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**REVIEW ARTICLE**

# A REVIEW BASED ON THE RELATIONSHIP AMONG DRYING, CURVE FITTING AND MATHEMATICAL MODELS IN FOOD SYSTEMS

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**ABSTRACT**: Drying process extends the shelf life stability of foods that preserve the quality and food stability by removal of water. Several drying methods are being used such as microwave, vacuum-microwave, freeze drying, convective air, spray drying, fluidized bed drying and infrared-convective for drying purposes.There is a close relationship between deteriorative reactions and final moisture contents in food materials. The final moisture content affects the storage capabilities and shelf-life of foods and to predict the moisture contents of foods mathematical models are being used at any drying time. The correlation coefficient (R2), the reduced chi-square (x2) and root mean square of error (RMSE %) are used to fit the models for drying curves. Increase drying temperature,drying air,microwave heating watts result an increase in drying rate and effective moisture diffusivity. Drying with microwave method is effective method for food preservation and rate of drying is higher than traditional drying methods.Microwave or infrared drying enhances drying rate and rapid process that creates a porous,crispy and delicious texture of the food samples.

## INTRODUCTION

Drying is a food preservation method that applied in food processing and storage to increase shelf life stability. This phenomena is based on the moisture removal from food materials in anyways. The heat required for the removal of water in foods is necessary to transfer the food materials by the way of conductive, convective and radiaton.The water is present in food materials in different forms such as chemically bounded, free and adsorbed water. In order to increase shelf life stability of food materials moisture content of foods should be decreased.Chemical, enzymatic, non-enzymatic and microbiologically induced reactions are related with moisture content and to prevent the deteriorative reactions that occured in foods, water content should be decreased (<15%) (Wiktor *et al.*, 2013). The water acts as a solvent for reactants and compounds that resulting from reaction products especially in enzymatic browning reactions in food systems.The physical, chemical and biological stabilities of food materials are affected by water content that related with water activity,desorption and adsorption isotherms. The sorption isotherms describe the sorption behavior, mechanism, food polymers and mutual effectiveness of water. By using the isotherm datas, optimum conditions of drying, storage and packaging process of foods can be achieved (Cemeroglu, 2004).

Drying process prolongs the shelf life stability of foods that preserve the quality and food stability by decreasing water activity (Puente-Diaz *et al.*, 2013). The mechanical properties of food sysytem is most important factor that reflects the final quality of food materials and the other factors are texture, firmness and chewing ability during drying process.It is reported that textural properties are correlated to the rheological parameters that are important in understanding the structure of food and biological materials during drying process (Markowski and Zielinska, 2013). Moisture is removed from the food materials at falling and constant rate period during drying process. The amount of water removed during drying remains constant per unit time at constant rate period while drying rate decreses at falling rate period. Drying rate is controlled by factors that affect heat and mass transfer. The factors are drying air temperature, humidity, air velocity, surface area to be

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dried, food contents and physical properties, part massiveness, shapes, particle size and etc. The most effective factor that affect drying rate is the characteristics of food materials.It means the chemical components are extremely important in drying rate whether containing oil, carbohydrates such as starch, pectines and the dissolved materials that present in foods (Cemeroglu, 2004).

Hot air is being used for preserving foods during drying process in general. However,microwave drying, vacuum-microwave drying, freeze drying, convective air drying, spray drying, fluidized bed drying, infrared-convective drying methods are being used for drying purposes (Markowski and Zielinska, 2013). Food materials dried with infrared method serve higher drying rate compared to the convective drying process and in infrared assisted drying, the power density is higher than that in convective drying with hot air. Thus, application of combined infrared and convectional convective drying is considered to be more efficient than radiation or convective drying alone (Puente-Diaz *et al.,* 2013). Food materials to be dried are heat sensitive materials and there is a close relationship food contents and drying methods that to be used in drying process. Deteriorative reactions, microbial spoliage, non-enzymatic browning reactions and lipid oxidation reactions are related with the presence of water and water activity of food materials. Feeding value of the dried products is depend on drying method used and drying conditions. Due to the chemical, enzymatic, non-enzymatic and microbiologically induced reactions in food materials are related with moisture content and as a result, the final moisture content affects the storage capabilities and shelf-life of foods.Mathematical models are being used for predicting the final moisture content and drying parameters and drying kinetics are required for modelling the constant/falling rate of drying process.Several mathematical models are present to describe drying curves such as emprical, semi-emprical models, exponential, logaritmic models and etc.The mathematical models are thin layer equations that predicts the moisture content of food at any drying time generally.Kinetic models allow the producers to choose most suitable drying conditions either to desribe drying equipment or minimize drying process time for the final product specifications (Vega-Galvez *et al.,* 2010).

## MATHEMATICAL MODELS FOR DRYING KINETICS OF FOODS

Mathematical modelling of drying kinetic is important for predicting moisture content of food materials at any drying time.Numerous models are being used for drying kinetics that used to evaluate the drying kinetics listed in Table 1. It is reported that theoretical mathematical models consider internal resistance to the moisture transfer between food and heating air while semi-theoretical and emprical equations consider external resistance during drying process.Theoretical kinetic models need assumptions of geometry of food materials, its mass diffusivity and conductivity whereas emprical models neglect the fundementals of drying process and present a relationship between average moisture and drying time due to statistical analysis (Kumar *et al.,* 2010). The semi-theoretical equations are being used mostly than theoreticals models and semi-theoretical equations are derived from Fick's second law of diffusion model.Food materials are being dried in many ways but especially thin layer drying is most popular according to faster drying rate compared to others and minimum loss of nutritive values.

**Table 1:** Mathematical equations used to describe drying kinetics of food materials in literatures

| Model No. | Name | Equation | References |
|---|---|---|---|
| 1 | Page | $MR=\exp(-k.t^{n})$ | Madamba *et al.,* (1996) |
| 2 | Henderson and Pabis | $MR=a.\exp(-k.t)$ | Henderson, (1974) |
| 3 | Newton (Lewis) | $MR=\exp(-k.t)$ | Demir *et al.,* (2004) |
| 4 | Logaritmic | $MR=a.\exp(-k.t)+b$ | Togrul and Pehlivan, (2002) |
| 5 | Midilli | $MR=a.\exp(-k.t^{n})+b.t$ | Midilli *et al.,* (2002) |
| 6 | Wang and Singh | $MR=1+a.t+b.t^{2}$ | Wang and Singh, (1978) |
| 7 | Polynommial | $MR=a+b.t+c.t^{2}+d.t^{3}$ | Gamli, (2011) |
| 8 | Logistic | $MR=b/[(1+a.\exp(k.t))]$ | Soysal *et al.,* (2006) |
| 9 | Weibull | $MR=\exp(x(t/b)\ )$ | Corzo *et al.,* (2010); Vega-Galvez *et al.,* (2010) |
| 10 | Fick's second law of diffusion | $MR=8/\ ^{2}.\exp(-(\ ^{2}D_{ef}.t)/4L^{2})$ | Ramaswamy and Nsonzi, (1998) |
| 11 | Two-factor | $MR=a.\exp(-k_{1}.t)+b.\exp(-k_{2}.t)$ | Gamli, (2011) |
| 12 | Modified Page | $MR=\exp(-(k.t)^{n})$ | White *et al.,* (1981) |
| 13 | Modified Henderson & Pabis | $MR=n_{1}.\exp(-k_{1}.t)+n_{2}.\exp(-k_{2}.t)+ n_{3}.\exp(-k_{3}.t)$ | Puente-Diaz *et al.,* (2013) |
| 14 | Approximation of diffusion | $MR=a.\exp(-k_{1}.t)+(1-a).\exp(-k_{2}.a.t)$ | Yaldiz *et al.,* (2001) |
| 15 | Verma | $MR=a.\exp(-k_{1}.t)+(1-a)\exp(-k_{2}t)$ | Verma *et al.,* (1985) |
| 16 | Thompson | $t=a.Ln(MR)+b.[Ln(MR)]^{2}$ | Thompson *et al.,* (1968) |
| 17 | Geometric | $MR=a.t^{-n}$ | Chandra and Singh, (1995) |

The equaiton of Fick's can be rewritten due to homojenity of inital moisture content, neglilible external resistance, shrinkage and constant diffusivity as:

$$MR=(M-M_e)/(M_o-M_e) = (8/\ ^2).exp(\ ^2D_{ef}/4L^2) \quad (1)$$

where M is the moisture content of food at any times (kg water/kg dr solid), $M_o$ is the initial moisture content of food sample(kg water/kg dr solid) and $M_e$ is the equilibrium moisture content of sample (kg water/kg dr solid).
It is reported that falling rate drying period can be described using Fick's diffusion model for the characteristics of food samples. Crank, (1975) developed an equation in order to solve diffusion model for various regularly sahped bodies such as cylindrical, rectangular and spherical samples as:

$$MR_i=8/\ ^2 \sum [1/(2n+1)^2exp(-(2n+1)2\ ^2D_{ef}.t)/4.L^2)] \quad (2)$$

Where, $D_{ef}$ is the effective moisture diffusivity ($m^2/s$), L the half thickness of slab (m). Equation (2) is simplified due to long drying process in terms of first term series as:

$$Ln\ MR = (Ln\ 8)/\ ^2- (\ ^2D_{ef}.t)/(4.L^2) \quad (3)$$

Moisture diffusivity is derived from plotting experimental drying in terms of MR versus drying time due to equation (3). The equation (3) is compared to y=ax+c where a represents the slope of straight line and c is the intercept. The slope is obtained by

$$slope= (\ ^2D_{ef}.t)/(4.L^2) \quad (4)$$

and

$$D_{ef}= (4.L^2)/(\ ^2).slope \quad (5)$$

Where, slope refers to $[(LnMR)_2-(LnMR)_1]/(t_2-t_1)$
Moisture diffusivity parameter is temperature dependent variable that be described by an Arrhenius relationship (Akgun and Doymaz 2005; Madamba *et al.*, 1996; Wang *et al.*, 2007; Puente-Diaz *et al.*, 2013) as:

$$D_{ef}= D_o\ exp\ (-E_a/RT) \quad (6)$$

Where, $D_o$ is the pre-exponential factor of Arhenius model ($m^2/s$), $E_a$ the activation energy in terms of kJ/mole, R the universal gas constants as kJ/mole.K and T absolute temperature as Kelvin (K). By ploting Ln $D_{ef}$ versus reciprocal temperature, activation energy is derived from slope of the straight line.

## FITTING MATHEMATICAL MODELS

Modelling of drying kinetics of food samples is important for drying process and used to predict moisture content of samples at any drying time.Drying curves are plotted as a function of time and dimensionless moisture ratio (MR) during process. MR is obtained by using equation (1). In order to select mathematical equation that describes the moisture content and time datas, we need the correlation coefficient ($R^2$), the reduced chi-square ($x^2$) and root mean square of error (RMSE %).

$$R^2=1- ([\sum_i^N (MR_{ip}-MR_{ie})^2])/( [\sum_i^N (MR_{av,ip}-MR_{ie})^2]) \quad (7)$$
$$RMSE= [\sum_i^N (MR_{ip}-MR_{ie})^2/N]^{0.5} \quad (8)$$
$$x^2= \sum_i^N [((MR_{ip}-MR_{ie})^2/(N-n)] \quad (9)$$

Where, $MR_{ip}$ is the predicted dimensionless moisture ratio, $MR_{ie}$ is the experimental dimensionless moisture ratio, $MR_{av,ip}$ is the average value of experimental moisture ratio,N is the number of observations, and n is the number of constants in the mathematical equations.
The higher values of $R^2$, lower values of RMSE and $x^2$ indicate better fitness of drying curves according to the moisture and time datas.

## APPLICATIONS OF DRYING KINETICS OF FOOD SAMPLES

Food materials are being drien by many ways such as convective, microwave, vacuum drying, vacuum-microwave and freze drying methods (Nawirska *et al.*, 2009). Drying process supplies heat to the food materials and removes moisture content (in vapour form) in drying methods. By means of contacting oxygen that present in the air, food materials become exposed to high drying temperature for a long time which resulting reduced content of valuable components except freeze drying. Freeze drying serves excellent final product quality due to slight decrease in color, flavour, chemical composition and physical shapes of food samples. Most important disadvantage of freeze drying method is high cost of application and time consuming that requires pre-freezing and long-lasting storage of raw materials (Nawirska *et al.*, 2009). Microwave and the combined microwave-vacuum serve very short of process time. In microwave methods, the wave penetrates directly in to the material that results fast volumetric heating and water molecules causes rapid evaporation of water during microwave drying at low temperature (Nawirska *et al.*, 2009; Puente-Diaz *et al.*, 2013). Drying with microwave method of food samples is effective methods for food preservation and rate of drying is higher than traditional drying methods.Microwave wattage is decisive factor enhancing for drying rate and rapid process of drying creates a porous texture of the food samples that obtaining a crispy and delicious texture (Figiel, 2010).

In most drying process in food samples, water loss is rapid at first drying stage at constant rate period while power that connecting the remaining water to the food materials increases which is known as falling rate period. When the drying curves of food materials are plotted due to the drying time and moisture ratio by means of constant and falling rate period, descending curve is obtained generally. The studies related with food drying show that drying rate is function of drying air velocity,drying temperature or microwave heating watts and the increasing drying temperature, drying air velocity or microwave watts, the drying time required to achieve certain moisture content of food materials decreases such as tomato slices (Gamli, 2011), apricot (Togrul and Pehlivan, 2002), apples (Togrul, 2005) opuntia ficus ndica fruits (Toujani *et al.*, 2013), olive-waste cake (Vega-Galvez *et al.*, 2010), tomatoes (Doymaz 2007; Gaware *et al.*, 2010), pine forest residues (Phanphanich and Mani, 2009), murta berries (Puente-Diaz *et al.*, 2013), pumkin slice (Nawirska *et al.*, 2009), susame seeds (Kahyaoglu and Kaya, 2006), giant pumpkin (Sojak and Glowacki, 2010), tomato paste (Jumah *et al.*, 2004), apple tissue (Wiktor *et al.*, 2013), silverside fish (Toujani *et al.*, 2013), bamboo slices (Kumar *et al.*, 2013), carrot (Markowski and Zielinska, 2013), pomegranate seeds (Sharma *et al.*, 2011), roasted green wheat (Al-Mahasneh *et al.*, 2013) and etc. Mathematical models that present in literature (listed in Table 1) are being used in order to predict final moisture content or process time for sufficient drying of food materials.

In order to determine mositure ratio of food materials as a function of drying time, mathematical models are fitted and curve fitting parameters ($R^2$, RMSE, $x^2$) which are used to describe drying time and final moisture content that give which expression is the best model for drying process.Fitting of mathematical models for drying kinetics of food materials differentiates due to foods to be dried.There is no definite rule for fitting of models which model is suitable for drying kinetics of food samples. Some studies based on drying kinetic studies and suitable mathematicals model for drying purposes are listed in Table 2 for some food materials.

**Table 2:** Some mathematical models that used to fit drying kinetics of food materials in literatures

| Mathematical Model | Food materials to be dried | References |
|---|---|---|
| Page and logaritmic | bamboo slices, roseship | Kumar *et al.*, (2013); Jena and Das, (2007) |
| Page, Henderson and Pabis, Weibull, two-term | olive waste cake | Vega-Galvez *et al.*, (2010) |
| Page | pumkin slice,purslane | Nawirska *et al.*, (2009); Akpinar and Bicer, (2007) |
| Polynommial | tomato slice | Gamli, (2011) |
| Midilli-Kucuk | silverside fish, murta berries, carrot pomace, apple tissue, opuntia ficus fruit | Puente-Diaz *et al.*, (2013); Wiktor *et al.*, (2013); Kumar *et al.*, (2013); Toujani *et al.*, (2013) |
| Henderson and Pabis | pine forest residue, giant pumkin | Phanphanich and Mani, (2009) |
| Two-term | green wheat | Al-Mahasneh *et al.*, (2013) |
| Page | tomatoes, pepper | Doymaz, (2007); Gaware *et al.*, (2010) |
| Two-term, Page | susame seeds | Kahyaoglu and Kaya, (2006) |
| Modified Henderson and Pabis | olive leaves | Erbay and Icier, (2007) |
| Thompson | pomegranate seeds | Sharma *et al.*, (2011) |

The drying constant, k that presents in models except model numbers of 6,7,9 and 10 in Table 1 represents the rate of moisture removal from food samples pere unit time.It is related with effective moisture diffusivity when the drying procedure takes place only falling rate period and liquid diffusion controls the drying process (Phanphanich and Mani, 2009). Increase in drying temperature and drying air result increase in drying rate and k values.Drying rate constant shows the higher values during microwave drying due to enhancing drying rate by generating more energy inside the food materials (Gaware *et al.,* 2010). Radiation energy is converted into heat and food samples exposed to infrared radiaton are intensely heated during microwave drying thus drying rate constant increases. In microwave drying process, due to increase in molecular vibration by means of absorption of radiation impinges on food surface and penetrates into the food materials.The increased in molecular vibration due to absorption of microwave radiation produces heat at the surface and iner layer of food materials.As a result of this, the rate of water removal from foods increases (Puente-Diaz *et al.,* 2013).

The effective moisture diffusivity for food materials is modelled by using the Arrhenius equaiton to determine its functional relationship with drying temperature.The logarithm of moisture diffusivity constant in equation (6) exhibits a linear behaviour against the reciprocal of temperaure and increase in drying temperature causes increase in moisture diffusivity for food samples (Vega-Galvez *et al.,* 2010; Gamli, 2011; Kumar *et al.,* 2010; Puente-Diaz, 2013; Doymaz, 2007; Toujani *et al.,* 2013; Gaware *et al.,* 2010). The moisture diffusivity of food materials increases with the increase in drying temperature and drying air velocity that causes an increase in diffusion in food sample.It is reported that moisture diffusivities of food samples under microwave conditions are higher compared to convective drying conditions. $D_{ef}$ values of food materials change between $4.3.10^{-10}$-$7.6.10^{-10}$ $m^2/s$ for prunes and $3.32.10^{-9}$-$9.10^{-10}$ $m^2/s$ for berries at 50-70 ºC, $4.6.10^{-10}$-$16.3.10^{-10}$ for pineapple rings at 40-60 ºC, $7.01.10^{-10}$-$8.10^{-10}$ $m^2/s$ for longan at 40-80 ºC (Puente-Diaz *et al.,* 2013), $2.6.10^{-9}$-$9.14.10^{-9}$ $m^2/s$ for tomato products at 60-90 ºC (Gaware *et al.,* 2010; Doymaz, 2007), $8.7.10^{-8}$-$2.17.10^{-9}$ $m^2/s$ for potato at 50-70 ºC, $2.10^{-10}$-$4.2.10^{-10}$ for garlic slices at 50-90 ºC (Madamba *et al.,* 1996), $8.9.10^{-10}$-$1.3.10^{-9}$ $m^2/s$ for apricot, $7.91.10^{-9}$-$2.5.10^{-9}$ $m^2/s$ for grape, $9.10^{-10}$-$3.3.10^{-10}$ $m^2/s$ for carrot (Vega-Galvez *et al.,* 2010). The effective moisture diffusivity of food materials ($D_{ef}$) lies within general range of $10^{-11}$ to $10^{-9}$ according to previous research results in literature.

## CONCLUSION

Storage capabilities and shelf-life of foods are dependent on the final moisture content and in order to obtain the final moisture content, food materials are being dried in many methods that prolong the shelf life stability of foods, preserving the quality and food stability, such as hot air, convective, microwave, infrared and freeze drying methods.In order to predict final moisture content of food samples, mathematical models are being used at any drying time. Drying kinetics are required for modelling the constant/falling rate of drying process and being used to describe moisture diffusivity, equilibrium moisure content and model parameters.In order to select models that fit the drying curves of food materials, correlation coefficient ($R^2$), the reduced chi-square ($x^2$) and root mean square of error (RMSE %) are used.There is no definite rules between describing drying curves and mathematical models. The effective moisture diffusivity increases with the increase in drying temperature or microwave heating watts. An application of combined infrared and convectional convective drying is more efficient than radiation or convective drying alone.

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