX}{dt}=(a+bq^n)(c+dT^m)\left(\frac{X}{X_0}\right)^k \tag{3}$$

where, q is the imposed heat load (W/kg), T is the sample's temperature, and a, b, n, c, d, m, and k are the fitting parameters.

The definition of a drying kinetics model for the secondary drying stage is based on the mechanism of bounded water removal through this stage. The following equation is proposed:

$$\frac{dX}{dt}=a'\left(\frac{X}{X_0}\right)^{n'}-b'\exp\left(\frac{c'}{T}-d'\right)(e'+q^{k'}) \tag{4}$$

where, a′, n′, b′, c′, d′, e′, and k′ are the fitting parameters.

The parameters of Eqs. (3) and (4) are obtained by fitting the proposed models to the experimental drying rate. Here, the models' parameters are estimated by the minimizing the mean relative percent deviation (MRD) directly. MRC was used previously by Garcia-Pascual et al. [17] and is expressed as follows:

$$MRD=\frac{100}{N}\sum\frac{\left|\left(\frac{dx}{dt}\right)_{i,exp}-\left(\frac{dx}{dt}\right)_{i,calc}\right|}{\left(\frac{dx}{dt}\right)_{i,exp}} \tag{5}$$

where, $(dx/dt)_{i,exp}$ is the i^{th} experimental drying rate that is obtained based on Eq. (2), $(dx/dt)_{i,calc}$ is the i^{th} predicted drying rate that is obtained by Eqs. (3) and (4) for the primary and the secondary stages, respectively; N is the number of data points. MRD values below 10% are indicative of a reasonably good fit for most practical purposes [17].

RESULTS AND DISCUSSION

1. Analysis of Drying Behavior

As mentioned, three sets of experiments were carried out, and the total mass of the sample was measured through the drying time. Figs. 2-5 show the variation of dimensionless moisture content as a function of drying time for different sets of experiments. These figures present the effects of different operating conditions on the drying rate. Figs. 2 and 3 illustrate the effect of heat loads on the drying rate for two initiation times of heating. In these figures, the drying time decreases by increasing the heat load, as it is expected. In Fig. 2, the heating load is applied after 30 minutes from the process start

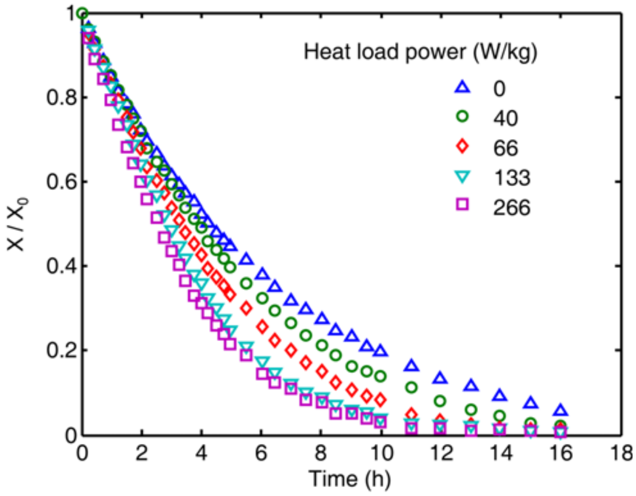

Fig. 2. Effect of heat load power on drying rate (t_s=30 min; X_0= 6.2 kg/kg).

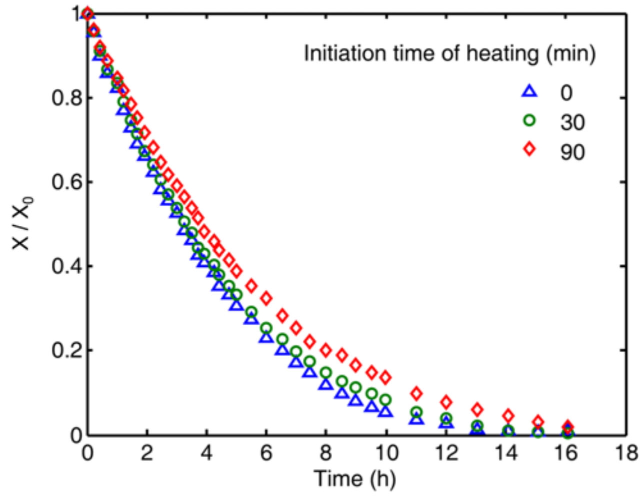

Fig. 4. Effect of time of heat application on drying rate (q=66 W/kg; X_0=6.2 kg/kg).

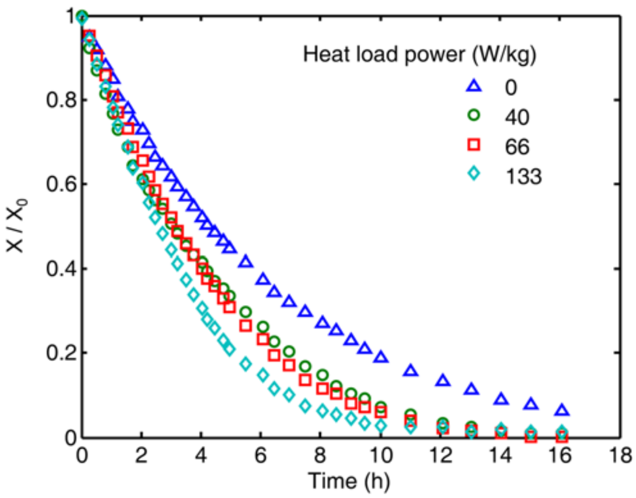

Fig. 3. Effect of power heat load on drying rate (the heat load was applied on bottom of the vial at start up of the process; X_0= 6.2 kg/kg).

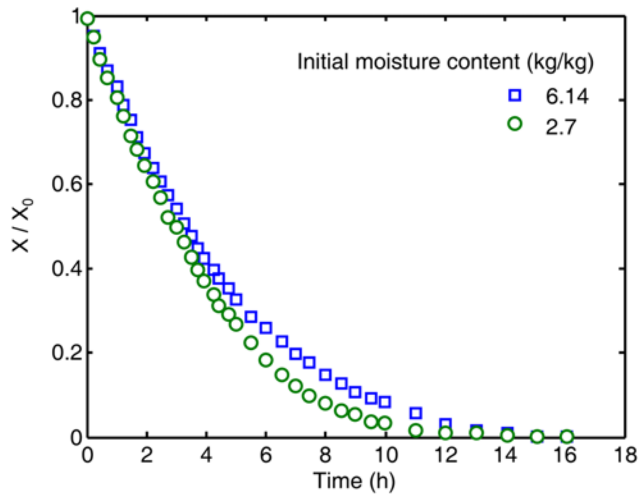

Fig. 5. Effect of initial moisture content on drying rate (q=66 W/kg; t_s=30 min).

up, and in Fig. 3 the heat load is applied at start-up of the process. Increasing the heat load power significantly intensifies the drying rate. Therefore, the heat load power is an effective parameter on the freeze-drying rate of quince. A comparison of the two figures reveals that the drying time is notably reduced when applying heat load at the beginning of the process compared to when it is applied after 30 min.

The effect of the initiation time of heating (0, 30, and 90 min) on the drying rate of quince at a constant heating load q=66 W/kg and a constant initial moisture content X_0=6.2 kg/kg is shown in Fig. 4. Here, the increase in the drying rate as a result of a lower initiation time of heating is evident. By imposing the heat load from the start-up of the process the drying rate is increased significantly. In general, this is an effective parameter for reduction of drying time.

Fig. 5 shows the effect of initial moisture content of the sample on the drying rate for heating loads of 66 W/kg. The initiation time of heating is 30 min. This figure indicates that a sample with more

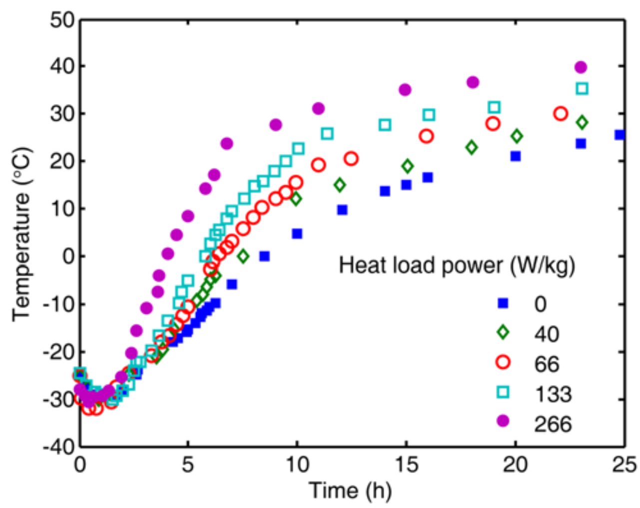

Fig. 6. Temperature of the sample in various heat load power (t_s= 30 min).

initial moisture content needs more drying time. Again, this figure reveals that increasing the heat load decreases the drying time for any initial moisture content value. It is noteworthy that this comparison is made for two other different heat loads and the same results are obtained.

The measured samples' temperatures for various operational conditions are shown in Fig. 6. At the beginning of the drying process, the temperature exhibits a reduction trend. This phenomenon has to do with the fact that the high sublimation rate causes a rapid reduction in the product temperature. In fact, the required energy for sublimation is absorbed from the frozen mass. The temperature increases then because with a reduction in the frozen layer thickness, the conductive heat transfer resistance that controls the heat transfer rate from the bottom heating plate is reduced.

2. Determination of the Parameters for Kinetics Models

The primary drying stage came to an end when all the ice crystals were sublimed and the sample temperature started to increase at a faster rate [3]. Here, this criterion was used to investigate the end point of the primary drying stage in all sets of experiments. The moisture content of each sample at the end of primary drying stage is presented in Table 1. Parameters of Eq. (3) were determined by using part of the experimental drying rates (obtained by Eq. (2)), related to the primary drying stage and the following correlation was acquired:

$$\frac{dX}{dt}=(0.0797+0.0007q^{0.9077})(1.1011+4.4060T^{-0.3246})\left(\frac{X}{X_0}\right)^{0.7954} \quad (6)$$

The obtained MRD by using Eq. (6) is 7.46%. The accuracy of the above equation was examined by experimental data of every set not utilized in the fitting procedure. Figs. 7 and 8 show the results of this comparison. The MRD values for each set of data are given in Table 2 also.

The average of MRD value reported in Table 2 for primary drying stage is equal to 5.2%. The good agreement confirms the validity of the obtained correlations for primary drying stage of quince freeze drying.

Similarly, the parameters of Eq. (4) were also determined by experimental drying rates of secondary drying stage, and the following correlation was obtained:

$$\frac{dX}{dt}=1.8224\left(\left(\frac{X}{X_0}\right)^{1.3716}-29.0836\exp\left(\frac{44.6125}{T}-8.7070\right)\right)(0.5844+q^{0.6116}) \quad (7)$$

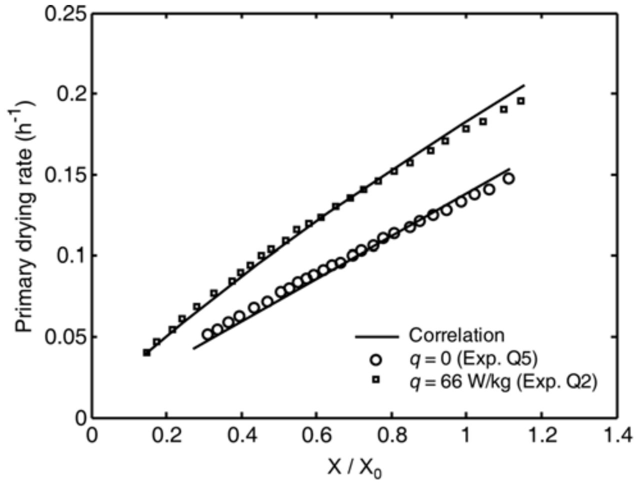

Fig. 8. Comparison of experimental data and model results for drying kinetics of the primary drying stage (the heat load was applied at start up of the process).

Table 2. The mean relative percent deviations, MRD, between the calculated results of Eqs. (6)-(7) and experimental values for each set data

Primary drying stage		Secondary drying stage	
Exp. #	MRD	Exp. #	MRD
Q2 (see Fig. 11)	5.1800	________	________
Q5 (see Fig. 10)	3.8615	________	________
Q6 (see Fig. 10)	7.2511	________	________
Q7 (see Fig. 10)	3.6667	Q7 (see Fig. 12)	2.3256
Q8 (see Fig. 10)	8.3934	Q8 (see Fig. 13)	5.1374

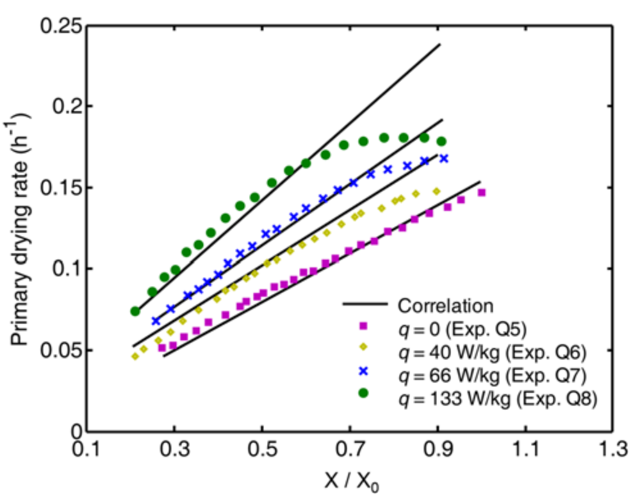

Fig. 7. Comparison of experimental data and model results for drying kinetics of primary drying stage (t_s=30 min).

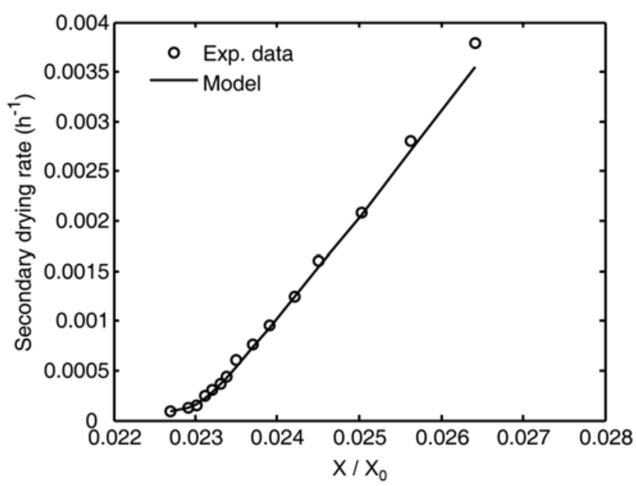

Fig. 9. Comparison of experimental data (Q7) and model results for drying kinetics of secondary drying stage.

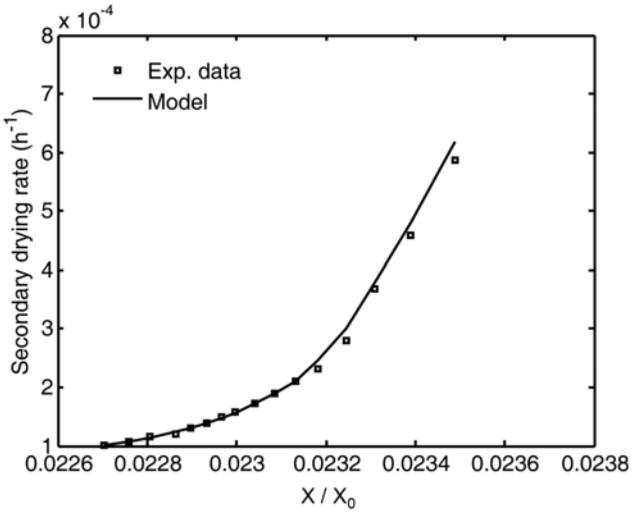

Fig. 10. Comparison of experimental data (Q8) and model results for drying kinetics of secondary drying stage.

The obtained MRD by using Eq. (7) is 5.94%. The accuracy of the above equation is examined by comparing the results of the experimental data Q7 and Q8 (reported in Table 1) which are not utilized in this fitting. Figs. 9-10 show the results of this comparison. The MRD values for each set data are given in Table 2 also. The average of MRD value reported in Table 2 for secondary drying stage is 3.73%.

CONCLUSION

The effect of head load, initiation times of heating, and initial moisture content were investigated on drying of quince in a lab-scale freeze dryer. The results reveal that the heat load is the most effective parameter on the rate of drying. Applying a high heat load power at the beginning of the process significantly reduces the drying time. In addition, two models are proposed on the basis of conceptual understanding of drying process in a freeze dryer, for correlating drying kinetics of primary and secondary drying stages. The good agreement between the experimental data and the calculated values obtained by the proposed models confirms the validity of the obtained correlations for drying kinetics of primary and secondary drying stages of quince.

NOMENCLATURE

a, b, c, d, e : fitting parameters in Eq. (1) [-]
a'', b'', n'', c'', d'', m'', k'' : fitting parameter in Eq. (3) [-]
a', n', b', c', d', e', k' : fitting parameter in Eq. (4) [-]
N : number of data points
q : the imposed heat load [W/kg]
t : time [h]
t_s : heating initiation time [min]
T : temperature of the sample [K]
X_0 : initial moisture content [kg/kg]

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