MATHEMATICAL MODELLING OF DRYING KINETICS OF *KINEMA*

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Mathematical Modelling of Drying Kinetics of *Kinema*

A dissertation submitted to the Department of Food Technology, Dharan Multiple Campus, Tribhuvan University, in partial fulfillment of the requirements for the degree of B.Tech. in Food Technology.

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Approval Letter

This *dissertation* entitled *Mathematical Modelling of the Drying Kinetics of Kinema* presented by Ranjana Poudel has been accepted as the partial fulfillment of the requirement for the B. Tech. Degree in Food Technology.

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Abstract

Kinema is an indigenous food of Nepal traditionally prepared by natural fermentation of boiled soybeans covered with a sticky, colorless material accompanied by pungent odor of ammonia. The effects of temperature variation on the drying kinetics of *kinema* samples were studied. The present investigation was conducted at drying temperatures of 50ºC, 60ºC, 70ºC and 80ºC in cabinet dryer and the drying kinetics of *kinema* were evaluated. The experimental data were fitted to five thin layer mathematical models including the Lewis, Page, Handerson and Pabis, Logarithmic and Midilli *et al.* models. These models were evaluated by comparing the coefficient of determination (R^2), chi square ($\chi 2$), root mean square error (RMSE) and sum of standard error (SSE).

The drying rate curve showed that the drying of *kinema* falls in falling rate period. The rate of drying continuously decreased as drying proceeded. Graphical and statistical analysis of result showed that Midilli *et al.* model was best fitted for cabinet drying with the value of R^2, RMSE, $\chi 2$ and SSE ranging from 0.982496-0.999538, 0.00784- 0.03271, 0.0000839-0.001399 and 0.000923- 0.018192 respectively. The effective diffusivity was calculated using Fick's diffusion equation and the value varied from 2.0258×10^{-10} m^2/s at 50ºC to 9.4219×10^{-10} m^2/s at 80ºC. Effective moisture diffusivity increased with increase in drying temperature. The activation energy was found to be 49.599 kJ/mol and the diffusivity constant was found to be 6.63×10^{-6} m^2/s respectively.

Contents

List of Tables

List of Figures

List of Plates

List of Abbreviations

Abbreviation	Full form
ASAE	American association of agricultural engineers
MR	Moisture Ratio
$MR_{exp,i}$	i^{th} experimental MR
$MR_{pre,i}$	i^{th} Predicted MR
M_{db}	Dry basis moisture content
M_e	Equilibrium moisture content
$MR_{exp,i}$	i^{th} experimental MR
M_t	Moisture at time
M_{wb}	Wet basis moisture content
M_o	Initial moisture content
R^2	Coefficient of determination
RMSE	Root mean square error
SSE	Standard Sum of Error
χ^2	Chi- square

Part I

Introduction

1.1 General introduction

Soybean (*Glycine max* L.) is a leguminous crop that was originated in China. Among the natural vegetable, known Soybean is nutritively richest food, because of high percentage of protein (40%), fat (19%) and low carbohydrate (33.3%) compared to other legumes. So soybean is called as king of legumes (Sharma, 1997). The soybean has many names depending on the country where it is grown and used. It is generally reported that the name was derived from Chinese Chiang yiu which means soy sauce; in Japanese it would be pronounced Sho yu. Rather recent names include soybean, sojabean, soy, so-yu, Chinese pea, Manchurian bean and soia. In Nepali, it is called Bhatmas (Katawal,1984).

Kinema is traditionally prepared by natural fermentation of boiled soybeans and after fermentation soybean is converted with a sticky, colorless material accompanied by pungent odor of ammonia. The major organism responsible for *kinema* fermentation is *Bacillus subtilis* (Karki,1986 and Tamang and Sarkar, 1994). It resembles with other oriental fermented foods like natto of Japan, thua-nao of Thailand and tempeh of Indonesia (Tamang et al, 1998 and Nikkuni et al, 1995). The other similar products are akhoni of Nagaland, troombai of Meghalaya, hawaijar of Manipur, and bekang-um of Mizoram. *Kinema* is consume in Darjeeling, Sikkim, eastern part of Nepal and Bhutan.

Kinema is a soybean product which have characteristics odor, slimy appearance and even though it is well popular in Eastern Nepal and certain parts of India. There is no industrial manufacture of *kinema* even small level production of *kinema* also not available. One obvious reason for limited *kinema* production is due to the virtual ignorance of this product. Another probable reason could be the typical ammonical odor which is not acceptable to other ethnic people living in other parts of the country (G.C, 1994). *Kinema* is prepared by traditional method by wrapping banana leaves or sal leaves. *Kinema* can also be made from pure culture method making the isolation of *Bacillus subtilis* from old *kinema* samples. Dhungel(2000) has concluded that *kinema* prepared from pure culture method is better in its quality than that prepared by traditional fermentation method.

1.2 Statement of the problem

The quality of dehydrated food is affected by the rate of drying. No study has been carried out about the effects of drying rate kinetics in *kinema* and its dehydration process till date. Drying or Dehydration simply refers to the removal of water from the tissue structure of food product. The physical, chemical, bio-chemical and microbiological changes which determine nutritional stability are closely connected with the status of water in food product. That means, process of dehydration imparts sufficient effect on nutritional profile of *kinema*. Drying is a complex thermal process in which unsteady heat and moisture transfer occur simultaneously, which is not easily understandable. The theoretical models may explain heat and mass transfer but it encounters unnecessary computational complexity and time commitment as well as less interpretable (Sahin and Dincer, 2005).

From engineering point of view, the drying process as well as drying parameters as it reflects the quality and acceptability of final dried product. In order to achieve a product of better quality the whole drying system (i.e., both process and parameters) must be closely controlled. Effects of various processing parameter on drying process must be identified for better process control (Hossain and Bala, 2002). The drying rate is strongly dependent on air velocity, temperature and relative humidity inside dryer. The study can be used to predict water removal rates and to generalize drying curves. Empirical models derive a direct relationship between average moisture content and drying time. This process is advantageous, because a full scale experimentation of different products and configurations of the drying system is time consuming and also costly (Erbay and Icier, 2010a).

1.3 Objectives

1.3.1 General objectives

- The general objective of the study was to develop the mathematical modelling of drying kinetics of *kinema*.

1.3.2 Specific objectives

To fulfill the general objectives, the specific objectives were undertaken as follows:

- To study the effects of temperature (50^{o}C, 60^{o}C, 70^{o}C and 80^{o}C) on the drying characteristics of *kinema.*
- To fit the experimental data to different models and calculate the model parameters.
- To determine the corresponding moisture diffusivity.
- To determine the activation energy and diffusivity constant.

1.4 Significance of the study

This study "Mathematical modelling of drying kinetics of *kinema*" helps in process of synchronization i.e. it provides suitable modelling formulation and hence model parameters. It also gives an idea about the effect of variable in dehydration process**.**

The best fitted drying models can be used in calculations involving the design and construction of new drying systems, optimization of the drying process, and the description of the entire drying behavior including heat and mass transfer. Thus, it is important to understand the basic idea of modeling the drying kinetics of food. The drying conditions, type of dryer, and the characteristics of the material to be dried all have an influence on drying kinetics. The drying kinetics model are therefore significant in deciding the ideal drying conditions by providing information on all drying parameters and model constants which are important in terms of equipment design, optimization, and product quality improvement. The most important aspects of thin-layer drying technology are the mathematical modeling of the drying process and the equipment design which can enable the selection of the most suitable operating conditions. Thus, there is a need to explore the thin-layer modeling approach as an essential tool in estimating the drying kinetics from the experimental data, describing the drying behavior, improving the drying process, and eventually minimizing the total energy requirement (Giri and Prasad, 2007).

1.5 Limitations of the study

i. The changes in physical and thermal properties during drying were not studied.
ii. The shrinkage during drying was not considered.

Part II

Literature review

2.1 Soybean

Soybean is the most popular legume of orient. It has a long history of use in this subcontinent with records of cultivation in China as early as 2838 B.C. Soybean is exceptionally high source of protein. The current global production of soybean during 2014/2015 was 320 million metric ton. The leading world's soybean producer was U.S.A (34%), followed by Brazil (30%), Argentina (18%), China (4%) and India (3.95%) (Faostat, 2015). Nepal produced 29220.5 metric tons in the year 2012/2013 whereas, the Eastern region of Nepal produced 4,745 metric ton, Central region 6,490 metric ton, Western region 3,616 metric ton, Mid-Western region 4,433 metric tons and Far- Western region 8,462 metric tons respectively in the same year. Soybean is the fifth most important legume in terms of acreage and mainly grown in mid hills and valleys. Both the local and improved varieties are grown (Tren, 2000).

In Nepal soybean is commonly known by the name 'Bhatmas'. The agriculture farms of Kumaltar, Kakani and Rampur collected 138 samples of soybeans from the different districts of height from 500 to 1800 meters and conclusion was derived that most dominant varieties of soybean in Nepal are of white, Brown, Grey and Black colors. It has different local name depending on the varieties, color of seeds and locations like Nepale, Hardi, Saathiya, Darmali, Maily, Kalo, Seto and so on (Shrestha, 2013).

2.2 *Kinema*

Yoshida (1998) reported the origin of *kinema* in Southern part of China. *Kinema* is use as a seasoning in Nepal, Burma, Thailand and Korea and as a food in Japan and Indonesia. While it is fermented food to those who eat it and may appear to be merely a "rotten bean" who don't. This is because *kinema* has powerful odor and slimy appearance like a rotten food. But to those who eat it the smell is delightful and its consistency or texture part of pleasant eating experience. It is eaten in the fresh form or as a fried curry dish along with boiled rice, and sometimes as soup, pickle, or mixed with other vegetables. It is sold in all markets of these regions by some rural women who are economically dependent upon this product (Shrestha, 2013; Chhetri, 1994).

The method of preparation of *kinema* differs from home to home, depending upon the localities, family convenience and materials available. General method of household preparation involves soaking, cooking, splitting beans, mixing with firewood ash, pack in bamboo basket lined with plant leaves, and overnight fermentation in warm place. The final product has a sticky texture, typical musty flavor and a detectable ammonical odor. *Kinema* is considered to be of good quality if longer mycelium is formed when beans are pulled apart (Karki, 1986). After fermentation, fresh *kinema* is sun dried and stored for months. During the fermentation of *kinema* Ash is used to facilitate the growth of Bacillus and increase the mineral level in the final product (Nikkuni *et al*., 1995). However, A variety of leaves e.g., banana (*Musa paradisica* (L), smith leaves (*Leucosceptrum canum*) and sal leaves (Shorea *robusta*) are used to wrapped the boiled beans before fermentation (Tamang *et al*., 1988).

Kinema prepared by traditional method contains a large amount of microorganisms besides Bacillus *subtilis* e.g., *Enterococus faecium*, *Candida Parapsilosis*, *Geotrichum candidum*, many yeast and mold strains in traditionally made *kinema* (Karki, 1986; Sarkar and Tamang, 1994). Unhygienic method of preparation, poor storage condition, substrate itself and materials used may influence the possibility of contamination of product causing health risks. The quality of *kinema* also inconsistent; products differ from method of preparation, raw materials used, and person making the product. The product appearance is rough as it wrapped in plant leaves and possesses distinct odor of that leave. Whereas the *kinema* prepared by using the pure culture is free of these shortcomings and better in overall quality (Shrestha, 2013; Chhetri, 1994)

2.3 *Kinema* making process

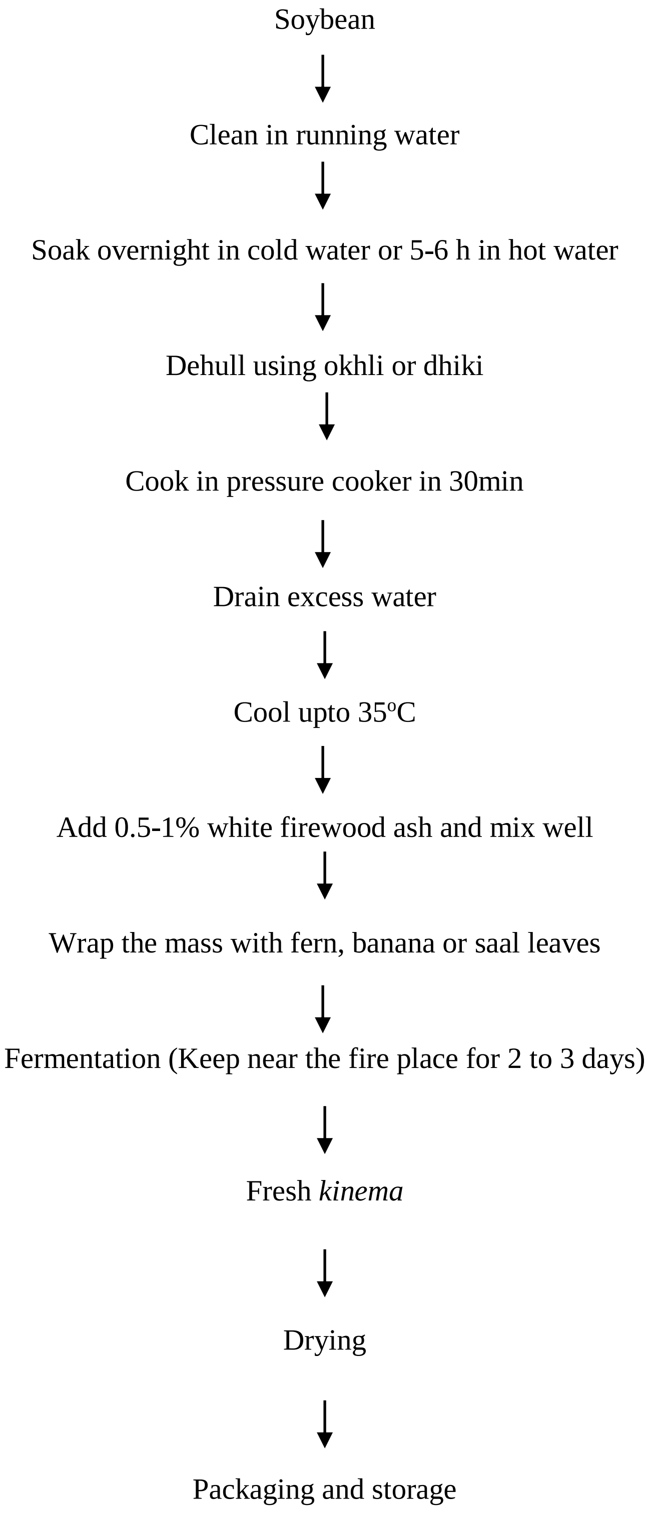


Fig. 2.1 Traditional method of *kinema* preparation (Kharel, 2006)

2.4 Physio- chemical changes during *kinema* fermentation

The *kinema* organism *B. subtilis* produces strong proteolytic enzymes which hydrolyze the protein into peptides, amino acids, ammonia and other flavoring compounds. Proteolysis increases the solubility of protein and improves other functional properties as well. The release of ammonia increases pH from neutral to 8.0. The combined effect of higher pH, ammonia and other metabolites inhibit the growth of other organisms in *kinema* (Karki, 1986). The fermenting organisms produce sticky mucilaginous gum on the surface of the soybean. These gummy substances are exopolypeptides of D-isomeric glutamic acid. The extent of production mucilaginous gum depends upon the strain of fermenting organism. (Chhetri, 1994).

A great increase in water soluble ammonia nitrogen was noted during fermentation and storage. The amino acid composition remains same. There is significant increase in the level of thiamine, riboflavin, and vitamin B_{12}. During traditional *kinema* fermentation the moisture content remain same throughout the period of fermentation (Karki, 1986). Several workers have reported a significant increase in the pH, protein, and reducing sugars and decrease in crude fiber and total sugar content (Chhetri, 1994; Karki, 1986). They found no significant change in the level of fat and mineral content. (Sarkar and Tamang,1994), reported a 33 times increase in free fatty acid value in as compared to raw soybean suggesting release of lipase during fermentation process.

2.5 Drying of fruits and vegetables

Drying means the fluid extraction in a material. In technical drying, outer intervention is applied to the drying operation and the moisture in the material is removed with the use of various methods. Therefore, drying is described as the mitigation of the moisture of the material to be dried to the desired drying values within a particular period of time. The whole units, which help the material achieve the drying values within a particular period and which comprise various components (heating, moisture extraction), are referred to as the drying system. Drying operation comprises the evaporation of the water first of all, and then extraction phase of the evaporated water from the system. During the evaporation there is a need for high energy. Therefore, drying operations are those in which high energy is used.

Drying involves the application of heat to vaporize the volatile substances (moisture) and some means of removing water vapor after its separation from the solid (Jayaraman and Gupta, 1995). The drying process is a heat and mass transfer phenomenon where water migrates from the interior of the drying product on to the surface from which it evaporates. Heat is transferred from the surrounding air to the surface of the product. A part of this heat is transferred to the interior of the product, causing a rise in temperature and formation of water vapor, and the remaining amount is utilized in evaporation of the moisture from the surface (Lopez *et al.*, 2009).

Drying is one of the oldest methods known for the preservation of agricultural products such as fruits and vegetables. Drying of agricultural products enhances their storage life, minimizes losses during storage, and save shipping and transportation costs. The terms "drying" and "dehydration" both refer to the simultaneous application of heat and removal of water by evaporation from a wet material (Brennan, 2006; Fellows, 2000). Therefore, they are used interchangeably in the literature. However, Vega *et al.*, (2007) point out the difference between drying and dehydration. According to them, dehydrated food products are those with no more than 2.5% water (dry basis, db) while dried food products have more than 2.5% water (db). From engineering point of view, drying is the unit operation in which nearly all the free moisture present in the food stuff is removed by evaporation or sublimation as a result of application of heat under controlled condition (Lilly *et al.*, 1976).

Drying of agricultural products has always been of great importance for the preservation of food. Many food products are dried at least once at some point in their preparation (Madamba, P.S, *et al*., 1996). Drying of fruits and vegetables is a complicated process involving simultaneous, coupled heat and mass transfer, under transient conditions (Diamante *et al*., 2010). The introduction of dryers in developing countries can reduce crop losses and improve the quality of a dried product significantly when compared to traditional methods. The major objective of drying food products is the reduction of moisture content to a level which allows safe storage over an extended period (Doymaz, *et al*., 2003). Drying consists of a critical step by reducing the water activity of the products being dried. High amount of energy are required due to high latent heat of water. Hot air drying of agricultural products is one of the most popular preservation methods because of its simplicity and low cost (Diamante *et al*., 2010).

To analyse the drying behaviour of a food product, it is essential to study the drying kinetics of the food. Thin layer drying is a common method and widely used for fruits and vegetables to prolong their shelf life (Kadam *et al*., 2011).

According to ASAE (2001), thin layer drying refers to a layer of material exposed fully to an airstream during drying. There is a wide range of thin layer drying models, thin layer drying models which have found application because of their ease of use. Thin layer drying equations are often empirical to describe drying phenomena in a unified manner regardless of the controlling mechanism (Kadam *et al*., 2011). Many mathematical models have been used to describe the thin layer drying process of agricultural products. Most workers describe their thin layer drying experiments with suitable mathematical models which can be theoretical, semi-empirical or purely empirical (Madamba *et al*., 1996). Thin layer drying equations are used to estimate the drying time of several products and also to generalize drying curves (Meisami *et al*., 2009).

Some of the selected thin layer models of agricultural products are presented in Table 2.1. A considerable amount of data has been reported in the literature regarding the thin layer drying model of various agricultural products, still continuous effort need to be carried out for further improvement of the drying process. The most important aspect of drying technology is the mathematical modelling of the drying processes and equipment where its purpose is to allow engineers to choose the most suitable operating condition for certain product. Therefore, the objective of this project was to study and investigate the thin layer drying characteristics of particular products and the mathematical models that have been used to describe the thin layer drying process. The result of analysis has been tabulated in Table 2.1.

Table 2.1 List of selected thin layer drying models of various agricultural products.

S.N	Agricultural products	Authors/year	Best Thin Layer drying model
1	Macadamia in-shell nuts and kernel	Palipane, *et al* (1994)	Two-term
2	White onion slices	Rapusas, *et al* (1995)	Single term exponential
3	Garlic slices	Madamba, *et al* (1996)	Page and two compartment
4	Black tea	Panchariya, *et al* (2002)	Lewis
5	Corn	Doymaz, *et al* (2003)	Page
6	Red pepper	Akpinar, *et al* (2003)	Diffusion model
7	Eggplant slices	Ertekin, *et al* (2004)	Midilli *et al* model
8	Soybean	Rafiee, *et al* (2009)	Midilli *et al* model
9	Cocoa	Hii, *et al* (2009)	Combination of Two-term Page
10	Grape seed	Robert, *et al* (2008)	Lewis model
11	Apple slices	Meisami, *et al* (2009)	Midilli *et al* model
12	Mint Leaves	Kadam, *et al* (2011)	Two-term
13	Kiwi and apricot	Diamante, *et al* (2010)	Empirical model
14	Litchi and peeled longan	Janjai, *et al* (2011)	Page
15	Rapeseed	Duc, *et al* (2011)	Page
16	Roselle	Suherman, *et al* (2011)	Newton/Lewis

2.5.1 Drying principles

Drying can be described as the process of thermally removing moisture to yield a solid product. Moisture can be found as bound or unbound in the solid. Moisture, which exerts a vapor pressure less than that of pure liquid, is called bound moisture while moisture in excess of bound moisture is called unbound moisture.

The most important thermodynamic process in food drying is heat and mass transfer. During hot air drying, there is a simultaneous exchange of heat and mass between the food and the drying air (Maroulis *et al.*, 1995).

a) Heat transfer
   - Convective heat (energy) transfer from the air to the food’s surface (external heat transfer).
   - Conductive heat transfers within the food (internal heat transfer).

b) Mass transfer
   - Moisture transport within the food toward its external surface (internal mass transfer).
   - Evaporation and convective transfer of the vapor into the air (external mass transfer)

Since the physical structure of the drying solid is subject to change during drying, the mechanisms of moisture transfer may also change with elapsed time of drying (Luickov, 1966). Energy transfer as heat from the surrounding environment to the wet solid can occur as a subsequence of convection, conduction, or radiation and in some case as a result of a combination of these effect, however convection is common and predominant mechanism (Aguilera and Stanley, 1990; Heldman and Hartel, 1997). In most cases heat is transferred to the surface of the wet solid and then to the interior. This heat transfer to the food surface increases the sample temperature and supplies the required latent heat of vaporization for both the surface water and the water within the product. At the same time, internal moisture (mass) migrates to the surface of the food and then it evaporates to the surrounding hot air (Aversa *et al.*, 2007; Ramaswamy and Marcotte, 2006).

Transport phenomena involve both external and internal resistance to heat and/or mass transfer. The factors that slow the rate of these processes determine the drying rate (Ramaswamy and Marcotte, 2006; Singh and Heldman, 1993). In other words, the resistance mechanisms control the drying rate. In general, it is accepted that the rate of the drying may be limited either by the rate of internal migration of water molecules to the surface or by the rate of evaporation of water molecules from the surface into the air, depending on the conditions of drying (Heldman and Hartel, 1997). This indicates that the resistance to mass transfer is considered to be the primary rate-limiting mechanism and the resistance to heat transfer may hence be neglected. The reason for this is that within the food, heat is usually transported more easily than moisture and thus the temperature gradients inside the food can be assumed to be flat (no resistance to internal heat transfer), especially when compared to the steep moisture content gradient (Fortes and Okos, 1981). In addition, it is known that heat transfer within the food may be limited by the thermal conductivity of the product as its water evaporates (Donsi *et al.*, 1996).

The air temperature, air humidity and velocity, and exposed surface area all influence the resistance to external heat and mass transfer whereas the internal mass transfer is only affected by the physical nature of the food, its moisture content and temperature. At the beginning of drying, since the internal resistance in the food is low enough to maintain the surface at saturation, evaporation takes place at a constant rate depending mainly on external heat and mass transfer. When the drying rate starts to decrease due to insufficient water at the surface, resistance to internal mass transfer governs the process. Most foods therefore switch from an external drying process during the initial stages to an internal drying process as the product dries out (Ramaswamy and Marcotte, 2006). In addition, the drying rate in the food sample, which decreases from the very beginning of the process (at a constant temperature), may also indicate that the internal resistance to mass transfer controls the drying (Uddin *et al.*, 1990; Yusheng and Poulsen, 1988).

2.6 Theory of drying

When hot air is blown over a wet food, heat is transferred to the surface, and latent heat of vaporization causes water to evaporate. Water vapor diffuses through a boundary film of air and is carried away by the moving air. This creates a region of lower water vapor pressure at the surface of the food, and a water vapor pressure is established from the moist interior of the food to the dry air. This gradient provides the driving force for water removal from the food. Fig. 2.2 shows movement of moisture during drying.

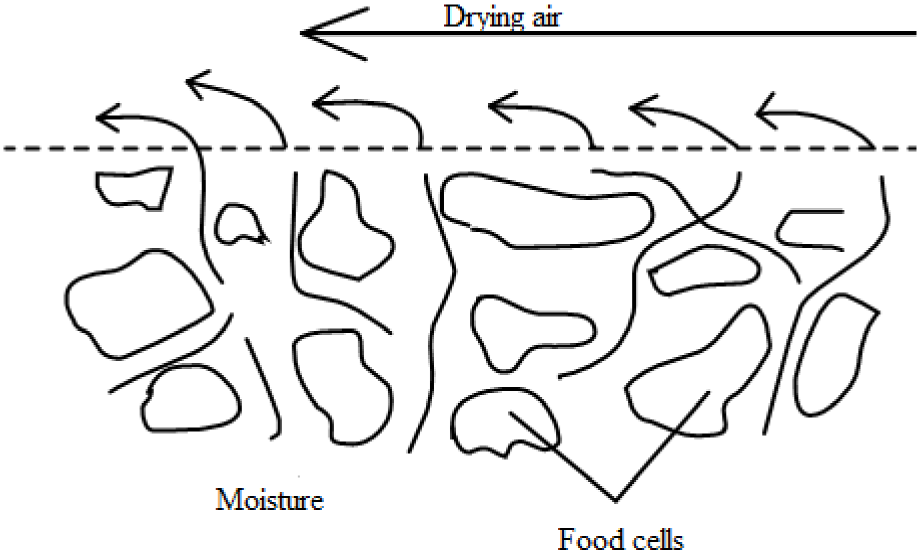


Fig 2.2 Movement of moisture during drying (Geankoplis, 2003)

Water moves to the surface by the following mechanisms:

a. Liquid movement by capillary forces.
b. Diffusion of liquids, caused by differences in the concentration of solutes in different regions of the food.
c. Diffusion of liquid which is adsorbed in layers at the surface of solid components of the food, and
d. Water vapour diffusion in air spaces within the food caused by vapour pressure gradients.

For a given food, the total amount of moisture that can be lost will vary with the humidity and temperature of the air. As water migrates out during drying, dissolved solids (sugar, acid, salt) are carried along to the surface. Here water evaporates into the air leaving the soluble solids which concentrate and may even precipitate at the surface. As the drying proceeds, the water removal may be restrained by the drying process itself. Food tissue often sinks as it loses moisture and the structure may change and blocks the exit of water. Such a condition is known as case hardening in which the outer trough surface is formed but still moist interior remains. The hard outer surface is more impermeable to water and such a product is susceptible to microbial spoilage. Less intense drying and intermittent conditioning alleviate this problem (Kharel, 2006).

2.7 The drying curve

Drying curve is the description of the changes of moisture content of material during drying. It can also be expressed as a drying kinetics or drying rate curve shown in Fig. 2.3 and Fig. 2.4

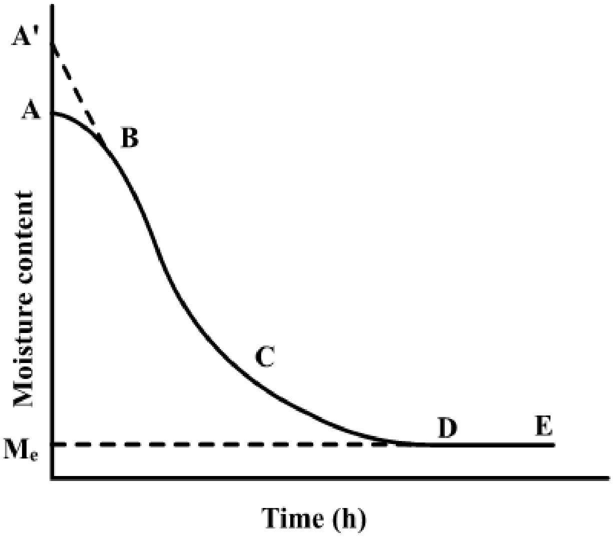


Fig. 2.3 Drying curve showing moisture content as a function of time (Geankoplis, 2003)

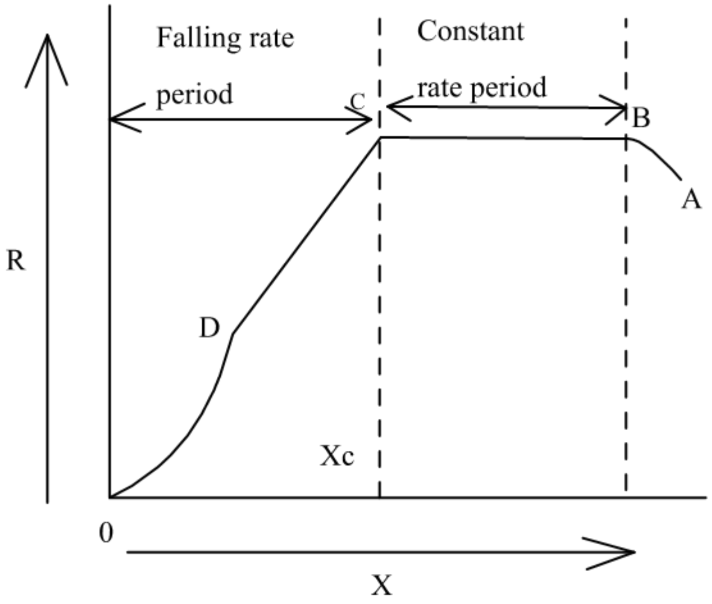


Fig. 2.4 Drying rate as a function of moisture content (Geankoplis, 2003)

Drying curve can be obtained experimentally by plotting the free moisture content versus drying time. This plot can be converted into a drying rate curve by calculating the derivative of the curve over time. From these two types of curve it is seen that drying is divided into two distinct portions. The first is the constant rate period (line BC) and second portion is falling rate period (line CD). Although the curve possesses two distinct phases, it contains total 3 stages.

I. *Transition phase (A/A'-B)*

It represents the setting down period during which the solid surface conditions come into equilibrium with the drying air. The point A and A' represent the initial conditions for a cold and hot material, respectively. It is often negligible proportion of the overall drying cycle but in some cases, may be significant.

II. *Constant Rate period (B-C)*

During this period mostly unbound water is removed. Water evaporates as if there is no solid present, and its rate of evaporation is not dependent on the material being dried. The rate of moisture migration from the interior to the surface of the food is equals to the evaporation rate at the surface (i.e. there is no internal resistance to mass transfer). In this stage of drying the rate controlling step is the diffusion of the water vapor across the air-moisture interface. This period continues until water from the interior is no longer available at the surface of food material. The rate of heat transfer from the air to the food surface, on the other hand, is balanced by the rate of energy removal due to the evaporating moisture (i.e. latent heat of vaporization). Thus, the surface temperature remains at some constant value, which is in fact lower than air temperature due to the cooling effect of the evaporating water on the surface. (Heldman and Hartel, 1997; Ramaswamy and Marcotte, 2006).

III. Falling rate period (C-D)

Evaporating moisture (i.e. latent heat of vaporization). Thus, the surface temperature remains at some constant value, which is in fact lower than air temperature due to the cooling effect of the evaporating water on the surface. Finally, water evaporates into the drying air as a result of the water concentration gradient and/or water vapor pressure gradient between the surface of the food and the drying air, and remains the same throughout the constant drying period Point C distinguishes the constant rate period from the subsequent falling rate period and is called the critical moisture content. As the free and loosely bound moisture contents in the product diminish and mass transfer from the surface to the drying air becomes smaller, the internal resistance to moisture transfer begins to drive the drying process. This is represented in Fig. 2.4 at the end of the second stage where the drying rate is no longer constant but falls progressively throughout the rest of the drying. The drying period beyond this point is termed as the falling-rate period, The surface of the solid is no longer wet (Fellows, 2000).

Drying of food material divided into different sub-periods depending on the structure of the dried material (e.g. hygroscopic and non-hygroscopic) (Hallström, 1992). In the case of non-hygroscopic materials there is a single falling rate period, while hygroscopic ones may exhibit two or more falling rate periods. This is explained by the fact that a non-hygroscopic material (e.g. sand, polymer particles and some ceramics) exerts the same partial water vapor pressure, at all moisture contents due to the negligible amount of physio-chemically bound water and the non-shrinkage property of such material. This partial water vapor pressure is equal to saturated water vapor pressure. In the case of a hygroscopic material, however, partial water vapor pressure is dependent on the moisture content due to the large amount of physio-chemically bound water and the occurrence of shrinkage during drying (Lewis, 1987).

The first falling rate period, the third phase (C-D), follows the end of equilibrium at the surface, which occurs when there is insufficient supply of water from the inner parts of the food. This results in the appearance of increasingly larger proportions of dry spots on the surface, leading to the reduction of surface area for evaporation and an increase in surface temperature (Heldman and Hartel, 1997). The second falling-rate period (D-E), the fourth phase, begins when the surface is completely dry, but the changeover between the periods is not always clear-cut. For example, in some cases no sharp discontinuity occurs at the end of the first falling-rate period due to the gradual change from partially wetted to completely dry conditions at the surface. During the second falling-rate period, the plane of evaporation slowly recedes from the surface and all evaporation occurs at the interior of the food. Therefore, changes in the external conditions such as air velocity and humidity no longer affect the rate of drying (Geankoplis, 2003).

In addition, the latent heat of vaporization of water at this stage of the drying process is higher than the latent heat of vaporization of pure water since water in the food sample is held in multiple layers (i.e. bound water). As a result, the amount of water removed is relatively small, while the time required is long. This causes the most heat damage to the food and therefore during this period the air temperature should be controlled to balance the rate of drying and extent of heat damage (Geankoplis, 2003).

The drying rate in the falling rate period is controlled by diffusion of moisture from the inside to the surface and then mass transfer from the surface. During this stage some of the moisture bound by sorption is being removed. As the moisture concentration is lowered by drying, the rate of internal movement of moisture decreases. The rate of drying falls even more rapidly than before and continues to drop until the moisture content falls down to the equilibrium value for the prevailing air humidity and then drying stops. Equilibrium between the material and the drying air is reached as the food temperature approaches the drying air temperature. At this point, the partial water vapor pressure of the food and the drying air become equal. The air fails to pick up any moisture from the product and thus drying ceases.

The moisture content at this stage is the level to which food can be dried under a given drying condition and is referred to as the equilibrium moisture content (Heldman and Hartel, 1997).

2.8 Intermittent drying

Intermittent drying is a non-continuous drying process with tempering periods. It involves strict control of the heat input (drying temperature) such that the food material is subjected to particular air conditions at different points over the course of drying. Heat is supplied intermittently rather than continuously throughout the drying process. That is, the drying cycle, which consists of a drying and a tempering period, is repeated until the moisture content of the food product is reduced to the desired level (Xing *et al.*, 2007).

Drying causes moisture gradients to develop within the food products, which in turn decrease the drying rate. Tempering periods allow for moisture diffusion from the interior to the external surface of the food sample, thus decreasing such moisture gradients. This happens when the sample surface and the pores close to the surface are saturated with water that has been transferred from the inner sections. The resultant uniform distribution of moisture contributes to a reduction in drying time in the oven, thus reducing the total cost of the drying process. Indeed, after tempering, the surface moisture is easily removed in subsequent drying periods in the oven, which improves the drying rate. This phenomenon is referred to in the literature as the “refreshing effect” (Nishiyama *et al.*, 2006).

The length of tempering periods used in intermittent drying varies widely. The tempering time should be as short as possible to minimize the damage to the food sample caused by chemical changes, respiration and microbial activity. The duration and frequency of tempering depend on the time intervals of both the drying phase and the tempering phase and are greatly affected by the drying temperature. Higher temperatures shorten the required tempering times. Consequently, the total drying time necessary for reaching the desired moisture content (<15% wb) depends on the lengths of both the drying period and the tempering period (Cihan and Ece, 2001).

2.9 Cabinet drying

The majority of industrial drying installations rely on convectional hot-air drying at atmospheric pressure since it is the simplest and most economical among the various methods. A wide variety of food materials such as fruit, vegetables, herbs and cereal crops has therefore been dried by convectional hot-air dryers. In addition, it is easy to set and control the optimum drying conditions in these dryers, especially in cabinet dryers. Common atmospheric hot-air dryers include kiln, cabinet (tray), tunnel, and belt or conveyor dryers (Jayaraman and Gupta, 1995). Fig 2.5 shows the example of cabinet dryer.

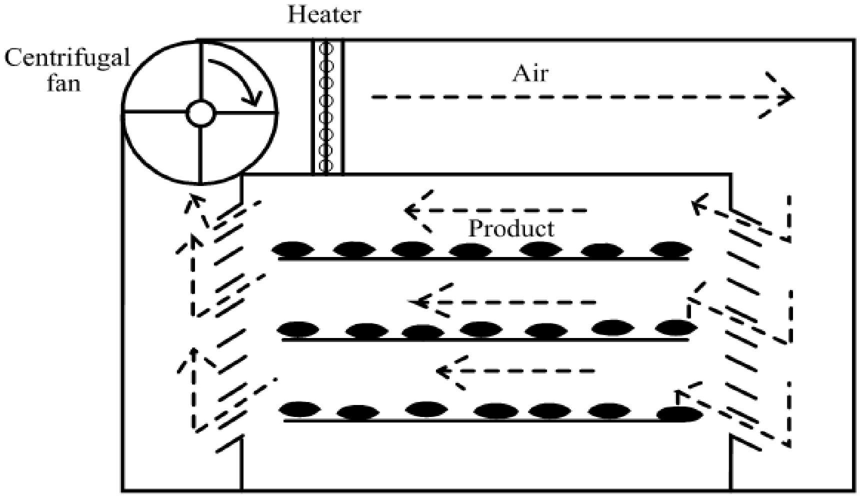


Fig 2.5 Cabinet dryer

The basic configuration of an atmospheric hot-air dryer is an enclosed and heated chamber where food material is placed. It is also equipped with a blower (i.e. fan) and ducts to allow the circulation of hot air around and across the food. When there is no fan the drying takes place under natural convection. The drying process in an atmospheric dryer involves both heating the product and removing water from the product surface (Rahman and Perera, 1999).

The food is spread out, generally quite thinly, on trays in which the drying takes place as shown in Fig. 2.5. This consists essentially of an insulated cabinet containing an air circulating fan which moves the air through a heater and then through adjustable baffles which direct air either horizontally between the trays of food materials or vertically through the trays and food. Air heaters may be direct gas burners, steam coil exchangers or electrical resistance heaters. The air is blown past the heaters and thus heated air is used for dying. It is relatively cheap to build and maintain, flexible in design, and produces variable product quality due to relatively poor control. It is used singly or in groups, mainly for small- scale production (1-20 ton/day) of dried fruits and vegetables (Geankoplis, 2003).

2.10 Some terminologies

2.10.1 Equilibrium moisture content.

The Term “EMC” is an acronym for equilibrium moisture content. The term is used in relation to a hygroscopic material. The term hygroscopic refers to a material that absorbs or bleeds moisture from or into the atmosphere. Equilibrium Moisture Content is defined as the point where stops absorbing moisture from or bleeding moisture into the surrounding air. At this point, the material is said to have reached equilibrium with the atmosphere (Heldman and Hartel, 1997).

2.10.2 Critical moisture content

At certain moisture content, dry regions begin to exist on the surface, and the drying rate begins to decrease. This moisture level is called the critical moisture content. In other word it is the moisture content at which constant rate of drying disappear and falling rate starts. Here the surface of the solid is no longer wet. The critical moisture content depends on the thickness of the bed of material and the degree of mixing between the gas and solids. The critical moisture content is therefore not a property of the material itself and must be determined experimentally (Geankoplis, 2003).

2.10.3 Moisture content

The quantity of moisture present in a material can be expressed either on the wet basis or dry basis and expressed either as decimal or percentage. The moisture content on the wet basis is the weight of moisture present in a product per unit weight of the undried material, represented as,

$$M_{wb} = \frac{W_o - W_d}{W_o} \text{ …………… (2.1)}$$

Where, M_{wb} = moisture content at wet basis

W_o = initial weight

W_d = final weight after drying

While the moisture content on the dry basis (M_{db}) is the weight of moisture present in the product per unit weight of dry matter in the product and represented as,

$$M_{db} = \frac{W_o - W_d}{W_d} \text{ .... } (2.2)$$

The moisture content on the wet basis is used normally for commercial purposes, while the moisture content on the dry basis has tended to be employed for engineering research designation, because the weight change associated with each percentage point of moisture reduction on the dry basis is constant as against the wet basis where the amount of water involved in a moisture content reduction of one percent changes as drying progresses, because the weight of water and total crop weight change.

2.10.4 Moisture ratio (MR)

Moisture ratio is one of the important criteria to determine the drying characteristics of agricultural product. MR can be determined according to external conditions. If the relative humidity of the drying air is constant during the drying process, then the moisture equilibrium is constant too. In this respect, MR is determined as in Eq**.** 2.3

$$MR = \frac{M_t - M_e}{M_o - M_e} \text{ .... } (2.3)$$

Where, MR = moisture ratio

M_t = moisture content at any time (t)

M_o = initial moisture content

M_e = equilibrium moisture content

If the relative humidity of the drying air continuously fluctuates, then the moisture equilibrium continuously varies, MR is determined as given by (Diamante *et al*; 2010).

$$MR = \frac{M_t}{M_o} \text{ .... } (2.4)$$

2.10.5 Drying rate

Agricultural products differ from most other materials dried frequently, such as textiles in a Laundry, sand, stone, dust or paper. Agricultural products (which are hygroscopic) has always some residual moisture after the drying while for non-hygroscopic material drying continued up to zero moisture content. Because of hygroscopic products moisture is trapped in closed capillaries. The rate of moisture flow is only approximately proportional to its vapor pressure difference with the environment because of the crop resistance to moisture flow. There are two main drying rate regimes for agricultural products, namely the constant drying rate period and the falling drying rate period;

$$\text{Drying rate} = \frac{M_{t+dt} - M_t}{dt} \text{ .... } (2.5)$$

2.11 Mathematical modeling of agricultural products

A mathematical object could be a system of equations, a stochastic process, a geometric or algebraic structure, an algorithm, or even just a set of numbers. The model should be usable for predicting either future behavior or behavior under different circumstances, or for better understanding the situation (Malkevitch *et al.*, 2011).

Reasons for modeling:

a) To gain understanding

Generally speaking, a mathematical model which accurately reflects some behavior of a real-world system of interest, it helps to gain improved understanding of that system through analysis of the model. Furthermore, in the process of building the model we find-out which factors are most important in the system, and how different parts of the system are related.

b) To predict or simulate

To know what a real-world system will do in the future, but it is expensive, impractical or impossible to experiment directly with the system (Neter *et al.*, 1990). Different types of Mathematical models have been used in order to explain different behavior and characteristic of agricultural products, such as Drying, Rehydration, sorption isotherm, fermentation etc. Here, Drying characteristic of product has been studied by different thin layer drying equations.

2.12 Thin layer drying

According to ASAE (2001), thin layer drying refers to a layer of material exposed fully to an airstream during drying. There is a wide range of thin layer drying models, thin layer drying models which have found application because of their ease of use. Thin layer drying equations are often empirical to describe drying phenomena in a unified manner regardless of the controlling mechanism. Thin layer drying equations are used to estimate the drying time of several products and also to generalize drying curves (Kadam *et al.*, 2011).

Drying is one of the most complex and least understood processes at the microscopic level, because of the difficulties and deficiencies in mathematical descriptions. It involves simultaneous and often coupled and multiphase, heat, mass, and momentum transfer phenomena (Yilbas *et al.*, 2003). In addition, the drying of food materials is further complicated by the fact that physical, chemical, and biochemical transformations may occur during drying, some of which may be desirable. Physical changes such as glass transitions or crystallization during drying can result in changes in the mechanisms of mass transfer and rates of heat transfer within the material, often in an unpredictable manner (Mujumdar, 1997). The underlying chemistry and physics of food drying are highly complicated, so in practice, a dryer is considerably more complex than a device that merely removes moisture, and effective models are necessary for process design, optimization, energy integration, and control. Although many research studies have been done about mathematical modeling of drying, undoubtedly, the observed progress has limited empiricism to a large extent and there is no theoretical model that is practical and can unify the calculations (Maroulis *et al.*, 1995).

The term “thin layer” has been applied to:

- A single material freely exposed to the drying air or one layer of the material.

-A polylayer of many materials slice thicknesses if the temperature and the relative humidity of the drying air can be considered for the purpose of the drying process calculations, as being in the same thermodynamic state at any time of drying.

It means that, the thickness of a thin layer can increase if the velocity of the drying air increases and also if the thermodynamic state of the drying air approaches the equilibrium state in heat and mass transfer with grain dried in this layer (Jayas *et al.*, 1991). According to Chakraverty (1994), layer thickness up to 20 cm can be consider as thin layer. Thin layer drying equations are important tools in mathematical modeling of drying. They are practical and give sufficiently good results. To use thin layer drying equations, the drying-rate curves have to be known.

2.12.1 Thin layer drying mechanism

The main mechanisms of drying are surface diffusion on the pore surfaces, liquid or vapour diffusion due to moisture concentration differences and capillary action in granular and porous foods due to surface force (Erbay and Icier, 2010b). Generally, fruits and vegetables dry in constant rate and subsequent falling rate periods and drying stops when equilibrium is established (Erbay and Icier, 2010b). During the constant rate period of drying, the physical form of the product and external conditions such as temperature, drying air velocity, direction of air flow and relative humidity have a great influence on the surface of the product being dried so called surface diffusion. Unlike the constant rate periods, the falling rate period is controlled by liquid diffusion as a result of moisture concentration differences and the internal conditions of the product. The internal conditions such as moisture content, the temperature and the structure of the product play an important role in the falling rate periods. In summary, an all-inclusive drying profile for fruits and vegetables may consist of 3 drying stages: an initial slight constant rate period (products with high moisture content), a first falling rate period, and a second falling rate period. In practice, recent evidence suggests that the drying of fruits and vegetables occurs only during the falling rate period with the initial slight constant rate period said to be negligible (Demir *et al.*, 2004).

2.12.2 Mathematical models of thin layer drying

Thin layer drying equation is fundamental to the drying simulation. The equation represents moisture exchange between a thin layer of the drying product with its surrounding air. From a mathematical point of view, a thin layer represents the spatial dx that is chosen infinitesimal small within which changes in humidity and temperature of the air can be assumed linear (Wang *et al.*, 2004). Thin layer drying models that describe the drying phenomenon of biological materials mainly fall into three categories, theoretical, semi-theoretical and empirical (Panchariya *et al.*, 2002).

2.12.2.1 Theoretical models

The theoretical model considers both the external and internal resistance to moisture transfer. They involve the geometry of the material, its mass diffusivity, and the conductivity of the material (Cihan and Ece, 2001).

It is further sub divided into two groups:

2.12.2.1.1 Distributed Model

Distributed models consider simultaneous heat and mass transfer. This model or system is based on the interaction between time and one or more spatial variables for all of its dependent variables. They take into consideration both the internal and external heat and mass transfer, and predict the temperature and the moisture gradient in the product better. Generally, these models depend on the Luikov equations that come from Fick's second law of diffusion or their modified forms (Luikov, 1975).

$$\frac{\partial M}{\partial t} = \nabla^2 k_{11} M + \nabla^2 K_{12} T + \nabla^2 K_{13} P \text{ .... } (2.6)$$

$$\frac{\partial T}{\partial t} = \nabla^2 K_{21} M + \nabla^2 K_{22} T + \nabla^2 K_{23} P \text{ .... } (2.7)$$

$$\frac{\partial P}{\partial t} = \nabla^2 K_{31} M + \nabla^2 K_{32} T + \nabla^2 K_{33} P \text{ …………… } (2.8)$$

Where, K_{11}, K_{22}, K_{33} are the phenomenological coefficients, while K_{12}, K_{13}, K_{21}, K_{23}, K_{31}, K_{32} are the coupling coefficients, M is the local moisture content on a dry basis (Brooker et al., 1974), T is temperature and P is partial pressure. For most of the processes, the pressure effect can be neglected compared with the temperature and the moisture effect, so the equations become as (Brooker *et al.*, 1974),

$$\frac{\partial M}{\partial t} = \nabla^2 K_{11} M + \nabla^2 K_{12} T \text{ …………… } (2.9)$$

$$\frac{\partial T}{\partial t} = \nabla^2 K_{21} M + \nabla^2 K_{22} T \text{ …………… } (2.10)$$

Nevertheless, the modified form of the Luikov equations (Eq. 2.10) may not be solved with analytical methods, because of the difficulties and complexities of real drying mechanisms. On the other hand, this modified form can be solved with the finite element method.

2.12.2.1.2 Lumped parameter models

Lumped parameter models do not pay attention to the temperature gradient in the product and they assume a uniform temperature distribution that equals to the drying air temperature in the product. This model or system considers the effect of time alone on the dependent variables with this assumption, the Luikov equations become as:

$$\frac{\partial M}{\partial t} = K_{11} \nabla^2 M \text{ …………… } (2.11)$$

$$\frac{\partial T}{\partial t} = \nabla^2 K_{22} M \text{ …………… } (2.12)$$

Phenomenological coefficient K_{11} is known as effective moisture diffusivity (D_{eff}) and K_{22} is known as thermal diffusivity (α). For constant values of D_{eff} and α, Equations 2.11 and 2.12 can be rearranged as:

$$\frac{\partial M}{\partial t} = D_{eff}\left[\frac{\partial^2 M}{\partial x^2} + \frac{a_1 \partial M}{x \partial x}\right] \text{……………} (2.13)$$

$$\frac{\partial T}{\partial t} = \alpha\left[\frac{\partial^2 T}{\partial x^2} + \frac{a_1 \partial T}{x \partial x}\right] \text{……………} (2.14)$$

Where, parameter a_1= 0 for planar geometries, a_1= 1 for cylindrical shapes and a_1= 2 for spherical shapes.

The resistance to moisture transfer in theoretical model involves the geometry of the material, its mass diffusivity, and the conductivity of the material (Cihan and Ece, 2001). Thus the resistances can be estimated from Eq. 2.11 and 2.12 because these equations describe the mass transfer (Erbay and Icier, 2010b). Equation 2.13 and 2.14 under some assumption and boundary condition can describe mass transfer with good degree of accuracy. Eq. 2.13 and 2.14 can be analytically solved with the assumptions, and the initial and boundary conditions, which are as follows;

Assumptions:

- The particle is homogenous and isotropic.
- The material characteristics are constant, and the shrinkage is neglected.
- The pressure variations are neglected.
- Evaporation occurs only at the surface.
- Initially moisture distribution is uniform and symmetrical during process.
- Surface diffusion is ended, so the moisture equilibrium arises on the surface.
- Temperature distribution is uniform and equals to the ambient drying air temperature, namely the lumped system.
- The heat transfer is done by conduction within the product, and by convection outside of the product.
- Effective moisture diffusivity is constant versus moisture content during drying.

Then analytical solutions of Fick’s law are given below for infinite slab:

$$\text{MR} = \left(\frac{\text{M}-\text{M}_\text{e}}{\text{M}_\text{o}-\text{M}_\text{e}}\right) = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left\{\frac{\left(-(2n+1)^2\pi^2 dt\right.}{4(h^*)^2}\right\} \ldots\ldots\ldots\ldots\ldots (2.15)$$

Where *D* is the effective moisture diffusivity in m^2/s, h* is the half thickness of slab (m), and n is the number of terms (as a positive integer).

However, in practice, for long drying period only first term of the series is often applied because the value of rest term is negligible. Hence, the above equation is simplified to

$$\text{Ln (MR)} = \text{Ln}\left(\frac{8}{\pi^2}\right) - \frac{\pi^2 D}{4(h^*)^2}\times t \ldots\ldots\ldots\ldots\ldots (2.16)$$

Here n= 1.

2.12.2.2 Semi-theoretical or Semi- empirical models

The semi-theoretical models are generally derived by simplifying general series solutions of Fick’s second law or modification of simplified models and are valid within the experimental temperature, relative humidity, air velocity and moisture content range (Panchariya *et al.*, 2002). Semi-theoretical models can also be derived from Newton’s law cooling. Here are some of the semi-theoretical models that are widely used in describing the thin layer drying characteristics of agricultural products (Erbay and Icier, 2010a). Factors that could determine the application of these models include the drying temperature, drying air velocity, material thickness, initial moisture content, and relative humidity (Erbay and Icier, 2010a). Furthermore, under these conditions it can be noted that the complexity of the models can be attributed to the number of constants, i.e. greater the number of constraints more complex will be the model and hence it is difficult to understand the mechanism.

On the basis of products nature, it is further subdivided in to two groups;

2.12.2.2.1 Models derived from Newton's law of cooling

A. Lewis Model

This model is analogous with Newton's law of cooling so many investigators named this model as Newton's model. Lewis described that the moisture transfer from agricultural materials can be seen as similar to the law of heat from a body immersed in cold fluid. First, (Lewis, 1921), suggested that during the drying of porous hygroscopic materials, the change of moisture content of material in the falling rate period is proportional to the instantaneous difference between the moisture content and the expected moisture content when it comes into equilibrium with drying air. So this concept assumed that the material is thin enough, or the air velocity is high, and the drying air conditions such as the temperature and the relative humidity are kept constant.

$$\frac{dM}{dt} = -K\ (M - M_e) \ \ldots\ldots\ldots\ldots\ldots \ (2.17)$$

Where, K is the drying constant. In the thin layer drying concept, the drying constant is the combination of drying transport properties such as moisture diffusivity, thermal conductivity, interface heat, and mass coefficients (Maroulis *et al.*, 1995). Newton's law of cooling assumes that, the internal resistance to moisture movement and thus moisture gradients within the material are negligible. It considers only the surface resistance (Madamba, 2003).

Assuming a boundary condition as $M=M_o$ at $t=0$, the solution of the above equation can also be rewritten as;

$$MR = e^{-kt} \ \ldots\ldots\ldots\ldots\ldots \ (2.18)$$

Where, k = drying constant, t = time

This is one of the simplest models describing moisture movement for food products. The most important drawback of this model is that, it generally underestimates late stages and overestimates early stages of the drying process (Hossain and Bala, 2002). This model has been widely and successfully used by some researchers to model the drying behavior of agricultural products such as strawberry (El-Beltagy *et al.*, 2007), red chili, grape seeds (Roberts *et, al.*, 2008) and black tea (Panchariya *et al.*, 2002).

B. *Page model*

The Page model or the Modified Lewis model is an empirical modification of the Newton model, whereby the errors associated with using the Newton model are greatly minimized by the addition of a dimensionless empirical constant (n). This parameter has an effect of moderating the time, and the model in this case gives better results for the prediction of moisture loss (Doymaz and Ismail, 2011).

$$MR = e^{-kt^{n}} \ldots\ldots\ldots\ldots\ldots (2.19)$$

This model has 2 constants and is widely used as the basis for most semi-theoretical thin-layer models. This model has been used by many researchers to describe the rate of moisture loss during thin layer drying of agricultural materials under constant drying conditions. It was successfully used to describe the drying characteristics of some agricultural products such as banana, date palm, green bean, kiwifruit, mango, onion, bitter melon etc.

C. *Modified Page model*

As the name implies, this is a modification of the Page model. Erbay and Icier (2010a) reported 3 forms of the Modified Page model (I, II, and III). For the purpose of this literature review, the following Modified Page models (Eq. 2.20 and 2.21) have been found to be the most suitable in describing the drying behavior of different fruits and vegetables.

$$MR = e^{-kt^{n}} \ldots\ldots\ldots\ldots\ldots (2.20)$$

Equation 2.20 is widely regarded as the Modified Page model. This model has 2 constants and has been applied in predicting the drying kinetics of mint leaves and basil leaves.

$$MR = ke^{\left(-\frac{t}{d^{2}}\right)^{n}} \ldots\ldots\ldots\ldots\ldots (2.21)$$

Where d is an empirical constant (dimensionless). Equation 2.21 can be called the Modified Page model. This model has 3 constants and can successfully describe the drying behavior of onion.

2.12.2.2.2 Models derived from Fick’s second law of diffusion

A. Henderson and Pabis model

This model is the first term of the general solution of the Fick's second law of diffusion as stated above i.e,

$$\text{Ln (MR)} = \text{Ln}\left(\frac{8}{\pi^2}\right) - \frac{\pi^2 D}{4(h^*)^2} \times t \text{ ....} \quad (2.22)$$

Assumptions:

- The surface moisture content of the food material is in equilibrium with the temperature and relative humidity of the surrounding air.
- Temperature of food material is in equilibrium with drying air.
- The diffusion coefficient remains unchanged during the course of drying.

Then above equation becomes;

$$\text{MR} = a\, e^{-kt} \text{ ....} \quad (2.23)$$

Where, $a = \frac{8}{\pi^2}$ and $k = \frac{\pi^2 D}{4(h^*)^2}$

This can also be regarded as a simple model with only 2 model constants. The Henderson and Pabis (1961) model has been effectively applied in the drying of crops such as corn and millet. However, it has not been quite so successful in describing the drying behavior of fruits and vegetables, since the model has been found applicable only to apple. This model effectively predicts the drying rate at the beginning of the drying process, but appears sometimes to be less efficient for the last stages of the process (Dissa *et al.*, 2008). The slope of this model, “k”, is related to effective diffusivity when drying process takes place only in the falling rate period and liquid diffusion controls the process (Panchariya *et al.*, 2002) and a represents the shape of the materials used (dimensionless).

B. Modified Henderson and Pabis model

The modified Henderson and Pabis model is a third term general solution of the Fick's second law of diffusion for correction of the shortcomings of the Henderson and Pabis model. It has been reported that the first term explains the last part of the drying process of food and agricultural products, which occurs largely in the falling late period, the second term describes the midway part, and the third term explains the initial moisture loss of the drying process (Erbay and Icier, 2010a). The model contains 6 constants and based on this, the model has been referred to as complex thin-layer model.

$$MR = ae^{-kt} + be^{-gt} + ce^{-ht} \ldots\ldots\ldots\ldots\ldots \quad (2.24)$$

Where, a, b, and c are defined as the indication of shape and generally named as model constants (dimensionless), and k, g, and h are the drying constants. These constants are obtained from experimental data.

This model does not effectively describe the drying process of most fruits and vegetables. This model has been found to only successfully describe the drying kinetics of pretreated pumpkin.

C. Logarithmic model

This model is also known as an asymptotic model and is another modified form of the Henderson and Pabis model. It is actually a logarithmic form of the Henderson and Pabis model with the addition of an empirical term. The model contains 3 constants and can be expressed as,

$$MR= ae^{-kt} +c\ldots\ldots\ldots\ldots\ldots \quad (2.25)$$

Where, c is a dimensionless empirical constant. This model has been found to be the fourth best thin-layer model in describing the drying kinetics of various fruits and vegetables. Consequently, the model has produced the best fit in predicting the drying kinetics of apple, basil leaves, beetroot, pumpkin, and stone apple.

D. Two - term model

The 2-term model is a second term general solution of the Fick's second law of diffusion. The model contains 2 dimensionless empirical constants and 2 model constants which can be derived from experimental data. The first term describes the last part of the drying process, while the second term describes the beginning of the drying process. For most fruits and vegetables with high moisture content, this model can well be suitable as it assumes a constant product temperature and diffusivity throughout the drying process. This model well describes the moisture transfer of the drying process, with the constants representing the physical properties of the drying process.

$$MR = ae^{-k_1t} + be^{-k_2t} \ldots\ldots\ldots\ldots\ldots (2.26)$$

Where a and c are dimensional less constant and k_1 and k_2 are drying constants. This model predicts the moisture transport well and its parameters represent the physical properties of the drying process. It is successfully applied to explain drying behavior of prickly pear fruit and cladodes (Lopez *et al.*, 2009), sultana grapes, garlic (Sacilik and Unal, 2005) and pumpkin (Zenoozian *et al.*, 2008).

E. Two - term exponential model

The 2-term exponential model is a modification of the 2-term model by reducing the number of constants and modifying the indication of shape constant (b) of the second exponential term. Erbay and Icier (2010) emphasized that constant "b" of the 2-term model has to be (1 – a) at t = 0 in order to obtain a moisture ratio of MR = 1. The model has 3 constants and can be expressed as,

$$MR = ae^{-kt} + (1-a)e^{-kat} \ldots\ldots\ldots\ldots\ldots (2.27)$$

This model has been found successful in describing the drying kinetics of only star fruit.

F. Approximate diffusion model

The Approximate Diffusion model is another modification of the 2-term exponential model with the separation of the drying constant k and t with a new dimensionless constant “b” in the second part of the model.

$$MR = ae^{-kt} + (1-a)e^{-kbt} \ldots\ldots\ldots\ldots\ldots (2.28)$$

Where, b is also a dimensionless model constant.

This model has been applied with great success in the determining the drying kinetics of green pepper, pumpkin, and tomato.

G. Verma and others model

This model is another modification of the 2-term model with 4 model constants. The Verma *et al.* (1985) model has been applied successfully in describing the drying kinetics of parsley and pumpkin

$$MR = ae^{-kt} + (1-a)e^{-gt} \ldots\ldots\ldots\ldots\ldots (2.29)$$

Where, g is also a drying constant.

H. Modified Midilli model

Midilli *et al.* (2002) proposed a new model by a modification of the Henderson and Pabis model by the addition of an extra t with a coefficient. The new model, which is a combination of an exponential term and a linear term, has been validated by testing the model on mushroom, pollen, and pistachio.

$$MR = ae^{-kt} + bt \ldots\ldots\ldots\ldots\ldots (2.30)$$

Where, a and b are the model constants and k is the drying constant (s^{-1}) to be estimated from the experimental data. This model is sometimes called the Midilli Kucuk model or the Midill *et al s*imodel. It contains 3 constants and has been found to be the best in describing the drying behavior of different fruits and vegetables. It has been found to be suitable in describing the drying kinetics of fruits and vegetables such as apple, chilly, golden apples, hawthorn, jackfruit, kiwifruit, mango, ginger, pepper, persimmon, pineapple, saffron, spearmint.

I. Midilli *et al*. model

Midilli *et al*. model is composed of an exponential and a linear term describing the moisture ratio as a function of drying time;

$$MR = ae^{-kt^n} + bt \text{ …………… } (2.31)$$

This model is also similar to Henderson and Pabis model with an addition of an empirical term to "t". The Midilli *et al.* model was successfully used in studying the drying characteristics of agricultural products such as savory leaves celery leaves, various vegetables like pumpkin and also fruits like apple (Menges and Ertekin, 2006).

J. Hii and others (modified 2-term model)

The Hii, *et al* (2009) can also be referred to as a Modified Page model or, more appropriately, a Modified 2-term model. The model involves a combination of the Page and the 2-term model. The first part of the model is exactly as the Page model. However, it more theoretically describes the model as a modified 2-term model with the inclusion of a dimensionless empirical constant "n." The model contains 5 constants and can be referred to as a complex model in this regard. Hii and others (2009) proposed this model for the drying of cocoa beans. However, it has been found appropriate in describing the drying kinetics of some fruits,

$$MR = ae^{-k_1t^n} + be^{-k_2t^n} \text{ …………… } (2.32)$$

The Hii and others model has been successfully applied to the drying of carrot pomace and pumpkin.

2.12.2.3 Empirical models

Empirical models give a direct relationship between the average moisture content and the drying time. The empirical models also have similar characteristics to semi-theoretical models. They strongly depend on the experimental conditions and give limited information about the drying behaviors of the product (Erbay and Icier, 2010a). The empirical method is based on experimental data and dimensional analysis. They are easily applied to drying simulation, as they depend on experimental data. Empirical models consider only the external resistance to moisture transfer between the product and air. The major limitation to the application of empirical models in thin-layer drying is that they do not follow the theoretical fundamentals of drying processes in the form of a kinetic relationship between the rate constant and the moisture concentration, thus giving inaccurate parameter values. Moreover, these models do not have a physical interpretation and are wholly derived from experimental data (Onwude *et al.,* 2009).

The 3 most widely applied empirical models for the drying kinetics of fruits and vegetables as reported in the literature are:

2.12.2.3.1 Wang and Singh model

This model was developed for the intermittent drying of rough rice (Wang and Singh, 1978).The model gives a good fit to the experimental data. However, this model has no physical or theoretical interpretation, hence its limitation.

$$MR = 1 + at + bt^2 \quad \ldots\ldots\ldots\ldots\ldots \; (2.33)$$

Where, *a* and *b* are dimensionless model constants gotten from the experimental data. This model has been found to successfully explain the drying behavior of banana.

2.12.2.3.2 The Thompson Model

The Thompson model is an empirical model obtained from experimental data by correlating the drying time as a function of the logarithm of the moisture ratio. The model cannot successfully describe the drying behavior of most fruits and vegetables because it has no theoretical basis and lacks physical interpretation. However, the model has been found to be suitable for describing the drying kinetics of green peas and blueberries. The model can be expressed as,

$$t = a + \ln(MR) + b + [\ln(MR)]^2 \quad \ldots\ldots\ldots\ldots\ldots \; (2.34)$$

Where, a and b are dimensionless empirical constants.

2.12.2.3.3 Peleg Model

This model is generally used to model the Rehydration characteristic of food products but Peleg model gives good fit for drying of some biological product. It has been applied successfully only in describing the drying behavior of banana.

$$M = M_o + \left(\frac{1}{a + bt}\right) \text{..............} \ (2.35)$$

Where, M = moisture content at time t (%), M_o = initial moisture content (%), a = Peleg constant ($hour^{-1}$), b = Peleg capacity constant ($\%^{-1}$), t = hour.

2.13 Evaluation of mathematical models of different products

Due to the complexity of transport mechanisms, semi-empirical models are often used to describe the thin layer drying behaviours of food materials. Of all semi-empirical models, two compartments or two terms model has been used widely in determining the thin layer drying characteristics of product. The thin layer drying characteristics of garlic slices, macadamia in-shell nuts and kernels, mint leaves and rough rice were satisfactorily described by the two compartment model. Palipane, *et al* (1994) proved that the two term model gave better predictions of the experimental values especially over long drying periods. Palipane, *et al* (1994) also indicated that the best correlation between moisture content and drying time covering all the drying runs was obtained with the two term model.

The two compartment model was chosen as an adequate model for certain products due to its lesser number of parameters and its physical significance. Obviously, product consists of several compartments is better described by more than a single term due to internal drying resistances of each compartment. Yodollahinia, *et al* (2008) used two-term model to explain the thin layer drying behaviour of rough rice with three compartments, the hull, bran and endosperm. Semi-theoretical models are generally derived by simplifying general series solutions of Fick’s second law or modification of simplified model. Based on the Crank solutions, diffusivity of a particular product is determined by assuming the geometry of the product itself. As most of the agricultural products are not uniform, it is difficult for researchers to specify the shape or geometry of the product.

The two compartment model is found to be an accurate model when dealing with long drying period but still it does not respond well to changing conditions such as air temperature. Due to moisture ratio differences between two layers during drying, it is expected to give better respond to experimental data and predict the drying behaviour of a product. Further experimental and research works need to be carried out in order to verify its expected outcome.

2.14 Effects of drying and product conditions on drying rate

Many variables involve in thin layer drying of agricultural products such as product temperature which is assumed to be equal to the drying air temperature, initial product moisture content, air velocity, relative humidity and product thickness. Based on literature, drying air temperature and product thickness are proved to be the major factors which affect the heat and moisture transfer rates whereas air velocity has a little effect on drying rate. Rapusas, *et al* (1995) agreed that temperature and the slice thickness were significantly affected the drying rate of white onion slices. Ertekin, *et al* (2004) found that the thinner slices of eggplant, the shorter the drying time. Madamba, *et al* (1996) also showed that both temperature and slice thickness had a significant effect on the drying rate while relative humidity and air flow rate had a very little effect.

However, relative humidity of the drying air has a vital impact on the final moisture content of the product as it controls the rate of water vapour transport from the product surface to the air. Duc *et al*., (2011) proved that the moisture ratio had a steeper decreasing slope with increasing air temperature as well as decreasing relative humidity. Obviously, increase in temperature of drying air reduces the time required to reach any given level of moisture ratio since the heat transfer increases whereas decrease in the relative humidity of drying air reduces the time required to reach any given level of moisture ratio since the mass transfer increase. In other word, an increase in relative humidity decreases the drying rate. Researchers generally agree that pre-treatment of product before drying plays an important aspect in reducing the drying time. Fig. 2.6 shows the effect of thickness moisture ratio at different temperatures of garlic slices.

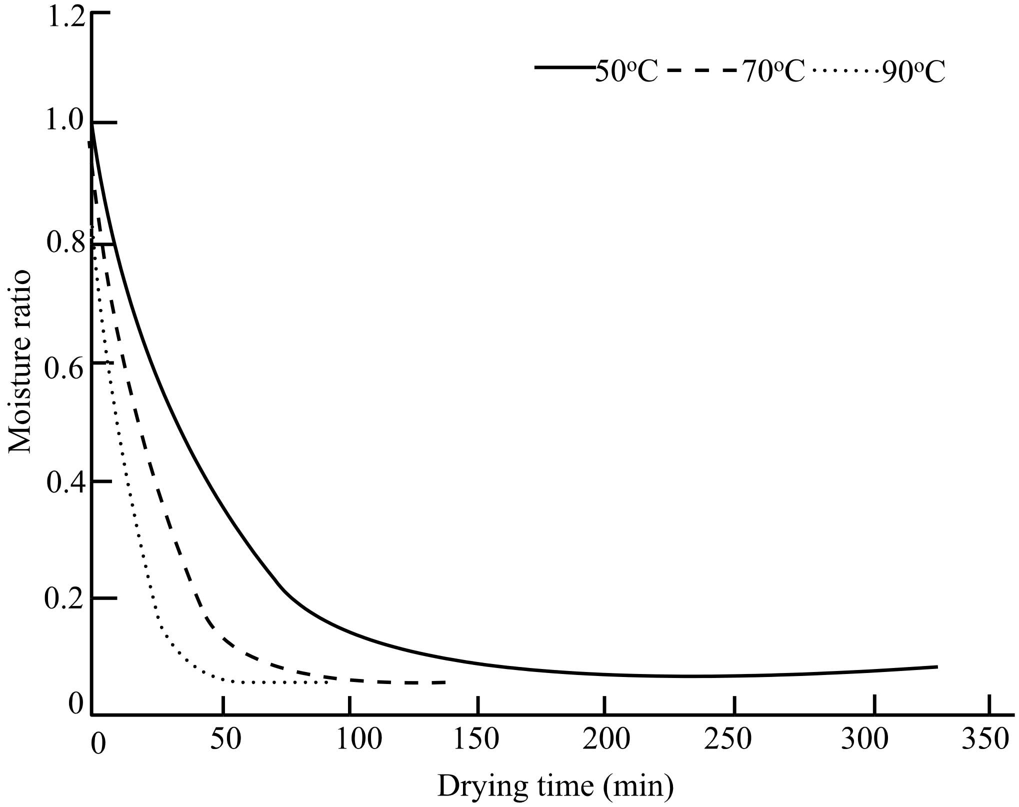


Fig. 2.6 The effect of thickness moisture ratio at different temperatures of garlic slices (Madamba, *et al* 1996).

As shown in Figure2.8 Doymaz, *et al* (2003) showed that there is a significant difference between the untreated and treated corn in term of drying rate as the drying time decreased by 35%, 25% and 16.7% for treated corn kernels. Doymaz, *et al* (2011) also compared various pre-treatments with the blanched samples had shorter drying time compared to other methods and untreated samples.

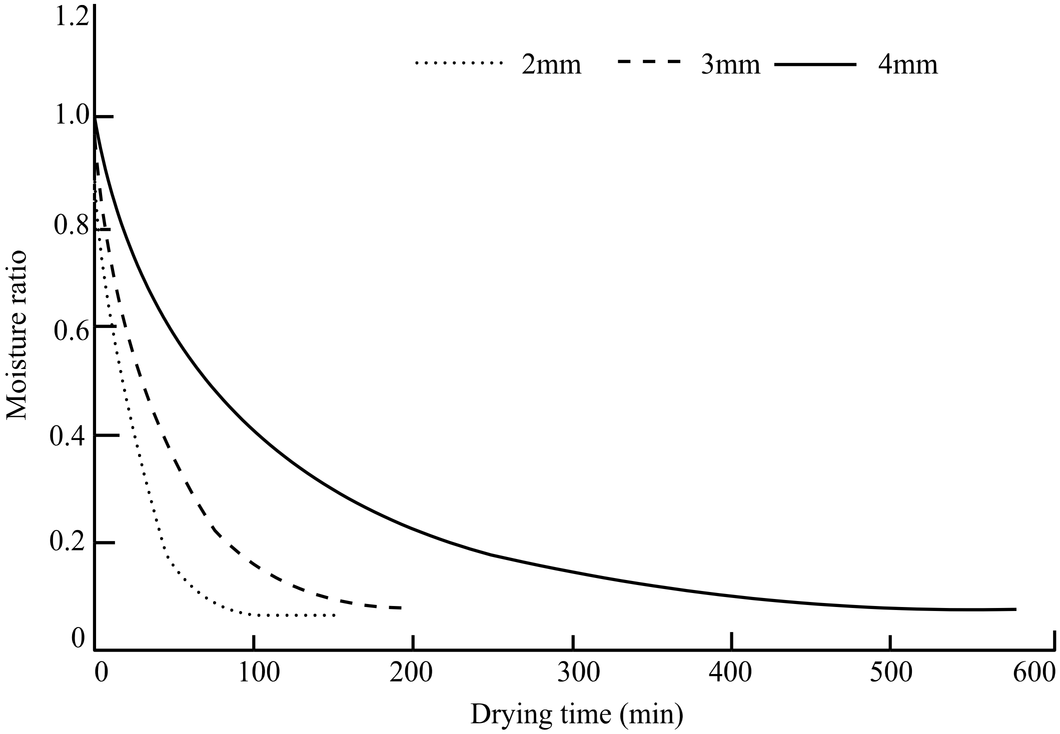


Fig. 2.7 The Influence of drying air temperatures on moisture ratio of garlic slices (Madamba, *et al* 1996).

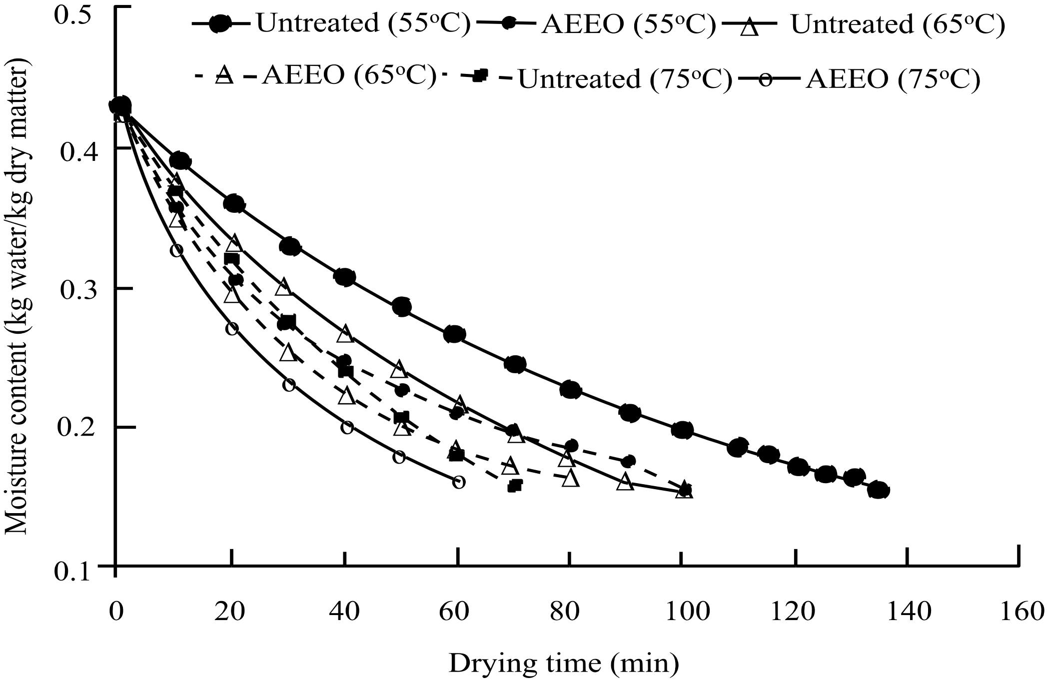


Fig. 2.8 Effect of ethyl oleate (AEEO) dipping on the drying curves at different temperatures of corn kernels (Doymaz, I., *et al* 2003).

2.15 Estimation of the activation energy

The relationship between effective diffusivity and temperature is assumed to be an Arrhenius function (Akpinar 2006a; Sacilik 2007; Vega and others 2007; Aghbashlo and others 2008; Pardeshi and others 2009; Perez and Schmalko 2009; Doymaz 2011; Guin´e and others 2011; Unal and Sacilik 2011; Kumar and others 2012b; Akoy 2014; Tzempelikos and others 2014; Da Silva and others 2015; Dianda and others 2015; Saxena and Dash 2015), of the type:

$$D = D_o \exp\left(-\frac{E_a}{R(T+273.15)}\right) \ldots\ldots\ldots\ldots\ldots (2.36)$$

where D_o is the pre-exponential factor of the Arrhenius equation in m^2/s, E_a is the activation energy in kJ/mol, R is the universal gas constant (R = 8.31451 J/mol/K), and T is the air temperature expressed in °C.

A plot of Ln(D) as a function of 1/ (T + 273.15) will produce a straight line with a slope equal to ($-E_a/R$), so E_a can be easily estimated.

However, Dadali and others (2007) developed another form to estimate the activation energy. They determined that D is a function of material mass and the microwave power level of an Arrhenius type equation:

$$D = D_o \exp\left(-\frac{E_a m}{P_m}\right) \ldots\ldots\ldots\ldots\ldots (2.37)$$

where E_a is the activation energy (W/g), m is the mass of the product (g) and P_m is the microwave output power (W). This equation has been applied in calculating the activation energy during the drying of spinach, date palm, pepper, mango and ginger.

Finally, the activation energy values in the literature, for various fruits and vegetables, for the specified for over 90% of the activation energy values are in the range 14.42 to 43.26 kJ/mol, while 8% of the values are in the range 78.93 to 130.61 kJ/mol. The large concentration of these values are found in the range 21.6 to 39.03 kJ/mol (Onwude *et al.*, 2009).

Part III

Materials and methods

3.1 Materials

3.1.1 Soybeans

White variety soybeans (*Glycine max* L.) was collected from the local market of Dharan, Nepal.

3.1.2 Apparatus

Following equipments were used in this study:

- Dryer: cabinet [hot air convective dryer PCD-E3000 Serials, volts - 220V, Temperature range {0-300} cabinet ^{o}C]
- Electronic balance (Volt: DC9V, Max: 500g, d:10 mg)
- Digital thermometer
- Hot air drying oven **(**oven temperature Max 250^{o}C, Volt 240V)

3.2 Methods

3.2.1 Preliminary operation

Kinema was prepared traditionally as per the procedure provided by (Kharel, 2006). Soybeans was washed and removed dust, mud, dirt and foreign materials.

3.2.2 *Kinema* making process

The traditional method of *kinema* preparation was derived from Kharel (2006) but small modification was done during drying process of *kinema*. Fig. 3.1 shows the method of *kinema* preparation and mathematical modelling.

Soybean
↓
Cleaning (Clean in running water)
↓
overnight soaking in cold water
↓
Dehulling by scrubbing on palm
↓
Cooking (Cooking up to 30 min)
↓
Draining (Drain excess water)
↓
Cooling (cool to 35^{0}C)
↓
Ash addition (1% White firewood)
↓
Wrapping (Wrap the mass with banana leaves)
↓
Fermentation (3days at room temperature)
↓
Fresh *kinema*
↓
Cabinet drying of fresh *kinema* at 50, 60, 70 and 80^{o}C till constant weight was obtained (bed thickness = 0.7 cm)
↓
Mathematical modeling of drying
↓
Checking for goodness of fit to models
↓
Calculation of activation energy and diffusivity constant

Fig. 3.1 Method of *kinema* preparation and mathematical modelling.

3.2.3 Drying kinetics modeling

3.2.3.1 Drying kinetics modeling procedures

Kinema was dried by hot air convective dryer PCD-E3000 Serials, volts-220V, temperature range (0-300) cabinet °C. *kinema* was subjected to drying in cabinet dryer at four different temperatures i.e 50°C, 60°C, 70°C and 80°C. Changes in weight were noted in regular basis until the change in weight was negligible. Observed readings were converted to dry basis moisture content. The dry basis moisture content was then converted to experimental Moisture ratio. The obtained data was fitted by using Microsoft excel (i.e. non-linear curve fitting) and then compared to standard curves. A graph between experimental MR vs. time was plotted. The plotted experimental graph was then compared with standard curve of particular equation. Then, Chi-squire, corrected correlation coefficient and root mean square was determined on the basis of experimental and predicted moisture ratio value. Finally, the best curve was selected by evaluating Chi-square (χ^2) test, correlation coefficient and Root mean squire error (RMSE).

3.2.3.2 Drying kinetics modeling equations

The Experimental moisture ratio value was then compared with 5 most popular and widely acceptable thin layer modeling equations. The compared equations are tabulated in Table 3.1.

Table 3.1 Mathematical models applied to the drying curves

Model name	Mathematical Equation	References
Lewis	$MR = \exp(-kt)$	Ceylan, 2007; Guiné *et al.*, 2011
Page	$MR = \exp(-kt^n)$	Ceylan, 2007; Guiné *et al.*, 2011
Henderson and Pabis	$MR = a \exp(-kt)$	Ceylan, 2007; Guiné *et al.*, 2011
Logarithmic	$MR = a \exp(-kt) + c$	Ceylan, 2007; Guiné *et al.*, 2011
Midilli et al.	$MR = ae^{-kt^n} + bt$	Ceylan, 2007; Guiné *et al.*, 2011

3.3 Statistical analysis for determination of appropriate models

In order to find best suitable model to explain drying behavior of any product with different drying methods or different conditions, statistical methods were generally used. The main methods used for drying studies in the literatures are discuss in the following sections.

3.3.1 Coefficient of determination

It is used by the statistical models whose main purpose is the prediction of future outcomes on the basis of other related information. It is the proportion of variability in a data set that is accounted for by the statistical model. The coefficient of determination is not likely to be 0 or 1, but rather somewhere in between these limits. The closer it is to 1, the greater relationship exists between experimental and predicted values (Neter *et al.*, 1990). This value is used for the quantitative comparison criteria and shows the level of agreement between measured and predicted values (Hossain and Bala, 2002). It is sometimes called as correlation coefficient or determination coefficient (Akpinar, 2006a; Sobukola *et al.*, 2008). Although there are several different definitions of R^2, it can be calculated by;

$$R^2 = \frac{\sum_{i=1}^{N}\left(MR_{exp,i} - MR_{exp}\right)\left(MR_{pre,i} - MR_{pre}\right)}{\sqrt{\sum_{i=1}^{N}\left(MR_{exp,i} - MR_{exp}\right)^2 \sum_{i=1}^{N}\left(MR_{pre,i} - MR_{pre}\right)^2}} \quad \text{..............} (3.3)$$

3.3.2 Reduced chi-square (χ2)

It is the mean square of the deviations between experimental and predicted values for the models and used to evaluate the fitting agreement of each model. Lower the values of χ^2, better the goodness of the fit (Yang *et al.*, 2007). It is called as mean squared deviation (Cihan *et al.*, 2007; Celen *et al.*, 2010), reduced mean square of deviation, mean square of deviation and standard deviation (Midilli *et al.*, 2002) and could be calculated as follows;

$$\chi^2 = \frac{\sum_{i=1}^{N}\left(MR_{exp,i} - MR_{pre,i}\right)^2}{N - n} \quad \text{..............} (3.4)$$

3.3.3 Root-mean-square error (RMSE)

It is a frequently used measure of the differences between values predicted by a model or an estimator and the values actually observed from the thing being modeled or estimated. RMSE is a good measure of accuracy and serves to aggregate the residuals into a single measure of predictive power. It is required to reach zero and can be calculated as (Wang *et al.*, 2007);

$$\text{RMSE} = \left(\frac{1}{N}\sum_{i=1}^{N}\left(MR_{pre} - MR_{exp,i}\right)^2\right)^{\frac{1}{2}} \ldots\ldots\ldots\ldots\ldots (3.5)$$

It is called as root mean square analysis, standard deviation, root mean sum error, standard error, root mean square difference and root mean squire deviation.

3.4 Procedure for finding best fit model

In order to select the most suitable model describing thin layer drying behavior and conditions for any specific application the following steps should be taken into consideration;

The values of correlation coefficient, the coefficient of determination, adjusted R^2, the reduced chi-square and the root mean square error was calculated. The highest values of the correlation coefficient, the coefficient of determination, modeling efficiency, adjusted R^2 was determined and selected. The lowest values of the reduced chi-square and the root mean square error was determined and selected. The drying curve model was determined that had the highest values of the criteria i.e. R^2 and the lowest values of the criteria i.e. reduced chi-square and root mean square error. This model can be assumed to be the best model describing the thin-layer drying curve.

3.5 Effective moisture diffusivity

The simplified form of Fick's second law of diffusivity is given as;

$$\text{Ln (MR)} = \text{Ln}\left(\frac{8}{\pi^2}\right) - \frac{\pi^2 D}{4(h^*)^2} \times t \ldots\ldots\ldots\ldots\ldots (3.6)$$

The diffusion coefficient is determined by plotting the experimental drying data in terms of ln(MR) versus time. A plot of ln(MR) versus time gives a straight line with a slope of;

$$\text{Slope} = -\frac{\pi^2 D}{4(h^*)^2} \quad \ldots\ldots\ldots\ldots\ldots \ (3.7)$$

3.6 Data analysis

The data obtained during the course of experiment was first processed and then analyzed. The experimental data of the ratio of moisture were used to fit the models. For mathematical modeling, the different semi theoretical equations were tested to select the best model for describing the drying curve equation. The goodness of fit of the tested mathematical models on the experimental data was evaluated using coefficient of determination (R^2) and chi-square test (χ^2) and Root Mean Square Error (RMSE) and with higher R^2 values and lower χ^2 and RMSE values indicating a better fit.

Part IV

Results and discussion

4.1 Physical properties of soybean seed

It’s obvious that the quality of finished product is dependent upon the quality of raw material used. Morphological analysis is a tool that provides essential information regarding the soundness of kernels. Hence, selection of suitable variety of raw materials can be done with the help of morphological analysis. Result of analysis of raw materials has been tabulated in Table 4.1.

Table 4.1 Physical properties of white soybeans

Parameter	Value*
Color	Yellowish white
Shape	Oblong and elliptical
Surface	Smooth
Length	8.65 mm (0.10)
Breadth	6.66 mm (0.32)
L/B ratio	1.17 (0.23)
1000 kernel weight	190.23 g (6.67)
Bulk density	0.78 g/cc (0.11)

*Values are the mean ± s.d. of triplicate determinations.

The L/B ratio gives the idea about shape (sphericity) of the seed (Shrestha, 2013). This ratio was found to be 1.17 for white soybean. 1000 kernels weight gives the information about the size of the seed. Higher the 1000 kernel weight, greater is the size of the seed. 1000 kernel weight for white soybean was 190.23 g. The value for white soybean was quite similar, 190 g, as determined by Dhungel (2000). The bulk density observed for white soybean was 0.78 g / cc. The bulk density of white soybean was quite higher than that obtained by Shrestha (2013) and Dhungel (2000).

4.2 Proximate composition of soybeans

The raw materials for the preparation of *kinema* were analysed and proximate composition of soybeans were comparatively equal to that given in nutrient content of Nepalese food, 1986. The proximate composition of soybeans is given in Table 4.2

Table 4.2 Proximate analysis of white soybeans

Parameter	**Value***
Moisture (%)	9.76±0.26
Crude protein (%)	39.4±0.254
Crude fat (%)	20.01±0.55
Total ash (%)	5.40±0.18
Crude fiber(%)	4.52±0.28
Carbohydrate (%)	30.04±0.45
pH (uncooked)	6.7

*Values are the mean ± s.d. of triplicate determinations.

The moisture, Crude protein, Crude fat, Total ash, Crude fiber, Carbohydrate of white soybean was found to be 9.76%, 39.4%, 20.01%, 5.40%, 4.52% and 30.04% respectively. Similarly, the pH of raw soybean was found to be 6.7. The results were close to the findings as obtained by Nepali (2007).

4.3 Drying curves

Fig. 4.1 illustrates the dry basis moisture content of *kinema* during the convective air drying at the different temperatures studied. The samples took constant rate period of 7.0, 5.66, 4.33 and 2.33 h, for the temperatures varying from 50^{o}C to 80^{o}C, and reached a final moisture content of 0.5197, 0.2198, 0.0612 and 0.0212 kg water/ kg dry solids respectively.

As expected, there is an acceleration of the drying process due to the increase in the temperature of the drying air from 50ºC to 80ºC. Moreover, the higher percentage of weight loss occurs in the early stages of drying, so that in the first 100 mins, the moisture content decreased from 1.1697 kg water/ kg dry solids to 0.1697 kg water/ kg dry solids when the temperature rises from 50ºC to 80ºC.

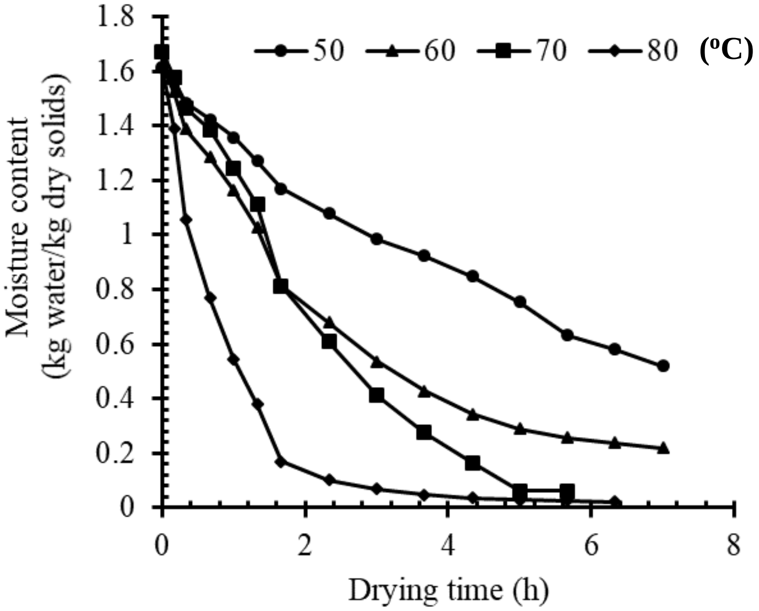


Fig. 4.1 Batch drying curve for *kinema* at different temperature

The drying temperature significantly affected the drying rate of *kinema*. This was found by Vega-Galvez *et al.* (2011), they also studied the effect of temperature and air velocity on the drying kinetics of apple slices, and found that the drying rate of apples increased with an increase in temperature. At high drying temperatures, the drying rate is faster due to the excitation of molecules in the samples (Jamali *et al.*, 2006). As the temperature increases, water molecules inside the sample move faster, which increases the distance between molecules and indirectly reduces the attractive forces between them. Thus, an increase in the drying temperature increases the amount of moisture removed from the samples.

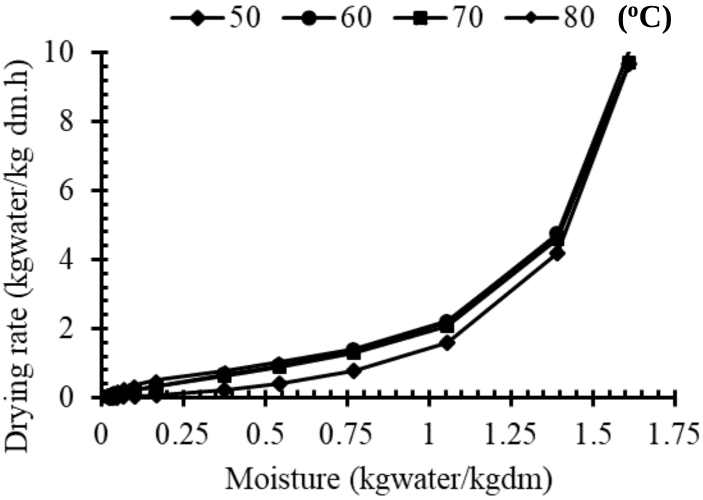


Fig. 4.2 Drying rate versus moisture curves of *kinema* dried at different drying temperatures

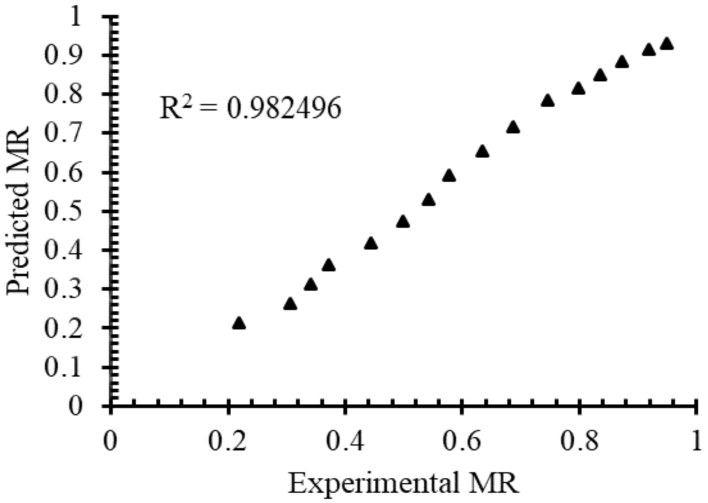
Based on the results shown in Fig. 4.2, samples dried at 50ºC, 60ºC, 70ºC and 80ºC showed a falling rate period. These results were in accordance with those obtained by Hii *et al.* (2009) and Doymaz (2007), who observed a falling rate period in their studies on the drying of fruit products. In the early stages of the drying process, a rapid loss of moisture was observed due to moisture loss at the surface of samples and capillary action, which transported unbound water to the surface through the capillaries of the samples. As the drying time increased, the surface layer of water slowly receded below the surface, and hot air filled the voids left by moisture removed from the samples. Moisture was continuously removed until there was insufficient water left to maintain a continuous film across the pores. At this stage, the limiting step in the drying process was the rate of water vapour diffusion in the pores because liquid water had to evaporate and move to the surface in the gas phase. This phenomenon explains the observed decrease in the drying rate at longer drying times (Geankoplis, 2003). In thin layer drying model, the rate of change in material moisture content in the falling rate drying period is proportional to the instantaneous difference between material moisture content and the expected material moisture content when it comes into equilibrium with the drying air (Menges and Ertekin, 2006).

4.4 Mathematical Modelling

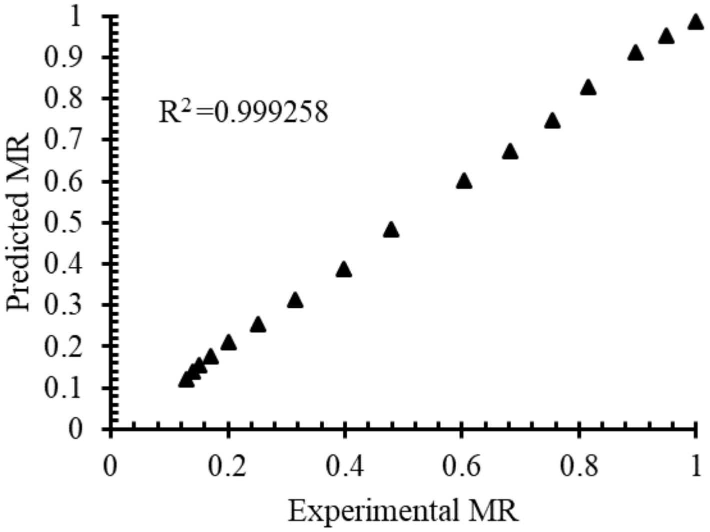
The moisture ratio (MR) was calculated using Equation 3.2, and regression analysis was performed using Microsoft Excel. Table 4.4 shows the calculated data for the selected thin layer drying model. Compared to other mathematical models, the Midilli *et al.* model was the best model for all of the drying temperatures because the lowest RMSE and χ^2 were observed with highest R^2 values (Table 4.4). The results were confirmed by plotting the graph of the experimental MR versus the predicted MR (Figure 4.3). All of the R^2 values were greater than 0.98, which indicates that the fit was good.

Table 4.3 Mathematical drying model constants

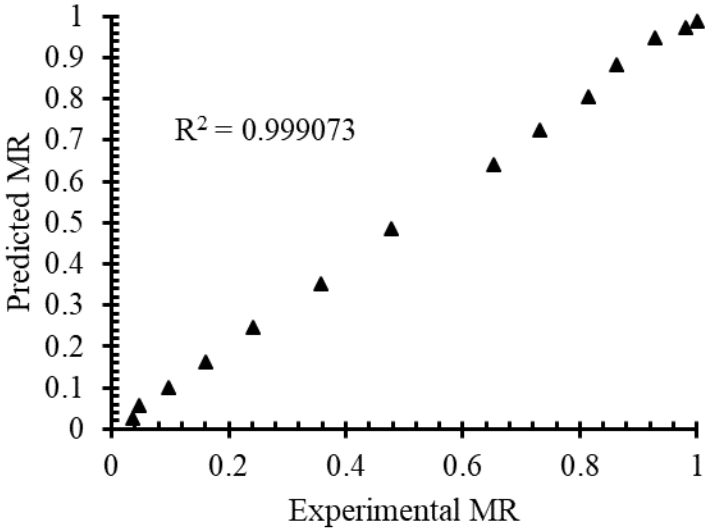
Temperature (ºC)	Model name	Model constants
50	Lewis	k = 0.1587
	Page	k = 0.1572, n = 1.0059
	Henderson and Pabis	a = 0.9833, k = 0.1545
	Logarithmic	a = 0.9833, k = 0.1545, c = 0
	Midilli *et. al*	a = 0.9467, n = 1.0960, k = 0.0779, b = -0.0254
60	Lewis	k = 0.3050
	Page	k = 0.3052, n = 0.9994
	Henderson and Pabis	a = 1.0010, k = 0.3054
	Logarithmic	a = 0.9779, k = 0.3276, c = 0.0293
	Midilli *et. al*	a = 0.9864, n = 1.1373, k = 0.2909, b = 0.0098
70	Lewis	k = 0.3425
	Page	k = 0.2107, n = 1.4726
	Henderson and Pabis	a = 1.0771, k = 0.3749
	Logarithmic	a = 1.0771, k = 0.3749, c = 0
	Midilli et. al	a = 0.9871, n = 1.4701, k = 0.1985, b = -0.0036
80	Lewis	k = 0.8197
	Page	k = 0.7877, n = 1.2389
	Henderson and Pabis	a = 1.1025, k = 0.9215
	Logarithmic	a = 1.0992, k = 0.9326, c = 0.0047
	Midilli *et. al*	a = 1.0819, n = 1.0973, k = 0.9018, b = 0.0023



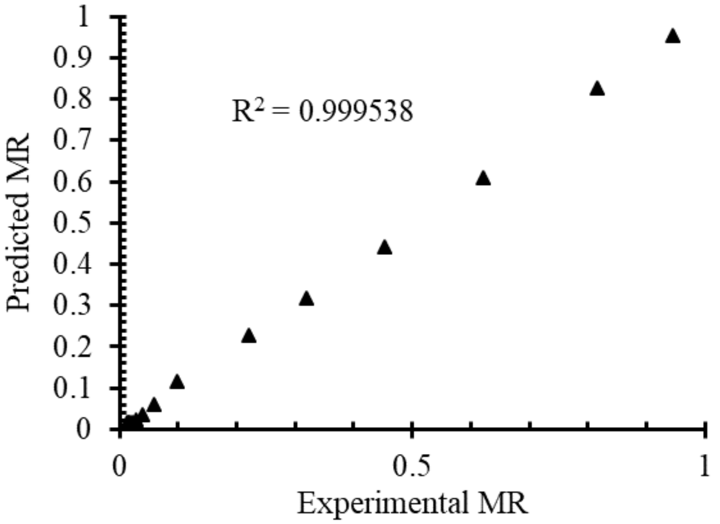
i. 50^{o}C



ii. 60^{o}C



iii. 70ºC



iv. 80ºC

Fig. 4.3 Calculated MR vs. actual MR for the Midilli *et. al* model at a drying temperatures of .i. 50ºC .ii. 60ºC .iii. 70ºC and .iv. 80ºC

Table 4.4 Statistical results for thin layer mathematical modelling with different drying temperatures.

Temperature (ºC)	**Model name**	**R^2**	**χ^2**	**RMSE**	**SSE**
50	Lewis	0.973897	0.00173	0.0404	0.027835
	Page	0.974045	0.00185	0.0404	0.027824
	Henderson and Pabis	0.974644	0.001771	0.0395	0.026565
	Logarithmic	0.974644	0.00189	0.0395	0.026565
	Midilli *et. Al*	0.982496	0.001399	0.03271	0.018192
60	Lewis	0.998011	0.000204	0.01384	0.003065
	Page	0.99801	0.000218	0.01383	0.003064
	Henderson and Pabis	0.998024	0.00021	0.0138	0.003061
	Logarithmic	0.998354	0.0001913	0.0124	0.002488
	Midilli *et. Al*	0.999258	0.0000934	0.00837	0.001121
70	Lewis	0.982491	0.004936	0.0677	0.064168
	Page	0.99865	0.002230	0.01382	0.002677
	Henderson and Pabis	0.97709	0.0037	0.0566	0.045003
	Logarithmic	0.9770	0.00409	0.05669	0.045003
	Midilli *et. Al*	0.999073	0.000162	0.01075	0.00162
80	Lewis	0.996074	0.00163	0.0390	0.022919
	Page	0.99655	0.000840	0.02699	0.010928
	Henderson and Pabis	0.998688	0.000206	0.0133	0.002687
	Logarithmic	0.998712	0.000214	0.0130	0.00257
	Midilli *et. Al*	0.999538	0.0000839	0.00784	0.000923

In all cases, the values of R^2 for the models are greater than the acceptable threshold of 0.90, which indicates a good fit (Madamba *et al.*, 1996). The higher the value of R^2 and the lower the values of, RMSE and χ^2 are chosen as the criteria for goodness of fit. From the table 4.4, it was seen that the value of coefficient of determination ranges between 0.9824 to 0.9738, 0.9992 to 0.9980, 0.9990 to 0.9770 and 0.9995 to 0.9960 at 50, 60, 70 and 80°C respectively. The lowest χ^2 value ranging 0.0013 to 0.0018, 0.00009 to 0.00021, 0.00016 to 0.0049 and 0.00008 to 0.0016 at 50, 60, 70 and 80°C respectively. The value of RMSE ranging between 0.0327 to 0.404, 0.0083 to 0.0138, 0.0107 to 0.0677 and 0.0078 to 0.0390 at 60°C at 50, 60, 70 and 80°C respectively. Also, the value of SSE ranging between 0.0181 to 0.2783 at 50°C, 0.0011 to 0.0030 at 60°C, 0.0016 to 0.045 at 70°C and 0.00092 to 0.0229 at 80°C was found.

At 80°C the value of R^2 obtained for the Midilli *et al.* model was highest (0.999538) than those obtained from the other models. Also the values of RMSE and χ^2 obtained for Midilli et. al model were lower than rest of the models. At 50°C the value of R^2 obtained for the Midilli *et al.* model was higher i.e. 0.9824 and also the values of RMSE and χ^2 obtained for Midilli *et al*. model is lower than rest of the models. At 60°C the value of R^2 obtained for the Midilli *et al*. model was higher i.e. 0.9992 on the other hand the values of RMSE, χ^2 is also lower than other rest of the models. Similarly, at 70°C, the value of R^2 obtained for the Midilli *et al.* model is higher i.e. 0.9990 with the values of RMSE and χ^2 obtained for Midilli *et al*. model lower than rest of the models.

Variations of experimental and predicted moisture ratio values with drying time are given in Fig. 4.3 which shows the moisture ratio values predicted by the Midilli *et al*. model compared with the experimental data for cabinet drying at temperatures of 50, 60, 70 and 80°C. Fig. 4.1 clearly shows that the moisture ratio decreases with increasing drying time. At the start of drying process, the rate of moisture removal is very high and decreases as the drying proceeds. The predicted data mainly banded around the straight line which showed the suitability of the model in describing single layer drying behavior *kinema*.

Graphical representation of predicted vs. experimental M.R. gives the relation between them. Correlation coefficient (R^2) indicates how well experimental and predicted moisture ratio correlates. Its value should be greater than 0.90 for good correlation. Here, the value of correlation coefficient is close to 1 in all drying temperatures. That means they are well correlated with each other. Here experimental data are generally banded around straight line representing data found computation. This indicates suitability of mathematical model in describing drying behavior of *kinema*.

The value of R^2 was higher for Midilli *et al*. model and also value of RMSE and χ^2 are lower for Midilli *et al*. model too. Hence, Midilli *et al*. model fits the curve with high degree of accuracy then other models. Hence, Midilli *et al.* is the best model for simulation of drying characteristic of *kinema* during cabinet drying at the range of temperature (50-80)°C. Midilli *et al.* model has been found suitable in describing the drying kinetics of many fruits and vegetables. This model has found excellent in describing drying kinetics of apple slices corresponding to similar statistical result having the value of R^2, χ^2 and RMSE 0.9979, 1.7×10^{-4} and 0.01357 respectively (zarein *et al.*, 2013). Similarly, Midilli *et al*. model has been found best fitted in in describing the drying behavior of various porous leaves such as celery leaves, spanich leaves (Simha and Gugalia, 2013). mint leaves such as spear mint leaves (Ayadi *et al.*, 2014) and also has described the dying kinetics of saffron. This model has also found excellent in describing drying kinetics of various vegetables such as pumpkin and fruits such as jack fruit, kiwi fruit, golden apples (Menges and Ertekin, 2006), mango, ginger and spice like pepper (Onwude *et al.*, 2009).

This Midilli *et al.* model having three constants have been found best in describing the drying kinetics of different fruits and vegetables as well as savory leaves. According to Onwude *et al.* (2009) this model is noted as most suitable model in over 24% literature sources reviewed. Thus statistical result as well as graphical curve models shows that the Midilli *et al* is the most suitable drying models that describes the drying kinetics of *kinema* during hot air convective drying at the temperatures of 50, 60, 70 and 80°C.

4.5 Effective moisture diffusivity

Fick's second law of diffusion was used to evaluate the effective diffusivity of *kinema* because all of the samples showed a falling rate period in their drying characteristics. Samples used in the present study were analysed in slab geometry form. The results have shown that internal mass transfer resistance controls the drying time due to the presence of a falling rate drying period. Therefore, it is essential to determine the values of the effective moisture diffusivities for given condition. The effective moisture diffusivity was calculated by using the method of slopes. Graphically, it is determined by plotting graph between Ln(M.R) with time.

4.5.1 Moisture diffusivity at 50°C.

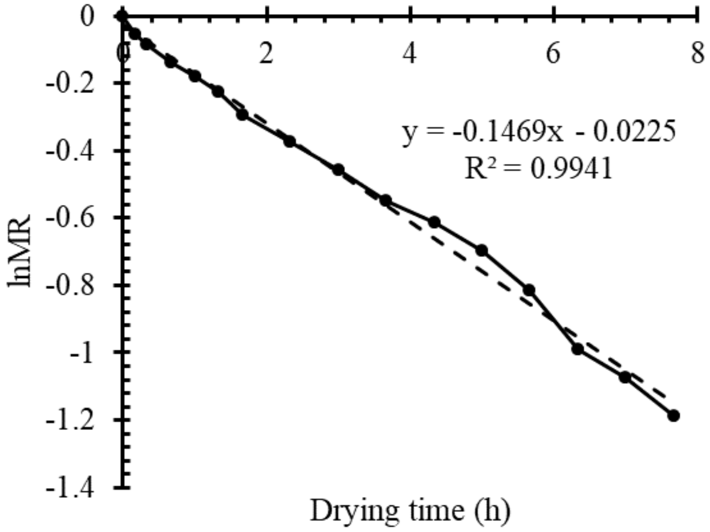


Fig. 4.4 Graphical representation of Ln(MR) vs. time at 50°C.

Average half thickness of slab (*kinema*) = 3.5×10^{-3}m

From graph,

Slope of curve = -0.1469

Now, slope = $-\frac{\pi^2 D}{4(h^*)^2}$

Diffusivity = 2.0258×10^{-10} m^2/s.

The effective moisture diffusivity of *kinema* during cabinet drying at 50°C was found to be 2.0258×10^{-10} m^2/s.

4.5.2 Moisture diffusivity at 60°C.

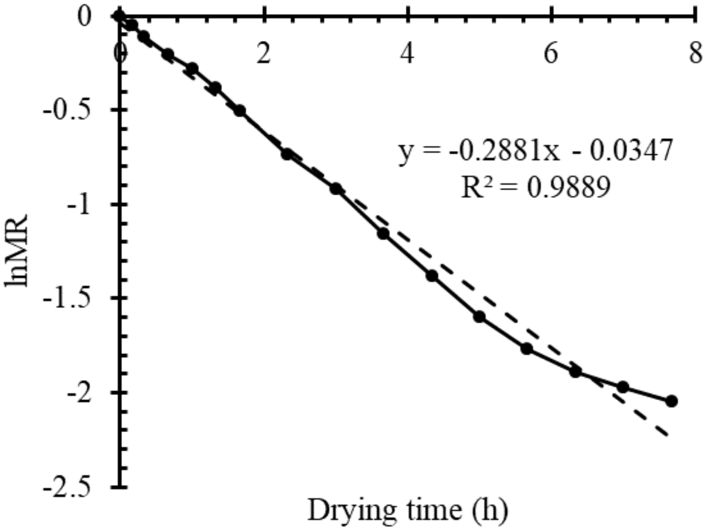


Fig. 4.5 Graphical representation of Ln(MR) vs. time at 60°C.

Average half thickness of slab (*kinema*) = 3.5×10^{-3}m

From graph,

Slope of curve = -0.2881

Now, slope = $-\frac{\pi^2 D}{4(h^*)^2}$

Diffusivity = 3.9730×10^{-10} m^2/s.

The effective moisture diffusivity of *kinema* during cabinet drying at 60°C was found to be 3.9730×10^{-10} m^2/s.

4.5.3 Moisture diffusivity at 70°C.

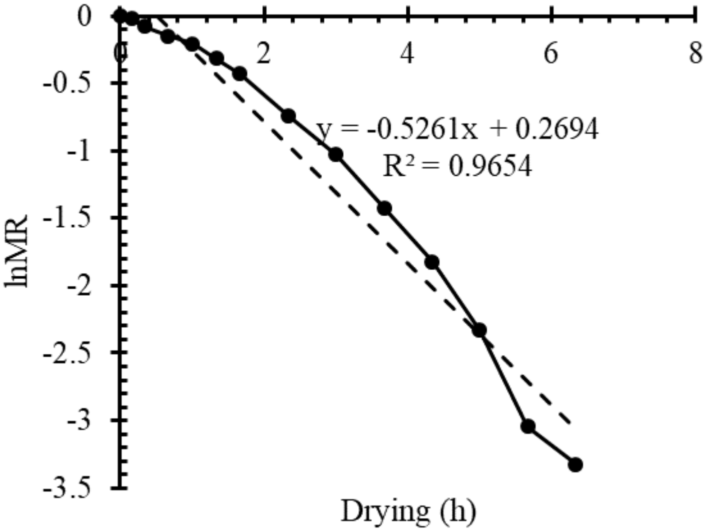


Fig. 4.6 Graphical representation of Ln(MR) vs. time at 70°C.

Average half thickness of slab (*kinema*) = 3.5×10^{-3}m

From graph,

Slope of curve = -0.5261

Now, slope = $-\frac{\pi^2 D}{4(h^*)^2}$

Diffusivity = 7.255×10^{-10} m^2/s.

The effective moisture diffusivity of *kinema* during cabinet drying at 70°C was found to be 7.255×10^{-10} m^2/s.

4.5.4 Moisture diffusivity at 80°C.

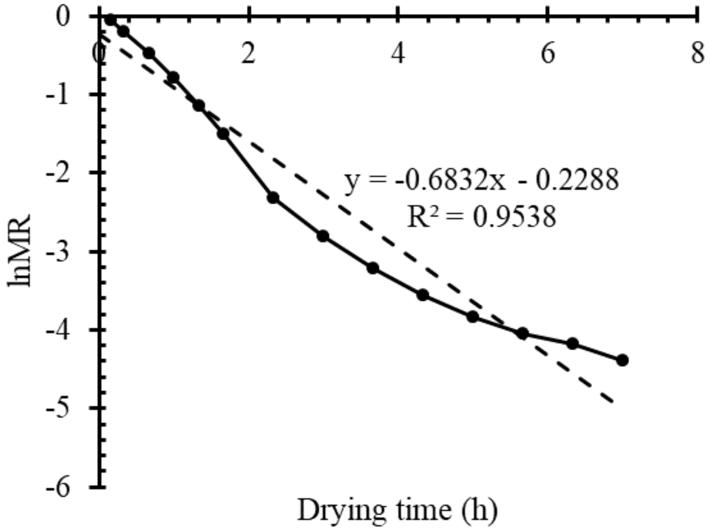


Fig. 4.7 Graphical representation of Ln(MR) vs. time at 80°C.

Average half thickness of slab (*kinema*) = 3.5×10^{-3}m

From graph,

Slope of curve = -0.6832

Now, slope = $-\frac{\pi^2 D}{4(h^*)^2}$

Diffusivity = 9.4219×10^{-10} m^2/s.

The effective moisture diffusivity of *kinema* during cabinet drying at 80°C was found to be 9.4219×10^{-10} m^2/s.

The results shows that the effective moisture diffusivity for *kinema* ranged between 2.0258×10^{-10} m^2/s at 50ºC, 3.9730×10^{-10} m^2/s for 60°C, 7.255×10^{-10} m^2/s at 70°C, and 9.4219×10^{-10} m^2/s for 80°C.

As the drying temperature increased, the value of effective moisture diffusivity also increased. Samples dried at 50ºC presented the lowest effective moisture diffusivity, which was .0258 × 10^{-10} m^2/s, and samples dried at 80ºC had the highest effective moisture diffusivity, which was 9.4219 × 10^{-10} m^2/s.

Table 4.5 Effective diffusivities of dried *kinema* at different Temperatures.

Temperature (ºC)	**Effective Diffusivity, D_{eff} (m^2/s)**
50	2.0258×10^{-10}
60	3.9730×10^{-10}
70	7.255×10^{-10}
80	9.4219×10^{-10}

The evaluated diffusivities were similar to a range of food stuffs for drying of fruits and vegetables as reported by (Ankita. and Prasad, 2013) (10^{-9} to 10^{-12} m^2/s) and in (10^{-11} to10^{-9} m^2/s) reported by Madamba *et al.* (1996) These diffusivities were also close to the range 2.61×10^{-10} to 1.09×10^{-9} m^2/s obtained by Dissa *et al.* (2008). The effective moisture diffusivity of masyeura was also found in range of 4.575×10^{-10} - $2.5797\times10^{-9}m^2/s$. Similar results have been obtained for various leaves drying such as spinach , parsley leaves and mint leaves (Akpinar, 2006). The above results showed that effective moisture diffusivity is higher at higher drying temperature and vice versa. A similar observation has been reported for increase in diffusivity coefficient as air drying temperature increases (Rahman and Kumar, 2007).

Different literature shows that diffusivity decreased with increase in drying time. That is due to the fact that when the product water content decreases during drying, its water activity also decreases simultaneously (because the remaining water to remove is increasingly bound water)(Demir *et al.*, 2004; Erbay and Icier, 2010b).

4.6 Activation energy and diffusivity constant

The activation energy is the energy barrier that must be overcome in order to activate moisture diffusion. It is one of the most important terminology that play significant role in drying. By increasing the temperature and hence the drying rate this energy barrier can be easily overcome but there should be a compromise between high temperature and acceptable product quality (Hii *et al.*, 2009). The Arrhenius equation was used to describe the relationship between the effective diffusivity and drying temperature.

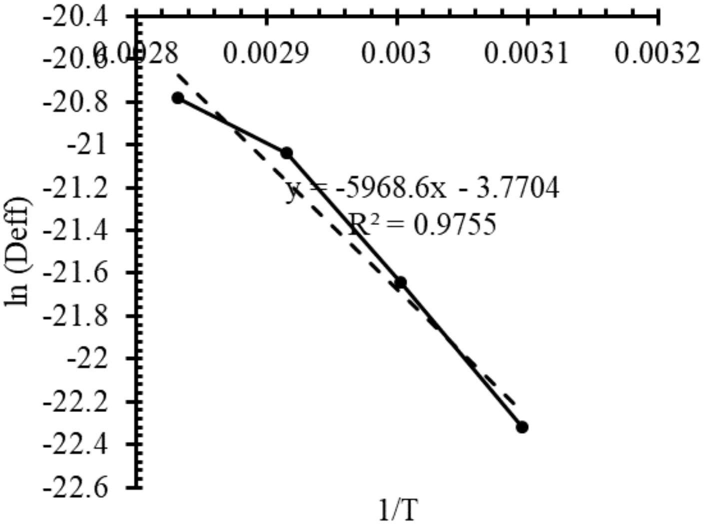


Fig. 4.8 Arrhenius-type relationship between effective moisture diffusivity and the reciprocal of absolute temperature.

We know Arrhenius equation is $D_{eff} = D_o \exp(-\frac{E_a}{RT})$ …………… (4.1)

On solving,

Slope = $-E_a/R$

Now, from graph,

Slope = -5965.8

E_a = 49.599 kJ/mol

For Diffusivity constant:

Using graph, from equation (4.1)

Intercept ($\ln D_o$) = -3.782

Therefore, $D_o = 6.63\times10^{-6}$ m^2/s

The Arrhenius equation (Equation 4.1) was used to describe the relationship between the effective diffusivity and drying temperature (Roberts *et al.*, 2008). The estimated diffusivity constant, D_o, and activation energy, E_a, were 6.63×10^{-6} m^2/s and 49.599 KJ/mol, respectively. These values were determined using the relationship shown in Figure 4.8. The value of Ea was within the range of Ea values reported in previous studies, which varied from 12.32 kJ/mol to 51.26 kJ/mol (Hii *et al.*, 2009).

The values of activation energy lies from 12.7 to 110 kJ/mol for most food material (Akpinar and Bicer, 2007). The activation energy is the energy barrier that must be overcome in order to activate moisture diffusion. By increasing the temperature and hence the drying rate this energy barrier can be easily overcome but there should be a compromise between high temperature and acceptable product quality (Hii *et al.*, 2009). The value of activation energy found for *kinema* is similar or comparable to the value various leafy vegetables or leaves such as spinach leaves and for that of parsley leaves and mint leaves (Vega *et al.*, 2007).

Part V

Conclusions and recommendations

5.1 Conclusions

On the basis of the results obtained, the following conclusions have been drawn:

i. Drying rates of *kinema* was affected by the temperature. It was observed that drying time decreased as the air temperature increased i.e. shortest drying time at 80°C and longest drying time at 50°C. According to drying rate curve, drying of *kinema* lied in falling rate period, which implied that moisture removal from the material was governed by diffusion phenomenon.

ii. The data obtained for kinema drying in cabinet dryer at 50, 60,70 and 80°C were best fitted to Midilli *et al*. based on R^2, χ^2, RMSE and SSE.

iii. The effective diffusivity was calculated using Fick's diffusion equation in the temperatures values varied from 2.0258×10^{-10} m^2/s at 50°C to 9.4219×10^{-10} m^2/s at 80°C. Effective moisture diffusivity range of 50 to 80°C increased with increase in drying temperature.

iv. The activation energy and Do for cabinet drying of *kinema* at temperature from 50 to 80°C were found to be 49.599 kJ/mol and 6.63×10^{-6} m^2/s. respectively.

5.2 Recommendations

i. Midilli *et al*. model can be used to predict the drying behavior of *kinema* in cabinet dryer.

ii. The effect of different drying temperatures on the sensory attributes of *kinema* can be studied.

Part VI

Summary

Soybean (*Glycine max* L.) is a leguminous crop that was originated in China. Soybean is nutritively richest natural vegetable food known. Because of very high percentage of protein (40%) and fat (19%) and less carbohydrate (33.3%) compared to other legumes. so soybean is called as King of legume (Sharma,1997). Drying is one of the feasible methods of preservation. Research needs to be done to explore the possibility of employing dehydration techniques for processing to minimize the losses and to make them available for consumption in the off-season. Drying or Dehydration is not only energy intensive process but also an important unit operation that determines the product final quality. Since it is very critical process, it must be closely controlled in order to get higher quality product with minimum cost and this is possible only if we formulate the whole drying process. The thin layer drying modeling helps us to formulate drying process as well as dryer itself.

A mathematical model is a simplified version of the word that is used to study key characteristics of that word. They are the representation of particular condition or idea. A model embodies a hypothesis about the study system, and lets you compare that hypothesis with data. Modeling is not perfect and usually is a simplification of reality. Model study provides information about the variable and their control to achieve desire result. Drying modeling is generally carried out by using thin layer models which are semi theoretical models based on Fick's law of diffusion.

Soybean (*Glycine max* L.) collected from the local areas of Dharan and was than dried at cabinet dryer at four different temperatures i.e. 50, 60,70 and 80°C. Change in weight was noted in fix interval and is processed. Drying curve was plotted between MR and Time. The curve obtain were then fitted to twelve different drying models. Experimental result showed drying of *kinema* falls in falling rate period. The rate of drying continuously decreased as drying proceeds. Graphical and statistical analysis of result showed that, Midilli *et.al* model was best fit model for cabinet drying at temperature range of (50-80)°C.

According to drying rate curve, drying of *kinema* lies in falling rate period.which implies that moisture removal from the material was governed by diffusion phenomenon. Drying rates of *kinema* is affected by the temperature. It was observed that drying time decreased as the air temperature increased i.e. lowest drying time at 80^{o}C and highest drying time at 50^{o}C. Midilli *et.al* model best described the drying characteristics of the *kinema* for cabinet drying at temperature ranging from 50, 60, 70 and 80°C with highest value of R^2 (0.982496-0.999538), lowest value of χ^2 (0.0000839- 0.001399), lowest value of RMSE (0.00784- 0.03271) and lowest value of SSE (0.000923- 0.018192) . The effective diffusivity (D_{eff}), was calculated using Fick's diffusion equation and the value of D_{eff} varied from 2.0258×10^{-10} m^2/s at 50^{o}C to 9.4219×10^{-10} m^2/s at 80^{o}C. This showed, effective moisture diffusivity value increased with increase in drying temperature. The minimum energy required to initate the process of the drying i.e triggering the moisture diffusivity during *kinema* drying to was found to be 49.599 kJ/mol which is comparable to other leafy vegetables and diffusivity constant was found to be 6.63×10^{-6} m^2/s.

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Appendices

Appendix A

A.1 Experimental MR during different drying conditions of *kinema.*

Table A.1. Cabinet drying

Time (h)	MR 50°C	MR 60°C	MR 70°C	MR 80°C
0	0.9999	1	1	1.09
0.166	0.9481	0.94955	0.981	0.9449
0.333	0.9184	0.8959	0.9277	0.8166
0.666	0.8721	0.8155	0.8615	0.6199
1	0.8355	0.7548	0.8137	0.4518
1.333	0.7981	0.6831	0.7315	0.3193
1.666	0.7463	0.60277	0.6531	0.2217
2.333	0.6868	0.4782	0.4778	0.0989
3	0.6336	0.3986	0.3571	0.0599
3.666	0.5776	0.3143	0.2413	0.0403
4.333	0.5416	0.252	0.16163	0.0285
5	0.4981	0.2016	0.0972	0.0215
5.666	0.4428	0.17	0.0476	0.0173
6.333	0.3716	0.1511	0.0359	0.0152
7	0.3411	0.1393		0.0124
7.666	0.3052	0.1291		
8.333	0.1289			

Appendix B

Color plates

Plate B.1 Soybeans soaking in cold water.

Plate B.2 Dehulling of soybeans by scrubbing on plam.

Plate B.3 Fermentation of soybean.

Plate B.4 Fresh *kinema.*

Plate B.7 Fresh *kinema* in tray.

Plate B.6 Dried *kinema* in tray.