

Effect of Drying Temperature on the Chemical Properties and Diffusivity of *belimbi* (*averrhoa belimbi*)

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Abstract. In recent years, many dried fruit products have been developed in response to a strong demand by the customer. This type of fruit has a different composition and hence different moisture diffusivity (D). During drying, Fick's Law of diffusion, which describes the movement of liquid water was used to calculate this diffusivity. However diffusivity has strong effects on the material drying characteristics and these must be determined. In this paper, Fick's Law of diffusion with different kinds of boundary conditions was solve using separation of variable (SOV). In order to get the value of D , results obtained using SOV will be compared with the results from the drying of *belimbi* at temperature of 40°C, 50°C and 60°C. Although the results show that variation in the values of diffusivity for different temperatures is relatively small, but the variation in the total time required for drying is significantly bigger: between 3-7 hours. Its shown that diffusivity is an important measurement and should be considered in the modeling of the drying process. The chemical properties of *belimbi* slices in terms of vitamin C, total ash and antioxidant activity with different air temperatures and pre-treatment were also investigated. Higher drying temperatures gives less drying time, a lower vitamin C and antioxidant activity but a greater total of ash, whilst pre-treatment can increased vitamin C and antioxidant activity. The results show that pre-treatment and the drying temperature are important variables to improve mass and heat transfer, as well as the *belimbi* chemical properties.

1. Introduction

It is generally accepted that world food production is not increasing at the same rate as population growth. Therefore, the primary goal of food processing should be to conserve the food we have so that it can be distributed [1]. The way to make food available for later use is to convert it into a stable form because it is difficult to control chemical and biological activities while it is in a fresh state. Hence, drying can be described as the reduction of product moisture to the required dryness values as a definite process [2]. This research centres on the drying of fruit, especially the drying of *belimbi* (*averrhoe belimbi*), which have high levels of initial moisture. Currently, most dehydrated fruits are produced by the technique of hot air drying, which is the simplest and most economical of the various method [3]. However, for modelling purposes, in this study, a combination of osmotic dehydration (sucrose pre- treatment) with conventional hot air drying is assumed to be applied to the surface. The main feature of such a system is its ability to predict moisture and temperature inside the product, which is a very important way of providing structural knowledge about the quality of the new product.



Even though experimentation is an important step for the enhancement of drying technology, with the aid of mathematical modeling and analytical solutions, fundamental research provides very useful information for investigating the complicated physics that evolve during the drying process. For example, diffusivity, D , is generally about transportation of the mass property of water and is an important parameter to be determined during the drying process. Most of the drying models used the 'method of slope' to find the diffusion coefficient, D (for example see [4, 5]). In this method, the Fick law of diffusion with specified boundary condition was solved analytically. Then, the solution is compared with the experiment drying curve by plotting the decay of moisture with drying time.

The basic requirement for drying, from an industrial point of view, is to achieve an amount of dried product in a reasonable time and to obtain acceptable product quality for minimal cost [6]. Hence, the optimisation of the processing variables, especially temperature and pre-treatment, is essential not only to achieve a precise control of the process but also to produce a high quality dried product. Thus, it is important to control this variable and generally achieve higher nutritional value.

Therefore, the aim of this study is to evaluate the behavior of the drying process of *belimbi* at different air temperatures with/without pre-treatment. Three different air temperatures of 40°C, 50°C and 60°C were used. In this study, a partial differential equation of mass transfer equation condition was solved analytically using separation of variable to simulate the drying process. The result from the analytical solution was compared with the experiment drying curve of *belimbi* to find the value of diffusivity, D . In addition, the effects of process treatment before drying and process temperature to chemical properties such as vitamin C, total ash, antioxidant capacity and total phenolic content were also evaluated.

2. Material and Methods

2.1. Mathematical Formulation

A mathematical model that used Fick's Law of diffusion, describing unsteady state mass transfer, is given as follows:

$$\frac{\partial M}{\partial t} = D \frac{\partial^2 M}{\partial x^2}, \quad 0 < x < L \quad (1)$$

where D = effective diffusivity ($\text{m}^2 \text{sec}^{-1}$), M = average local moisture content (kg water/ kg dry matter) and t = time.

2.1.1. Model 1

By assuming that the initial moisture content is uniform ($M=M_0$) throughout the solid, the surface of the solid is in equilibrium with the air for the time considered; the shape of the solid remains constant during the drying period(see [7]), thus giving the boundary and initial condition as below:

$$\text{at } x=0, \quad \frac{\partial M(0,t)}{\partial x} = 0, \quad \text{and } x=L, \quad M(L,t) = M_e, \quad (2)$$

Decompose the equation and solve, using separation of variable. The solution is given by:

$$\frac{M(x,t) - M_e}{M_0 - M_e} = \sum_{n=1}^{\infty} \frac{4(-1)^{n+1}}{(2n-1)\pi} e^{-Dt \left(\frac{(2n-1)\pi}{2L} \right)^2} \cos \left(\frac{(2n-1)\pi x}{2L} \right) \quad (3)$$

Integrate the solution between $0 < x < L$ to find the moisture ratio (MR) and, for a long diffusion time (taken $n=1$), Equation (3) becomes

$$MR = \frac{8L}{\pi^2} e^{-\frac{1}{4L^2} \pi^2 Dt} \quad (4)$$

M_o shows the initial moisture, M_e is the moisture at equilibrium and L is the half thickness of the slice.

2.1.2. Model 2

Dincer [8] used another assumption on the boundary condition, which is given by

$$\text{at } x=0, \quad \frac{\partial M(0,t)}{\partial x} = 0, \quad \text{and } x=L, \quad -D \frac{\partial M(0,t)}{\partial x} = h_m(M - M_e), \quad (5)$$

Using separation of variables, the solution for Equation (1) with boundary conditions Equation (5), is given by

$$\frac{M(x,t) - M_e}{M_o - M_e} = \sum_{n=1}^{\infty} \frac{2 \sin \mu_n}{\mu_n + \sin \mu_n \cos \mu_n} e^{-Dt \left(\frac{\mu_n}{L}\right)^2} \cos\left(\frac{\mu_n x}{L}\right) \quad (6)$$

Taking ($n=1$) for long time diffusion, and the value of μ_1 is given by [8], Equation (6) becomes,

$$MR = Ge^{\left(-\frac{\mu_1^2}{L^2} Dt\right)} \quad (7)$$

On measuring the drying moisture content M with time, t , the drying curve of each experiment is obtained by plotting the decay of dimensionless moisture (MR) in the sample with the drying time. The basic decay equation that is normally used is an assumed exponential model for the moisture ratio, such as the Handerson and Pabis models (for example see [9]), given by,

$$MR = Ae^{-kt} \quad (8)$$

The data from the experiment were fitted with the Handerson and Pabis (Equation (8)) for drying temperatures 40°C, 50°C, and 60°C to get the value of A and k ; comparison was made with analytical solution (Equation (4) for Model 1 and Equation (7) for Model 2). From the comparison, the value of diffusivity, D , was determined at different drying temperatures.

2.2. Chemical Analysis and Antioxidant activity measurement

2.2.1. Drying of belimbi slices and moisture content determination

The *belimbi* fruits were selected on the basis of their appearance and state of ripeness, which was evaluated for the total soluble solid content by using a digital hand held refractometer (N-1 α , ATAGO, USA). The selected *belimbi* were washed and sliced into 0.5cm thickness. Each slice was separated between control and pre-treatment. A pre-treatment was carried out using syrup blanching 70°Brix sugar solutions for 10 minutes at room temperature. The fruit slices were removed from the syrup, rinsed, drained and the dehydration process continued. The slices were spread on stainless sieves in a convective drier with a horizontal air flow (0.2 m/s) at 40°C, 50°C and 60°C for about 8-15 hours. The *belimbi* were weighed every hour on an electronic balance with precision 10-3 g. The drying tests were terminated when 20% moisture content was reached.

The moisture content in the dried *belimbi* slices was analyzed by using the moisture content determination method by AOAC [10]. The percentage of moisture (wt/wt) of the dried *belimbi* slices calculated using the following formula:

$$\text{Percentage moisture (wt/wt)} = \frac{\text{Wt of wet sample} - \text{Wt of dried sample}}{\text{Wt of wet sample}} \times 100\%$$

2.2.2. Vitamin C Determination

The vitamin C or ascorbic acid content in the dried *belimbi* slices was determined by using the 2, 6-dichlorophenol indophenols titrimetric method. The 2, 6-dichlorophenol indophenol solutions is a

solution that has a blue colour in alkaline conditions and pink colour in acidic conditions. Upon titration, these colours are reduced by ascorbic acid to become colourless. The vitamin C content was calculated as follows:

$$\text{mg ascorbic acid per 100g sample} = (X - B) \left(\frac{F}{W} \right) \left(\frac{V}{Y} \right),$$

where, X = Average volume, in ml, of dye used for sample titration, B= Average volume, in ml, of dye used for blank titration, F= mg ascorbic acid equivalent to 1.0 ml indophenols dye solution, V = Total volume, in ml, of the initial assay solution, Y= Total volume, in ml, of the sample aliquot titrated, W= Weight, in g, of sample

2.2.3. Total Ash determination

In the total ash determination for dried *bilimbi* slices, the method of AOAC [10] was followed. The total ash content of the dried *bilimbi* was calculated using the following formula:

$$\text{g ash per 100 g the total sample} = \frac{\text{Weight of sample after ashing}}{\text{Weight of fresh sample taken}} \times 100\%$$

2.2.4. Determination of Total Phenolic Content (TPC)

The total phenolic content (TPC) of the crude extracts was determined using Folin-Ciocalteu reagent following the method of Wolfe et al. [11], using gallic acid as a standard (1.0 mg of crude extract was diluted in 1.0 ml distilled water). The absorbance was measured at 760 nm using a UV-Vis Spectrophotometer (Lambda 35, Perkin Elmer, USA). The total phenolic content was determined as mg of gallic acid equivalent (GAE) per milligram of crude extract, using the equation obtained from the standard gallic acid calibration graph.

2.2.5. Ferric reducing antioxidant power (FRAP)

The FRAP assay was performed with some modifications [12]. FRAP reagent (10:1:1), 10 volumes of 300 mM acetate buffer, pH 3.6 were added with 1 volume of 10 mM 2,4,6-tripyridyl-s-triazine (TPTZ) in 40 mM HCl and 1 volume of 20 mM Fe₂Cl₃. The solvent mixture was incubated at 37°C for 10 minutes. 0.1 ml sample then was added with 2.9 ml of the solvent mixture and incubated again for another hour. The absorbance was measured at 593 nm using UV/ Vis spectrophotometer Five different concentrations of trolox (100, 250, 500, 750, 1000 µmol/l) were used to construct a standard curve and the results for the samples were expressed as µmol/g (edible part).

2.2.6. DPPH Radical scavenging activity

The effect of plant extracts on 2,2 diphenyl-1-picrylhydrazyl (DPPH) radical is estimated according to the method of [13] with some modifications. 600 µl of the extracts (0.2 mg /1 ml distilled water =200 ppm) with increasing concentration were added to 4.5 ml of DPPH (1 mM in ethanolic solution) in a 10 ml bottle with a screw cap. The mixture was shaken and left to stand at room temperature for 20 minutes in a dark place. The absorbance of the resulting solution was measured spectrophotometrically at 517 nm. The radical scavenging activity was measured as a decrease in the absorbance of DPPH and was calculated by the following formula:

$$\text{Scavenging affect (\%)} = 1 - \frac{A_{\text{sample}(517\text{nm})}}{A_{\text{control}(517\text{nm})}} \times 100\%$$

3. Results and Discussions

3.1. Effective Diffusivity

With reference to the drying process of *belimbi* slices with length 4cm, thickness $L=0.5\text{cm}$, $M_0=0.8$ and $M_e=0.1$, the results from the experiment were fitted with 40°C, 50°C, and 60°C to get the value of A and k. The non-linear least square regression based on the Levenberg-Marquardt algorithm was used. The values of k and A and the overall statistical analysis results of Sums Square Error (SSE),

Root Square Mean Error (RMSE) and coefficient of determination (R^2) are shown in Table I. The values of SSE and RMSE are relatively small. From these data it can be seen that there is an adequate fit of the statistical analysis results. Figure I show the result from curve fitting of the pre-treatment and control *belimbi* data. The lines show the data that have been fitted on the basis of their SSE, RMSE and R^2 .

Table 1. Result of statistical analysis of drying of Belimbi at 40°C, 50°C and 60°C

Temperature(°C)	Condition	A	k	SSE	RMSE	R^2
40	Control	1.0448	0.0774	0.0089	0.0235	0.9879
	Pre-treatment	1.0429	0.0716	0.0047	0.0191	0.9908
50	Control	1.0549	0.1014	0.0082	0.0252	0.9885
	Pre-treatment	1.0485	0.1140	0.0976	0.0312	0.9798
60	Control	1.0481	0.1428	0.0097	0.0348	0.9756
	Pre-treatment	1.0591	0.1208	0.0154	0.0393	0.9714

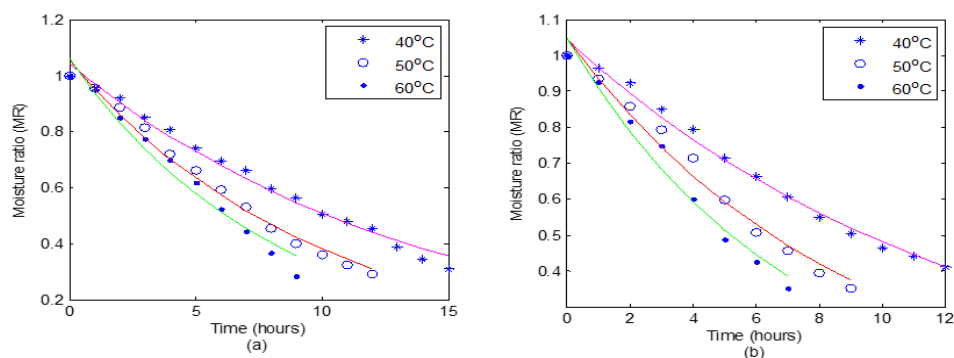


Figure 1. Predicted and experiment moisture ratio for control and pre-treatment, using three different temperatures.

Table 2. Diffusivity Value for control and pre-treatment of Belimbi using different air temperatures

Type of data	Temperature (°C)	Diffusivity(m^2/s) Model 1	Diffusivity(m^2/s) Model 2
Control	40	5.4516×10^{-11}	4.3326×10^{-10}
	50	7.315×10^{-11}	4.5467×10^{-10}
	60	8.4997×10^{-11}	4.9992×10^{-10}
Pre-treatment	40	5.0386×10^{-11}	2.2879×10^{-10}
	50	8.0209×10^{-11}	6.6808×10^{-10}
	60	1.1004×10^{-10}	7.3773×10^{-10}

Table 2 shows the value of diffusivity (D) of the control and pre-treatment of *belimbi*. The value of D from the results lies in the range between 1.1004×10^{-10} to 8.2112×10^{-11} (m^2/sec) for Model 1 and 2.28×10^{-10} – 7.37×10^{-10} (m^2/sec) for Model 2 and is comparable with the data collected [14] for different kinds of food. These values depend on the experimental drying temperature: if the temperature is increased, the diffusivity will increase, which leads to a faster decrease in moisture content. The value of diffusivity for Model 1 is smaller than that of Model 2 and this value depends on the assumption at the boundary. Thus, it can be concluded that the diffusion process is a very slow process and it takes around 8-15 hours to dry *belimbi*, depending on the temperature.

3.2. Effect of temperature and pre-treatment on chemical properties of dried Belimbi

Many biochemical reactions can be induced during the drying of food. These reactions can be linked to product composition, temperature and water content (or chemical potential, or water activity), all of which may vary from one point to another point inside the food [15]. The results of the total ash,

vitamin C and antioxidant properties of dried *belimbi* after drying at different temperatures are given in Table 3. Vitamin C (ascorbic acid) is an important nutrient, and is often taken as an index of the nutrient quality of processes. From the result, syrup blanching gives higher vitamin C compared to the control and this value decreased as the temperature increased. Ascorbic acid was mainly lost due to heat sensitive reactions, especially oxidation. This could explain the lower value of ascorbic acid in high temperature drying. A similar result obtained by [16] showed that higher osmotic temperature affects ascorbic acid content. [17] found out that a maximum loss of 98.2% of vitamin C occurred in a sample dried at 90°C. The amount of ash is an index of the mineral content in fruit. From the Table 3, the value of ash increases with the use of pre-treatment compared to the control; this value also decreased when the air temperature increased.

Table 3. Temperature and pre-treatment effect on chemical properties of dried *belimbi*

Temperature	Condition	Moisture Content	Ash (%)	Vitamin C(mg/g)	Antioxidant			
					Total Phenolic content(mg GAF/100g)	Scavenging effect (%)	FRAP Activiy	
40	Control	69.26	70.20	5.95	15	56	0.72	
	Pre-treatment	58.19	90.29	8.2	28	75	0.85	
50	Control	71	60.17	5.5	14	56	0.58	
	Pre-treatment	57.46	87.72	7.95	18	75	0.65	
60	Control	71	65.47	4.5	13	56	0.4	
	Pre-treatment	57.15	81.12	6.95	15	75	0.52	

Antioxidant is a substance that has the ability to delay the oxidation of a substrate by inhibiting the initiation or propagation of oxidizing chain reactions caused by free radicals [18]. Estimation of the total phenolic content using the Folin-Ciocalteu reagent revealed that pre-treated *bilimbi* slices contained the highest amount of polyphenol, which is between 15-29 mg GAE/100 g extract, compared to control slices. A lower polyphenol amount was achieved by control slices, where the values ranged between 13-15 mg GAE/100 g extract. Drying using syrup blanching gives a higher total phenolic content compared to the control, and this value decreased as the temperature increased. This behavior could be related to the drying process at low temperatures, which implies that long drying times may promote a decrease in antioxidant capacity. Results by [19] showed that the highest antioxidant activity of dried pulp and peel oranges was determined when dehydration took place at 60°C. The total antioxidant activity was higher at a lower drying temperature in both unblanched and water blanched orange peel [20]. However, data on the effects of total phenolic content are conflicting due to several factors such as the drying method, type and extraction, pre-treatment and so on

From the results in Table 2, drying temperature has no effect on percentage of scavenging. However, the experiment by [17] shows that radical scavenging activity produces more antioxidant activity at high temperatures (80°C and 90°C) than at low temperatures (40°C-70°C). When drying using syrup pre-treatment, a higher scavenging effect is given, compared to control slices.

A ferric reducing antioxidant power (FRAP) assay was performed to measure the total reducing capacity of a compound, based on its ability to reduce Fe³⁺ or tripyridyltriazine complex to its blue-colored ferrous form. Table 2 also shows the relationship between FRAP activity of control and pre-treatment dried *bilimbi* slices with the increment of drying temperature. The results show that both the control and pre-treatment dried *bilimbi* slices have decreasing FRAP activity as the drying temperature increases. Pre-treated slices had higher FRAP activity when compared to the control slices. According to [12], a strong correlation between total phenolic content and FRAP assay existed as the phenolic compounds have redox properties, which allow them to act as reducing agents, hydrogen donators, and

singlet oxygen quenchers. Thus, this redox potential of phenolic compounds can be used as the indicator to determine the antioxidant potential of foods

4. Conclusion

The quality of a dried product depends critically on the process parameters. Specifically, drying characteristics, such as temperature and pre-treatment, play an important role in the determination of physical and chemical properties. The optimization of drying temperature and pre-treatment concentration in order to get a desired product quality can be determined through mathematical modeling. Hence, the value of effective diffusivity has been investigated through the Fick Law of diffusion that is solved using separation of variable. We can conclude that, with the aid of an analytical solution, the parameter values involved in the fundamental physics equation can be determined. In this paper, different drying temperatures of 40°C, 50°C and 60°C and sucrose pre-treatment have been used. The major findings of this study are that the drying time is reduced when the air temperature increases and, furthermore, the use of pre-treatment can further reduce the drying time. A higher temperature can reduce the Vitamin C content in *belimbi* but the value of ash increased as the temperature increased. A lower temperature, which implies long drying times, may promote a decrease in antioxidant capacity, decreasing FRAP activity but this has no effect on the percentage of scavenging. There are close relationships between temperature and drying time with respect to the heat treatment of food. As a general rule, high drying temperatures tend to spoil the chemical properties of food products.

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