Best-fitted mathematical model to represent the moisture desorption characteristics of whole limes

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Abstract: Three commonly cited models for drying of agricultural products i.e. Page, Approximate form of diffusion, and Exponential were compared for their ability to the fit the experimental drying data of whole limes based on the root mean square error of estimate (*RMSE*) of the measured and simulated moisture contents. The comparison shows the Page model is the most suitable model having average *RMSE* = 0.046 wet-basis (decimal) while the Approximate form of diffusion and the Exponential models have 0.132 and 0.128 wet-basis (decimal), respectively. This indicated that the Approximate form of diffusion and the Exponential models both have less fitting ability then the Page model for the entire period (> 7 days) of drying in 30 tests at different combinations of temperatures (35°C – 80°C) and relative humidity (12.5% – 33.5%). The Page model was found to be most suitable equation, to describe the drying characteristics of whole mature limes over a typically seven days drying. The Page models can be used for the simulation of bulk volume of whole limes occurring during ventilated storage as commonly used in the middle east region.

Keywords: best-fitted, mathematical model, whole limes, drying

Citation: Basunia, M. A. 2021. Best-fitted mathematical model to represent the moisture desorption characteristics of whole limes. Agricultural Engineering International: CIGR Journal, 23(4): 256-264.

1 Introduction

Limes are seasonal, small and perishable citrus fruits. It is usually harvested when these become green or yellowish. It is normally harvested at moisture content approximately at 88% wet-basis it must be reduced to 10%-12% wet-basis within 7 days (Basunia, 2013) in order to preserve at normal temperature. They are used as a common food ingredient in many parts of Asia and as well as Central America. It is known as amani or Omani in Iran, named after the main production country, Oman. Dried lemons are usually used to add a distinct citrus flavor and a sour tang to legumes and meat dishes. The dried lemons are crushed before usage, and then added to foods like an aromatic rice dish prepared in the Gulf States.

There are various methods and techniques to dry limes. Each method has its own advantages and limitations. Dried products are becoming highly alternative to marketing than the freshly harvested products because of many advantages. Annual production of limes in Oman is estimated about 6340 metric tons (MAF, 2017). The limes are still dried by traditional method of open-air natural sun drying. This method of drying normally takes days, which are 25-35 days in Oman (Basunia et al., 2012, 2013). The traditional open-air natural sun drying methods often yield poor quality. In most cases the drying yard is not properly fenced. So, the product is not protected against dust, rain and wind, or even against insects, birds, rodents and domestic animals

Received date: 2020-07-29 **Accepted date:** 2021-06-12

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while drying. Soiling, contamination with microorganisms and infection with disease-causing germs are the result. The limes dried in this way have short shelf-life and may not be free from contamination. The solar drying facilities combine the advantages of traditional and industrial methods, namely low investment costs and high product quality. Basunia et al. (2012, 2013) carried out an experimental study with a solar tunnel dryer in drying 300 kg freshly harvested limes and reported that the limes were dried within seven days while the average temperature inside the tunnel dryer was approximately 50^0C while the average ambient temperature was approximately 37^0C. In order to describe these processes, particularly during drying and storing of freshly harvested limes through deep bed simulation, data on the moisture transfer and equilibrium characteristics of limes are needed.

Unfortunately, there is little information available on moisture transfer characteristics of whole limes, particularly at near ambient temperature and at high temperatures. Basunia (2016) reported a study on moisture transfer characteristics of whole limes over a wide range of temperature and relative humidity, and fitted a single thin-layer drying model only to describe the moisture transfer characteristics of whole limes. So, there is need to find out the best fitted equation to describe the drying characteristics of whole limes from low to high temperature which is commonly used in whole limes drying (Basunia et al., 2012). Similar studied were reported by Basunia and Rabbani (2011), Basunia (2013), and Paliwal and Sahrma (2019) to select the best fitted equation in rewetting rough rice, barley, and millets, respectively.

The object of this work is to determine the rate of moisture transfer in drying whole limes over a range of temperature and relative humidity, and to find the most suitable drying model for whole limes which can be used in the simulation of moisture transfer during ventilated storage of bulk volume of freshly harvested whole limes commonly practiced in the middle east regions.

2 Mathematical equations to predict whole lime drying

The drying characteristics of food materials have been examined by many researchers (Jamil et al., 2020) and various models for the prediction of the drying rate have been performed with success. Mathematical modeling of drying is crucial for the optimization of operating parameters and performance improvements of the drying systems. The most commonly used models of drying agricultural products are Page (Page, 1949), Approximate form of diffusion (Boyce, 1965), and Exponential (Jayas et al., 1991).

The following three models were therefore chosen for this study to fit the observed drying data of whole limes.

(1) The most commonly used empirical equation to describe the drying of cereals is that of Page (Page, 1949):

$$M_R = \frac{M_t - M_e}{M_e - M_i} = \exp\left(-K \times t^N\right) \qquad (1)$$

where, M_R is the moisture ratio, M_t is the moisture content at any time, decimal wet-basis, M_e is the equilibrium moisture content, decimal wet-basis, M_i is the initial moisture content, decimal wet-basis, t is the drying time in hour, K is drying constant in hour^{-1}, N is the drying parameter (unitless).

(2) It is generally agreed that the mechanism of moisture movement within food materials is controlled by the diffusion phenomenon as stated by Fick's law (Newman, 1931; Parry, 1985). The theoretical model employed in this study is based on Fick's law of diffusion described in a spherical coordinate. Chu and Hustrulid (1968) derived the following liquid diffusion equation in which the diffusion coefficient is a function of moisture content:

$$\frac{\partial M}{\partial t} = D\left(\frac{\partial^2 M}{\partial R^2} + \frac{2}{R}\frac{\partial M}{\partial R}\right) + \left(\frac{\partial M}{\partial R}\right)^2 \frac{\partial D}{\partial R} \qquad (2)$$

Simplifications of the well-known diffusion model (Equation 2) for large drying times that is frequently used to predict the drying of food material and grain are given as:

$$M_R = \frac{M_t - M_e}{M_i - M_e} = C \times \exp\left(-\frac{\pi^2 D t}{R^2}\right) \qquad (3)$$

where $C = 6/\pi^2$, M_R is the moisture ratio, M_t is the moisture content at any time, % wet-basis, M_e is the equilibrium moisture content, % wet-basis, M_i is the initial moisture content, % wet-basis, t is the drying time, h, D is the diffusion coefficient, $m^2\ h^{-1}$, R is the sphere radius, m. Equation 3 may be used to predict the drying of whole limes with known diffusivity, radius, initial moisture content and equilibrium moisture content. An individual lime is assumed to be a spherical, homogeneous, isotropic material drying under isothermal conditions. In applying Equation 3 it is implied that the diffusion process occurring into the whole limes dominates the drying rate.

Equation 3 has been used by many investigators for simulating the drying of grain (Basunia and Abe, 1997, 2000).

(3) Exponential model (Lewis, 1921) can be written as

$$M_R = exp\ (-K \times t) \qquad (4)$$

Where, t is the drying time, h, K is the drying parameter, h^{-1}.

3 Materials and methods

3.1 Sample preparation

The range of drying conditions for the experiment is presented in Table 1. The procedure to determine weight data of the samples of whole lime was described elsewhere (Basunia, 2016). Whole lime drying characteristics were determined at temperature ranging from 35°C to 80°C and for relative humidities ranging from 12.5% to 35.3%, with initial moisture contents in the range of 90% weight-basis.

Figure 1 Freshly harvested limes

About three kilograms limes, freshly harvested (Figure 1), was obtained from the local market. The samples were then sealed into double-layer polyethylene bags and stored in a refrigerator at 5°C. The limes sample was removed from storage one day prior to the drying test and kept overnight in double-layer plastic bags at room temperature. This step brought the sample into thermal equilibrium with the room temperature and prevented any condensation on the limes when it was placed in the test chamber. It also eliminated any transient heat transfer effects on the moisture desorption rates.

3.2 Apparatus used

A convection oven with a self-contained air conditioning unit, which can control the temperature and relative humidity for a wide range, was used for this study. Instead of using the automated displayed values of relative humidity and temperature by the oven, measured values were used in order to get a more accurate measurement. The temperatures and humidity of the drying air were measured using copper constantan thermocouples with an accuracy of ± 0.5°C and ± 3% relative humidity. Temperature and relative humidity data were recorded continuously at 15 minutes interval throughout the drying period. The oven was started 3-4 hours prior to every test to attain the desired drying condition. The air velocity inside the constant temperature and humidity chamber of the oven was almost constant at 0.1 m s^{-1} for different drying conditions. An electronic balance was used to quickly record the mass of the sample taking out from the drying chamber at particular interval. The capacity and sensitivity of the balance were 320 g and 0.001 g, respectively. A randomly selected three whole limes sample were placed inside the constant temperature and humidity chamber. The final and initial moisture contents were determined from the initial and final weight of the individual limes. The data were recorded at 1-2 hours intervals for the first day of drying than at approximately 3-6 hours interval for the remaining period of drying. The drying process was continued till the 24 hours change of moisture content was less than 0.5%, wet-basis (weight change was less than 0.05 g). Normally such an experiment was last for 7-35 days and it took almost 250 days to complete the whole experiment. The final moisture was considered as the dynamic equilibrium moisture content (EMC). The final moisture content of the samples of each test was determined by drying the whole limes sample for 20 hours in an oven at 100°C. The final points were recorded as the dynamic equilibrium moisture contents. Each data file consisted of more than 50 measured points.

3.3 Determination of model parameters

Drying parameters of each the models were found for each test run using non-linear regression. The coefficients of determination R^2 were all above 0.90 with the page model. While it was within 0.77 - 0.92 with other two models. Thirty sets of values for different parameters were used in a non-linear regression procedure to find expressions for each parameter of the model equations.

The measured and simulated moisture contents were compared and statically analyzed for determining the best fit equation. The standard error of estimate (*SEE*) indicates the fitting ability of a model to a data set. The smaller the SEE value, the better the fitting ability of an equation. For the same data set, the equation giving the smallest *SEE* value represents the best fitting ability.

The *SEE* is expressed as

$$SEE = \sqrt{\frac{\sum_{i=1}^{m} (M_t - M_s)^2}{df}} \quad (5)$$

where M_s is the simulated measured moisture content at any time in wet-basis and *df* is the degree of freedom, *m* is the number of data points.

For large data set, as in this experiment, it is defined as

$$SEE = \sqrt{\frac{\sum_{i=1}^{m} (M_t - M_s)^2}{m}} \quad (6)$$

where *m* is the number of data points

4 Results and discussions

The range of drying conditions for the experiment along with the root mean square error (*RMSE*) of each test is listed in Table 1. To complete this whole experimental plan, about seven months were required. The weight data collected as a function of drying time were processed and presented as moisture content versus drying time as did by earlier researchers (Basunia and Abe, 1997, 2000; Basunia, 2013; Mohite et al., 2016).

The typical drying curves at temperatures 35°C, 45°C and 57°C , and at 62°C, 72°C and 80°C and at different relative humidity are shown in Figures 2 and 3, respectively. It is clear from the figures that relatively smooth drying curves were obtained. The figures indicate that to obtain a complete drying curve and equilibrium moisture content point a considerable drying period was required. From Figures 2 to 3 it can be observed that the drying rate increased with the increase of temperature.

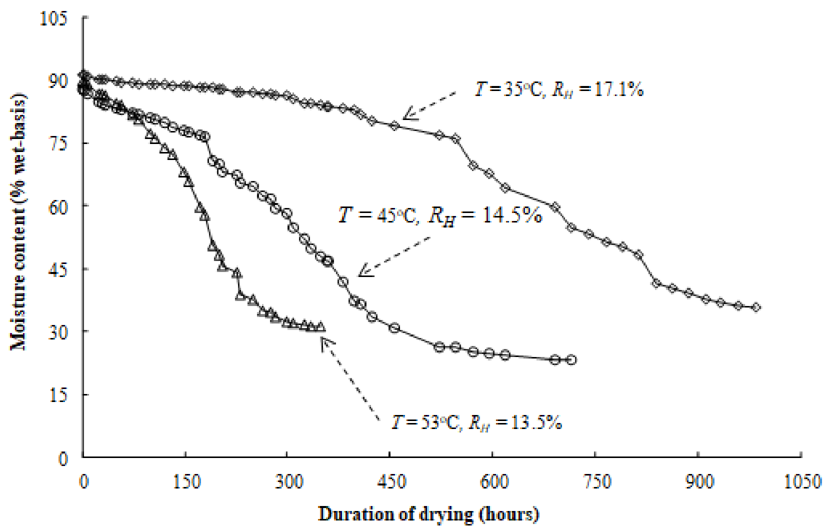

Figure 2 Drying curves of whole limes at temperatures 35°C, 45°C and 53°C respectively

4.1 Expressions for the parameters of Model Equation 1 (Page model)

The 30 sets of values for K and N were used in a non-linear regression procedure to find expressions for K and N. The non-linear regression analysis for K as a function of temperature T in °C and relative humidity R_H in decimal, yielded:

$$K = -0.00502 + 0.0001 \times T + 0.00596 \times R_H \quad (7)$$

with a coefficient of determination R^2 of 0.90.

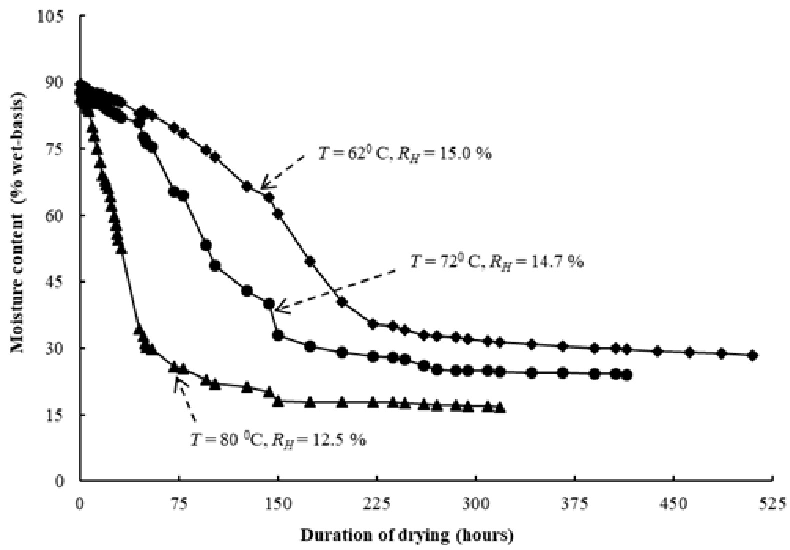

Figure 3 Drying curves of whole limes at temperatures 62°C, 72°C and 80°C respectively

Table 1 Experimental conditions initial moisture content and values of the root mean square errors (*RMSE*) of each test

Sl no.	Drying conditions: Temperature (⁰C)	Drying conditions: Relative humidity (%)	Initial moisture content (% w. b.)	Page Model (decimal w.b.)	Approximate form of diffusion model (decimal w.b.)	Exponential model (decimal w.b.)
1	35	33.5	91.37	0.095	0.259	0.340
2	35	33.5	89.18	0.078	0.224	0.311
3	35	33.5	90.48	0.062	0.268	0.354
4	39	23.5	87.91	0.069	0.267	0.159
5	39	23.5	87.72	0.078	0.271	0.206
6	39	23.5	88.90	0.082	0.325	0.199
7	44	20.0	87.81	0.036	0.108	0.085
8	44	20.0	87.48	0.039	0.107	0.093
9	44	20.0	87.77	0.031	0.102	0.081
10	49	17.1	89.63	0.027	0.097	0.071
11	49	17.1	90.06	0.027	0.099	0.075
12	49	17.1	86.62	0.032	0.100	0.078
13	53	14.5	89.87	0.047	0.101	0.077
14	53	14.5	91.17	0.049	0.124	0.113
15	53	14.5	91.32	0.046	0.102	0.095
16	57	17.0	88.78	0.077	0.146	0.155
17	57	17.0	88.83	0.038	0.103	0.107
18	57	17.0	87.73	0.041	0.110	0.115
19	62	15.0	89.94	0.051	0.135	0.134
20	62	15.0	90.25	0.043	0.128	0.126
21	62	15.0	89.35	0.034	0.115	0.111
22	66	13.5	85.30	0.026	0.085	0.088
23	66	13.5	87.16	0.041	0.101	0.106
24	66	13.5	86.67	0.020	0.081	0.081
25	72	14.7	86.98	0.025	0.103	0.101
26	72	14.7	85.34	0.031	0.089	0.062
27	72	14.7	85.40	0.037	0.089	0.056
28	80	12.5	86.70	0.035	0.083	0.099

29	80	12.5	86.30	0.043	0.079	0.081
30	80	12.5	88.00	0.025	0.0969	0.077
		Average *RMSE*		0.046	0.132	0.128

Note: **RMSE* of estimate of predicted moisture content with more than 50 observations for each test

The non-linear regression analysis for N as a function of function of temperature T in °C and relative humidity R_H in decimal, yielded:

$$N = 0.3017 + 0.0148 \times T + 1.4152 \times R_H \quad (8)$$

with a coefficient of determination R^2 of 0.91.

Moisture simulated by Equation 1 with K and N calculated with Equations 7 and 8, respectively, was compared to observe moisture in Figures 4 and 5. Moisture content variations was within 85.3%-91.3% (w.b), which was a very narrow range, and no significance variations of values of N and K were observed within this narrow range of variations of moisture content of limes. Also, the coefficient of determination R^2 became less than 0.70, if moisture content term is included in the expressions of N and K. The predicted and observed values were in good agreement. Similar agreements were also observed in other drying conditions. The average *SEE* between the measured and predicted values of moisture contents for the full data set was only 0.046 (decimal) wet-basis. This relatively low root means square error (0.046 decimal, wet-basis) shows the accuracy of the model to predict the moisture content at any time during the drying period. The root mean square error of individual tests is shown in Table 1.The highest root mean square error was 0.095 decimal, wet-basis and the lowest was only 0.020 decimal, wet-basis. From Table 1, it can be observed that for most of the tests *RMSE* was below 0.05 decimal wet-basis. It was found the that numerical difference between the moisture contents predicted by Equations 1, 7 and 8 and the observed moisture content did not exceed 6.5% wet-basis points in any test conducted at all temperature and relative humidity combination. This amount of error can be accepted for most practical purpose when working with biological products. Equation 1 with K and N values calculated with Equations 7 and 8, respectively, can be used in a deep bed simulation model to predict the moisture transfer in deep bed drying and storing of freshly harvested limes in arid and semiarid regions. The deep bed drying models for agricultural products are based on thin-layer drying model. The optimization of operating parameters and performance improvements of the deep bed drying systems is largely depending on the accuracy of prediction of the thin-layer drying model. So, Equation 1 with K and N values calculated with Equations 7 and 8, respectively, can be used in a deep bed simulation model. The SEE of individual test is shown in Table 1.

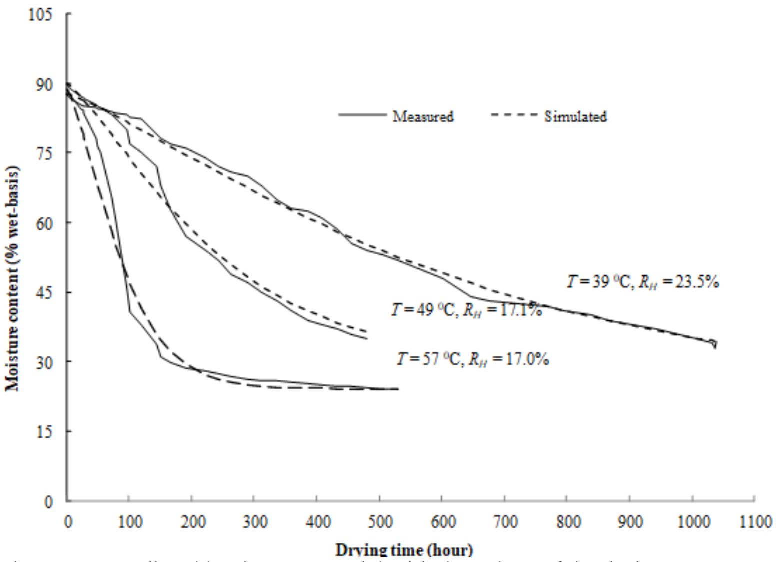

Figure 4 Comparison between the curves predicted by the Page model with the values of the drying parameter K with Equation 7 and N with Equation 8 and experimental points at temperature (T) of 39°C, 49°C and 57°C , and various relative humidities (R_H)

4.2 Expressions for the parameter of Model Equation 2 (diffusion model)

It was observed that C varies between 1.04 – 1.60 within the ranges of temperatures and relative humidities studied without showing any trend of variation with *T* and R_H. The most of the cases *C* was around 1.3. Hence for analysis and interpretations of the results, an overall average value of *C* from all tests was used. The average value of *C* for 30 tests was 1.3. This effectively assumes *C* to be a product-dependent constant instead of 0.608 for a perfectly spherical product as in Equation 3.

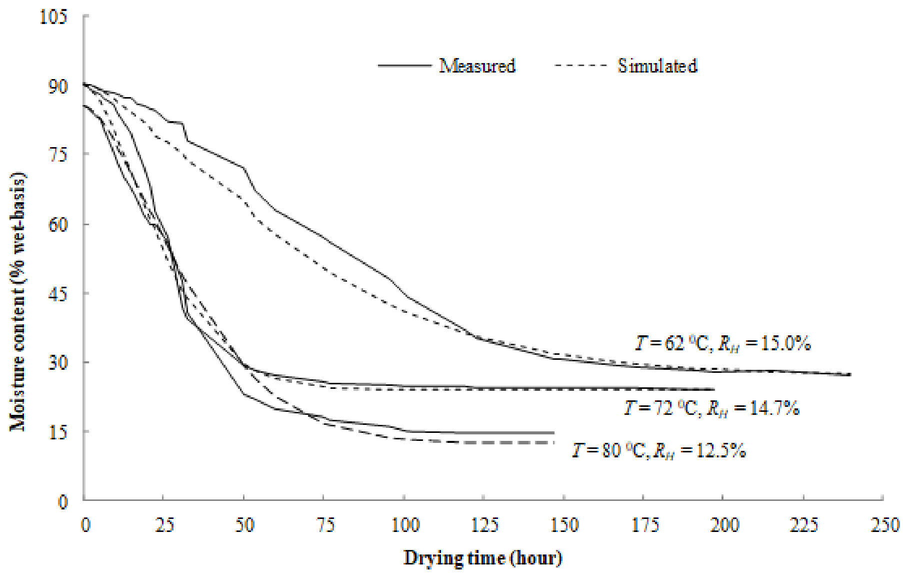

Figure 5 Comparison between the curves predicted by the Page model with the values of the drying parameter *K* with Equation 7 and *N* with Equation 8 and experimental points at temperature (T) of 62°C, 72°C and 80°C, and various relative humidities (R_H)

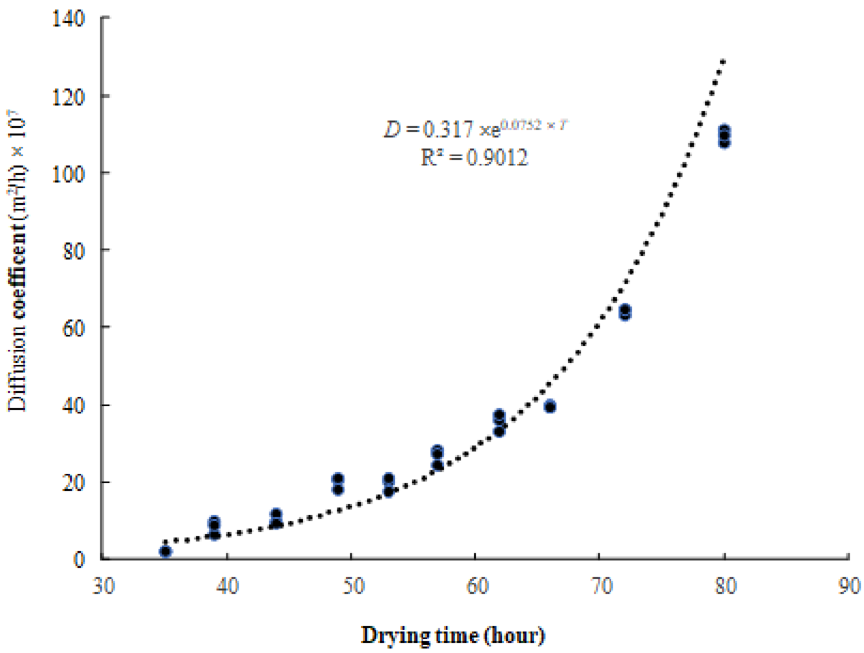

Figure 6 The variations of diffusivity of whole limes with drying air temperatures

Table 1 shows the values of *RMSE* of moisture content of all tests when the parameter *C* was fixed at this overall average of 1.3. The average SEE value of 30 tests was 0.1321 decimal wet-basis for a fixed value of $C = 1.3$. From Table 1 it is also clear that *D* values does not change considerably with relative humidity at a constant temperature. To quantify the effect of temperature on diffusion, an experimental relationship between *D* as a dependent variable and *T* as an independent variable was establish. The expression relating diffusivity, *D* in $m^2\ h^{-1} \times 10^7$, and drying air temperature, *T* in °C, was found as

$$D = 0.317 \times \exp(0.0752) \times T \quad (9)$$

with a coefficient of determination 0.90.

Diffusion coefficients, plotted against drying air temperatures in °C, are presented in Figure 6.

Alternatively, the diffusivity, D in m^2 h^{-1}, can be expressed by an Arrhenius-type equation:

$$D = 2E + 12 \times \exp\left(-\frac{8216}{T + 273.15}\right) \quad (10)$$

with a coefficient of determination 0.91.

Analogous to Equations 9 and 10, the modified diffusivity parameter, D_m, which is defined as $D_m = D/R^2$ (Basunia and Abe, 1997, 2000), can be expressed as

$$D_M = 156.54 \times \exp(0.0752) \times T \quad (11)$$

and

$$D_M = 2E + 14 \times \exp\left(-\frac{8216}{T + 273.15}\right) \quad (12)$$

The *RMSE* of individual tests is shown in Table 1. The highest root mean square error was 0.222 decimal wet-basis and the lowest was only 0.031 decimal wet-basis. From Table 1 it can be observed that for most of the tests *RMSE* was below 0.15 decimal wet-basis. However, the predictability of this model is poor compare to Page model as shown by *RMSE*. The average radius value used in the prediction equation was 45×10^{-3} m which is obtained by randomly nine selected sample of limes used for this experiment.

4.3 Expression for the parameter of model Equation 3 (Exponential)

The multiple regression analysis for K as a function of temperature T in °C and relative humidity R_H in decimal, yielded:

$$K = 0.07585 - 0.0012 \times T - 0.12408 \times R_H \quad (13)$$

with a coefficient of determination R^2 of 0.92.

The highest SEE was 0.354 decimal wet-basis and the lowest was only 0.056 decimal wet-basis. The average *SEE* between the measured and predicted values of moisture contents for the full data set was 0.128 decimal wet-basis which is higher than the Page model (0.046 decimal wet-basis). So, it is clear that the Page model is the most suitable equation to predict the moisture desorption of characteristics of whole lime at commonly used temperature for drying whole limes.

5 Conclusions

The drying rates of whole limes from near ambient temperature to high temperatures have been determined. Three commonly used models were compared based on *RMSE* values. The Page model, based on the ratio of the difference between the initial and final moisture content and the equilibrium moisture content, fits the data well with a standard error of 0.046 decimal wet-basis. The Page model is found to be the most appropriate models for representing the drying characteristics of whole limes. Other two models, the Approximate form of diffusion and the Exponential did not fit well compared to the Page Model. The values of *RMSE* for the approximate form of diffusion and the Exponential models were 0.132, and 0.128 decimal wet-basis, respectively. The result presented here, over a typical seven-day drying period, are useful in the longer-term moisture transfer process occurring during ventilated storage.

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Nomenclature

D diffusivity of rough rice, m^2 h^{-1}

D_m modified diffusivity of rough rice ($= D/R^2$), m^2 h^{-1}

M_e equilibrium moisture content of grain, wet-basis (w.b.)

M_i initial moisture content of grain, wet-basis (w.b.)

M_t moisture content of grain at any time, wet-basis (w.b.)

M_s simulated moisture content of grain at any time, wet-basis (w.b.)

R_m moisture ratio

r radial distance from the center of the sphere, m

R radius of sphere, m

R_H relative humidity, decimal

t drying time, hr

T drying air temperature, ^oC