USE OF PESTİL AS AN EDIBLE FILM AND COATING

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By

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ABSTRACT

USE OF PESTİL AS AN EDIBLE FILM AND COATING

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Pestil, a well known fruit leather in Turkey, was prepared from boiled grape juice and starch mixture by using traditional technique. Drying of pestil was carried out by hot air drying and sun drying. The factors investigated in hot air drying were air temperature (55, 65 and 75°C), sample thickness (S_1=0.71, S_2=1.53, S_3=2.20 and S_4=2.86 mm) and air velocity (V_1=0.86, V_2=1.27 and V_3=1.82 m/s). The effects of drying time temperature and slab thickness on moisture content of pestil during drying were significant ($P<0.05$) and of air velocity was not ($P>0.05$). Depending on sample thickness and air temperature, the drying time ranged between 50-140 min to achieve the commercial moisture content of pestil (11 % wet basis) in air drying. Whereas, sun drying took 180 to 1500 min. Almost all samples dried in the falling rate period, except S_2, S_3, S_4 of sun drying and S_4 at 55°C. The latter had a short (negligible) constant rate period. Effective moisture

diffusivity values were estimated from Fick's diffusion model. These values were between 3.00-37.6x10^{-11} m^2/s for hot air drying and 1.93-9.16x10^{-11} m^2/s for sun drying. Activation energy value of water diffusion was calculated using an Arrhenius-type equation. The estimated values were 21.7, 16.5, 12.0 and 10.3 kJ/mol for S_1, S_2, S_3 and S_4, respectively.

The Hunter colour parameters (L, a, b) of grape juice during boiling and of pestil samples during drying were investigated. It was found that most of the colour destructed during boiling. All Hunter parameters changed significantly. However, either during hot air or sun drying, only Hunter-a value changed. The colour destruction reaction followed a zero order reaction kinetics.

The water vapour permeability (WVP) properties of pestil at three different temperatures (15, 25 and 37°C) and four relative humidity gradients (20, 50, 70 and 100% RH) were tested. It was found that water vapour permeability was strongly dependent on relative humidity. Pistachio nut meat was coated with pestil solution and kept at 15°C and three different relative humidities. Results showed that when the coated pistachio nut samples were kept at about 55% relative humidity, weight of the samples were almost constant. The coated samples absorbed moisture at high relative humidity (76.46%) and lost water at low relative humidity (33.33%) environments.

Key words : Grape, pestil, drying, colour change, edible film, water vapour permeability, pistachio nut meat.

ÖZET

PESTİLİN YENİLEBİLİR FİLM VE KAPLAMA OLARAK KULLANIMI

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Türkiye'de pestil olarak bilinen meyve derisi, geleneksel yöntemle, kaynatılmış üzüm suyu ve nişasta karışımından hazırlandı. Pestilin kurutulması sıcak hava ile ve güneşte yapıldı. Sıcak hava ile yapılan kurutmada, hava sıcaklığı (55, 65 ve 75°C), örnek kalınlığı (S_1=0.71, S_2=1.53, S_3=2.20 ve S_4=2.86 mm) ve hava hızı (V_1=0.86, V_2=1.27 ve V_3=1.82 m/s) gibi faktörler incelendi. Kuruma zamanı, hava sıcaklığı ve örnek kalınlığının kuruma sırasında pestilin nem içeriği üzerine olan etkileri anlamlı bulundu ($P<0.05$) ve hava hızının ise etkisi anlamlı bulunmadı ($P>0.05$). Örnek kalınlığı ve hava sıcaklığına bağlı olarak, pestilin ticari nemine (% 11 yaş baz) ulaşmak için havalı kurutmada gerekli olan zaman 50 ile 140 dakika arasında gerçekleşti. Halbuki bu zaman, güneşteki kurutmada 180 ile 1500 dakika arasında bulundu. Güneşte kurutmada S_2, S_3 ve S_4 ile 55°C havalı kurutmada S_4 örneklerinde çok kısa ve ihmal edilebilir sabit kuruma hızı

dönemi görüldü. Diğer bütün şartlarda kuruma tamamen azalan kuruma hızı döneminde gerçekleşti. Suyun efektif difüzyon değerleri Fick'in difüzyon modelinden elde edildi. Bu değerler havalı kurutmada 3.00 ile 37.6×10^{-11} m^2/s ve güneşteki kurutmada ise 1.93 ile 9.16×10^{-11} m^2/s aralıklarında gerçekleşti. Su difüzyonunun aktivasyon enerjisi Arrhenius tipi bir denklemden hesaplandı. Hesaplanan değerler S_1, S_2, S_3 ve S_4 örnekleri için sırasıyla 21.7, 16.5, 12.0 ve 10.3 kJ/mol olarak bulundu.

Üzüm suyunun kaynatılması ve pestil örneklerinin kurutulması sırasında Hunter renk parametreleri (L, a, b) incelendi. Rengin önemli bir bölümünün kaynama sırasında bozulduğu bulundu. Bütün Hunter parametreleri önemli ölçüde değişti. Bununla birlikte, gerek havalı kurutmada gerekse güneşte kurutmada sadece Hunter-a değeri değişti. Renk bozunum reaksiyonu sıfırıncı mertebeden bir reaksiyon kinetiği izledi.

Pestilin su buharı geçirgenliği (WVP) özellikleri üç farklı sıcaklık (15, 25 ve 37°C) ve dört farklı bağıl nemde (%20, %50, %70 ve %100) test edildi. Su buharı geçirgenliğinin bağıl neme bağlı olduğu bulundu. İç Antepfıstığı pestil çözeltisine daldırılarak kaplandı ve 15°C'de üç farklı bağıl nem ortamında tutuldu. Sonuçlar, kaplamalı fıstığın %55 bağıl nem civarında saklandığında hemen hemen ağırlık kaybının olmadığını gösterdi. Kaplamalı örnekler yüksek bağıl nemli (%76.46) ortamlarda su aldı ve düşük bağıl nemli (%33.33) ortamlarda ise su verdi.

Anahtar kelimeler : Üzüm, pestil, kurutma, renk değişimi, yenilebilir film, su buharı geçirgenliği, iç antepfıstığı.

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LIST OF ABBREVIATIONS

ANOVA : Analysis of variance

C : Colour concentration at any time

C_0 : Initial colour concentration

D_0 : Constant in Arrhenius equation

D_{eff} : Effective moisture diffusivity (m^2/s)

D.f. : Degrees of freedom

DS : Dry solids

E_a : Activation energy (kJ/mol)

HPMC : Hydroxypropyl methyl cellulose

Hunter a : Hunter parameter defining redness/greenness

Hunter b : Hunter parameter defining yellowness/blueness

Hunter L : Hunter parameter defining whiteness or brightness/darkness

k : Rate constant (min^{-1}) in equations 1 and 2

L : Film/slab thickness (mm)

LSD : Least squares difference

MR : Moisture ratio

MS : Methyl cellulose

p_1 : Apparent pressure (kPa)

p_2 : Water vapour pressure (kPa)

r : Correlation coefficient

R_g : Gas constant (8.314 kJ/mol.K)

R : Drying rate (kg water/min)

RH : Relative humidity

S_1 : Sample with a thickness of 0.71 mm

S_2 : Sample with a thickness of 1.53 mm

S_3 : Sample with a thickness of 2.20 mm

S_4 : Sample with a thickness of 2.86 mm

SPI : Soy protein isolate

T : Absolute temperature (K)

t : Time (min)

V : Air velocity (m/s)

WPI : Whey protein isolate

WVP : Water vapour permeability (g water.mm/kPa.h.m^2)

WVTR : Water vapour transmission rate (g water/m^2.h)

X : Moisture content at any time (kg water/kg DS)

X_0 : Initial moisture content (kg water/kg DS)

X_e : Equilibrium moisture content (kg water/kg DS)

CHAPTER I

INTRODUCTION

1.1. Drying of Food Materials

Food drying is one of the oldest methods of preserving food for later use. It is a complex operation involving transfer of heat and mass which may cause changes in product quality. Physical changes that may occur include shrinkage, puffing and crystallization. In some cases, desirable or undesirable chemical or biochemical reactions may occur leading to changes in colour, texture, odour or other properties of the food product. Drying can either be an alternative to canning and freezing or complement these methods. Drying occurs by affecting vaporization of the liquid by supplying heat to the wet feedstock. Heat may be supplied by conduction (contact or indirect dryers), by convection (direct dryers) by radiation or volumetrically by placing the wet material in a microwave or radio frequency electromagnetic field. Over 85 % of industrial dryers are of convective type with hot air or direct combustion gases as the drying medium [1]. The air drying may be divided into two main categories; one in which drying occurs as if the system was pure water being evaporated (constant rate drying period) and one with internal control (falling rate drying period). The constant rate period may be only relatively important for such situations in which, for example, the drying

potential of air is very low or the moisture content of the food is very high [1, 2]. Mass transfer during constant rate period involves diffusion of water vapour from the material surface through a boundary layer into the drying medium. However, it has been found that drying of biological products occurs entirely in falling rate. During the falling rate period, the drying decreases with time, and the rate of internal mass transfer to the material surface typically controls the process. The mass transfer mechanisms that have been proposed in this period are capillar movement of liquid and diffusion. Capillarity refers to the flow of liquid through the interstices and over the surface of a solid due to molecular attraction between the liquid and the solid. Diffusion means the distribution of the molecules within a single phase brought about by molecular motion of translational and mutual bombardment. In most studies carried out on drying, diffusion is generally accepted to be the main mechanism during the transport of water to the surface to be evaporated [3].

Drying of various foods is needed for one or several of the following reasons:

1. need for easy to handle free-flowing solids
2. preservation and storage (extending shelf-life)
3. reduction in cost of transportation
4. achieving desired quality of product etc.

The drying of fruit on a commercial scale has received a resurgence of interest during the past years few especially in the production of fruit "leathers". Leathers are made by removing moisture from a large flat tray of wet puree until the desired cohesive "leathery" composition is obtained. The

fruit to be processed can be harvested mechanically and the purees lend themselves to automated handling because of their pumpability [4].

In many processes, improper drying may lead to irreversible damage to product quality and hence a non-salable product. With modern dehydrators whole fruits, fruits leather like products (like pestil), fruit chips and pieces can all be dried year-round. Dried foods are ideal for backpacking and camping. They are lightweight, take up little space and do not require refrigeration. Dried fruits and fruit products are unique, tasty and nutritious. It might be argued that they are even tastier than fresh fruits. They have been called nature's candy. Dried fruits and fruit products taste sweeter because the water has been removed thus concentrating the fruit's flavour and calories. They can be eaten as a snack or added to various food preparations [5, 6].

Because of the short harvest season and the sensitivity to storage even at refrigerated conditions, most fresh grapes and grape derivatives are preserved in some form. Drying is among the methods which commonly used. Sun drying permits one to produce a product with a rich colour, a translucent appearance and a desirable gummy texture; however, it has many disadvantages. Notable among these are the slowness of the process, the exposure to environmental contamination, the dependency on whether and the hand labour requirement. In recent years, air dehydration has been applied to avoid these disadvantages [7].

Sun dried fruits and fruit products are the best known of all dried foods. In our country, raisins, apricots, figs and pestil are the most popular sun dried foods. To dry fruits out of doors hot, dry/low humidity breeze days are the best. A minimum temperature of about 30°C is needed with higher

temperatures being better. It takes several days to dry foods out doors. Because weather is uncontrollable, drying fruits out doors can be risky. If it rains when grapes are drying, the entire supply of raisins can be destroyed. Besides these, fruits dried out doors must be covered or brought under shelter at night. The cool night air condenses and could add moisture back to the food, thus slowing the drying process. Due to these difficulties and operation disadvantages of out doors drying, a rapid, safe and controllable drying operation is required. The drying operation is conventional drying which is known as hot air drying commercially. This drying method both decreases drying time and improves the quality of dried product [8, 9].

1.2. Colour Change During Processing

Thermal processing is one of the most important methods of food preservation primarily intended to inactivate enzymes, deteriorative microorganisms and reduce water activity by dehydration. During manufacturing process changes in the structure of derivative fruit products are produced, therefore these modify the colour and final aspect of the product. Thermal treatments during the preservation processes can affect the quality of juices, fruit purees and derivatives through non-enzymatic browning reactions and pigment destruction [10, 11, 12].

The first quality judgement made by a consumer on a food at the point of sale is its visual appearance. Appearance analyses of foods (colour, taste, odour and texture) are used in maintenance of food quality throughout and at the end of processing. Colour is one of the most important appearance attribute of food materials, since it influences consumer acceptability. And

abnormal colours, especially those associated with deterioration in eating quality or with spoilage, cause the product to be rejected by the consumer [13, 14, 15].

It has been reported that many reactions can affect colour during thermal processing of fruits and their derivatives. Among them, the most common are pigment degradation, especially carotenoids, anthocyanins and chlorophyll, and browning reactions such as Maillard reactions of reducing sugars present (mainly glucose and fructose) and amino components, and oxidation of ascorbic acid [10, 16, 17]. Other factors affecting colour include fruit pH, acidity, processing temperature and duration, fruit cultivar and heavy metal contamination [18, 19, 20]. In order to minimise the colour deterioration, suitable designs are needed for manufacturing and treatment equipment. And also, some combined processes such as high hydrostatic pressure-temperature [21] and blanching-high hydrostatic pressure [22] have been used for colour retention of fruits and fruit products.

1.2.1. Kinetic Considerations of Colour Change

For the design process, kinetic modelling is necessary to derive basic kinetic information for a system in order to describe the reaction rate as a function of experimental variables and, hence, to predict changes in a particular food during processing and storage [23]. There are numerous references on the kinetics of colour of food materials in the literature. The majority of these works report zero order (Equation(1)) or first order (Equation(2)) degradation reaction kinetics.

$$C = C_0 \pm k\,t \quad (1)$$

$$C = C_0 exp(\pm k\,t) \quad (2)$$

where (+) and (-) indicate formation and degradation of any quality parameter, respectively.

The colour measurements can be used in an indirect way to estimate colour change of foods, since it is simpler and faster than chemical analysis. Hunter colour parameters (L, a, b) have previously been proven to be valuable in describing visual colour deterioration and providing useful information for quality control in fruits and fruit products such as blackcurrant syrup [19], sultana grapes [24], diced apples [25], concentrated fruit pulp [10], double concentrated tomato paste [16], pear puree [12], and banana [26].

1.3. Water Vapour Properties of Films

Quality and shelf life are reduced when food, through interaction with its environment, gains or losses moisture or aroma, takes up oxygen (leading to oxidative rancidity), or becomes contaminated with microorganisms [27]. Packaging protects foods from environment [28]. Edible films by regulating transfer of moisture, oxygen, carbon dioxide, lipid, aroma and flavour compounds in food systems, can increase food product shelf-life and improve food quality [29]. Edible films can also decrease conventional synthetic packaging materials needed to preserve and protects the foods, as well as improve package recyclability by decreasing the need for coating, laminating and co-extrusion [30].

Edible films and coatings can be defined as thin layers of edible materials applied on (or even within) foods by wrapping, immersing, brushing, or spraying in order to offer a selective barrier against the transmission of gases, vapours, and solutes while also mechanical protections.

There is no distinction between films and coatings, and often two terms are used interchangeably. Usually coatings are directly applied and formed on the surface of the product, while films are formed separately as thin sheets and then applied on the products [31].

1.3.1. Advantages of Film

Advantages for edible films over other traditional nonedible polymeric packaging material are summarized below [31]:

1. The films can be consumed with the packaged product.
2. Even if the films are not consumed they could still contribute to the reduction of environmental pollution. The films are produced exclusively from renewable, edible ingredients and therefore are anticipated to degrade more readily than polymeric materials.
3. The films can enhance the organoleptic properties of packaged foods provided that various components (flavouring, colouring, sweeteners) are incorporated to them.
4. The films can supplement the nutritional value of the foods. This is particularly true for films made from proteins.
5. The films can be used for individual packaging of small portion of food, particularly products that currently are not individually

packaged for particular reason such as peas, beans, nuts and strawberries.

6. The films can be applied inside heterogeneous foods at the interfaces between different layers of components. They can be tailored to prevent deteriorative intercomponent moisture and solute migration in foods such as pizzas, pies and candies.
7. The films can be very conviently used for microencapsulation of food flavouring and leavening agents to efficiently control their addition and release into the interior of foods.
8. The films can function as carriers for antimicrobial and antioxidant agents. In a similar application they also can be used at the surface of the foods to control the diffusion rate of preservative substances from the surface to the interior of the food.
9. Another possible application for edible films could be their use in multilayer food packaging materials together with nonedible films. In this case the edible films would be the internal layers in direct contact with food materials.

1.3.2. Film Components

Components of edible films and coatings can be divided into three categories: hydrocolloids, lipids, and composites [32].

1.3.2.1. Hydrocolloids

Suitable hydrocollids include proteins, cellulose derivatives, alginates, pectins, starches, and other polysaccharides These films possess good

barrier properties to oxygen, carbon dioxide, and lipids, but poor resistance to water vapour because of their hydrophilic nature. Most of these films also have desirable mechanical properties, making them useful for improving the structural integrity of fragile products. In terms of composition, hydrocolloids can be either carbohydrates or proteins. Film forming carbohydrates include starches, plant gums (alginates, pectins, and gum arabic), and chemically modified starches. Film-forming proteins include gelatin, casein, soy protein, whey protein, wheat gluten, and zein.

1.3.2.2 Lipids

Suitable lipids include waxes, acylglycerols, and fatty acids. Lipid films are often used as barriers to water vapour, or as coating agents for adding gloss to confectionery products. Their use in a pure form as free-standing films is limited, because most lack sufficient structural integrity and durability. Waxes are commonly used for coating fruits and vegetables to retard respiration and lessen moisture loss. Shellac coatings, when formed on a supporting matrix, provide effective barrier to gases and water vapour.

1.3.2.3. Composites

Composites films can be formulated to combine the advantages of the lipid and hydrocolloid components and lessen the disadvantages of each. When a barrier to water vapour is desired, the lipid component can serve this function while the hydrocolloid component provides the necessary durability. A composite film can exist as a bilayer, in which one layer is a hydrocolloid

and other a lipid, or as a conglomerate, where the lipid and hydrocolloid components are interspersed throughout the film.

1.4. Film Formation

Many techniques have been developed for forming films directly on food surfaces, or as separate, self supporting films.

1.4.1. Coacervation

Coacervation involves separation of a polymeric coating material from a solution by heating, altering pH, adding solvents, or altering the charge on the polymer involved. Coacervation may also be classified according to the type of phase separation: aqueous or non-aqueous. Aqueous phase separation requires a hydrophilic coating such as gelatin or gelatin-gum acacia that is deposited on a water insoluble core particle. Non-aqueous phase separation usually involves a hydrophilic coating that is deposited on a core which may be either water-soluble or water-insoluble.

1.4.2. Solvent Removal

For film-forming materials dispersed in aqueous solutions, solvent removal is a necessity for solid film formation. Rate and temperature of drying has been found to influence crystallinity and mechanical properties of cellulosic films.

1.4.3 Solidification of Melt

Solidification of the melt by cooling is a common technique for preparing lipid films. Similar to the rate of cooling plays an important role in the overall physical properties of the resulting films.

1.5. Film Application

1.5.1 Dipping

This method lends itself to food products that require several application of coating materials or require a uniform coating on an irregular surface. After dipping, excess coating material is allowed to drain from the product, and it is then dried or allowed to solidify.

1.5.2. Spraying

Films applied by spraying can be formed in a thinner, more uniform manner than those applied by dipping. Spraying, unlike dipping, is more suitable for applying a film to only one side of a food to be covered.

1.5.3. Casting

Casting can be accomplished by controlled-thickness spreading or by pouring. Controlled-thickness spreading requires a spreader with a product reservoir and an adjustable gate, the height of which can be set accurately and good reproducability

1.6. Films Based on Starch and Fruit Juice

There have been increasing demands last decades for application of edible films, although this approach is not new. Mainly waxing fruits, chocolate or sugar coated candies are well known by everybody. To prepare fruit leather has been arranged as changing the form of fruit to improve the stability. Such an approach has been observed for grapes, a fruit leather has been prepared known as (pestil or basdık). Literature survey revealed that there is little works done on pestil preparation and pestil properties.

1.6.1. Starch Films

Starch, the food preserve of plants, occurs widely in nature and is the most commonly used food hydrocolloid [28]. Starch is an important raw material, either for food industry or a renewable source of biodegradable material for packaging [33, 34, 35]. Scientists have thus begun to seek alternative source for plastic material [36]. The production-based biodegradable products is easier to control and with lower cost. Starch based resins have been made as composed bags disposable food-service items (cutlery, plates, cups, etc.), packaging materials (loose-fill, films, etc.), coatings and other specialty items. However a major concern of the starch based materials is moisture sensitivity due to the hygroscopicity of the starch components [37]. Starch is hygroscopic and will gain or lose water to achieve equilibrium with the ambient air [38]. Amylose, high amylose starch have been used to form self-supporting films by casting from aqueous solution. These films appear to have moderate oxygen barrier properties but are poor moisture barriers and their mechanical properties are generally

inferior to synthetic polymer films [36]. Starch exhibit thermoplastic behaviour, when a plasticizer such as water is added [33]. Since water is a plasticizer changing the water content of the film will change the properties of the film [35, 38]. Amylose and hydroxypropylated high amylose starch can also be extruded to form films [33]. Starch are known to exhibit very low oxygen permeability. However, the barrier properties of starch films are greatly affected by air humidity. In industrial barrier applications, starch films must be made less water-sensitive or be protected from water contact. For synthetic polymers, an increased crystallinity is known to increase the barrier properties of the material [36].

1.6.2 Pectin Films

Pectin are a complex group of structural polysaccharides which occur widely in land plants. The major commercial sources of pectin are citrus peel and apple pomace. Pectin substances are polymers composed mainly of 1,4-α-D-galactopyranosyluronic acid units. One aspect of difference among the pectic substances is their content of methyl esters or degree estreification, which has a vital effect on their solubility and gelation properties.

1.7. Fruit Leathers

Considerable interest exists in finding new uses for fruit purees. As consumer are becoming more health conscious, consumption of fruit products at various occasions is increasing [32]. Advantages of fruit purees over fresh, whole fruit are the inclusion of mechanically harvested fruit (thus lowering costs) as well as potential for year round processing [39]. Past

research has focused on incorporation of fruit and vegetables purees into sheets, commonly called "leathers" without regard to potential barrier properties [4, 32]. Leathers are made by removing moisture from a large flat-tray of wet puree until the desired cohesive "leathery" composition is obtained. The resulting product is light, pleasant to chew, and for many fruits, quite tasty. Since it is light and low in moisture it has few storage problems, and is economical to ship [4].

Pectic and cellulosic substances are the primary polysaccharides in fruit purees; consequently, the matrix of fruit puree edible films is comprised mainly of those components. The variety of sugar in fruit puree function as placticizing agents in fruit puree edible films. Percentages of polysaccharides in fruit purees vary depending on fruit cultivar and maturity, as well as cultural and environmental conditions [32]. Cemeroğlu [39] suggested that the influence of the year, cultivar and maturity on the food quality of fruit purees especially for apples.

1.7.1. Production of Pestil

Turkiye is an important grape producer country and it is the fifth grape producer in the world. Approximately 3,600,000 tons/ year of grapes is produced in our country. That's why grapes and its products have significant effect on Turkish economy [40]. In Turkiye 23 % of the grapes produced is consumed as fresh grapes, 37 % dried, 3 % is processed for wine production and approximately 37 % processed to pekmez, pestil, sucuk, tarhana, etc.

Since grapes have high nutritional value due to its composition shown in Table 1, marketing opportunities, alcoholic drink production and

consumption trade cause great variance in processing and consumption of grapes.

Maturation of grapes is a long time progress and consumption of grapes as fresh fruit is possible only between June-October. Different types of grapes mature at different time intervals depending on climatic condition and type of grapes. However during this time intervals large amount of fresh grape is supplied to market for consumption. Since grapes have very short shelf-life, significant amount of grape loss occurs due to deterioration. This situation cause the fresh grapes price to be too low. For that reason it is required to process the grapes into a form that can be stored for long time without loss within nutritional value. So that it is required to process the grapes to get its nutrition value where there is no fresh grapes to consume.

Some of that known processes are [41];

1. Drying of grapes to produce raisin
2. Production of grape juice and concentrate
3. Production of pekmez, pestil, and others
4. Production of alcoholic drinks

Pestil is produced from different fruits, mainly grape, apricot, foamed grape, plum, etc., and using starch or wheat flour [41] as a thickener.

Table 1. Composition of grapes and grape juice [40, 42].

Component	Grape	Grape juice
Energy (kcal/100 g)	56.0	53.0
Moisture (%)	84.4	85.2
Protein (%)	0.5	0.3
Oil (%)	0.2	0.2
Carbohydrate (%)	14.2	14.0
Cellulose (%)	0.2	0.0
Total ash (%)	0.3	0.3
Calcium (mg/ 100 g)	6.0	5.0
Phosphorous (mg/100 g)	13.0	10.0
Iron (mg/ 100 g)	0.2	0.2
Sodium (mg/100 g)	1.0	2.2
Potassium (mg/100 g)	130.0	45.0
Ascorbic acid (mg/100 g)	4.0	0.0

Table 2 shows the typical composition and thickness of the pestil produced from different types of fruits.

Table 2. Thickness and composition of pestil types produced from different fruits [41].

Composition	Pestil types			
	Mulberry	Plum	Apricot	Grape
Thickness (mm)	0.5	1.4	1.1	0.6
Moisture (%)	14.3	19.5	17.3	11.3
Total dry matter (%)	85.7	80.5	82.7	88.7
Total sugar (%)	83.4	79.0	80.1	87.6
Total acid (%)	0.2	2.3	6.2	0.7
Protein (%)	2.0	2.0	1.9	4.1
Ash (%)	1.4	1.6	3.5	1.6
Raw oil (%)	0.4	0.1	2.6	0.6

1.8. Water Vapour Permeability of Edible Films

One of the most useful functions of edible films is their ability to act as water, gas (mainly, oxygen and carbon dioxide) and oil barriers. Water vapour permeability (WVP) is one of the most important and widely studied property of edible films [28, 30]. WVP of edible films, like that of flexible, non-edible films, is normally measured using a 100-0% RH gradient. In the past, results derived using a 100-0% RH gradient were generally regarded as "worse case" data, since exposure to a smaller RH gradient was assumed to be a less severe condition. However, recent studies have shown that for most types of films, a 97-65 % RH gradient represents a more severe test condition [28, 30, 32]. These studies demonstrate the necessity of testing films under conditions of temperature and RH that will be encountered in practice. Water vapour permeability is usually measured gravimetrically. A film is sealed over the opening of special impervious cup containing a

desiccant, and the cup is then placed in a chamber at constant temperature and RH. The desiccant maintains a constant low RH environment (usually 0.0 %RH) inside the cup. More rapid techniques, which are generally more expensive, have been developed, and these involve detection of water vapour by means of electrical resistance, electrolysis, or infrared absorption [32]. WVP of some edible films are represented in Table 3. The source, plasticizer used, processes applied for film formation, RH and thickness of the films are all affect the barrier and mechanical properties of the produced films.

Table 3. WVP of different types of some edible and non-edible films with their measurement conditions [43].

Film	L (mm)	T (°C)	RH (out/ in,%)	WVP
WPI:G (1.6:1)	0.11	25	0/11	0.3
WPI:G (1.6:1)	0.12	25	0/65	4.9
WPI:G (4:1)	0.13	25	0/77	2.9
Chocolate	0.612	20	80.8/0	0.05
Peach puree	0.19	25	0/80	4.1
Apricot puree	0.19	25	0/80	4.3
Apple puree	0.21	25	0/76	5.8
Pear puree	0.26	25	0/74	7.8
Gluten	0.4	25	0/85	2.2
MC 13000*	0.013	25	50/0	0.02
MC 13000*	0.083	30	0/11	0.3
HPMC 22000*	0.014	25	50/0	0.05
Zein	0.12-0.33	21	85/0	0.4
Polyethylene (low density)	0.025	25	100-90/0	$2*10^{-4}$
Polyethylene (high density)	-	38	90/0	$8*10^{-4}$

WVP: water vapour permeability ($g.mm/m^2$ h kPa), WPI: whey protein isolate, SPI: Soy protein isolate, MS: Methyl cellulose, HPMC: Hydroxypropyl methyl cellulose

* Molecular weight, RH: relative humidity.

1.9. The Aim of The Present Study

One of the important agricultural products of Türkiye is grape. Gaziantep and its vicinity is the largest grape producer with the widest land for grape production. Since not all of the grape produced is consumed right away, some problems existed as its preservation. However, grape juice has been used for many years in Anatolia for production of pekmez, pestil, sucuk and some other typical products for improving utilization of excess grape produced. There were so many studies for standardization and modernization of pekmez, whereas a few study exists showing the production steps of pestil.

The aims of present study were summarized as the determination of some properties of pestil.

1. Drying of pestil is the most important step in the pestil production. Nevertheless, drying characteristics of pestil has not been studied yet. Determination of drying characterization of pestil was one of the aims of the present study. Drying of pestil was carried out at different air temperatures, velocities and different pestil thickness using a tray dryer. The effects of sun drying was also studied.

2. While there are many literature studies on the kinetics of changes in fruits and fruit derivatives, little work has been conducted on the production of pestil, and no kinetic studies related with the colour change during concentration of grape juice and drying of pestil were found in the literature.

Therefore, another aim of this study was measurement of colour change during concentration of grape juice and drying of pestil.

3. One of the important property of a fruit leather is WVP, so in this study the prediction of WVP of pestil was studied at three different temperatures and four different relative humidity gradients. Pestil can be used as a leather (film) or a coating material for pistachio nut and hazel nut (defined as sucuk). Another aim of this study was the determination of the optimum relative humidity for storage of sucuk.

CHAPTER II

MATERIALS & METHODS

2.1. Materials

Grapes (dökülgen), for pestil production with an initial total soluble solids (°Brix) of 20 g/100 g, were obtained from a farm in Gaziantep in September 1999 and stored at 4±0.5°C. Prior to pestil preparation, grapes were taken out of storage and processed. All grapes used for pestil making were from the same batch. Gaziantep white earth used for fruit juice clarification was obtained from grape producers. All chemicals used were of reagent grade and deionised water was used for all experiments.

2.2. Preparation of Pestil

Flow sheet for pestil production was shown in Figure 1. The first step was washing of grapes to remove dirts, leaves, and foreign materials. Then, the grapes were crushed and pressed manually in the laboratory. The seeds were separated from juice by filtration using cheese cloth. The juice obtained had a pH of 4.4 ± 0.1. In order to reduce acidity and clarify the juice 7 g earth (70 % $CaCO_3$)/L was added. The mixture obtained was boiled for 3-5 minutes in order to inactivate enzymes which cause colour change [42]. The foams formed on the surface of the juice was separated. Then, it was waited until

some parts of tartaric acid has been precipitated as calcium tartarate [35]. The juice was separated by filtration using cheese cloth.

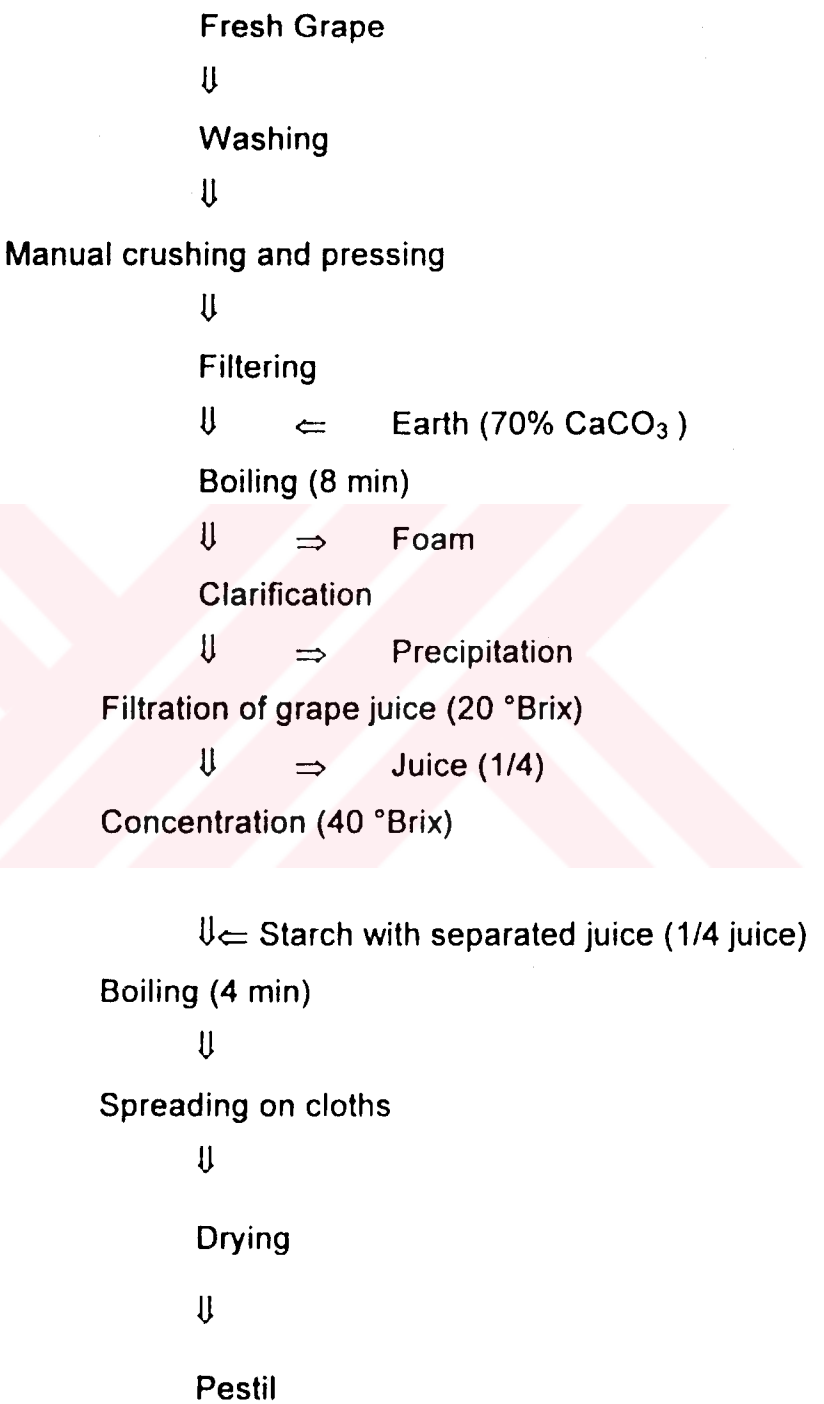

Figure 1. Flow sheet of pestil production.

It had a pH of 7.6 ± 0.3. °Brix of clean juice was 20±1.0. The juice was divided into two parts. A 3/4 part of juice was boiled for 30 minutes while constant stirring to obtain concentrated juice with 40° Brix. Then, freshly prepared wheat starch-juice mixture (starch dissolved in 1/4 part of juice) was added to the boiling juice. It was boiled for 4 minutes more. The concentration of starch was 4 g/100 g juice. Depending on the purpose of study, required amount of boiled grape juice-starch mixture was cast onto specially prepared circular cheese cloth (diameter was 8 cm) to minimize thickness variations between treatments. The mixture was spread evenly with a bent glass rod and allowed to dry around 24 h at 23°C (± 2.0) and 40 % (± 5.0) RH.

For dehydration tests, different thickness of pestil sample was required, so different amount of concentrated grape juice-starch mixture was spread on the cloths.

2.3. Film Preparation and Thickness Measurements

Cooked grape juice-starch mixture was evenly spread on 8 cm diameter disc of a cloth. The sample thickness was measured with a dial micrometer. At least six measurements of the thickness were made at different points. Only 5% deviation of the average thickness was allowed for the samples. The samples were used for drying process and water vapour permeability studies. Film thickness measurements were also done after permeability test completed.

2.4. Drying Equipment

The hot air drying experiments were performed in a pilot plant tray dryer (UOP 8 tray dryer, Armfield Ltd, UK) as shown in Figure 2. The dryer consisted of a temperature controller. Air was blown into the dryer through a mesh guard by a motor

driven axial flow fan impeller whose speed can be controlled in the duct. The air flow was parallel to the drying surface of the sample. Dry bulb and wet bulb temperatures of drying air were monitored in the drying chamber. Temperature measurements were made with a temperature sensor placed in front of the sample holder.

2.4.1. Drying Procedure

The drying regimes were as follows:

1) Hot air drying: In this study, various factors were investigated. These factors were temperature (55, 65 and 75°C dry and 27, 30 and 33°C wet bulb temperatures, respectively), air velocity (V_1: 0.86±0.03, V_2: 1.27±0.04 and V_3: 1.82±0.09 m/s) and sample thickness (S_1: 0.71+0.035, S_2: 1.53±0.070, S_3: 2.20±0.110 and S_4: 2.86±0.071 mm). Moisture loss was recorded at 10 min intervals during drying for determination of drying curves by a digital balance (Avery Berkel, CC062D10ABAAGA). Pestils were dried until equilibrium (no weight change) was reached.

2) Sun drying: Sun drying of pestils was achieved under direct sunlight and during night in September with no rain. The sun drying took place during the 1999 crop season. The samples were spread on drying clothes and exposed to sunlight directly.

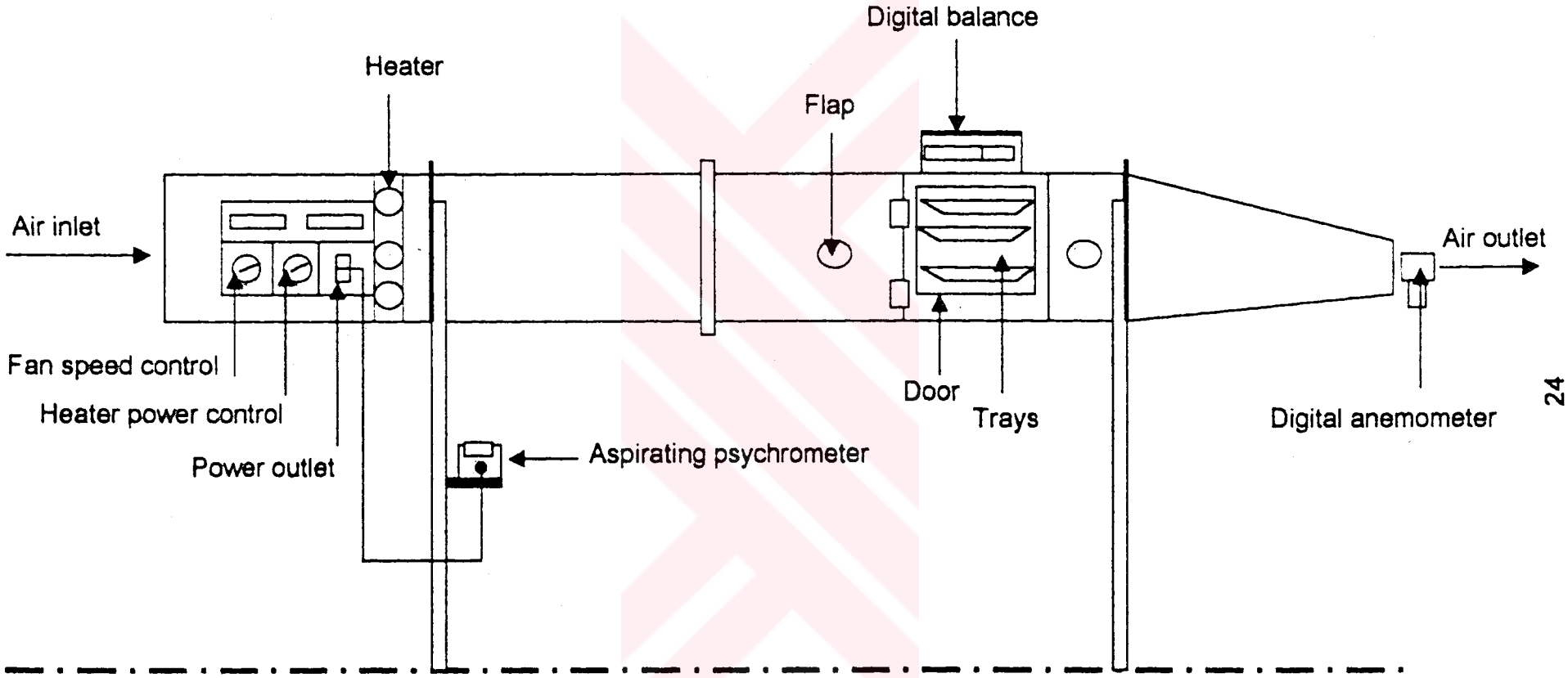

Figure 2. Schematic diagram of the hot air drying equipment (not to scale).

2.5. Colour Measurements

Colour measurement was made during grape juice concentration process, before drying and at pre-specified time intervals during drying by a HunterLab ColorFlex, A60-1010-615 model colourmeter (HunterLab., Reston, VA). Only colour changes of pestil sample S_2 was studied for simplicity. The colour values were expressed as L (whiteness or brightness/darkness), a (redness/greenness) and b (yellowness/blueness) at any time, respectively.

2.6. Water Vapour Permeability

Water vapour transmission of pestils was measured using procedures described by Kamper and Fennema [44]. Circular glass test cups with a diameter of 3 cm and a depth of 3 cm were used as shown in Figure A1. Relative humidity of inside and outside of the test cups were arranged using saturated salt solutions to provide different relative humidity gradient (Table 4). In addition, P_2O_5 (0.00 % RH) and deionised water (100.00 % RH) were used to control relative humidity.

Table 4. Relative humidity of saturated salt solutions used at the temperature studied.

Temperature	Salt solution		
(°C)	$MgCl_2$	$Mg(NO_3)_2$	$NaNO_3$
15	33.33	55.87	76.46
25	32.78	52.89	74.25
37	31.87	49.67	71.64

After replacing 10 ml of saturated salt solution or distilled H_2O in each cup, they were covered with the edible films. Films were cut circularly with a

diameter slightly larger than the diameter of the cup and then they were sealed using melted paraffin. Prior to each experiment cabinets were stored in laboratory desiccators each maintained at constant relative humidity with a saturated salt solution [28]. Each cup was placed in a desiccator containing the deionised water or saturated $MgCl_2$ solution at the bottom and weighed with their contents at two hours interval. The desiccators were kept in the incubator (Nüve ES 500) at 15, 25 or 37°C. Water vapour pressure on P_2O_5 and distilled water side of the films were assumed to be zero and hundred, respectively.

2.7. The Water Vapour Permeability Calculation

The amount of water vapour transferred through the films was calculated from the increasing or decreasing the weight of the cup kept in the desiccator and is plotted as a function of time. A linear variation in weight versus time indicates a steady transfer rate. Slopes of them (calculated by applying least square analysis, correlation coefficients of them were larger than 0.997) obtained linear least square method used to calculate water vapour transmission rate (WVTR) in the following equation [45];

$$WVTR = \frac{Slope}{Film\ Area} \tag{3}$$

where slope = weight loss vs. time. Film area is the cup test mouth area (6.6×10^{-4} m^2). WVP or permeability values (equation (4)) were determined by using the methods described by Chinnan and Park [45] and Kaya and Kaya [46].

$$WVP = \left[\frac{WVTR}{(p_2 - p_1)}\right] * L \tag{4}$$

where WVP is the water vapour permeability, p_1 is the apparent pressure (kPa) inside the cup, p_2 is the water vapour partial pressure (kPa) at the film outer surface in the system. L is the average film thickness (mm). The p_1 and p_2 values were calculated from the product of vapour pressure of pure water and the relative humidity of the medium at the defined temperatures and given in Table 4. Vapour pressure of pure water are 1.705, 3.169, and 6.306 kPa at 15, 25 and 37°C, respectively.

2.8. Coating of Pistachio nut With Grape Juice-Starch Mixture

The dry pistachio nut meat samples were dipped completely into pestil solution for about 5 s at room temperature and then taken out. This process was repeated twice. Before the application of pestil to pistachio samples, the samples were bound with thread as using same length of thread to eliminate error due to the adsorption of water by thread. After coating finished, samples were placed in glass cup carefully to eliminate the contacting the sample with the cup as suspended, and were kept at room temperature for about 3 h and then transferred into a desiccator (Figure A2). The saturated salt solution was changed as $MgCl_2$, $Mg(NO_3)_2$ and $NaNO_3$ to provide constant relative humidity in the desiccator. The coated samples were weighed one by one with the cup to the nearest 0.1 mg and replaced in the desiccator as before. The weighed samples in the desiccator were kept in the incubator at 15C for 7 days. Weighings of samples were repeated every 24 h in order to measure the moisture loss or gain as a function of time.

2.9. Statistical Analysis

Analysis of variance (ANOVA) was conducted to determine the effect of variable factors on drying parameters using Statgraphics software [47]. LSD multiple range test method was used when difference in means detected. The parameters of Fick's model (equation (5)), Arrhenius equation (equation (6)) zero and first order kinetic models (equations (1) and (2)) were estimated by the linear regression procedure of the SigmaPlot (Scientific Graph System, version 4.00, Jandel Corp.).

CHAPTER III

RESULTS AND DISCUSSION

3.1. General

Analysis of drying processes requires a fundamental knowledge of water-solid interaction, composition of complex food systems and prediction of quality change. When deciding which process conditions produce the best quality dried products, it is necessary to compare drying time and quality parameters. Good quality can be defined as fast rehydration capacity, little shrinkage and an attractive colour. In this study, neglecting shrinkage, the effect of drying method (hot air/sun) on drying rate and colour of pestils was evaluated. WVP properties of pestil at different environments (relative humidities) were also studied. The result of experimental studies and the treatment of the resultant data are given in graphical and tabular forms and discussed separately for pestil samples.

3.2. Drying of Pestil Samples

3.2.1. Hot Air Drying

The effects of drying time temperature, thickness and air velocity on moisture content of pestil during drying were analysed using analysis of

variance (ANOVA). Three-way ANOVA clearly showed that drying time, temperature and pestil thickness were significant ($P<0.05$) factors in drying (Tables A1-A4). The influence of air velocity, by one-way ANOVA within the range studied, through the product were statistically insignificant ($P>0.05$) as shown in Tables A5-A12 and Figures 3, 4, 5 and 6 for S_1, S_2, S_3 and S_4 respectively at 75°C. This is similar to that observed in potato drying by Yusheng and Poulsen [48], on sugar beet root by Vaccarezza et al. [49] and for thin layer drying of garlic slices by Madamba et al. [50].

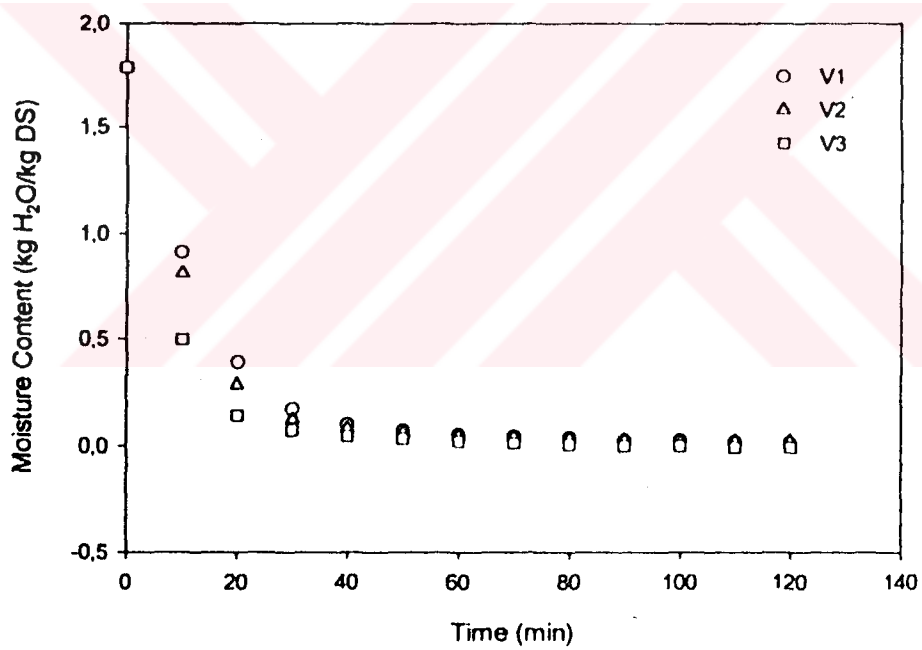

Figure 3. Drying curves at different air velocities for pestil slab (0.71 mm) at 75°C.

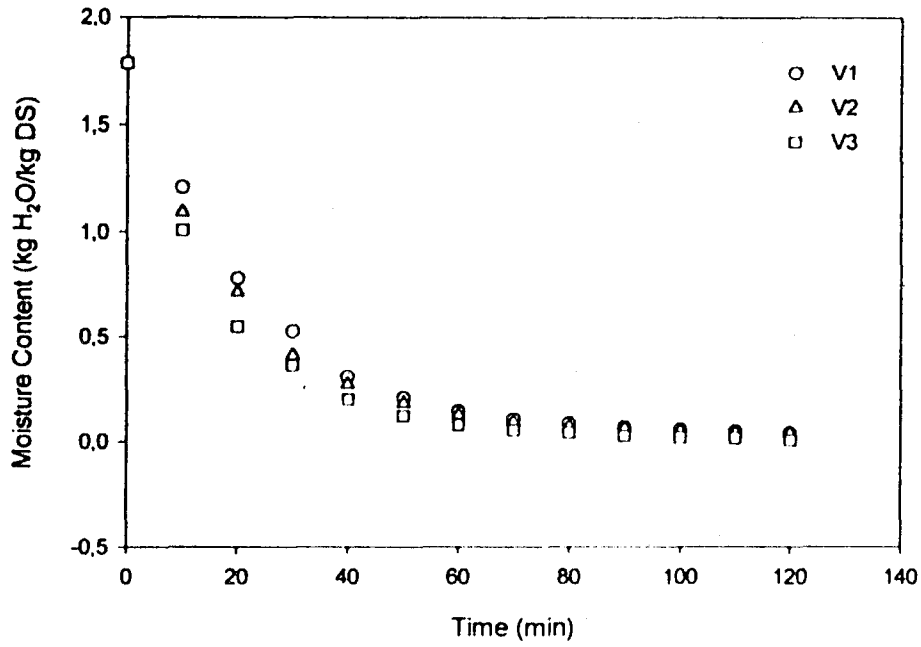

Figure 4. Drying curves at different air velocities for pestil slab (1.53 mm) at 75°C.

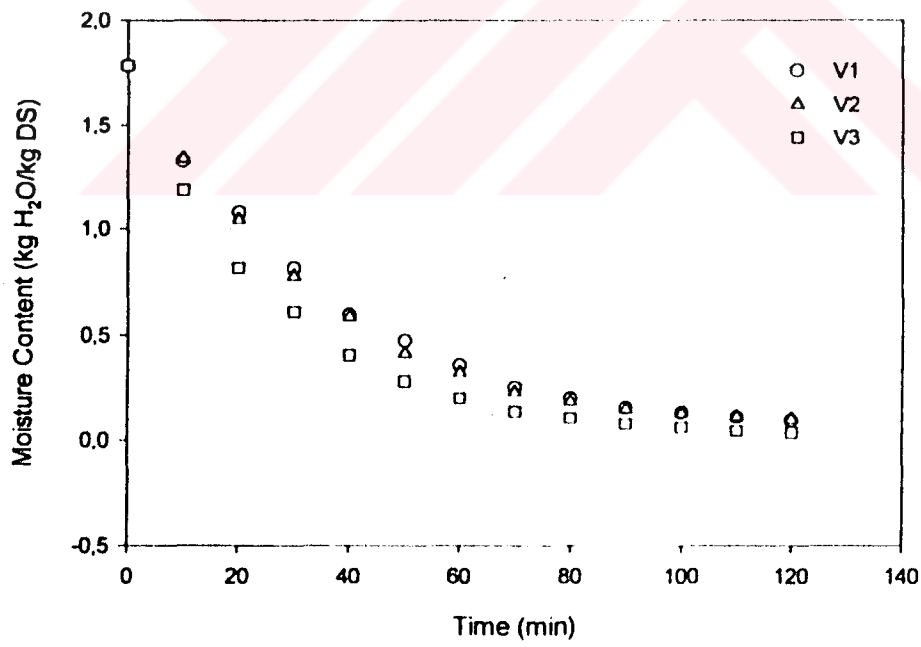

Figure 5. Drying curves at different air velocities for pestil slab (2.20 mm) at 75°C.

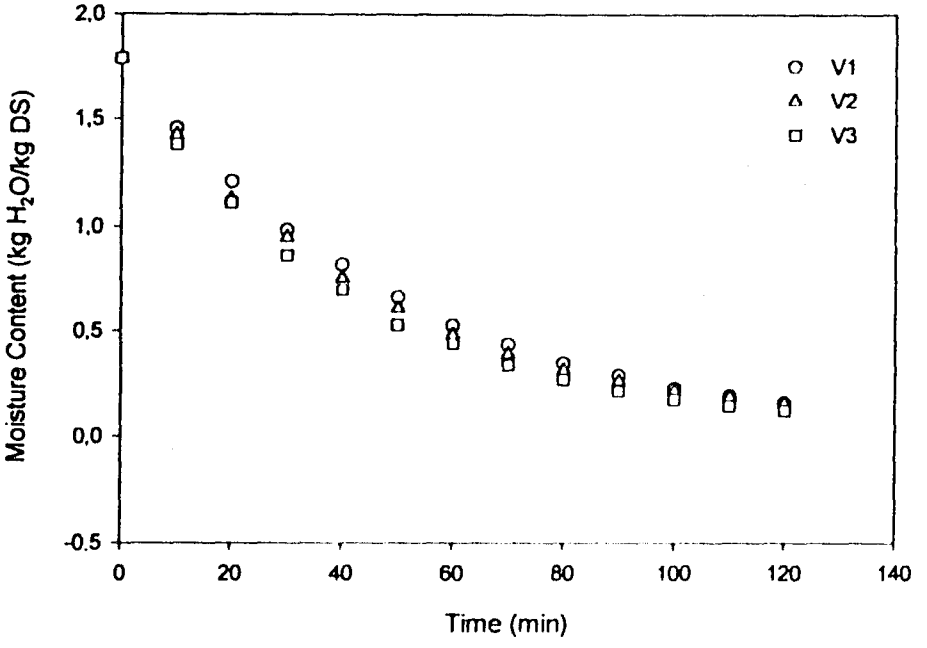

Figure 6. Drying curves at different air velocities for pestil slab (2.86 mm) at 75°C.

It was found that the trend was the same for 65 and 55°C. However the numerical data were different. Hence, the main study was limited to only an intermediate velocity V_2 (1.27 m/s) at all the temperatures and thicknesses defined for the sake of simplicity. In general, the time required to reduce the moisture content to desired level was dependent on drying conditions and sample thickness, being the highest in sun drying and the thickest sample, and lowest with 75°C and the thinnest sample.

When the experimental data of moisture content versus drying time were plotted, a concave downward curves were obtained. These are typical of the drying curves obtained during drying. Figures 7 to 10 show the effectiveness of increasing the drying air temperature in accelerating the dehydration of samples S_1, S_2, S_3 and S_4 respectively. It can be seen that the increase in temperature, at constant sample thickness, reduced the time needed to reach equilibrium moisture content. This is, according to kinetic

theory, due to the increased energy of water molecules as temperature is increased. Hence, escaping of molecules becomes easier from the medium and faster. It has been reported that [51] the higher temperatures provide a larger water vapour pressure deficit (wvpd, the difference between the saturated water vapour pressure and partial pressure of water vapour in air at a given temperature), which is one of the driving forces for the outward moisture diffusion process (drying). Similar behaviours were observed by Vergara et al. [52] for osmotically dehydrated apples, Moyls [4] for apple purees drying and Salgado et al. [53] for sugar beet root and sugar beet pulp, respectively.

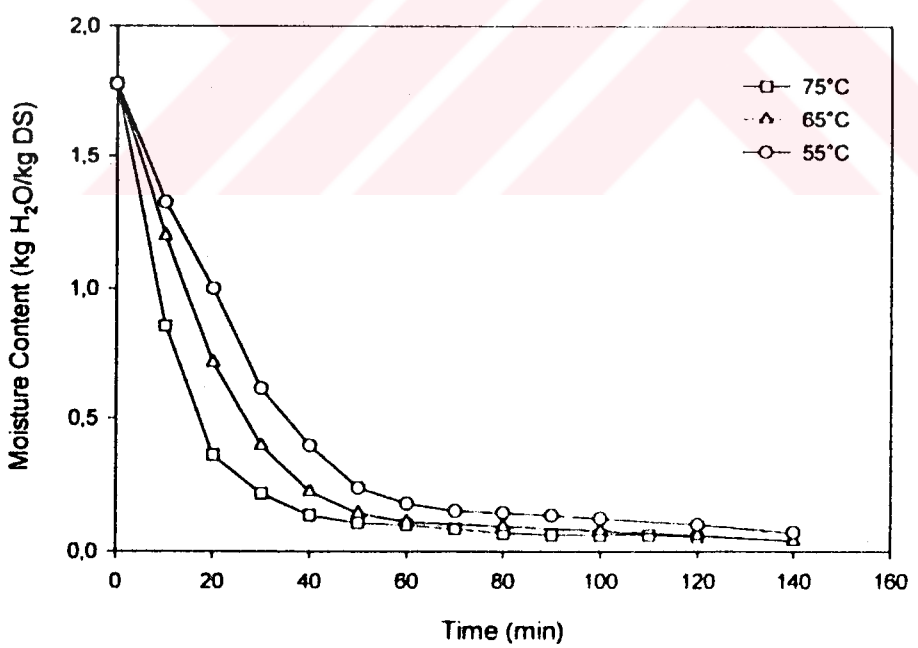

Figure 7. Effect of air temperature on drying of pestil slab (S_1=0.71 mm, V=1.27 m/s).

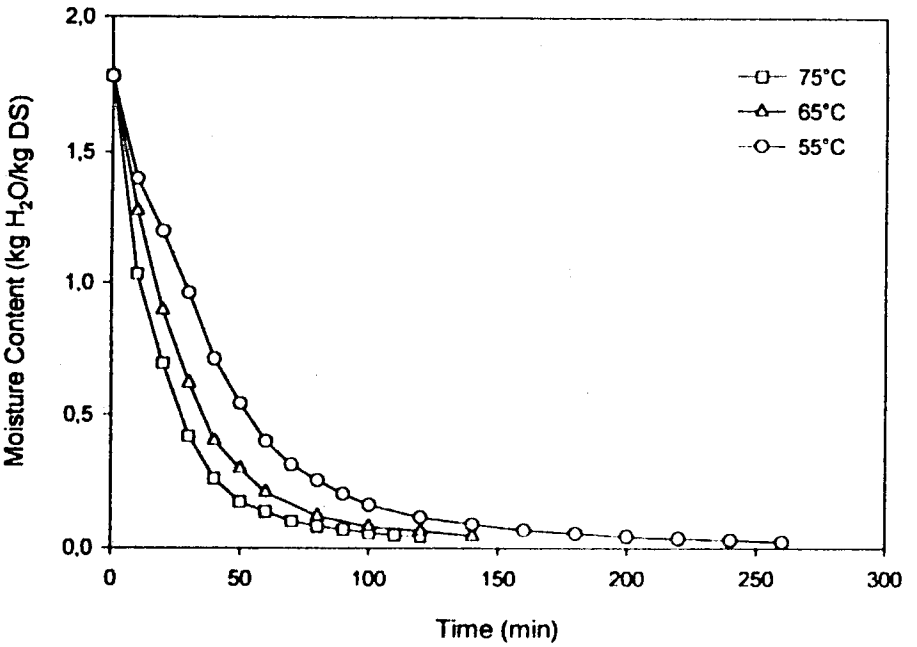

Figure 8. Effect of air temperature on drying of pestil slab (S_2=1.53 mm, V=1.27 m/s).

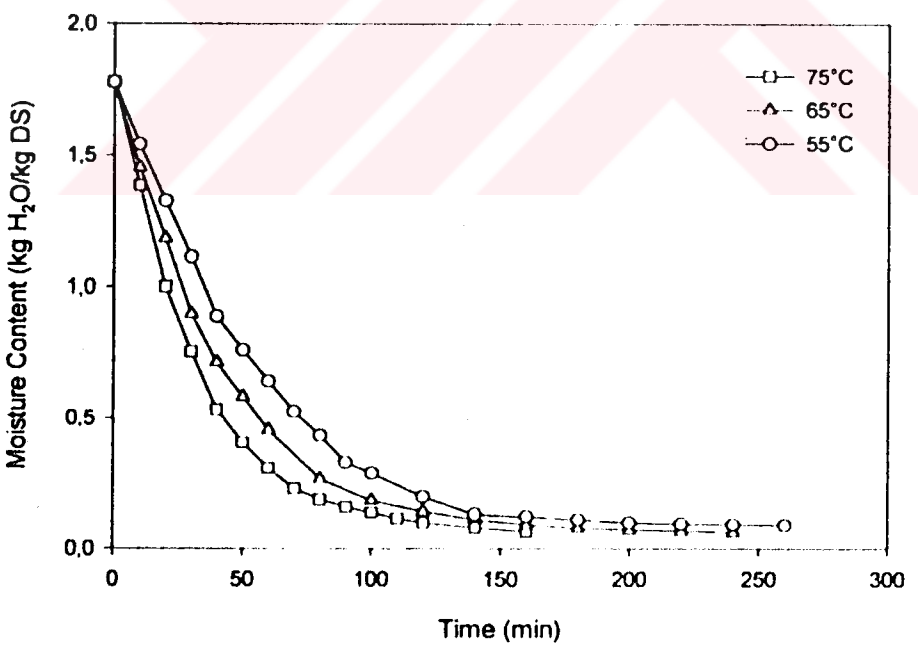

Figure 9. Effect of air temperature on drying of pestil slab (S_3=2.20 mm, V=1.27 m/s).

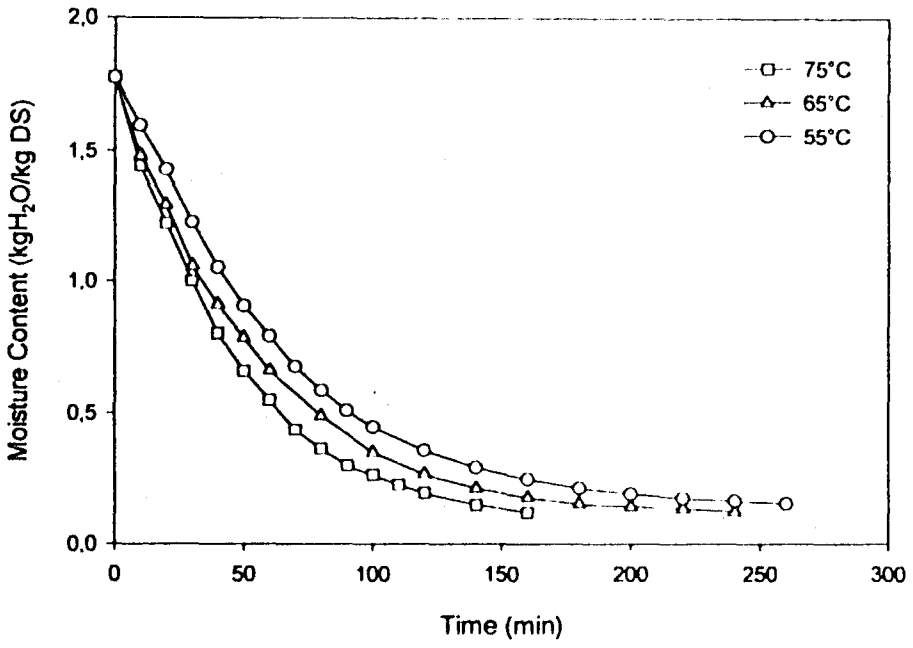

Figure 10. Effect of air temperature on drying of pestil slab (S_4=2.86 mm, V=1.27 m/s).

Drying times in order to reach moisture content of about 0.12 kg H_2O /kg DS (11 % wet basis) were given in Table 5. This moisture content was selected since it gives the final moisture content of commercial grape pestils [41, 42]. It has also been speculated that [54] moisture contents at or below 15 % (wet basis) for most fruits (especially for grapes and its products) is a rather safe indication that there is no microbial or mould growth and the reaction rate of a number of other deteriorative reactions (sugar crystallisation, non-enzymatic browning, flavour deterioration, lipid oxidation etc.) is significantly reduced.

Table 5. Drying time (min) for pestil samples to reach 0.12 kg H_2O /kg DS.

T (°C)	S_1	S_2	S_3	S_4
55	70	120	140	240
65	50	80	120	180
75	40	60	100	140

Figures 11, 12 and 13 show the influence of sample thickness on drying at 55, 65 and 75°C respectively. The effects of sample thickness were similar to studies on air drying of banana slices at 60°C [26], drying of potato slices [48] and drying of apple slices [55] with all authors concluding that thinly sliced products dried faster due to the reduced distance the moisture travels. The analysis of variance showed that the effect of drying time and slice thickness was more pronounced than the air temperature due to a significantly higher F-values.

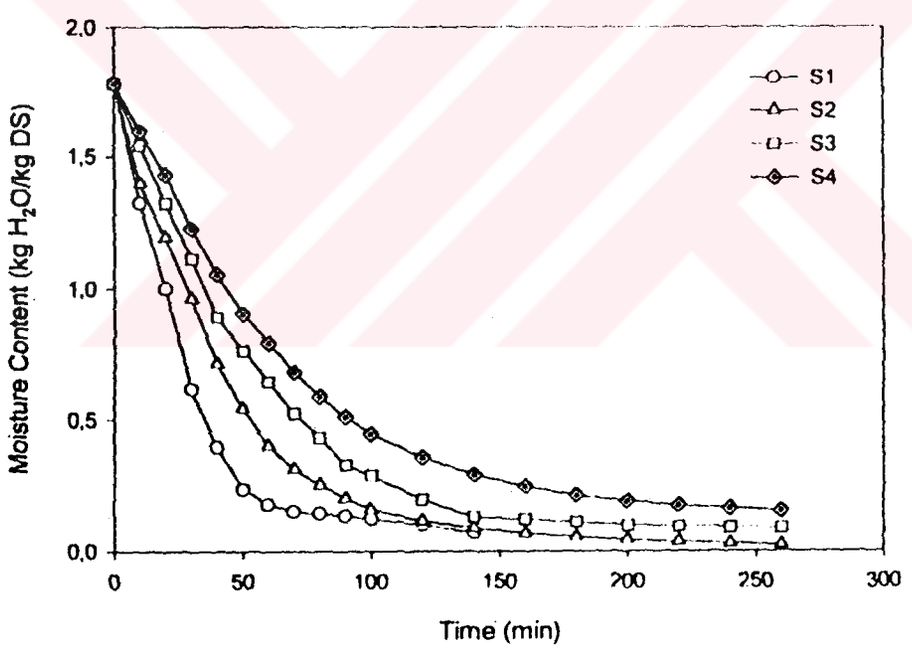

Figure 11. Effect of sample thickness on air drying of pestil slabs at 55°C.

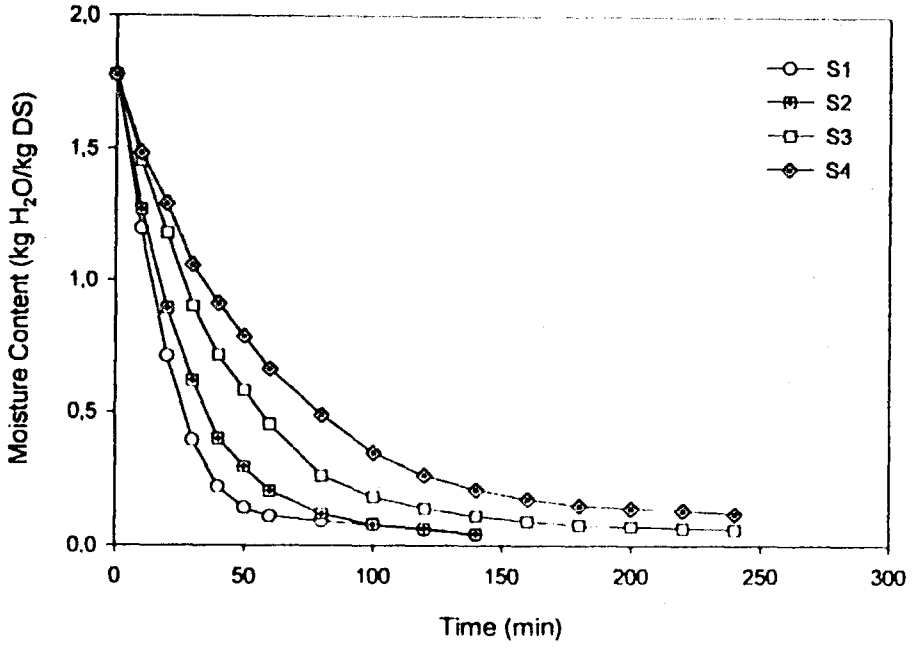

Figure 12. Effect of sample thickness on air drying of pestil slabs at 65°C.

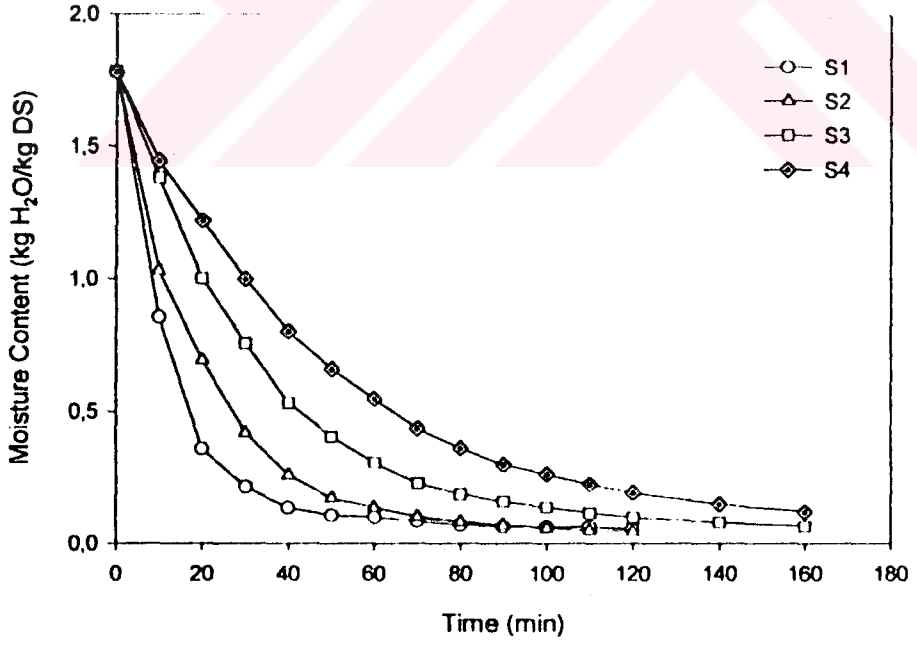

Figure 13. Effect of sample thickness on air drying of pestil slabs at 75°C.

3.2.2. Sun drying

The moisture content versus time curves for sun drying of pestil samples were given in Figure 14. The thin sample (S_1) dried appreciably faster than the others. The time to reach the moisture content of 11 % (wet basis) was 3, 5, 15 and 25 hr for S_1, S_2, S_3 and S_4 respectively. These results are quite higher than those of hot air drying (Table 5) and lower than those of sun dried sultana raisins which required 740 hr of drying [6]. This abnormality is due to the difference in shape/size and nature of the two products and the skin on the raisins. Because the outer skin results in an overall larger resistance to the water vapour movement. The comparison of drying time for sun drying of pestil and raisins is important in order to present the difference in drying behaviour of grape and its derivative, pestil.

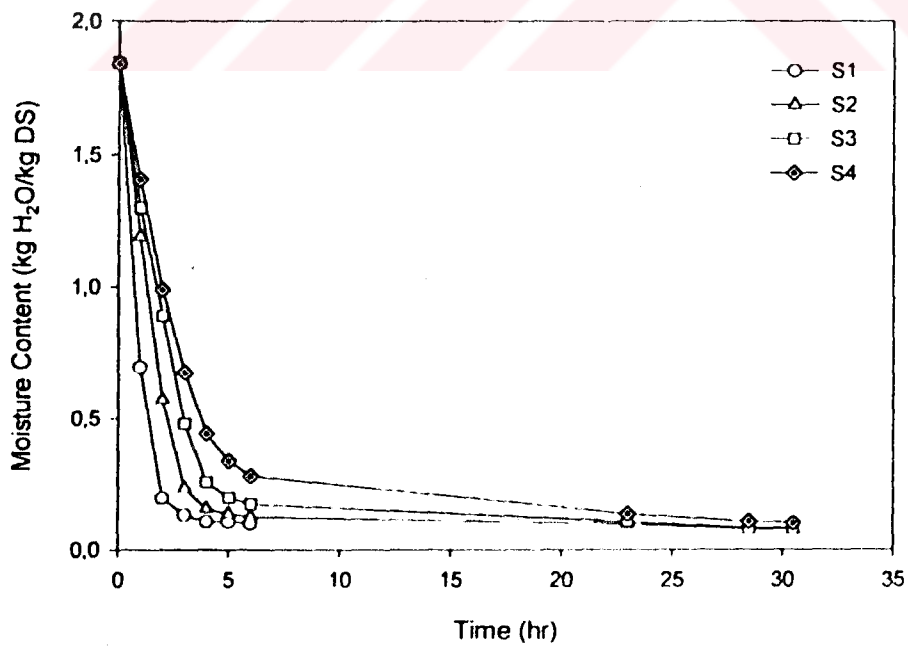

Figure 14. Typical drying curve for sun drying of pestil slabs at different thicknesses.

3.2.3. Analysis of Drying Rates

The drying rate was determined from the slopes of the curves, at each measurement point, presented in Figures 11-14. The variation of the drying rates against moisture content were shown in Figures 15, 16, 17 for hot air drying (at 75, 65, 55°C respectively) and Figure 18 for sun drying. Statistically, a significant difference ($P<0.05$) was found between drying rates of hot air and sun drying processes. The drying rates for the tested conditions were as follows; according to

a) drying method : air drying > sun drying
b) sample thickness: $S_1 > S_2 > S_3 > S_4$
c) temperature : 75°C > 65°C > 55°C.

From the results of previous works on drying of apple puree [4], apple slabs [55] and banana slabs [2] both constant and falling rate drying periods have been observed. In this study, at 75°C and 65°C all the samples, at 55°C S_1, S_2, S_3 and in sun drying only S_1 dried in falling rate drying period.

However, a short constant drying rate period was observed in sun dried samples of S_2, S_3, S_4 and sample S_4 of 55°C prior to falling rate period. This constant rate period was neglected in our diffusivity calculations and it was assumed that the entire drying process for pestil occurred in the falling rate period, as it has been commonly found in biological products, for all of the test conditions. Another reason for non-existence of a constant rate period either at high temperatures (65 and 75°C) and the thin samples may be explained by the fact that at high temperatures the surface of products dries out very quickly (especially of the thin samples) and a partial barrier is generated to moisture movement. This caused pestil to dry in the falling rate period.

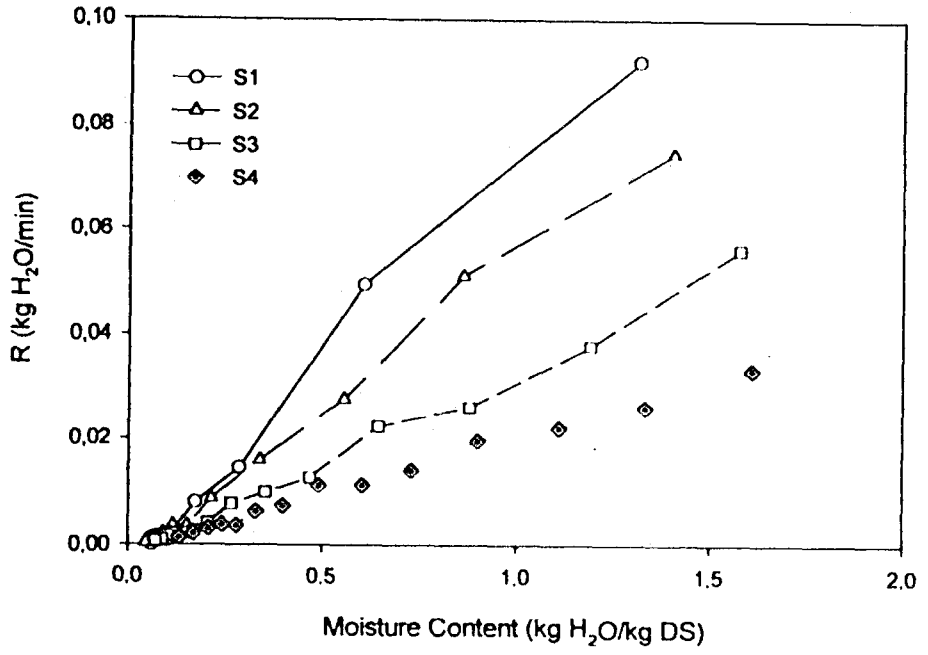

Figure 15. Drying rate curves for pestil slabs at air temperature of 75°C (V=1.27 m/s).

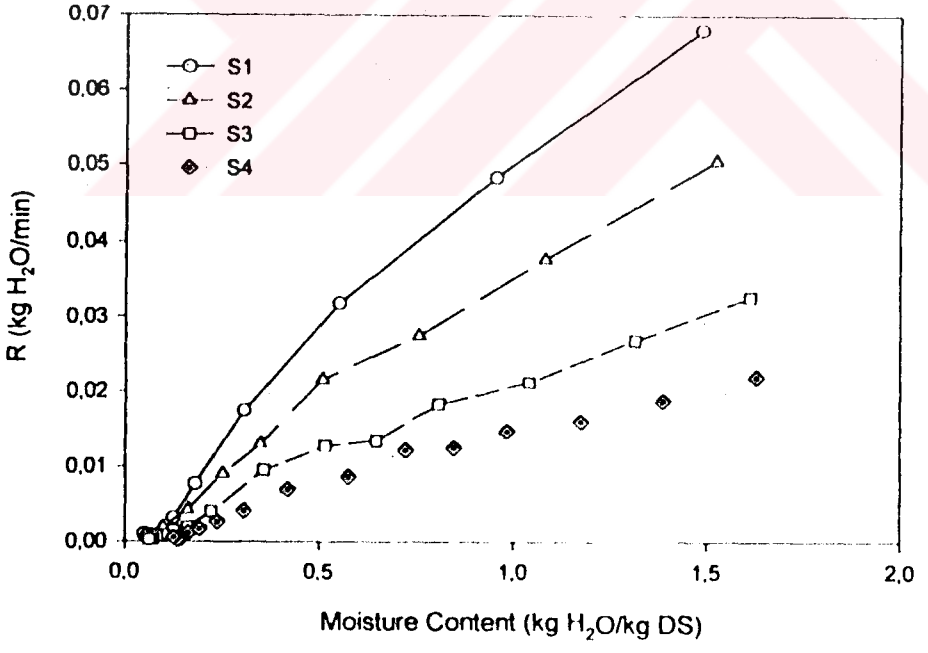

Figure 16. Drying rate curves for pestil slabs at air temperature of 65°C (V=1.27 m/s).

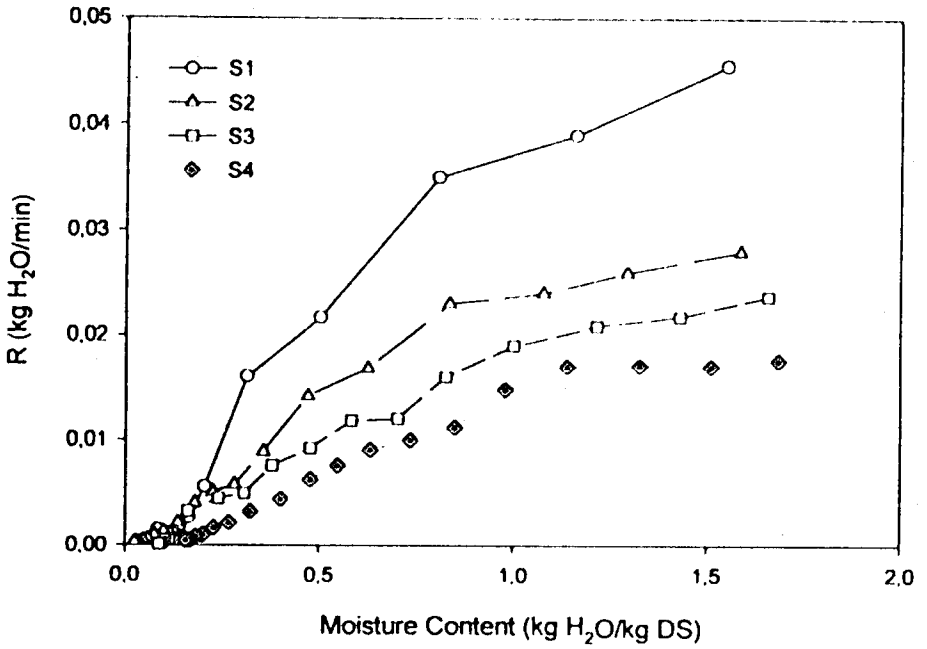

Figure 17. Drying rate curves for pestil slabs at air temperature of 55°C (V=1.27 m/s).

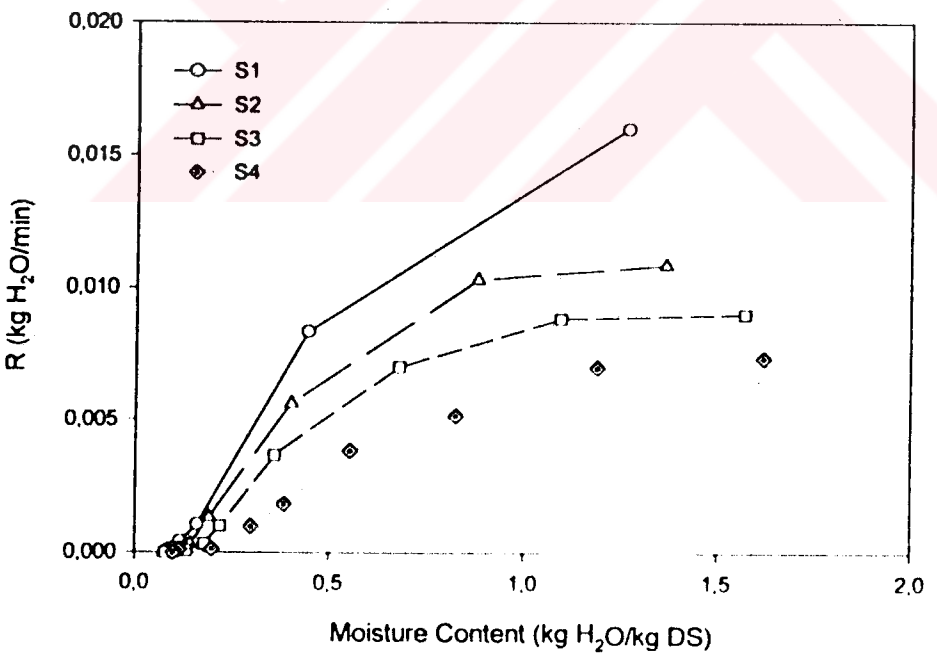

Figure 18. Drying rate curves for sun dried pestil slabs.

Non-existence of a strong constant rate period, as existed in apple puree, apple slabs and banana slabs, may be due to addition of starch to grape juice for pestil preparation. This may add additional hydrophilic interaction to the system. In the water-starch system, each water molecule is hydrogen bonded to two hydroxyl groups either on adjacent starch chains or on the same coiled chain. In order to form this structure, the starch must be arranged in a precise manner to bind the water. The extent of water sorption depends on the availability of these sites where starch-water-starch-hydrogen bonds can form [56]. These sites, probably, form during cooking of grape juice and starch mixture, hence, makes water-solid interaction difficult to break. Therefore, there is no available water at the pestil surface at any time, the surface is not covered by wet regions and the evaporation of water does not take place entirely at the surface for occurrence of a constant drying rate period. Since, at that point there are no free water regions the evaporation front may be moved into the interior of the pestil. The mass transfer is then by molecular (liquid) diffusion or vapour diffusion or by capillary forces in the interior (wet) region of the pestil and the water is evaporated as it reaches the surface (negligible resistance to mass transfer). And also the starch molecules form a close-knit matrix resulting in the encapsulation of water molecules in small cavities. The diffusion process of water through the dry outside layers is activated by high temperatures [6, 57].

As mentioned previously, the air velocity had no effect on the drying curves in the all cases studied. It means that the resistance to moisture movement at the surface of sample (external resistance) is negligible. From the results shown in Figures 15-18 it can be seen that the internal moisture

movement (internal resistance) is the main resistance to the rate of loss of moisture for which the drying rate is not affected by air velocity. Internal resistance is evident from presence of only falling rate period in any drying process as reported by several authors [49, 58].

3.3. Calculation of the Effective Moisture Diffusivity and Activation Energy

As mentioned above, the results obtained have shown that the drying process is entirely controlled by internal mass transfer resistance (falling rate drying period), so that the experimental results can be interpreted by using Fick's diffusion model. Assuming uniform initial moisture distribution and negligible external resistance (no constant rate period), the solution of Fick's diffusion equation developed for particles with slab geometry by Crank [59] is applicable and is of the form of equation (5):

$$MR = \frac{(X - X_e)}{(X_0 - X_e)} = \frac{8}{\pi^2} exp\left(\frac{-\pi^2 * D_{eff} * t}{L^2}\right) \quad (5)$$

where MR is the moisture ratio, X is the average moisture content (kg H_2O/kg DS), X_e is the equilibrium moisture content (kg H_2O/kg DS), X_0 is the initial moisture content (kg H_2O/kg DS), L is the thickness of the slab (m) for drying from one side (from the top surface of pestil), D_{eff} is the effective moisture diffusivity (m^2/s) and t is the drying time (min).

The effective moisture diffusivity was calculated using the method of slopes. When logarithm of MR values versus drying time were plotted in

accordance with equation (5), straight lines were obtained at all temperatures and sample thickness investigated. Figures 19-22 show such lines for 75, 65, 55°C hot air and sun drying processes respectively. The pattern of the curves was similar to that reported by Yusheng and Poulsen [48] and Madamba et al. [50]. Linear regression analysis was employed to obtain values of diffusion coefficients for different drying conditions from the slope of the straight lines. Values of D_{eff} for different conditions together with correlation coefficient of estimation were presented in Table 6.

Table 6. Effective diffusivity values (m^2/s) for drying pestil slabs ($D_{eff}*10^{11}$).

Slab Thickness (mm)	Hot Air Drying						Sun Drying	
	Temperature (°C)							
	75	r	65	r	55	r	D_{eff}	r
0.71	4.76	0.987	3.18	0.966	3.00	0.977	1.93	0.997
1.53	17.3	0.998	15.2	0.999	12.2	0.873	4.35	0.978
2.20	27.3	0.998	22.3	0.999	21.1	0.995	7.33	0.990
2.86	37.6	0.993	30.8	0.998	27.8	0.995	9.16	0.997

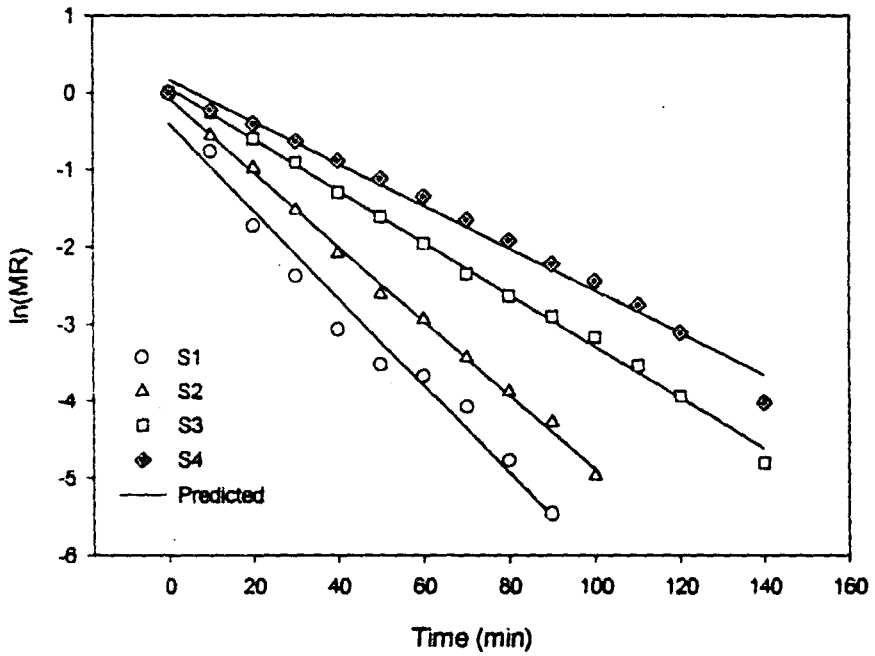

Figure 19. Comparison of Fick's diffusion model with experimental moisture content values of pestil slabs at 75°C (V=1.27 m/s).

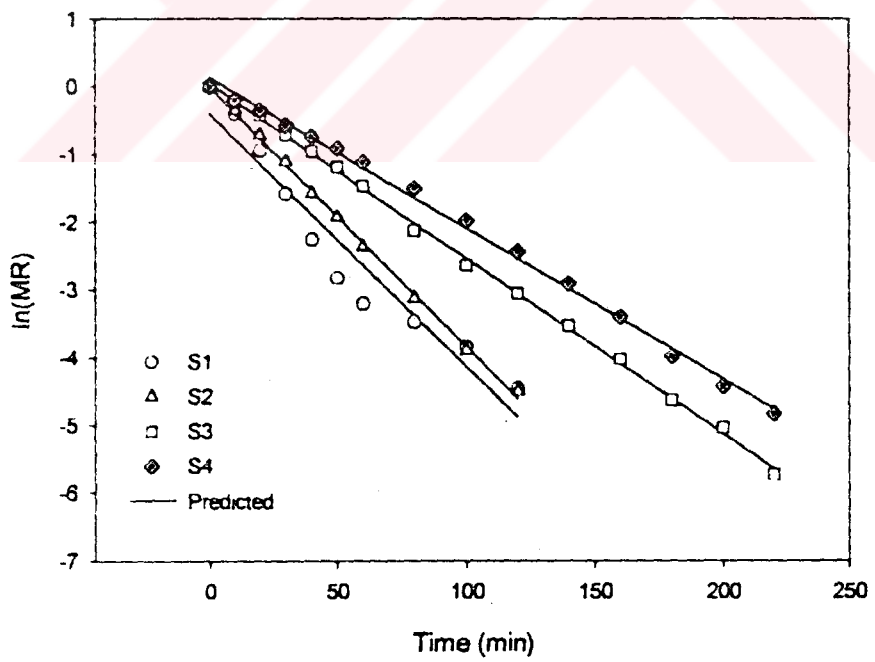

Figure 20. Comparison of Fick's diffusion model with experimental moisture content values of pestil slabs at 65°C (V=1.27 m/s).

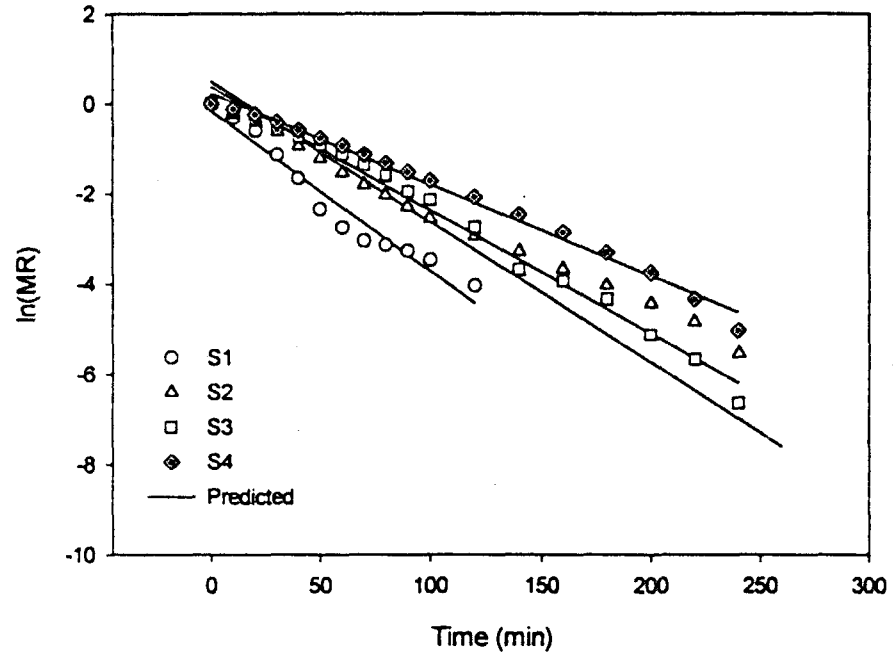

Figure 21. Comparison of Fick's diffusion model with experimental moisture content values of pestil slabs at 55°C (V=1.27 m/s).

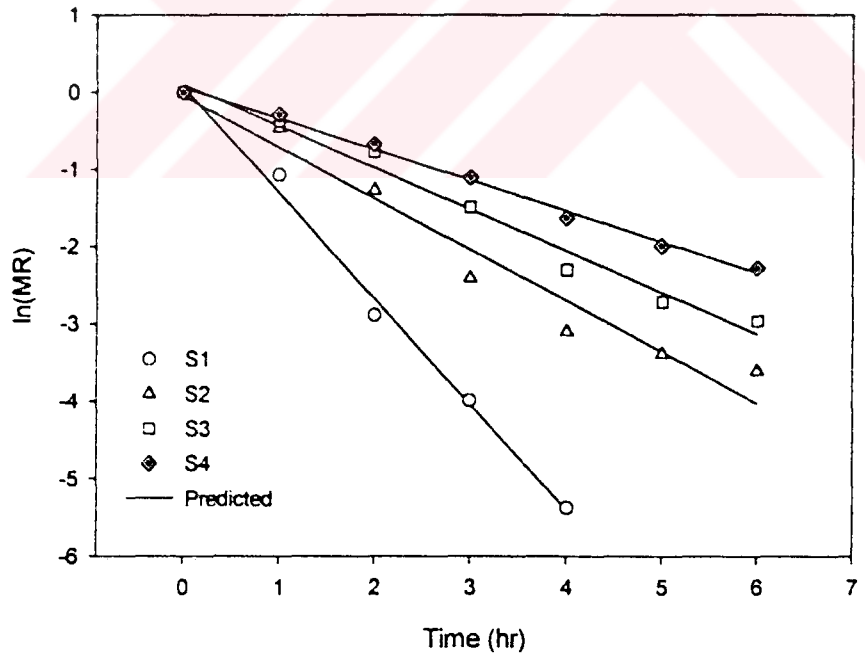

Figure 22. Comparison of Fick's diffusion model with experimental moisture content values of sun dried pestil slabs.

It can be seen from Table 6 that the drying air temperature has a pronounced influence on the drying rate and as a consequence, markedly affects the value of the diffusion coefficient. As was expected, the drying rate increased greatly with increasing temperature. Drying at 75°C gave the highest D_{eff} values. The lowest values were obtained with sun drying. The values for hot air drying ranged from 3.00 to 37.6×10^{-11} m^2/s and for sun drying 1.93 to 9.16×10^{-11} m^2/s depending on temperature and sample thickness. These values are within the general range of 10^{-9} to 10^{-11} m^2/s and comparable to the reported values of 1 to 3×10^{-11} m^2/s for air drying of apricots [7], sun drying of differently treated grapes 10.4 to 9.9×10^{-11} m^2/s [9] and hot air drying of banana slices at 60°C 8.33×10^{-10} m^2/s [2].

Activation energy for diffusion was estimated using an Arrhenius-type equation:

$$D_{eff} = D_0 exp\left[\frac{-E_a}{R_g T}\right] \quad (6)$$

where D_0 is a constant equivalent to the diffusivity at infinitely high temperature and E_a is the energy of activation (kJ/mol). The activation energy was calculated by plotting $\ln(D_{eff})$ versus the reciprocal of the absolute temperature (1/T) as presented in Figure 23. The slope of the straight line is $-E_a/R_g$, where R is 8.314 kJ/mol.K. Then, the activation values for water diffusion (calculated from the slopes of straight lines of Figure 23) were found to be 21.7 ($r = 0.912$), 16.5 ($r = 0.992$), 12.0 ($r = 0.943$) and 10.3 ($r = 0.979$) kJ/mol for S_1, S_2, S_3 and S_4 respectively. It is obvious that activation energy values decreased with increasing sample thickness. These values are in the

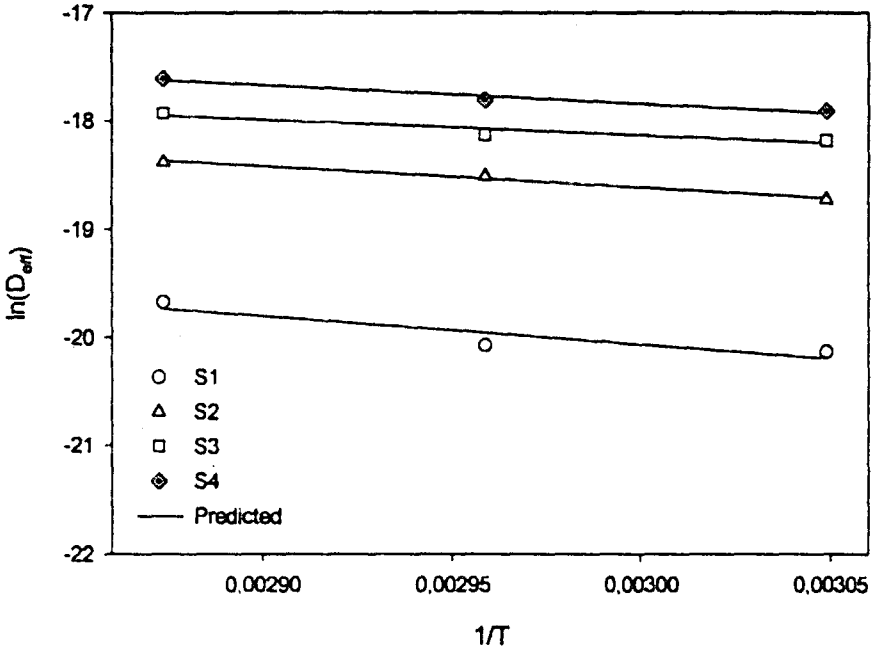

Figure 23. Effect of temperature on the diffusion values of water in pestil slabs.

range or close to the E_a values reported (15-40 kJ/mol) by Rizvi [60] for various foods.

The value of E_a shows the sensitivity of the diffusivity against temperature. The greater the value of E_a, the more sensitivity of the diffusivity to the temperature. The greater value for S_1 shows the sensitivity of the thin sample against temperature, i.e., a small variation in temperature during drying results in significant changes in diffusivity value compared to the thicker samples.

3.4. Colour Evaluation

Colour change in juices and fruit purees during manufacture and storage is of vital interest for the industry. Different indicators are assayed to determine the extent of colour change. These include colorimetric

evaluations and qualitative and quantitative determinations of intermediate and final products of non-enzymatic browning (spectrophotometric method at 420 nm), such as sugars and, especially, hydroxymethylfurfural (HMF). In this study, only colorimetric determinations were carried out in order to express colour change during grape juice concentration, cooking and pestil drying. Browning enzymes, such as polyphenoloxidase, are very heat sensitive [8]. Therefore, they were assumed to be inactivated during cooking process and, hence, their influence on browning was neglected also.

The order of reaction for the colour parameters during concentration, cooking and drying was determined by the adjustment of the experimental data to the integrated kinetic equations (equations (1) and (2)) for zero and first orders using linear regression analysis. In each case the best fit was selected and the rate constant at each process was determined from the slope of the straight line. These analysis revealed that zero order described the data better than the first order. The kinetic study of the colour change of grape juice during cooking showed that all the Hunter colour parameters (L, a, b) investigated changed significantly. The results obtained are presented in Figures 24, 25 and 26 respectively, for L, a and b values. The parameters a and b increased, an L value decreased during cooking processing. These results compare well with those of Lozano and Ibarz [10] for heating fruit pulps (apple, plum and peach) and Ibarz et al. [12] for pear puree during heating. It has been reported that grapes contain a variety of different anthocyanin pigments [9, 13]. They are sensitive to temperature and more stable at low pH values. Since grape juice used had a pH value of 7.6 and temperature of cooking is about 98°C, the decrease in L and increase in a

and b values may be attributed to destruction of anthocyanins and Maillard reactions during cooking resulting in a colour change from a natural red or purple to a more dull brownish colour [19]. Different authors have reported that decreases in L value correlated well with increases in browning of foods [15, 61].

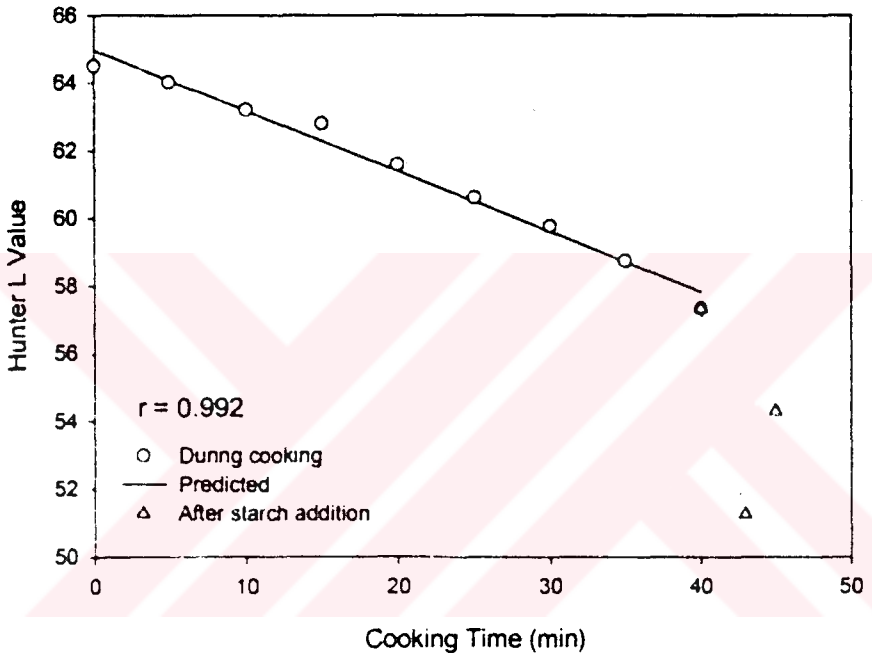

Figure 24. Effect of cooking time on the Hunter L-value of grape juice.

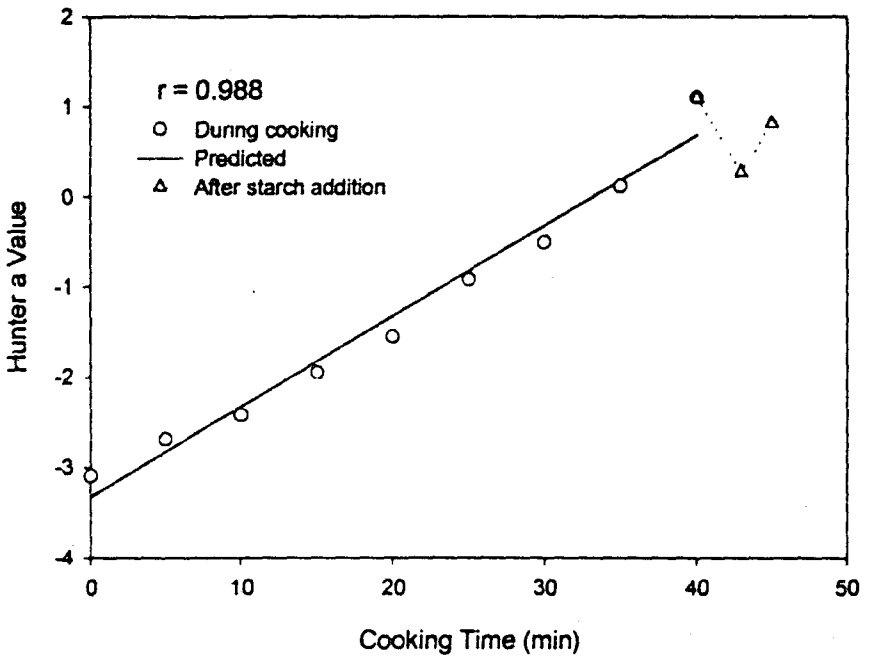

Figure 25. Effect of cooking time on the Hunter a-value of grape juice.

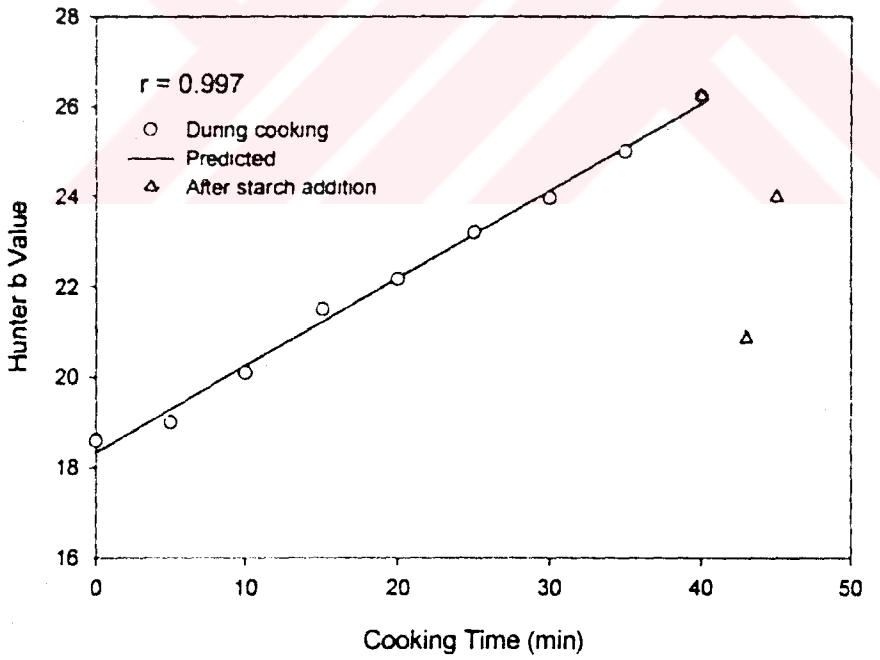

Figure 26. Effect of cooking time on the Hunter b-value of grape juice.

On the other hand, only Hunter a-value of pestil slab (1.53 mm) changed significantly upon both hot air and sun drying. The change in this value as a function of time is presented in Figures 27 and 28 for hot air and sun drying respectively. L and b values showed little difference during drying (Tables 7-10). Therefore, only kinetics of a-value (of zero order) was evaluated for drying processes.

Table 7. Hunter L and b values of pestil slab (1.53 mm) during hot air drying at 75°C.

Time (min)	L value	b value
0	53.83	21.28
20	52.84	20.77
50	52.35	19.29
80	52.8	19.32
130	54.87	19.70
150	54.17	20.07

Table 8. Hunter L and b values of pestil slab (1.53 mm) during hot air drying at 65°C.

Time (min)	L value	b value
0	52.9	20.20
30	52.18	20.04
60	53.87	19.14
90	53.61	19.69
120	53.20	19.62
150	53.11	20.00
180	53.16	20.20
210	53.32	20.29

Table 9. Hunter L and b values of pestil slab (1.53 mm) during hot air drying at 55°C.

Time (min)	L value	b value
0	53.40	19.15
60	54.71	20.75
110	55.00	20.20
170	56.89	20.40
230	55.96	21.00
260	55.63	19.90

Table 10. Hunter L and b values of pestil slab (1.53 mm) during sun drying.

Time (min)	L value	b value
0	53.42	20.20
30	53.55	18.51
120	53.07	21.00
210	52.76	22.00
270	53.22	20.56
330	53.15	19.65
1350	53.55	20.60
1680	52.86	21.03
1800	53.24	20.80

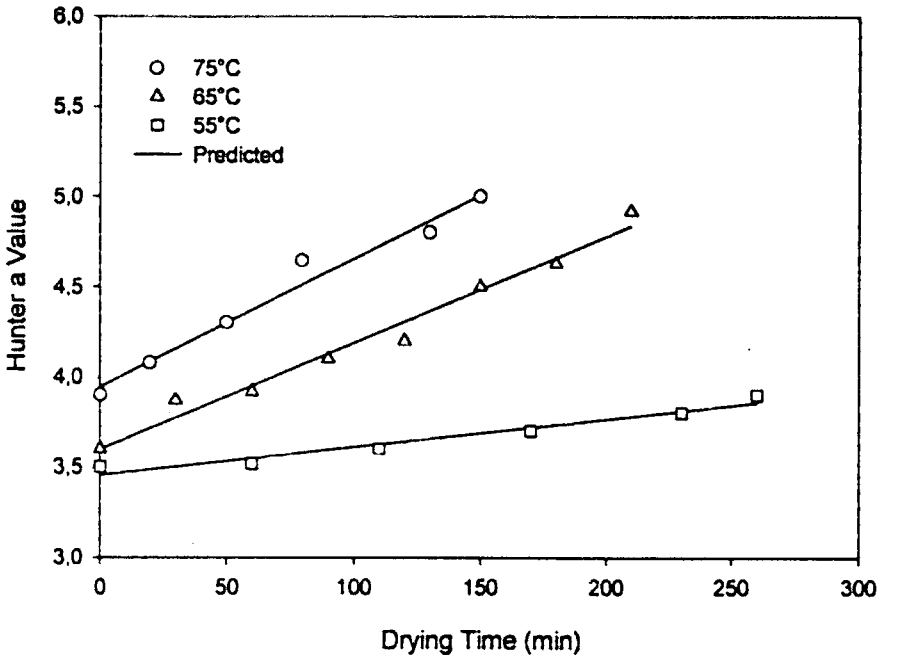

Figure 27. Effect of temperature on Hunter a-value of pestil slab (1.53 mm) during air drying.

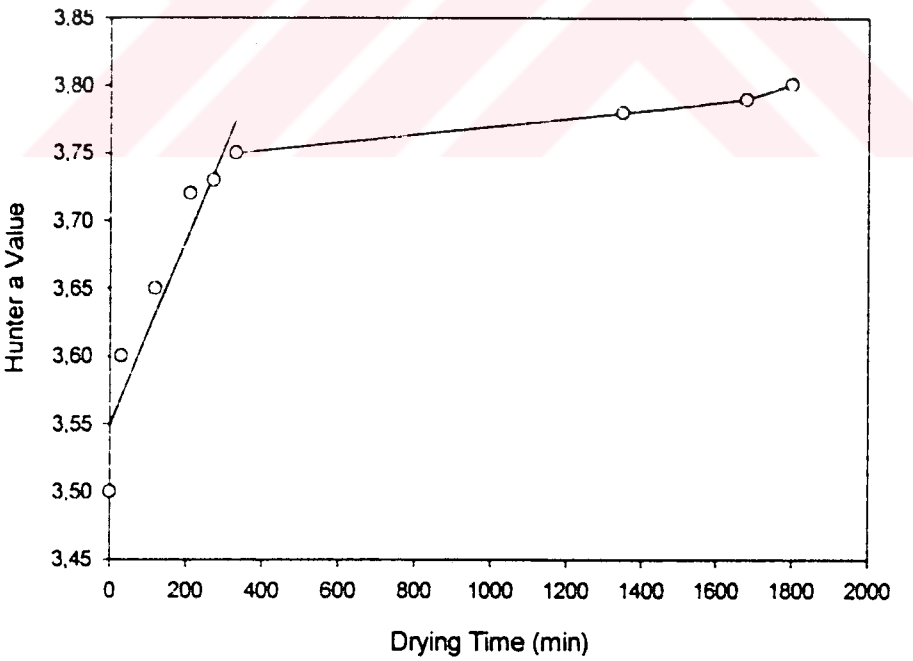

Figure 28. Change in Hunter a-value of pestil slab (1.53 mm) during sun drying.

The evolution of L, a and b values during cooking of grape juice and, of a-value during drying with the treatment time were fitted to the zero order kinetics model. The values of the parameters obtained from these fittings were given in Table 11. The activation energy value for colour change during air drying of pestil for Hunter a-value also was presented in the same table. The correlation coefficient changed between 0.943 to 0.997, representing good fits. Only the first linear portion of a-value of sun dried pestil was considered in kinetics calculations (Figure 28).

Table 11. Kinetic parameters for colour evolution during grape juice cooking and pestil drying (slab thickness of pestil = 1.53 mm).

Operation type		Parameter	C_0	k (min^{-1})	r	E_a (kJ/mol)
Grape juice cooking		L	64.96	0.178	0.991	
		a	-3.33	0.100	0.988	
		b	18.3	0.900	0.997	
Air drying	75°C	a	3.94	7.09×10^{-3}	0.987	72
	65°C		3.59	5.90×10^{-3}	0.988	r = 0.923
	55°C		3.45	1.56×10^{-3}	0.988	
Sun drying		a	3.55	6.82×10^{-4}	0.943	

where C_0 is estimated initial concentration of colour parameters and k is the zero order reaction rate constant.

It can be seen that rate constants for L, a and b values for cooking process are higher than the rates values of drying, meaning that most of the colour change occurred during cooking. Among the drying processes, hot air drying had more influence on colour change than sun drying due to higher air temperature application. It can be considered that zero order kinetics model gave good fit, examining correlation coefficients of estimation, for all treatments except sun drying (r = 0.943). It was attributed to variation in air

conditions through day and night. The changes in air conditions might have speeded or lowered down the colour change reactions, since there is not a constant trend. The rate constant values increased with an increase in drying air temperature. These values for Hunter a-parameter were from 7.09 to $1.56x10^{-3}$ min^{-1} for hot air drying for the air temperature range of 75 to 55°C and $6.82x10^{-4}$ min^{-1} for sun drying. It is obvious that sun energy has less destructive effect on the colour of pestil samples. The dependency of temperature on k was determined using the linearised Arrhenius type equation. The value obtained for the activation energy for hot air drying of pestil based on change in a-value was 72 kJ/mol. This value was slightly higher than the value (62.8 kJ/mol) given in colour change of pear puree at high temperature [12] and lower than the value given in colour change of grape juice (131.3 kJ/mol for a-value) using linearly increasing temperature treatment [13].This difference in values could be due to the variation in type of treatment or process and compositional change in samples being treated.

3.5. Effect of Relative Humidity Gradient and Temperature on Weight Loss and Gain of Pestil

Weight loss of pestil at three different temperatures (15, 25, 37°C) with three different relative humidity gradients (in / out: $Mg(NO_3)_2$ / $MgCl_2$, $NaNO_3$ / $MgCl_2$, H_2O / $MgCl_2$) were given in Figures 29-31. Saturated salt solutions were used to provide a constant relative humidity environment. The relative humidity values of the salt solutions were given in Table 4 (Chapter 2). The data obtained for weight gain of pestil when the water was placed outside the test cups at 15, 25 and 37°C when the relative humidity inside was arranged

as zero using (P_2O_5) were represented in Figure 32. As the relative humidity gradient increased, the weight loss and gain were increased. It was given in literature that for edible films, temperature increasing also increased effect of relative humidity gradient on the weight gain and loss [29, 44, 62].

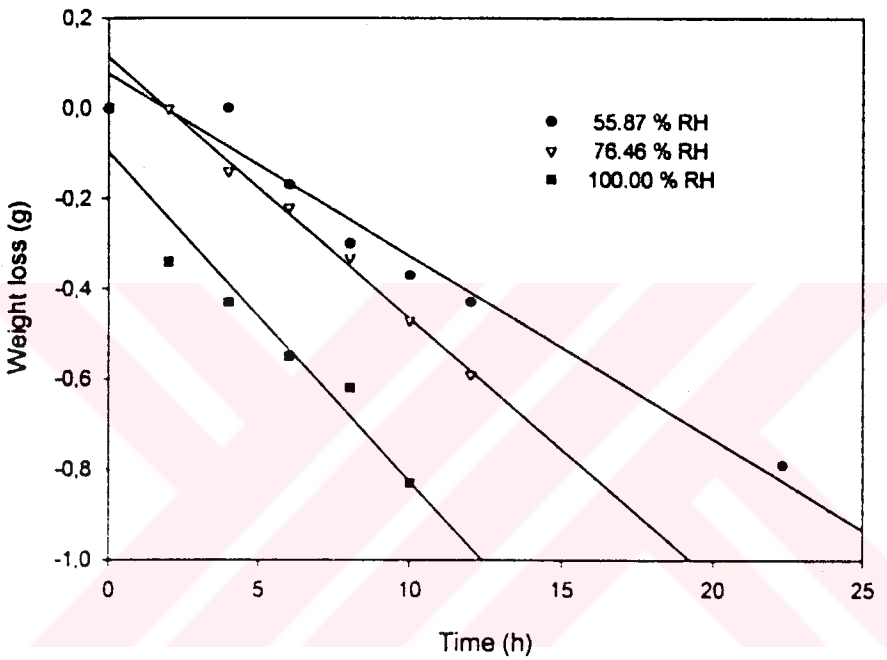

Figure 29. Weight loss of pestil at 15°C with different relative humidity inside of the cup (outside of the cup was 33.33 % RH).

3.6. WVTR and WVP of Pestil

The appearance of pestil was light yellow with smooth surface. Average thickness of pestil before the experiment was approximately 0.60 (±0.05) mm and after the experiment the thickness of the pestil was measured and tabulated in Table 12.

It can be stated that increasing RH of the environment increased the thickness of the pestil. The WVTR and WVP values obtained using three different temperatures and five different relative humidity gradients were tabulated in Table 12. WVTR of pestil for all cases were calculated using the slopes of the weight loss and gain plots (Figures 29, 31 and 32) of pestil using equation (3).

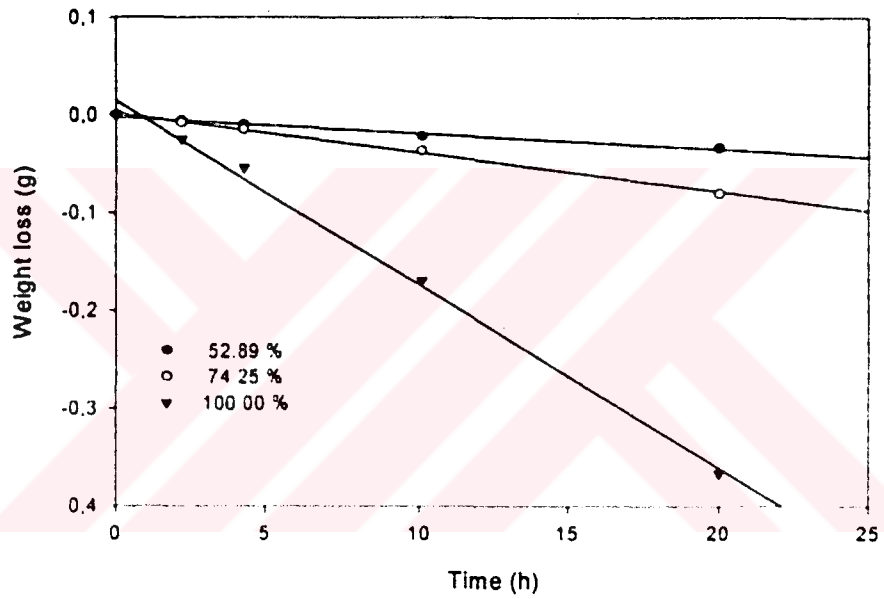

Figure 30. Weight loss of pestil at 25°C with different relative humidity inside of the cup (outside of the cup was 32.78 % RH).

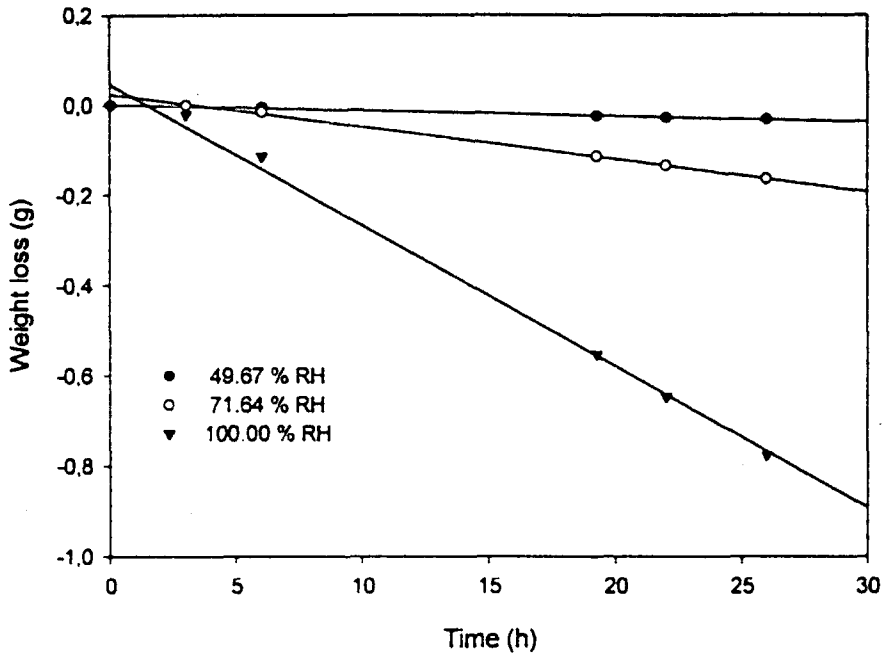

Figure 31. Weight loss of pestil at 37°C with different relative humidity inside of the cup (outside of the cup was 31.87 % RH).

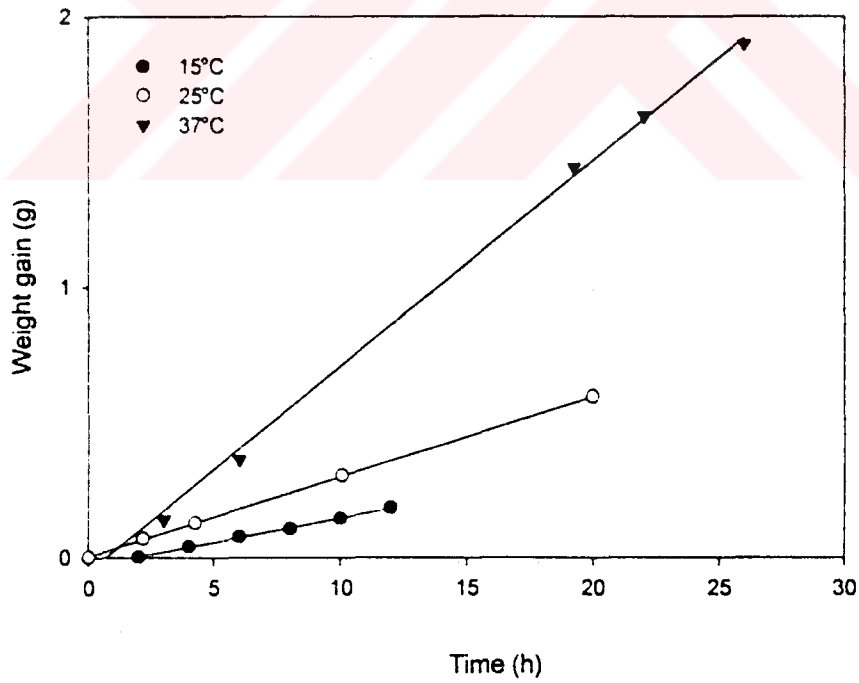

Figure 32. The effect of temperature on weight gain of pestil (inside and outside of the cup were 0.0 and 100 %).

Table 12. Water vapour transmission rate and permeability values of pestil subjected to different relative humidity gradients at three different temperatures.

Temperature (°C)	L (mm)	Relative humidity (%, in-out)	WVTR ($g/m^2.h$)	WVP ($g.mm/kPa.h.m^2$)
15	0.50	55.87 / 33.33	0.55	0.71
	0.62	76.46 / 33.33	0.87	0.73
	0.67	100.00 / 33.33	1.31	0.77
	0.66	0.00 / 100.00	27.07	10.47
25	0.62	52.89 / 32.78	2.30	2.23
	0.55	74.25 / 32.78	6.01	2.51
	0.54	100.00 / 32.78	28.33	7.18
	0.75	0.00 / 100.00	44.69	10.57
37	1.2	49.67 / 31.87	2.45	2.62
	0.83	71.64 / 31.87	10.94	3.60
	0.88	100.00 / 31.87	47.39	9.74
	1.12	0.00 / 100.00	114.91	20.42

Increasing the relative humidity gradient at a constant temperature increased the WVTR of pestil. As it was expected in a hydrophilic and edible film, increasing RH gradient increased WVTR [29]. Same trend was observed for WVP but not as high as in the WVTR. The effect of temperature on WVTR was represented on Figure 33. WVP values at 15, 25 and 37°C were not significantly different ($p>0.05$) for all RH gradients (Tables A13 and A14). RH

gradient significantly affected ($P<0.05$) the WVP values (Tables A15 and A16). During the preparation of pestil, starch was gelatinised and pestil contains high amount of sugar (87.6%), lower porosity and lower diffusivities were obtained by addition of sugars or gelatinisation of starch materials [27, 63]. The WVP of the pestil was lower than WVP's of peach, apricot, apple, and pear puree edible films (4.18, 4.29, 5.83, and 7.77 g.mm/ kPa.h.m^2, respectively) [64].

McHugh [64] reported that temperature had little effect on WVP due to strong penetrant/ polymer interactions. However, WVP of most edible films have been strongly affected by relative humidity and temperature [29, 62] as in case of this study. A large increase of WVP has been frequently observed in high water activity ranges [29, 44]. In the results of pestil, it can be noted that WVP was strongly dependent on relative humidity in the studied range, and like WVTR, effect of temperature increased the effect of relative humidity on WVP.

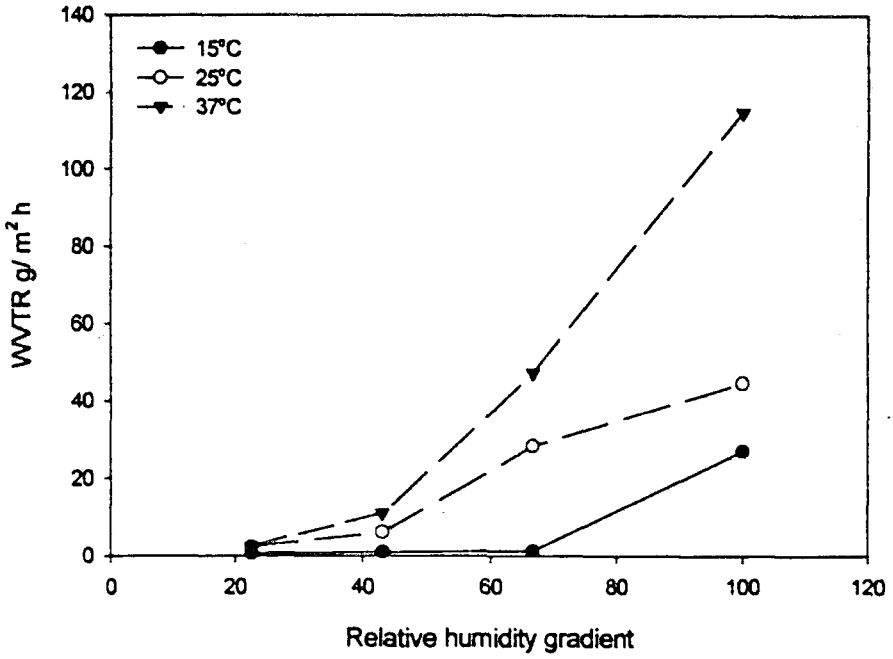

Figure 33. Effect of relative humidity gradient on WVTR of pestil at different temperatures studied.

Krochta and De Mulder-Johnston [33] reported that starch films have moderate oxygen barrier properties but are poor moisture barriers, and their mechanical properties are generally inferior to synthetic polymer films. The results of this study showed that the films have water barrier properties as in acceptable level when compare to WVP of films presented in Table 3 (Chapter 1). The addition of grape juice and gelation of starch during cooking might improve the water barrier property of starch used in this study. Since the pestil is well known and consumed widely in our country, the water barrier property might provide useful information for coating nuts with pestil solution prior to drying. Mechanical property and gas barrier properties must be studied and also some possible additives can be applied for improving water barrier property in later studies.

3.7. Application of Pestil to Pistachio nut

Pistachio nut samples were coated with pestil, and placed in desiccators containing different saturated salt solution to provide different relative humidity environment (33, 55, and 76 % RH) at 15°C. Weight (water) gain or loss from the samples coated with pestil with respect to time were represented in Figure 34. It can be seen from Figure 34 that coated pistachio nut did not gain or loose water at 55 % RH, means that the water activity of coated pistachio nut was around 0.55. From the plot, it was also understood that increasing RH increased the weight gain in a higher rate than decreasing RH although increasing and decreasing RH from 0.55 at the same level (difference in RH was around ± 0.2). It is important to note that if the pestil coated pistachio nut (sucuk) kept at 55 % RH, the weight of the sucuk will be kept constant.

Some of the sucuk samples kept over the deionised water in desiccator at 15°C to provide 100 % RH (data not shown). Weighting could not be possible due to the destruction of structure. From this observation, it was possible to report that keeping at high RH caused the softening and melting of the sucuk samples.

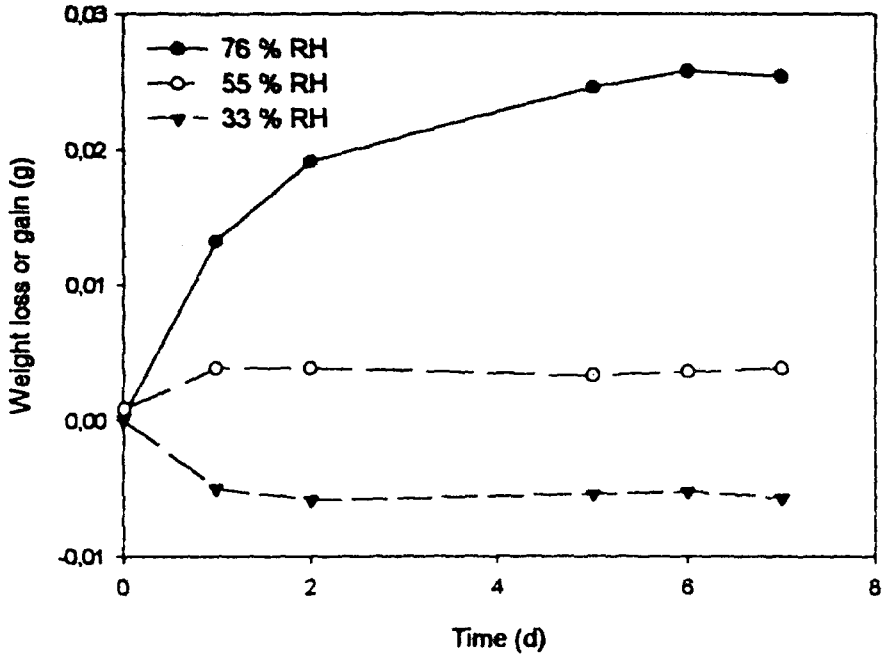

Figure 34. Water loss or gain at 15°C from pistachio nut coated with pestil.

CHAPTER IV

CONCLUSIONS

The study of production of pestil from boiled grape juice-starch mixture and drying and water vapour permeability of grape pestil revealed the following conclusions:

1. The optimum starch to fresh grape juice ratio was 4/100 with respect to easy spreadabilityi drying and good appearance
2. Hunter colour parameters (L, a, b) significantly changed during grape juice boiling
3. Drying time, sample thickness and air temperature influenced moisture content of pestil during drying
4. Air velocity was not very effective on drying of samples
5. Almost all samples dried in the falling rate drying period
6. Sun drying took longer time than hot air drying that is a risk for microbial growth
7. Fick's model of water diffusion fitted all experimental data with acceptable correlation coefficients
8. Hunter a-value was the most sensitive parameter during both air and sun drying

9. Colour change reactions followed a zero order reaction kinetics
10. Both diffusivity values and Hunter colour parameters followed an Arrhenius-type temperature dependence
11. WVTR and WVP of pestil were strongly affected with the changing relative humidity gradient
12. Temperature had no effect on WVP values
13. Thickness of the pestil was around 0.6 mm. After exposure to high RH environment, thickness of the films were increased, showing the adsorption of water by the film itself
14. Weight of pestil coated pistachio samples were increased or decreased as the RH of the environment increased or decreased from 55 % RH.

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APPENDICES

Table A1. Analysis of variance (3-way) for moisture content of pestil by drying temperature, time and sample thickness.

Source	Sum of Squares	D.f.	Mean Square	F-ratio	P-value
Main effects:					
Temperature	0.0812	2	0.5406	40.04	0.0000
Thickness	3.3452	3	1.1151	82.60	0.0000
Time	31.4067	9	3.4896	258.48	0.0000
Residual	1.4175	105	0.0135		
Total (Corrected)	37.2507	119			

All F-ratios are based on the residual mean square.

Table A2. Multiple range tests for moisture content by temperature (Method: 95 % LSD).

Temperature (°C)	Count	Least Squares Means	Homogeneous Groups*
75	40	0.5814	A
65	40	0.6802	B
55	40	0.8131	C

* Different letters in the last column denote significant difference.

Table A3. Multiple range tests for moisture content by pestil thickness (Method: 95 % LSD).

Sample thickness (mm)	Count	Least Squares Means	Homogeneous Groups*
0.71	30	0.4798	A
1.53	30	0.5961	B
2.20	30	0.7731	C
2.86	30	0.9172	D

* Different letters in the last column denote significant difference.

Table A4. Multiple range tests for moisture content by drying time (Method: 95 % LSD).

Drying time (min)	Count	Least Squares Means	Homogeneous Groups*
120	12	0.1385	A
100	12	0.1852	AB
80	12	0.2564	B
60	12	0.3780	C
50	12	0.4661	C
40	12	0.5858	D
30	12	0.7726	E
20	12	1.0250	F
10	12	1.3301	G
0	12	1.7778	H

* Different letters in the last column denote significant difference.

Table A5. Analysis of variance (One-way) for moisture content of pestil by velocity for S_1.

Source	Sum of Squares	D.f.	Mean Square	F-Ratio	P-Value
Between Groups	0.0018	2	0.0009	0.00	0.9971
Within groups	8.6151	27	0.3191		
Total (Corrected)	8.6171	29			

Table A6. Multiple range tests for moisture content by air velocity for S_1 (Method: 95 % LSD).

Air Velocity (m/s)	Count	Mean	Homogeneous Groups*
0.86	10	0.3561	A
1.27	10	0.3561	A
1.82	10	0.3729	A

* Different letters in the last column denote significant difference.

Table A7. Analysis of variance (One-way) for moisture content of pestil by velocity for S_2.

Source	Sum of Squares	D.f.	Mean Square	F-Ratio	P-Value
Between Groups	0.0461	2	0.0230	0.07	0.9320
Within groups	8.8290	27	0.3270		
Total (Corrected)	8.8752	29			

Table A8. Multiple range tests for moisture content by air velocity for S_2 (Method: 95 % LSD).

Air Velocity (m/s)	Count	Mean	Homogeneous Groups*
1.82	10	0.4181	A
1.27	10	0.4670	A
0.86	10	0.5142	A

* Different letters in the last column denote significant difference.

Table A9. Analysis of variance (One-way) for moisture content of pestil by velocity for S_3.

Source	Sum of Squares	D.f.	Mean Square	F-Ratio	P-Value
Between Groups	0.1042	2	0.0521	0.16	0.8506
Within groups	8.6457	27	0.3202		
Total (Corrected)	8.7005	29			

Table A10. Multiple range tests for moisture content by air velocity for S_3 (Method: 95 % LSD).

Air Velocity (m/s)	Count	Mean	Homogeneous Groups*
0.86	10	0.5500	A
1.27	10	0.6583	A
0.1.82	10	0.6869	A

* Different letters in the last column denote significant difference.

Table A11. Analysis of variance (One-way) for moisture content of pestil by velocity for S_4.

Source	Sum of Squares	D.f.	Mean Square	F-Ratio	P-Value
Between Groups	0.0488	2	0.0240	0.08	0.9199
Within groups	7.88662	27	0.2913		
Total (Corrected)	7.9150	29			

Table A12. Multiple range tests for moisture content by air velocity for S_4 (Method: 95 % LSD).

Air Velocity (m/s)	Count	Mean	Homogeneous Groups*
1.82	10	0.7371	A
0.86	10	0.8170	A
1.27	10	0.8274	A

* Different letters in the last column denote significant difference.

Table A13. Analysis of variance (One-way) for WVP of pestil by temperature.

Source	Sum of Squares	D.f.	Mean Square	F-Ratio	P-Value
Between Groups	70.75	2	35.37	0.997	0.4063
Within groups	319.30	9	35.47		
Total (Corrected)	390.05	11			

Table A14. Multiple range tests for WVP of pestil by temperature (Method: 95 % LSD).

Temperature (°C)	Count	Mean	Homogeneous Groups*
15	4	3.17	A
25	4	5.64	A
37	4	9.09	A

* Different letters in the last column denote significant difference.

Table A15. Analysis of variance (One-way) for WVP of pestil by RH gradient.

Source	Sum of Squares	D.f.	Mean Square	F-Ratio	P-Value
Between Groups	276.28	3	92.09	6.449	0.0158
Within groups	114.24	8	14.28		
Total (Corrected)	390.52	11			

Table A16. Multiple range tests for WVP of pestil by RH gradient (Method: 95 % LSD).

RH Gradient	Count	Mean	Homogeneous Groups*
23	3	1.8596	A
43	3	2.2856	A
67	3	5.9003	A
100	3	13.8200	B

* Different letters in the last column denote significant difference.

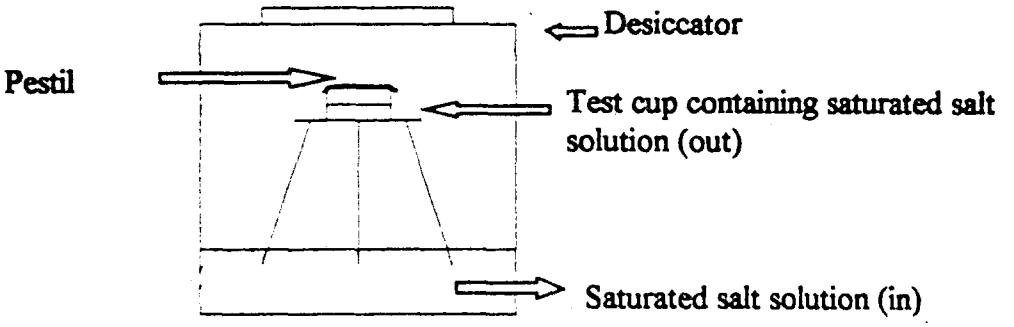

Figure A 1. Schematic representation of water vapor permeability experiment.

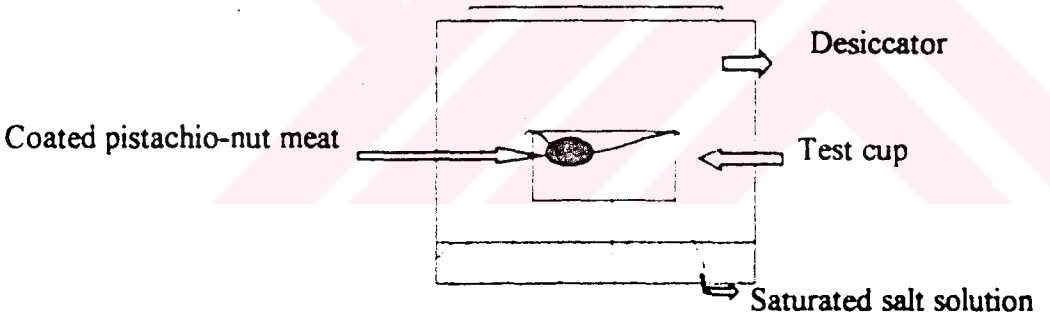

Figure A 2. Schematic representation of placing coated pistachio-nut meat into desiccator