FREEZE-DRYING KINETICS AND DIFFUSION MODELING OF HAWTHORN

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I certify that in my opinion the thesis submitted by Khaled Ali HAGIG titled “FREEZE-DRYING KINETICS AND DIFFUSION MODELING OF HAWTHORN” is fully adequate in scope and in quality as a thesis for the degree of Master of Science.

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“I declare that all the information within this thesis has been gathered and presented in accordance with academic regulations and ethical principles and I have according to the requirements of these regulations and principles cited all those which do not originate in this work as well.”

Khaled Ali HAGIG

ABSTRACT

M. Sc. Thesis

FREEZE-DRYING KINETICS AND DIFFUSION MODELING OF HAWTHORN

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This study has been carried out to test freeze-drying (FD) technology, which has been used in the recent years for preserving different food products' beneficial flavors because it reportedly extends their shelf life; so, this approach is considered as the healthiest drying procedure. Hawthorn is a commonly used food product, which needs drying to preserve its rich potassium and fiber contents. A freeze dryer brand, which is widely used for experimentation, is Scanvac Coolsafe model of the Labogene brand. First, 100g sliced hawthorn was frozen and placed in a drying freezer to start the drying process, and kinetic models were conducted by registering the loss of weight during the drying process. The total freeze-drying experimentation duration was 14 hours, and after every two hours, the weight of the hawthorn sample was measured besides calculating the sample's moisture ratio. Several mathematical models have been presented in the literature to assess the agrarian plants' drying properties; however, eight specific models are suitable for processing the experimental data obtained during and after drying hawthorn using MATLAB. Results clearly depict that the root mean square error (RMSE) and the lowest chi-square (X^2) values were 0.011063 and 1.959 x 10^{-4}. Additionally, the highest determination coefficient (R^2) value was 0.9987, which is almost 1. The best model, in this context, is the Diffusion approach model, which has provided these results that were the best for all the eight models. The specimens' effective diffusivity was $2.33742 \times 10^{-10} m^2/s$.

**Keywords : ** Freeze-Drying, drying kinetics, drying of hawthorn, kinetic drying model, diffusion approach model

Science Code : 92808

ÖZET

Yüksek Lisans Tezi

ALIÇIN DONDURULARAK KURUTULMA KİNETİĞİ VE DİFÜZYON MODELLEMESİ

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Bu çalışma, son yıllarda farklı gıda ürünlerinin faydalı aromalarını korumak için kullanılan dondurarak kurutma (FD) teknolojisini test etmek için yapılmıştır çünkü söylendiği üzere dondurarak kurutma raf ömrünü uzatmakta ve dolayısıyla bu yaklaşım en sağlıklı kurutma süreci olarak kabul edilmektedir. Alıç, zengin potasyum ve lif içeriğini korumak için kurutulması gereken yaygın olarak kullanılan bir gıda ürünüdür. Deney yapılması bakımından olarak yaygın olarak kullanılan bir dondurarak kurutma markası olan Labogene markasının Scanvac Coolsafe modeli kullanılmıştır. İlk olarak 100 gr. dilimlenmiş alıç dondurulmuş ve kurutma işlemini başlatmak için kurutma dondurucusuna konulmuştur. Kurutma işlemi sırasındaki ağırlık kaybı kaydedilerek kinetik modeller yapılmıştır. Toplam dondurarak kurutma deney süresi 14 saat olup, her iki saatte bir alıç numunesinin nem oranını hesaplanmanın yanı sıra numunenin ağırlığı da ölçülmüştür. Tarım bitkilerinin kuruma özelliklerini değerlendirmek için literatürde çeşitli matematiksel model sunulmuştur; bununla birlikte, MATLAB kullanılarak alıç kurutulması sırasında ve sonrasında elde edilen deneysel verilerin işlenmesi için sekiz özel model uygundur. Sonuçlar, kök ortalama kare hatası (RMSE) ve en düşük ki-kare (X^2) değerlerinin 0.011063 ve $1.959 x 10^{-4}$ olduğunu açıkça göstermiştir. Ayrıca en yüksek determinasyon katsayısı (R^2) değeri 0.9987'dir, ki bu değer yaklaşık olarak 1 ‘dir. Bu bağlamda en iyi model, sekiz modelin tümü için en iyi olan bu sonuçları sağlayan Difüzyon yaklaşım modelidir. Numunelerin etkin yayılma katsayısı $2.33742 \times 10^{-10} m^2/s$ olarak bulunmuştur.

Anahtar Kelimeler : Dondurarak kurutma, kurutma kinetiği, alıçın kurutulması, kinetik kurutma modeli, difüzyon yaklaşım modeli

Bilim Kodu : 92808

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SYMBOLS

a, b, c, n : Dimensionless drying constants in the models used
DR : Drying rate (g water/g dry matter)
D_{eff} : The effective diffusivity (m)
G : Gibbs energy (kJ)
H : Enthalpy (kJ)
h_1 : Specific enthalpy of the refrigerant at the compressor inlet, (kJ / kg)
h_2 : Specific enthalpy of the refrigerant at the compressor outlet, (kJ / kg)
h_3 : Specific enthalpy of the refrigerant at the condenser outlet, (kJ / kg)
h_4 : Specific enthalpy of the refrigerant at the evaporator inlet, (kJ / kg)
H_{sub} : Sublimation latent heat (kJ / kg)
k, k_0, k_1 : Drying rate constants in the models used, (min^{-1})
L : Half-thickness of samples (m)
m : Mass flow rate, (kg / s)
M_a : Molecular weight of air in the drying cell, (kg / mol)
MC : Moisture content (g water/g dry matter)
M_d : The final equilibrium moisture content (g water/g dry matter)
M_0 : The initial moisture content (g water/g dry matter)
MR : The moisture ratio (dimensionless)
MR_{exp} : Experimental moisture ratio
MR_{pre} : Predicted moisture ratio
M_t : The moisture content at a time t (g water/g dry matter)
N : Number of observations
P_{atm} : Atmospheric pressure, (Pa)
P_{ev} : Evaporation pressure, (Pa)
P_a : Air pressure in the drying cell, (Pa)

Q_C : Condenser capacity, (kW)

Q_E : Evaporator capacity, (kW)

Q_L : Absorbed cooling load by the evaporator from the cooled environment, (kW)

R : Gas constant (J / mol)

RMSE : Root mean square error

R^2 : Coefficient of determination.

S : Entropy, (kJ / K)

S_v : Vacuum pump speed, (m / s)

T : Temperature (^{0}C)

T_k : Temperature (k)

$T_{k.vc}$: Absolute temperature (k) of the vacuum chamber (drying cell)

t : Time (min)

t_{ev} : Evaporation time, (s)

V_f : Free volume of the drying cell, (m^3)

W_C : Compressor power, (kW)

χ^2 : Reduced chi-square

z : Number of drying constants in the model

η : Vacuum pump efficiency

ρ_a : The density of the air in the drying cell, (kg / m)

ABBREVITIONS

FD : Freeze-drying technique

PART 1

INTRODUCTION

It is not easy for us to get foodstuff whenever we want. In such cases, the goods produced during the abundance period of the commodity must be kept in a good condition for a long period of time and can be used when prerequisite. Many techniques are used to store foods for a long time and drying is one of these strategies. Drying is the act to extract the water which exist in the product. It is mainly used in the food sector, medicine, pharmacy, paint industry, agriculture sector, furniture sector and paper industry. The sun drying is the traditional method used in food industry. It is the most commonly used and cheapest food preservation method. Drying of many products in Turkey is made naturally by laying the sun. However, with the sun drying method, the product dries in a longer time with poor quality. As well as, at this method, unwanted bacteria are formed in the product and unwanted microbiological deterioration occurs. Moreover, direct exposure to the sun increases the amount of radiation in the product and its presence in the open-air damages the product by volatile insects.

An important approach that enables food to be dried with a special method is freeze-drying technique. It is the technique that is used in this study to dry hawthorn fruits. In this experimental study, we will use about 100 g of hawthorn where the fruit will slice and place inside containers and 7 sliced hawthorn samples will be prepared by using SCANVAC COOLSAFE device, at a temperature of -55° C and vacuum pressure up to 0.01 kPa, for a period up to 14 hours.

Hawthorn (or Crataegus) belongs to a significant family of plants called the Rosette family (or Rosaceae), which is a native plant for Northern Hemisphere (Asia, North America, and Europe). The number of species belonging to this genus is estimated to be about 200 and the number varies according to different scientific classifications.

Many colors of this nice mature fruits (yellow, green, red and dark purple) are available in Turkey and they are spherical in shape. Hawthorn fruit mostly ripe during the early days of mid-autumn. Hawthorn fruit has several proven health benefits such as protection against cardiovascular issues, hypercholesterolemia and hypotension. It has been used in medicine for a long time. The Turkish wild hawthorn showed plenty of beneficial minerals including potassium, calcium, sodium and magnesium.

In freeze-drying technology, food is firstly frozen with chemical dehumidifier or low temperature condenser and then, the high vacuum is taken with the connection to the applied volume. Heat transfer is provided to the frozen food by conduction. Meanwhile, the water in the solid phase evaporates (sublimation) and the drying process takes place. During the freeze-drying process, it is inevitable to have some amount of water in an unfrozen state called bound water in every food item. However, the very low transition temperature in the moist region where this water is located increases the quality of the dried product considerably. The existence of sufficient amount of frozen water in the substance to be dried is very important for freeze drying. Provided that they are processed correctly, many products can be stored for a long time until they are used, preserving their initial physical, chemical, biological, and organic properties. In order to obtain a product with as much pre-drying structure and appearance as possible, freeze-dried products are usually dissolved in the original amount of water or solvent that they originally contained. Food Vacuum freeze dryers are always used for foods, vegetables, and spices, as well as for marine products, for instant food, and finally for specialty products. Consumer demand is increasingly growing because the consistency of the freeze-drying goods is consistent with the green climate at present and is convenient and healthy. As we mentioned above, this process reduces the internal humidity of foodstuff such as meat, vegetables, and fruits, all of which makes them maintain the correct system of dried products. There is no need to keep freeze-drying goods cooling and can be stored at natural temperature for a long period, which means the same after soaking similar to the fresh materials and therefore it is very common with consumers.

Freeze drying technology is especially used in instant coffee production and is known as the food technology that best preserves the aroma of coffee. In addition, freeze drying products are used in many areas such as pharmaceuticals, pharmaceutical industry, bacteria cultures, fruit juices, vegetable and tea extracts, meat and milk drying, etc. Freeze drying is an expensive process and suitable for heat sensitive materials. With freeze drying, a better-quality dried product is obtained compared to other drying methods. Freeze-drying technology have many features including extend the shelf life of product, decrease its weight and avoid the need for additional storage process such as cooling. There are many purposes for drying applied to foodstuffs, and perhaps the most apparent of these is to avoid product spoilage during long time storage. At the end of the drying process, by reducing the humidity of the product to an appropriate amount to decrease microbial growth or other reactions, the product can be preserved for a long time without being spoiled. In addition, quality characteristics such as scent and nutritional value are maintained by reducing the product's moisture content. At the same time, it improves productivity in the transport and storing of food by reducing the size of the product at the end of the drying process. It must be mentioned that there is no study has been conducted to determine the kinetic model of hawthorn fruit. Our study aims to determine suitable kinetic drying model and effective diffusivity for a freeze-dried hawthorn and to observe the loss of weight while freeze-drying hawthorn.

PART 2

LITERATURE RESEARCH

It is hard to acquire food in all seasons, as it is said. For this, it is important to ensure that these items are stored for a long period when there are plenty of foods. The drying technique is the process that guarantees the long-term storage of foods to be used in need. Foods may include all sorts of vegetables, meat, and milk, as well as fruits such as hawthorn that was used in this study by using the freeze-drying technique. Many methods are used for drying foods. Studies on these drying methods are given below.

2.1. DRYING WITH SOLAR ENERGY

Kholliev et al. (1982) built a drying hothouse of 50 x 5.86 m in order to dry crops in the summer and grow vegetables and seedlings in other seasons. They divided the hothouse into two parts with a partition in the east-west direction. They painted the base of the south-facing section black, and the drying process provided by radiation and convection. Drying of the products in the northern part was carried out by transporting the air heated in the other section [1].

Özel and Özil (1987) dried apricots, grapes and peppers under natural conditions, using solar energy at the exhibition and using an indirect type cupboard sun dryer with hot airflow. As a result of the experiments, it was found that apricots were dried in 7 days, grapes in 10-15 and peppers in 5-10 days under natural conditions; In controlled conditions, it was observed that apricots, grapes and peppers dried in 2, 5, 3 days respectively by reducing to the targeted moisture amount in a sunny dryer [2].

Güner (1991) used a shelf-trope sunny fruit dryer to determine the airflow rate of 10, 20, 40, 60, 80, 100, 200 and 400 l / s, the drying time, drying speed, and air and temperature values needed for drying apricots. As a result of the experiments; it has been found that the drying time decreases as the air temperature increases, the mass transfer increases and the drying time decreases, the drying speed increases, the air flow properties are more effective than the solar radiation in the rack dryers [3].

The drying characteristics of chili pepper were studied by Tunde-Akintunde using sun and solar drying. Chilli pepper was pre-treated by blanching water and steam and soaking in 60 and 70 ° brix osmotic solutions. Chilli pepper was taken untreated as a control. The pretreated chilli pepper dried quicker than the untreated chilli pepper, although in the dropping rate era the drying of both samples took place. To pick an appropriate drying equation, four thin-layer drying models (Newton, Henderson and Pabis, Logarithmic and Page) were attached to the experimental results. In order to better explain the drying actions of chili pepper for sun and solar drying, the Page model was discovered [4].

Yağcıoğlu et al. (1991) studied the drying characteristics of bay leaf under different drying conditions. They saw that when faced with unsuitable weather conditions in the sun drying method, losses occur and unfavorable situations such as long drying time occur. They have observed that drying under controlled conditions eliminates many problems compared to conventional drying. They stated that there is no loss in the basic oil composition amounts and quality of bay leaves with drying at 50 ° C or 60 ° C. They also stated that the drying time of the moisture content leaves up to 10% was shortened 120 times compared to the traditional drying process or 8 times compared to drying conditions at 40 ° C, and there was no loss [5].

Olgun and Rzayev (2000) experimentally investigated the drying of hazelnuts with solar energy in three different systems, cabinet type, cupboard type and tent type. In the systems, it was determined that hazelnut dries in the open air for about 82 hours; 28 hours if additional heater is used in cabinet type dryer, without additional heater is used they found that hazelnuts dried with only solar energy in 50 hours in the first case, in 73 hours in a tent-type dryer, in 72-76 hours in a cupboard type dryer. When the samples taken from the dried hazelnuts were also subjected to taste analysis, they did not find any deterioration in the products. They saw that the drying time was considerably shorter when additional heater is used in the system [6].

Sarsılmaz et al., stated that drying apricot is usually carried out by laying on wide soil floors, moreover, the drying time is prolonged, homogeneous drying is not achieved, it causes product loss and quality loss. The specially designed air solar collector with increased convection effect and rotary column cylindrical dryer has been developed. The system consists of three parts. These; blowing zone (fan), air heating zone (collector), drying zone (dryer room). Thus, the moisture changes of dried apricots in the dryer were compared and as a result of experiments, it has been determined that the moisture content of apricots decreases to 25% within 4 days and on the other hand, in the rotary column cylindrical dryer, it decreases to the same humidity in about 2 days [7].

El-Sebaii et al. (2002) dried seedless grapes, figs, apples, tomatoes, onions and peas in a solar indirect dryer. The area of the solar collector where they are used to heat the drying air is 1 m^2, the absorber surface is black painted 2 mm thick copper plate, the cover material of the collector is 5 mm made of thick glass. The gap between the glass and the absorber surface is 8 cm. 8 cm thick insulation material was used to prevent heat loss from the rear surface of the collector. The prototype drying cabinet is manufactured in 1x1x1.5 m dimensions, the 5 cm long chimney, painted black, is attached to the dryer to speed up natural circulation. A wire mesh attached to an aluminum frame of 0.855 x 0.8 m in length have formed. The air heated in the collector directly enters the drying chamber. The 0.1 m thick part between the absorption surface of the collector and the isolation material is heated to continue drying even at night conditions. The storage was also filled with materials such as clay, granite and sand, and drying trials were made. In their experiments with tomatoes, they determined that cut dried tomatoes reached 7% moisture content within 28 hours. The dryer unit they prepared is suitable for drying the agricultural products they have examined in the experiments in the range of 45-55 ° C, using heat storage material helps to decrease the humidity during the night, and if the system is used at full capacity, the places of the trays should be changed after a certain period of time for a homogeneous drying, and large materials should be cut into pieces. They stated that it should be separated and dried [8].

Tarhan et al. (2003) by calculations, found that the average temperature of the ambient air should be increased by 3 ° C in September and 6 ° C in November for a successful corn drying process in Tokat region. This result indicates that it is very difficult to dry fruits and vegetables in outdoor exhibitions in the Tokat region, reveals the necessity of using dryers for drying. They suggested the use of solar dryers in terms of both reducing drying costs and ease of use [9].

Midilli and Küçük (2003) studied the mathematic models of drying behavior of shelled and unshelled pistachio samples in a natural and forced solar dryer. Eight different mathematical energy models were used in order to find the appropriate solar drying model. The models used are semi-theoretical and experimental. Semi-theoretical and experimental models were compared by nonlinear regression analysis using Statistica Computer Program, they chose the most suitable model according to chi-square and correlation coefficients [10].

Aktaş et al. (2004) examined the applicability of solar drying systems to hazelnut drying. Researchers argue that hazelnuts cannot be dried at international standards in Turkey that leads to market share loss. And in their study, they designed a solar-powered hazelnut drying oven with low energy cost and temperature, weight and humidity control. In the study, they stated that the producers preferred drying ovens with low initial investment and low energy costs [11].

Tarhan et al. (2007) stated that none of the dryers used commercially today can provide the most economical and highest quality drying process together. In this study, the success criteria have expected from solar dryers and the factors related to the dried product quality are explained. Necessary data on dryer design and practical rules related to solar dryer design are tried to be given. They explained the work that the manufacturer should do for the economical and long-term use of solar dryers [12].

Aktaş et al. (2005) modeled the heat pump industrial hazelnut drying oven considering the hazelnut drying conditions. With the modeling, they stated that while less energy was consumed by using solar energy on sunny days, the continuity of the drying process could be provided with the help of a heat pump at other times [13].

Doymaz (2005) examined the drying of figs by laying them in the sun. Samples with a diameter of 5.42 cm and a weight of approximately 50.2 g were used in the study. Approximately 300 g of sample was placed in the tray as a single layer during drying and drying was performed. Experiments were carried out at 35 and 47 ° C. Seven different models were used to explain the drying behavior of figs, one of them was Verma et al. This model was found to be suitable for experimental data. According to the Verma et al model results; R^2 0.9944, χ^2 0.000483 and RMSE 0.062857. The effective moisture diffusion coefficient was calculated as 2.47x 10^{-10}m²/ s [14].

Mutlu and Ergüneş (2008) researched the drying conditions of tomatoes, which are produced intensively in Tokat, in different periods with a shelf-type sunny dryer for the drying of agricultural products using solar energy. The dried tomatoes were examined in terms of color, and it was observed that the change in color increased with the prolongation of the drying time. It has been determined that the tomato samples on the upper shelves are more exposed to oxidation reactions that cause changes in colors by reacting with oxygen in the air, as they dry longer and lose moisture more slowly [15].

2.2. DRYING WITH HEAT PUMP

Ceylan et al. (2005) experimentally investigated the use of a heat pump drying oven for apple drying. In this study, they ensured that the humidity of the system air was decreased by taking the outdoor air with lower relative humidity into the system with the adjustable cover (damper). They dried apples at 40º C, average relative humidity of 20%, air speed of 2.8 m / s, moisture content of 4.8 (g water / g dry matter) to 0.18 (g water / g dry matter) in 3.5 hours. The researchers stated that the heat pump drying system they built in regions with low relative humidity could work efficiently. They found the water activity value of apples after drying as 0.65. Thus, they found that the activities of some toxigenic molds and toxin production were prevented due to the low water activity in apples [16].

2.3. VACUUM DRYING

Jaya and Das (2003) vacuum dried the mango pulp. During drying, 30-50 mmHg absolute pressure, 2, 3, 4 mm pulp thickness and 65, 70, 75°C heating surface temperature values in the vacuum chamber were taken into consideration. They stated that the color change of pulp made from mango powder depends on pulp thickness rather than the heating surface temperature. It is stated that in vacuum drying, the heating surface temperature in the vacuum chamber should be 72.3°C and the pulp thickness should be a maximum of 2.6 mm in order to minimize the color change [17].

Jaya and Das (2004) in vacuum drying of mango pulp; investigated the effects of maltodextrin (MD), glycerol monostearate (GMS), and tricalcium phosphate (TCP) on dried mango powder properties. The desired 710-730 mmHg vacuum in the system (30-50 mmHg absolute pressure), 3.7 kW, 0.0236 m^3/ h capacity aqueous vacuum pump was used. Considering the properties such as adhesion degree, fluidity and color, the optimum feeding composition was obtained by mixing 0.43-0.57 kg maltodextrin into 1 kg solid mango. The optimal condition for tricalcium phosphate and glycerol monostearate was 0.015 kg per 1 kg solid mango [18].

Cui et al. (2004) dried the carrot slices with microwave vacuum and developed a theoretical model. Carrots sliced to 3-5 mm; they were dried at 336.5, 267.5, 162.8 W microwave powers and under vacuum of 30, 51, 71 mbar. Theoretical and experimental data have determined that the rate of drying is linear with the output power of the microwave and inversely proportionate to the latent water evaporation heat at vacuum pressure [19].

Madamba (2002) chose carrot for vacuum drying. The most suitable conditions for drying the carrot under vacuum is drying of 1.6 mm thick carrot slices at 68°C at 10 kPa pressure. During the drying of the carrot under vacuum, all features such as pressure, temperature, slice thickness have affected the final moisture content of the carrot to a large extent (90%). Average drying rate was affected only by product thickness. Moisture recovery rate and color are unaffected by any independent parameters and conditions [20].

2.4. FLUIDIZED-BED DRYING

Nitz and Taranto (2007) designed a pulsed fluidized bed (PFB) dryer to dry the seeds of fresh carioca beans. In this study, the kinetic parameters of Page's equation, which are air inlet temperature, airflow rate, and frequency of vibration, have been analyzed and developed. The only important variable was the inlet temperature of the air. Drying was done at 60ºC with conventional fluidization. No difference was observed between pulsed and conventional fluidisers. The fluid-dynamic assessment showed that the maximum pressure drop was approximately the same in both regimes. Whereas, under vibratory fluidisation the highest value is affected by the initial bed height [21].

Yüzgeç (2005) has developed two models for a batch fluidized bed drying process of baker's yeast (Saccharomyces cerevisiae), a biological product. The first model is the homogeneous mathematical dual model based on energy and mass balance. In this model structure, the bed temperature was found as a first order differential equation and its solution was made by the fourth order Runge-Kutta method in discrete time. The model was tested with the data obtained from the industrial fluidized bed drying process of baker's yeast. The second model consists of model equations that calculate the moisture fraction and temperature changes in the granule during drying. Moisture diffusion and temperature changes in the granule are described by second order parabolic nonlinear partial differential equations. Nonlinear partial differential equations are solved in discrete time using the Crank-Nicolson method. Considering the physical changes in the structure of the granules that are dried during drying, the model has been developed as a shrinking granule-based drying model [22].

Vitor et al. (2004) aimed to find the heat and mass transfer coefficients of the biological product "tapioca" depending on the gas and solid phases of the drying process in a batch fluidized bed dryer. They developed a math dual model by considering three phases, one solid and two liquid phases, and evaluated the results [23].

Topuz et al. (2004) made a numerical and experimental study of drying hazelnuts in a fluidized bed. In their study, they compared numerical and experimental results and determined that numerical values were close to experimental results [24].

Romero et al. (2004) investigated the viscoelastic parameters and rehydration capacities of mango in fluidized bed and convection tray dryer. First, the mango was peeled, cut into small 6 mm (± 3 mm) cubes and processed with osmotic solutions before drying. $CaCl_2$ was added to the main structure using glucose osmotic solutions. It has been observed that the melts at $40^{\circ}C$ ($\pm 0.9^{\circ}C$) are ideal for 6 hours for osmotic processing of mango cubes before the process. The squeeze release tests have been shown to work well on mangoes rehydrated using the two element Maxwell method. They found that tray dried mangoes spread the compressed stream faster than mangoes dried in a fluidized bed dryer. They observed that both pre-drying treatment and drying type affect the shrinkage-shrinkage efficiency of mangoes. It has been presented that several equations can predict the shrinkage efficiency as a function of the moisture content of mangoes. As expected, the minimum fluidization speed of the pretreated mango cubes was higher than the air velocity for the non-pretreated samples [25].

Temple et al. (2000) a resistance study was carried out for fluidized bed tea drying. In their studies, they designed controller forms. Under normal operating conditions, it was possible to tune these controllers using a transfer function estimated from the frequency conduct of a validated simulation model. A number of operational conditions that deviated from the normal conditions is analyzed in this work. Over the spectrum of conditions tested, controller tuning calculated by the Cohen & Coon or Ziegler-Nichols methods was not found to be robust. They have developed a different method based on desiccant modeling to make a series of controller settings that give a minimal integral square error. They have determined that these settings are suitable for all conditions tested. They have shown that a simplification is validated for the controllers using only the gains, rather than all transfer functions in the inferential calculator [26].

Soponronnarit et al. (1999) described drying rice in a fluid bed in Thailand. In this study, a mathematical model of a fluid bed rice dryer is developed. Fluid bed rice dryer is completely commercial in many countries and creates an economical market. He stated that although rice quality is provided especially for grains with very high moisture, energy consumption is relatively low [27].

Hajidavalloo and Hamdullahpur (1999) made the hydrodynamic and thermal analysis of the fluidized bed drying system. They established the experimental setup of the fluidized bed drying system and determined that it was in good harmony by comparing the experimental results with the three-phase mathematical model they developed. They observed that the three-phase model gave realistic results compared to the two-phase models [28].

Hajidavalloo (1998) has investigated the characteristics of granular material in the fluidized bed drying process. The experimental work was carried out in a laboratory-sized fluidized bed system. He studied how the changes caused by the circulating air of the distributor screen and the moisture content of the particles at the inlet would affect the hydrodynamics of the fluidized bed. In the theoretical part, a mathematical model is developed to simulate heat and mass transfer in a fluidized bed and nonlinear partial differential equations without correction parameters are obtained. As a result of the solution, it was determined that there is a very good agreement between the developed model and the experimental data. It has been determined that this model can also be used in the sprayed and still bed, in the fluid bed drying process, each characteristic spindle, air velocity, particle diameter etc. He determined how effective it was and also made studies on how to increase the thermal efficiency of the fluidized bed [29].

Soponronnarit et al. (1997) investigated the drying characteristics of maize in a batch fluidized bed dryer. In order to increase the thermal efficiency of the bed, they recycled some of the air released back to the fluidized bed. By comparison with the experimental results, they tried many experimental thin layer drying equations and found that the Wang and Singh equation gave good results [30].

Kiranoudis et al. (1997) have developed a method to optimize the total cost of each fluid bed and rotary dryer according to the production capacity. They used a simple mathematic auxiliary model to determine the convection drying process for both dryers. When the design structure of the dryers was examined, they stated that the rotary dryer is quite expensive compared to the fluidized bed dryer [31].

Grabowski et al. (1997) experimentally investigated the drying process of yeast in a laboratory-scale fluidized bed and spouted bed dryers. They determined that the spouted bed needs 25% more air than the fluidized bed. In addition, in this study, they determined that the spouted bed or the fluidized bed and the spouted bed combination was better than the fluidized bed alone in terms of fluidization, spraying behavior, drying kinetics, and calculations [32].

Albini et al. (2018) the principle of this experiment is to dry the barley by means of a fixed bed dryer. The first two methods were to reverse the airflow every 10 minutes and the second was to introduce a conventional airflow, while preventing reflection, the moisture distribution along the fixed layer was measured and the effect of the initial moisture content and temperature on the drying data. The air temperature during the drying process was (40° C and 50° C), with the air velocity constant (4.0 m / s), with initial moisture contents in three patterns (25%, 20% and 13.5% were moist content). During fixed bed height, the rates for drying were variable. This was expected. With regard to the higher initial moisture content of the grains, the heterogeneity of the process was found to be higher than that of the grains with lower initial moisture content. At 50° C, the use of reversible airflow in the drying process was shown to have better process uniformity, and the share of conventional drying was to improve energy performance. The results indicate the shortest time required to provide 12% moisture content at 50° C [33].

2.5. DRYING WITH TUNNEL TYPE DRYER

Johnson et al. (1998) in their studies on the air-drying characteristics of Plantain (Musa AAB), a banana variety, examined Plantain cylindrical parts of various thicknesses, drying behavior at different air temperatures, shrinkage and moisture distribution with a hot air dryer. As a result, they found the appearance methodology effect of air temperature and the thickness of the parts in drying rates. They determined that hot air has the greatest effect on drying behavior. They calculated the motion energy for air drying of the plantain as 38.81 kJ / g mol. By monitoring the changes in the volume and dimensions of the shrinking parts during drying, they defined the changes in volume with a core drying model very well and defined the changes in dimensions with linear moisture content. With this model, they have determined the local moisture content rather than the average moisture content in the food pieces, using it to give them an exact estimate of the susceptibility of food to rotting [34].

Boudhrioua et al. (2002) aimed to characterize the rheological properties of banana slices during the hot air drying process in their studies on the effect of maturity and air temperature on the changes in the structure during the drying of banana. They monitored firstly changes in fresh bananas during storage at chamber temperature and humidity, because the grade of maturity of fresh bananas has a direct effect on the rheological properties of the dried product. This research made it possible to establish the parameters that characterized fruit ripeness levels-humidity content, pulp sugar content, peel banana firmness (S) and peel color (a). Two associations in non-linear regression connected (S) and (a) to storage time. The glucose content and the safe moisture content values are often matched to avoid time consumption. Changes in rheological properties were monitored throughout the experiments with a penetrometer. As a result of this study, they determined that drying banana slices at 80ºC caused a radical change in banana fruits after 4, 6 or 8 hours, and banana's perishability and sudden fragility properties disappeared. As a result of the analysis of the thermal and thermodynamic properties of banana slices, they revealed that the banana showed a sudden change in the cooling transition temperature after drying [35].

Doymaz and Pala (2002) presented a theoretical and experimental study of drying red peppers under different process and air-drying conditions in their studies on hot air-drying characteristics of red pepper. They obtained the drying curves of the chipped peppers using the exponential equation and the Page equation. By comparing the R^2 values of both equations. They conclude that the equation that produces the good drying characteristics is the Page equation [36].

Arıcı (2006) determined the drying characteristics of mushroom (Agaricus bisporus) under different drying air temperature and air speed conditions. In the experiments, the air temperature was 50°C, 60°C and 70°C, and the air velocity was 1, 2 and 3 m / s. Newton, Page, Developed Page, Henderson and Papis, Logarithmic, binomial, binomial and exponential, Wang and Sign, Thompson, diffusion approach, Developed Henderson and Papis, Verma et al. and Midilli et al., models have been compared with each other. According to the results, Midilli et al., model has explained drying behavior of the fungus (Agaricus bisporus) better than others [37].

İzli (2007) has determined drying parameters in drying corn with hot air flow. As a result of the experiments, the best results are obtained from drying at 75°C in terms of drying time, energy consumption and cost in drying with and without agitators, while the best results in terms of germination speed and germination power are at 55° C in drying with stirring and 45°C in drying without stirring [38].

Akosman and Kalender (2004) examined the drying characteristic of soybeans in a tray dryer. In their experimental studies, they dried soybeans at different temperatures between 30° - 50° C and at different air flow velocities (0.5, 1.0 and 1.5 m / s) using a laboratory type tray dryer. They determined that the drying rate for all solid samples increased with temperature and air flow rate. They observed that solid moisture reached equilibrium humidity in a very short time at high temperatures. They analyzed the experimental data by solving the unsteady state diffusion equation [39].

Granella et al. (2019) in their study, the experiment of artificial drying with hot air convection was applied to corn and soybeans at temperatures (30, 40 and 50 degrees Celsius), as corn and beans are of great importance today, especially in biofuels and the food industry because of their vital and nutritional advantages. This was done by means of a central composite design (CCD). The effective diffusion coefficient, D_{eff}, has been adopted considering that it is thermodynamic properties and in two different ways by integrating ozone into the air for drying and also without combining both beans and corn. It was found that the CCD showed different D_{eff} values and during ozone drying (DOP) a numerical model was made in order to spread moisture during the process. It was also noted that the activation energy decreased from 43.90 to 35.20

kJ mol^{-1} for corn and 38.23 to 34.29 kJ mol^{-1} for soybeans when the drying air was ozone added. Enthalpy and entropy were the same. Thus, ozone drying can be useful in technological stages to improve the energy in steps that are after harvest [40].

2.6. DRYING WITH CABINET DRYER

Yılmaz et al. (1999) used a cabinet type drying system. This drying system consists of an air collector, drying chamber and air circulation system. 45 W of power generated from photovoltaic panels was used to run the fan to circulate the drying air. The air collector has an area of 27.50 m^2 and there are 8 shelves of 2.8 m^2 in the cabin. The capacity of the dryer is to take 25 kg of fresh tomatoes. Accordingly, the loading rate is around 9 kg /m^2. They stated that in this dryer, the moisture content of the material was reduced from 95% to 17% in 5 days during the drying season [41].

2.7. DRYING WITH MICROWAVE

Tuncer (1990) aimed in his research to determine the behavior and changes of the product when vegetables are placed under the effect of high frequency microwave magnetic field and to find the most suitable drying method experimentally. According to the results of the research, by selecting the appropriate microwave power level of leeks, red and green peppers, eggplants, onions and potatoes placed in the microwave area, without any loss of quality, with the arrangements that prevent the microwave and vegetables from reacting, he decided it was possible to dry in a shorter time, between 1 / 5-1 / 12, compared to heat drying [42].

Pappas et al. (1999) investigated the effects of product size on drying time and re-water absorption capacity in mushrooms dried by microwave oven equipped with vacuum apparatus. 25, 36 and 54 mm diameter in tests used mushrooms. According to the results of the experiments, they reported that the drying time decreased with the decrease in the sample size in drying at 425 W power level. They found that the re-water intake capacity was higher in the microwave drying method compared to conventional drying, and with the increase of time, the water intake rate of the product increased to a certain level and then remained unchanged [43].

During their study, Maskan et al (2001) studied the kiwi fruits' drying properties for 5:03 ± 0:236mm slices using microwave, hot air, and hot air-microwave combined method. They studied shrinkage, rehydration capacities and drying rates of the samples of kiwi. They found that microwave drying or drying using a combination of hot air and microwave drying increased drying rates, which significantly reduced drying time. Kiwi fruit showed greater shrinkage levels with microwave drying rather than hot air drying. When hot air was combined with microwave, lower shrinkage level was observed as compared to other drying processes. Finally, when kiwi slices were dried using microwave drying, a rapid water absorption rate and lower rehydration capacity were observed in comparison [44].

Özkan and Işık (2001) dried the apricot and cherry using a combination of microwave and hot air drying. Apricots with 82.8% moisture have been heated up to 12.7% humidity at 6 microwave levels for 32 minutes, and to 100C for the next 13 minutes. Drying in a fan oven. Apricots with 86.5% moisture were dried up to 13.2% humidity with microwave for 40 minutes and in the oven with a fan for the next 10 minutes. They have observed that the materials do not lose their color, odor and taste at the end of the drying processes [45].

Özkan and Işık (2001) used the tomato with a humidity value of 88.12% first in the oven with a fan for 30 minutes, then at the 90 W microwave level for 6 minutes, at the 160 W microwave level for 10 minutes, at the 350 W microwave level for 5 minutes, at the 500 W microwave level for 5 minutes, and 9 minutes at 650 W microwave stage with a total 65-minute drying period with hot air. In fan oven drying, the material center temperature is 24° C in 1 minute and 160° C in 30 minutes. It is 166° C in 31 minutes when the microwave drying period starts, and 393° C at the end of 65 minutes. They determined that tomatoes do not lose their color, odor and taste after drying [46].

Çelen et al. (2015) investigated the effects of microwave power (1500W and 2100W) and belt speed (0.175, 0.210 and 0.245 m / min) on drying time, color change and energy consumption in the microwave conveyor dryer of a 5mm piece of potato. According to the results, energy consumption decreased with the increase in microwave power and decrease in band speed. The correlation coefficient (r), standard error of estimate (e_s) and (χ^2) were calculated in order to determine the nine drying models by considering the experimental and theoretical moisture ratios. It has been determined that the Page model is the most suitable model for all drying conditions. As a result, working with as low power and low belt velocity as possible in belt microwave dryer drying applications can be said to be more beneficial in terms of quality criteria [47].

Dehghannya et al. (2018) investigated the effect of a process of drying apple pretreated osmotically with sucrose solution at five different concentrations by using the intermittent microwave at four power levels, four pulse ratios, and convective hot air (40°C) on drying kinetics, effective moisture diffusion coefficient, energy consumption, shrinkage, bulk density, and rehydration ratio. Results showed that the use of intermittent microwave coupled with forced convection of hot air (at low temperature) in drying of apple pretreated by sucrose osmotic solution led to products with improved properties in terms of both quality and quantity [48].

Keser et al. (2020) carrots are an important human food. In this study, the effect of various microwave powers on each of the antioxidant properties, phenol and odor was shown in this study on dried carrots with various samples and MW powder. They dried fresh and varied carrots (Daucus carota 'Nantes') by applying seven different power levels of 150, 200, 250, 300, 350, 400, and 450 watts (0.50, 0.67, 0.83, 1.00, 1.17, and 1.33). And 1.50 W / g and they are respectively). The aromatic compounds were extracted from the carrot samples by disinfection, whereas, the carrot samples extracted the aromatic compounds by disinfection and traps, as they were determined by gas mass spectrometry (GC MS). Regarding fresh carrot samples, the terpenes were relied on as the predominant aroma group, where a large decrease in the amount of these compounds was observed due to the total dependence on the applied MW energy level. Terpinolene and (E) -bisabolene, elemicin, and myristicin were also recognized as the dominant terpenes. With regard to fresh dried eyes, alcohol, furans, aldehydes, pyrazines, and acids were used as the main component, depending on the applied MW energy levels. Hexanal, 3-methylbutanal, acetic acid and hexanoic acid were the most dominant ones in the dried carrot samples. In order to assess the phenolic compounds, the method was approved using liquid chromatographic separation in addition to tandem mass spectrometry (LC MS / MS). This was the result of the analysis, it was found that there are seven phenolic compounds in a group, the most common was the share of two of them (3caffeoylquinic acid and a derivative of di-caffeic acid). The total phenolic content of carrots and their dried fresh samples were determined at an energy level below 150 and 200 W (0.50 and 0.67 W / g). When both smell and phenolic compounds were estimated, it was found that they were better preserved in carrots and their dried fresh samples by means of low energy levels of MW (150 and 200 watts) [49].

2.8. DRYING WITH INFRARED

Toğrul et al. (2005) in their study, determined the drying behavior of 0.5, 1.0 and 1.5 cm thick cubed mushrooms at different drying air temperatures (50° C, 60° C and 80° C) in an infrared dryer. They examined and emphasized that with increasing the temperature from 50° C to 80° C, 0.5 cm, 1.0 cm and 1.5 cm slice thicknesses decreased by 170, 140, 104 minutes in the drying time, respectively. They also examined the effect of mushroom thickness on the diffusion coefficient and found that the increase in temperature and slice thickness caused an increase in diffusion coefficient [50].

Toğrul et al. (2005) examined the drying quality of banana slices by drying the banana slices cut in four different thicknesses in an infrared dryer at temperatures of 50, 60, 70 and 80°C. As a result, the researchers found that both the drying speed and the diffusion coefficient increased with increasing drying air temperature, and that the drying speed decreased with increasing banana slice thickness [51].

In order to dry Quince slices from 3,89 g water/g dry matter initial moisture content to 0,16 g water/g dry matter final moisture content, Aktaş et al. (2013) constructed an infrared radiation dryer and monitored the required drying air temperature. Quinces were dried at 35° C and 40° C drying air temperature and 1,22 m/s, 1,83 m/s and 2,45 m/s drying air velocities, cut into 4 mm thickness. For six tests, energy analysis of the infrared radiation dryer was conducted. Drying time and heat recovery system performance were evaluated at the average specific moisture extraction rate (SMER).

They observed that the shortest drying period occurred at 40° C drying air temperature and 1.22 m/s air velocity within 240 minutes, while the longest drying time occurred at 35° C drying air temperature and 2.45 m/s air velocity within 390 minutes. Product drying time improved with increasing drying air velocity in all drying trials and decreased with increasing drying air temperature [52].

During an investigation, Apinya et al. (2019) analyzed drying kinetics and energy consumption using infrared-assisted freeze-drying (IRAFD) to produce a snack containing banana chips. They found that infrared assisted freeze-drying IRAFD significantly reduced the drying time as compared to freeze-drying (up to 213 minutes or 70% time). Using the diffusion models and drying kinetics, IRAFD found out the suitable drying model [53].

2.9. DRYING WITH CYCLONE TYPE DRYER

Akpınar and Biçer (2003) experimentally investigated the drying behavior of the pumpkin in a cyclone dryer. In the experiments, three different air inlet temperatures of 60, 70 and 80° C are used, while the selected drying air velocities are 1 and 1.5 m / s. The researchers have mathematically modeled the drying rate-moisture content change curves obtained from the experimental results using nonlinear regression analysis. According to the experimental results, it was observed that the drying speed of the pumpkin samples dried in the rotating flow environment in the cyclone fiber dryer was high. The highest drying speed was obtained at 80° C drying air inlet temperature and 1.5 m / s drying air speed, the lowest drying rate was obtained at 60° C drying air inlet temperature and 1.0 m / s drying air speed. It was understood that the drying speed of the samples dried at different inlet temperatures and speeds was more influenced by the air temperature than the air velocity. In addition, the researchers stated that as the drying air temperature and speed increased, a markedly rapid decrease was observed in the moisture content of the pumpkin samples and the drying speed increased [54].

2.10. FREEZE DRYING

Acar et al. (2015) performed an experimental analysis on the drying of saffron plants containing heat-sensitive volatile and aroma-yielding compounds, such as crocin, picrocrocin and saffron, using freeze-drying techniques and showing that heat-sensitive volatile and aroma-yielding compounds of saffron can be more preserved using this technique compared to other traditional drying methods. The freeze-drying characteristics of saffron were experimentally determined in their analysis. The data on drying kinetics were used in 10 different empiric diffusion drying models from literature to find the best one that reflects the weight loss of saffron during freeze-drying. Among the models evaluated in this analysis, it was observed that the Page model was the best model to reflect the drying kinetics of saffron during freeze-drying. The value of the effective diffusivity was determined. Results have demonstrated that freeze-drying is a more effective dehydration process for products containing heat-sensitive volatile and aromatic compounds [55].

Janaani (2021) dried approximately 100 g of carrots, which were cut into circular slices with different thicknesses of 5 mm and 7 mm, using the freeze-drying method by device SCANVAC COOLSAFE. In his study, firstly the slices were frozen then the dried operation was started. Weighing freeze-dried carrot slices over a total of 14 drying hours every two hours and using different temperatures, loss data were reported. And with many measurements taken, it was observed that the moisture level had decreased by more than 30%. This means that the product does not deteriorate, improves the process of storage of the product and does not fade its colour. Data was applied on 10 different mathematical models using the MATLAB program. The error analysis of the predicted and experimental results was made using the estimated standard error (RMSE), chi-square (x^2), and regression coefficients (R^2) in the models used. Based on the findings, it was determined that the Page model was similar to the experimental results in comparison to the other models [56].

Mellor (1978) examined the effect of pressure during freeze drying on transfer of mass and heat. The researcher mentioned that the driving force of mass transfer is increased by the low pressure but the heat flow on the dried surface is decreased due to the relation between the heat transfer coefficient and pressure. The researcher has developed a cyclic pressure freeze drying process that tries to overcome this problem. In this process, he briefly increased the pressure in order to increase the heat flow and later briefly reduced it to increase the steam flow [57].

Nail (1980), examined the impact of pressure in drying chamber on drying. Nail (1980) dried the drug in liquid solution. He placed the frozen medicine contained in glass bottles on a metal tray on the heating rack in the drying chamber. Nail (1980) stated that there is a resistance to the heat transfer from the heat source to the sublimation surface. The tray and bottle, and the air gap between the tray and the heater rack cause this resistance of the heat transfer. Found that it is more pronounced in low pressure environment. This situation was clarified from decreasing the gas thermal conductivity in the range of pressure when the heat flow of free molecules arises. He studied the drying rates by measuring them at 1.3, 0.25 and 0.04 mm Hg pressures. The findings of the confirmed Nail's theory by presenting that the drying ratio reduces with the reduction of pressure [58].

Wolf and Gibert (1989) carried out the freeze drying of milk in glass bottles. In this study, they identified the factors limiting the freeze-drying process. By applying their own models to the measurement data, the model included the determination of three transfer parameters. It is represented by the spread of water evaporation in the dried layer, the mass transfer coefficient in the product and heat transfer resistance from the heated shelf to the ice. As the resistance of contact between the shelf and glass bottle is an important obstacle to heat transfer, they determined that this resistance is a complete control parameter and therefore controls drying kinetics [59].

From Pikal et al. (1983) during the freeze-drying process, the dried surface layer resistance was tested. They determined that the dried surface layer resistance reduced when reducing the pressure. The dry layer resistance was calculated directly according to the results of sublimation ratio. Pikal et al. (1983) determined that low pressure increases the sublimation process. They conducted the trials with a container specially made and heat, not by conduction, but by radiation. By experimentally calculating the sublimation speeds, they have produced a model. Via estimation, they calculated the dry product resistance normalized to the steam flow from the results. They later used dry product resistance as relevant data for numerically calculating drying rates [60].

Pikal et al. (1984) studied the heat and mass transfer in freeze drying process. They measured the drying rates and estimated the heat flux by placing a few vials with frozen product on the heating rack. According to the study, as the pressure in the drying chamber decreases, the rate of sublimation decreases. In addition, the resistance associated with the semi stoppered vial is analyzed. The mass transfer coefficients combined with the resistance of the dried-product layer; it is determined by the measurements. The radiation and conduction were used to evaluate the heat transfer. An effective hat transfer coefficients depending on measured temperature has been used in the equations [61].

There have been many attempts to create the mechanism involved in the lyophilization process mathematically. Zamzow and Marshall (1952) were the first to study the freeze-drying process. Their method included the measurement of either conduction or radiation of the motion of the sublimation interface front and maximum heat supplied through the frozen area. The fundamental purpose of their work was to predict the shortest possible drying period under the melting temperature constraint of the frozen product. Their model yielded very good results [62].

Hill and Sunderland (1971) used the fake steady state model. However, free molecules evaluated from the continuum and transition flow regimes from momentum equations. They considered the flow rate as constant throughout the dried layer due to the pseudo steady state assumption. Due to the theoretical predictive data and characteristics of the model available, they compared it with published data for beef. They treated small differences between predictions and experimental data as experimental errors [63].

A model that involves both ice sublimation and water desorption in the dry zone has been developed by Liapis. This model uses a transient analysis, unlike the models previously discussed, that helps both desorption and sublimation to arise concurrently. The sorption-sublimation model is called this model [64].

Liapis and Bruttini's (1994) temporary sublimation model is a sensitive model that estimates the first 60-90% of the moisture removal. However, they concluded that they did not predict secondary drying [65].

Dyer and Sunderland (1968) took into consideration the transfer of moisture between the steam flow in the dried zone and the dried material in the sorption-sublimation model. In previous freeze-drying models, this feature of the drying process was neglected and thus caused errors in the data expected [66].

With the assumption of the typical non-real steady state that has been used in the modeling of classic freeze drying, Copson (1958) modelled the mechanism of microwave freeze drying. Ma and Peltre (1973) mentioned that this assumption is not valid in case of faster microwave free drying. They thought that the dry layer had hydrodynamic flow in the Copson analysis. The measurements of vapor flux were based on the difference in pressure between the mobile sublimation interface and the dry layer's outer surface. There were major variations in projected information and experimental information. These discrepancies exposed a misleading steady-state presumption that existed and Unidentified transport properties [67].

Ma and Peltre (1973) with microwave heating, presented a temporary one-dimensional freeze-drying examination. It was the first microwave-heated freeze-dried transient study. For the dry and frozen areas, they wrote the temporary mass and energy equations. They measured the heat by conduction in the frozen zone and by conduction and convection in the dry zone [68].

The sublimation rates of the ice were measured by Jennings. The calculation findings, the results of the studies carried out by Nikal and ch on the contrary, showed that as the pressure decreases, the sublimation rate rises [69].

Litvin et al. (1998) examined the drying on carrot slices by using the combination with freeze-drying, short-time microwave application and air or vacuum drying. In experiments, carrots were cut 7 to 10 mm thick, steam-boiled for 1 minute, cooled under running water, frozen at -18° C and stored at -18° C until further processing.

Freeze drying for 2 h at a plate temperature of 30°C followed by 1.5 h at 55 °C was adequate to extract all water by sublimation and to obtain a product moisture content of about 40 per cent. Then samples were subjected to microwave heating for 50 seconds and then vacuum and air dried up to 5% humidity. The colour, dimensions and rehydration ratio of the partially freeze-dried, microwave treated, and air-dried product were identical to the same as freeze-dried product with the final moisture value and the same quality parameters. The final drying performed in the vacuum oven has been determined to have some beneficial effects on color. Combining freeze drying with air drying after microwave operation, a substantial improvement in freeze drying time was achieved. 3.5-3.75 hours of partial freeze drying accompanied by quick microwave application and 3.75 hours of air drying, a total of 7.25-7.50 hours, while only the total time of freeze-drying time 9.5 hours at 30°C [70].

Khallouf et al. (2000) freeze dried strawberries, blueberries and mushrooms. In the analysis, the products were dried using a freeze-drying process for 72 hours and the relative humidity with saturated salt solutions improved from 11% to 87%. The weight changes and the water behavior of the fruit during the drying process were analyzed and it was reported that the GAB model was best for experimental data [71].

Shishehgarha et al. (2002) have experimentally examined drying kinetics, color and volume variations in freeze drying of 5 mm, 10 mm sliced and whole strawberries at various shelf temperatures (30, 40, 50, 60 and 70° C). As a result of freeze drying, the drying time for strawberries was 5 hours for 5 mm, 10.7 hours for 10 mm and 50 hours for whole strawberries. They observed that strawberries were of decent quality at temperatures below 50° C and that strawberries had collapsed at temperatures above 50° C [72].

In the freeze-drying process, Araki et al., experimentally examined 15 mm thick sliced and crushed apples in a temperature range of-10 to 70 °C heater surface temperature and 20 to 30 Pa pressure. They observed that the rate of crushed apples to dry was 2.5 higher than that of sliced apples [73].

Sadıkoğlu and Özdemir (2001) underlining the concept of freeze drying, pointed out the important points to be noted in freezing drying by stressing the freezing process during drying, the microwave drying, which is a process that increases drying speed, is faster than the traditional freeze drying method [74].

Carapelle et al. (2001) examined by experience the freeze-drying of frozen wet papers. By analyzing various physical parameters (pressure, heater power v, b.), the freeze-drying system needed for operation was developed. The study defined optimum parameters to minimize the time and cost of freeze drying and produced a basic example to promote research in this field [75].

Krokida et al. (2001) apples, bananas, carrots and potatoes were dried in five separate methods and the impact of drying on colour was investigated. Newly harvested apples, bananas, carrots and potatoes have a diameter of 20 mm and a thickness of 10 mm. In air drying, the temperature during drying is 70 ± 0,2 °C, the relative moisture of the air is 7% and the pressure is 1 ± 0,03 bar. During vacuum drying, the temperature for vacuum drying is 70 ± 0.2 °C and the pressure is 33 ± 0.03 mbar. Microwave drying was achieved power 810 W at atmospheric pressure. In freeze drying, the samples are sliced to 20 mm in diameter and 8 mm in thickness. Samples were frozen at-35 °C for 48 hours and dried in a freeze-dried laboratory cell for 24 hours. Significant browning has resulted in air, microwave and vacuum dried goods. During freeze drying, there was no browning in the color of the samples [76]

Marques and Freire (2005) experimentally examined modeling the freeze-drying kinetics of pineapple, guava and mango with "Chen and Douglas", "Van Meel" and "Page" models. The Page Model was considered to be the best explanatory model for experimental findings [77].

Sadıkoğlu (1997) focused on the estimate of the parameter and the separation of the model to decide the functional form of the mechanism that can be used to explain the removal of bound water during primary drying. They compared experimental results from the first drying process with theoretical models and found that the elimination of bound water did not greatly impact the overall mass flow during the first drying phase [78].

In their experimental research, Sadıkoğlu and Liapis (1998) found that an increase of 2 °C in the melting temperature of skim milk will decrease the drying time by 8.28% in the first stage of drying [79].

Duran (2002) contrasted the water and the fat content of fresh, frozen and frozen dried chicken and beef. Through experimental results, the water and fat ratios of chicken and beef were found to be lower during freezing drying [80].

Kwok (2006) compared drying saskatoon berry fruit by freeze drying (DK), vacuum microwave drying (VMK), air drying (AK) and CD-method, which is a mixture of AK and VMK, with other drying processes, fresh frozen fruits. The findings revealed that the other methods dramatically decreased overall phenol and anthocyanin content and also decreased antioxidant action, whereas DK drying showed the highest levels of anthocyanin and antioxidant activity, followed by VMK. CD drying was the average of VMK and AK [81] .

Rahman et al. (2002) investigated the pore characteristics of tuna dried by air, vacuum, and freeze-drying. Air drying is done at 70^o C, 1 m / s air velocity, and 3.4% relative humidity, and vacuum drying is done in a vacuum oven at 70^o C and pressures less than 2 kPa. In freeze-drying, fish are frozen at -40^o C for at least 24 hours. The condenser surface temperature is $–65^o$ C, the plate temperature of the room is $- 20^o$ C and the vacuum is 108 Pa. The volume weight of the meat part of the fresh tuna fish was measured as 1098 kg / m^3, while the volume weights of the air, vacuum, and freeze-dried tuna fish were 960, 709 and 317 kg / m^3, respectively. The porosity of the freeze-dried sample was higher than the air and vacuum dried samples [82].

Acar et al. (2011) conducted a study to compare freeze drying technology with natural sun drying on the saffron plant. The saffron samples were dried by both methods. It was observed through experimental results that the quality standards of saffron plants, such as saffron content and crocin content, were significantly higher in freeze drying than in natural sun drying. It was found that sun drying causes a loss of heat-sensitive volatile and aroma-yielding compounds [83].

Wang et al. (2007) used three different drying methods to dehydrate banana puree: Freeze-drying (FD), air drying (AD) and vacuum belt drying (VBD) to obtain banana powder. A solid-phase micro-separation (SPME) was used on the dried banana powder, which was separated and identified using a process called gas chromatography-mass spectrometry (GC–MS). Statistical analysis was conducted to assess the variables. They concluded that banana powder should be preferably produced using FD and then VBD rather than AD to maintain its optimum flavor [84].

Kırmacı (2008) designed and manufactured the freeze-drying system, 5 and 7 mm sliced strawberries were dried in this system. In order to determine the moisture content at any time during the drying process, the data obtained from the experiments were compared with the Newton, Page, Enhanced Page I, Enhanced Page II, Henderson and Papis, logarithmic, Two term, Two-term exponential, Wang and Sing, and diffusion approach models. It was determined that the results of the page model by using the root means square error(RMSE), chi-square (X^2) and coefficient of determination (R2) were found to be closer to the experimental results than the other models according to the results obtained by performing error analysis [85].

Xu et al. (2020) researched the effects of various drying methods on the chemical and physical properties of Cabbage using freeze-drying (FD), hot air drying (HAD), microwave vacuum drying (MVD), vacuum drying (VD), MVD mixed with HAD (MVD + HAD) and VD (MVD + VD). After these tests, observations were made in terms of antioxidant function, dietary ingredients, microstructure, texture, etc. Results have shown that HAD has had a worse effect, with a dietary portion loss of more than 45%. However, two combination approaches achieved higher nutrient retention, greater antioxidant activity and lower energy intake than the individual HAD. However, the MVD + HAD products still had a higher hydrolysis capability and a more uniform porous honeycomb composition as they had lower hardness relative to HAD. This study was important for the collection of better quality drying methods to achieve excellent quality [86].

Guo et al. (2018) in their research, a new path has been taken in the qualitative analysis of different slices of lemon by using a large-capacity electron Volta metric pulse. By using several methods of pre-processing the date, the principal component analysis (PCA) was also used, as well as by separate wavelet transfer (DWT). Including the use of linear discrimination analysis (LDA) it was intended to compare stress and its effect. Through the results of the linear discrimination analysis (LDA), it indicated the choice of DWT and its adoption as a method for extracting the characteristics. Then they used an Extreme Learning Machine (ELM) that was intended to analyze lemons and their different aromas qualitatively in order to compare the results with a common classification model: Random Forest (RF) and Support Vector Machine (SVM). Then they use the models and compare them depending on the accuracy of the training set [87].

Kurza et al. (2018) in their study, the accidental freezing of aluminum vaccines was used for transportation and storage. Knowing that the freezing of these aluminum vaccines harms them in the aid that is sensitive to freezing, this is done by separating the network between the antigen and aluminum adjuvant, meaning this leads to the formation of aluminum clumps that lead to loss of effectiveness. Then, Alhydrogel^{TM} ([AlO (OH)]xnH_2O, aluminum hydroxide, hydrated for absorption) were examined which were stored under certain conditions, and then subjected to freezing temperature to solidify. The aim of this study was to determine the destruction areas of frozen solid AL hydrogel by several methods selected from energy-dispersive x-ray spectroscopy, electron microscopy, Raman spectroscopy, as well as infrared spectroscopy for the purpose of Fourier transform, and electron microscopy was used for the purpose of transmission because it works in diffraction mode. Zeta potential readings, albumin absorption strength measurements, thermogravimetric analysis and mass loss estimate after drying. There are significant structural (physical) and chemical differences between the non-frozen and frozen spoilage vaccine material. These advanced results were of importance in order to understand the type and nature of damage that aluminum-based vaccines may be damaged by freezing [88].

Tan et al. (2019) in their study, the method used was the spray drying method, in which the acidified casein was treated and the resulting gel was somewhat similar to shampoo foam at a certain pH where it was 1, after which the tablets were placed for the purpose of releasing applications that control it. Then it was found that the casein gel, which is ergonomically designed, has higher moisture content and lower Tg / dehydration temperature compared to the other type of casein (gel casein), in light of the results of the analyzes of DSC and FTIR. It was discovered that casein is sensitive to thermal exposure (DSC), knowing that there is no significant change in casein during the FTIR process. During the spray drying process, it was observed that the size of casein gel particles increased with the decrease in temperature during the process. With the use of high temperatures on the particles in the spray drying process, these particles are subject to wrinkling surfaces, for example, raisins. To make microencapsulation of ascorbic acid (Vitamin C), in the spray drying process the dried powders work to reduce the relative moisture content with a temperature higher than Tg / dehydration. This is done by increasing the inlet temperature (100-190° C), the retention of ascorbic acid is observed (80-60%) with an increase in yield (0-70%). The gel casein disk results were more flexible upon DMA, and the hardness was 0.8 N / mm. According to the controlled release, then the casein gel was to exhibit a slow-character release of ascorbic acid for 24 hours and at a pH of 2 or 12 hours at a pH of 7.4. The results were slightly slower release at high a compression pressure (320 MPa) [89].

Getahuna et al. (2020) in their study, energy recovery and safe disposal of fecal sludge (FS) is done through drying processes. Knowing that there is little data for this process for FS. The purpose of this study is to know the characteristics of drying FS, as it was done by relying on samples belonging to ventilated improved pit toilets. With another attached to dry toilets was a urine diversion (UDDT) with an anaerobic reactor (ABR) for wastewater and its systems, which was decentralized. As the solids content and moisture content were depended, and in order to measure the calorific value to characterize the drying method of the FS content, the water activity, volatile solids, differential thermal analysis (TGA - DTA), and thermocouple measurement were used. Different humidity on drying (100° C) was very similar to samples belonging to sanitation facilities. As shown in the process of the results of the drying process, with respect to the experimental temperature, the FS depends on two to three times the latent heat for the purpose of evaporating the water necessary for drying. The source of the sludge was less important compared to the drying temperature when the solids content that was volatile and of the dried samples was known was the drying temperature. The thermodynamic thermogravimetric analysis showed a large percentage of thermal decomposition (2-11%). This ratio of dry mass stiffness was close to 200° C and it was below 200° C, and it did not show a significant difference. The calorific values of the samples were average VIP, UDDT, and ABR at 100 °C, 14.78, 15.70, and 17.26 MJ / kg were for dry solids, respectively. The drying temperature, which is not less than 200 ° C, does not affect the value of FS fuel to the sanitation facilities [90].

Liu et al. (2020) the instant soups have a high percentage of starch. In this study, the focus was on treating the low starch during the freeze-drying process and its degradation, which leads to a reduction in the viscosity of the soup. It is important to monitor the starch and to know the regression that will occur during the drying process in this study and its processes. In this study I use creamy mushroom soup because it is a soup with high starch content. The first time the freeze-drying process was observed and an understanding of the soup quality and drying properties. Knowing that the quality of the soup is preserved during the drying process, however, the viscosity is greatly reduced. The starch was regressed, that the drying quality and its advantages (for both rehydration behavior and whiteness, and shrinkage rate) of the product that was dried, there were three stages of hybrid drying. Microwave drying (0.8 W / g, for 1 hour) + freeze drying (50° C, for 4 hours) + microwave drying (0.8 W / g, until end of drying) It has been successfully improved to preserve the properties of the auxiliary soups as well as to prevent a decrease in its viscosity [91].

The purpose of this study is to freeze drying the hawthorn, which is a commonly consumed fruit product due to it contains wide benefits for humans as it is a rich plant by the content of potassium and fiber, determination the kinetic model for hawthorn, and calculation its moisture content or effective diffusivity during the freeze-drying process. Literature shows that so far, no study has been conducted to determine the kinetic model for hawthorn or its moisture content. Literature proves that freeze-drying dehydrates fruits and a variety of other agricultural products. To eliminate this research deficiency in the literature, we froze hawthorn and dried it using a Scanvac Coolsafe device and regression analysis with the aid of MATLAB software using information of the weight loss of freeze-dried hawthorn during drying. We have demonstrated the results using graphs and determined the most suitable empirical drying model among 8 different mathematical models as a result of these analyzes and effective diffusivity was determined.

PART 3

THEORETICAL BACKGROUND OF FOOD STORAGE METHODS

Several techniques are used to store foodstuffs. The cooling and drying applications are the most commonly used of these processes.

3.1. FOOD STORAGE TECHNIQUES WITH REFRIGERATION

Although refrigeration is an essential storage medium nowadays. Storing food at a low temperature is the simplest and safest way to store many types of food as the food you plan to cool requires the least amount of preparation or the food is already ready for cooling. Refrigerators maintain the quality and safety of food because cold slows bacterial growth and reduces spoilage. Depending on the type of food, it can last between a few days and a few weeks in the refrigerator before the texture and taste deteriorates.

Refrigeration is the process of removing heat to reduce the temperature of a substance or an environment below its surrounding volume temperature and to maintain it at that temperature [92–94]. With the cold preservation process, food can last between 5 and 50 times longer. The process of freezing food is defined as a preservation technique based on lowering the water contained in the food to a temperature where it can form ice crystals. Microbiological development is stopped in frozen foods. By reducing the temperature of the food to a temperature between -18° C and -30° C, possible damage to the product at room temperature is prevented or minimized in this way. These temperature levels prevent microbiological spoilage and extend the shelf life of the product. In general, the freezing process consists of four stages:

- Cooling the product called pre-cooling from the initial temperature to the freezing point.

- The first ice crystals in the product begin to form and the freezing temperature remains constant until a significant portion of the water in the product freezes.
- Freezing of the remaining water as a result of the decrease in product temperature.
- In the last stage, after the free water completely freezes, the product temperature decreases without a phase change.

The main purpose of the freezing process is to preserve the natural structure of foods as much as possible. Significant changes occur in the structure of the food by lowering the temperature in relation to the water content of the food. When the freezing temperature of the product is carried out rapidly between the freezing temperature and the temperature below 5° C, the crystal structure formed in the product becomes small. If the freezing process is slow in this process, the size of the crystal formed in the product increases. This situation especially destroys the cell wall of fruits and vegetables and the product cannot maintain its fresh quality because its structure changes when the product is thawed again. At the same time, during the prolonged freezing process, the water in the cells of the fruit and vegetable spreads out of the cell depending on the concentration, and this leads to the dehydration of the cell. Therefore, the rapid freezing process ensures that the product surface remains smooth and does not disrupt the cell structure [95]. The freezing methods used in the food industry are given below.

3.1.1. Freezing with Cold Air

Freezing with cold air has two main applications freezing with still (natural convection) air and freezing with accelerated air (forced convection) [96,97].

3.1.1.1. Freezing with Still Air

As the name suggests, the cold air used in the freezing process is still. The essence of such a freezer is a fully insulated cold room. The evaporator of the refrigeration equipment can be found on the ceiling, wall or in the middle of the room in the form of a tube bundle extending from top to bottom, or in the form of vertical racks. The products to be frozen are stacked between these shelves [96].

These types of freezers are simple and inexpensive in terms of the equipment used. There is no mechanism that provides air movement in still air-freezing rooms. Air is subject to only natural convection. However, since it is impossible to see this as an air movement, it is accepted that the air is still. Even in some still air-freezers, a limited air movement is provided with the help of a fan. However, due to this low air velocity, such an arrangement should not be confused with the "freezing in air flow" method. Because, in freezing in the air flow, a high freezing rate can be achieved by circulating the air at a high speed with a forced circulation. In the still air-freezing method, the temperature of the cold room is between -15° C and - 30° C. Since the thermal conductivity of the still or very slow-moving air is very low, it takes a long time for the foodstuff to freeze. The freezing time can vary from a few hours to several weeks, depending on various factors such as the size of the frozen material, the shape of the packaging, the space between the frozen units and the like. This method was mainly applied for fish freezing and is still widely used for the same purpose [96].

3.1.1.2. Freezing with Accelerated Air

The general principle of this type of freezer is that air moves rapidly between the frozen food and the evaporator. The air, which is moved with the help of powerful fans, cools while passing over the cooling spirals (evaporator) and then passes over the frozen product at a speed of 10 - 15 m /s. Since the heat transfer coefficient increases depending on the airspeed, the foodstuff is rapidly frozen. In air circulation freezing, the air temperature varies between -30° C and -45° C. Food freezing process with air flow can be designed as tunnel or belt. Accordingly, tunnel freezers can be belt or wagon. The speed of the band or wagons in the tunnel is adjusted according to the freezing time. On the other hand, the movements of the frozen product and the cold air inside the tunnel may be parallel or countercurrent. Countercurrent In tunnels, the product to be frozen is given from one side of the tunnel and cold air from the other side. Accordingly, the coldest air encounters the frozen product at the exit of the tunnel with a very low temperature. Then it continues on its way to the tunnel entrance. In this system, the moisture content of the air that cools the product increases. In this case, when it comes back to the evaporator, snow occurs on the evaporator surface. Due to this disadvantage, which occurs especially in long tunnels, the air movement in the tunnels is arranged diagonally to the product movement. So the air is given from the sides of the tunnel. In this application, the distribution of cold air in the tunnel is homogeneous. Cold air is mostly blown up from the bottom of the belt. With this blowing, the material on the belt gains a slight vibration depending on the air speed and particle size, thus increasing the freezing speed. However, this limited vibration is far from causing the frozen particles to freeze to stick together and thus turn into a mass. However, today, many products are desired to be frozen in individual pieces without becoming a block. For this reason, a new system called fluid bed freezer has been developed based on the very high velocity air emitted from the belt freezers under the belt to keep the particles on the belt floating in the air. In fluid bed freezers, each of the particles rising in the air and falling back, making a boiling-like motion, freezes rapidly by making full contact with the cold air from all their surfaces. Fluid bed freezers are actually a belt freezer. However, there are many different types of fluid bed freezers. Figure 3.1 shows a fluid bed freezer [97].

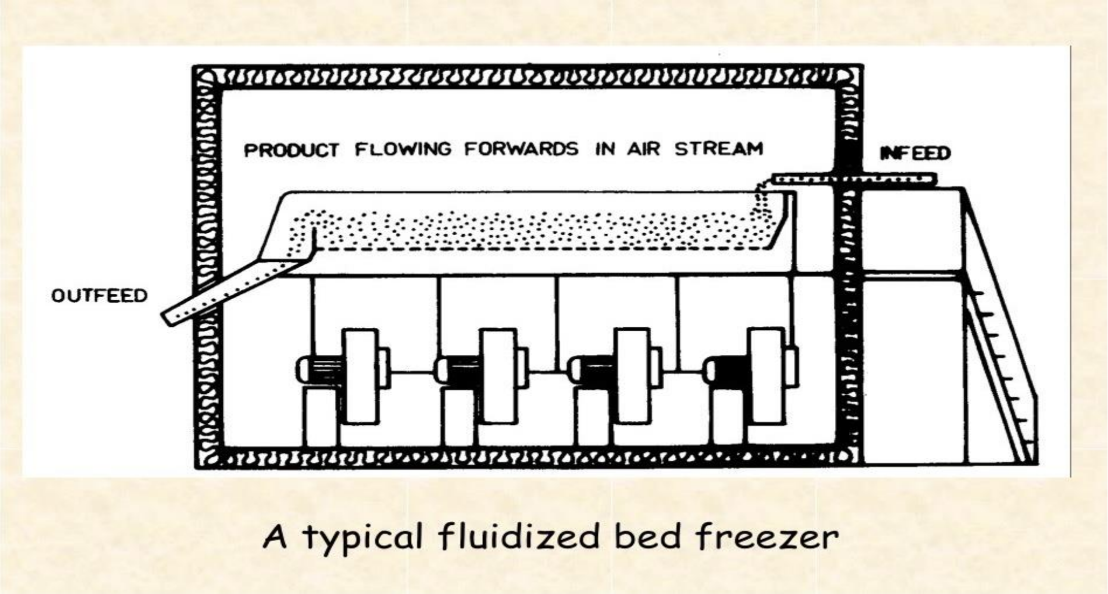


Figure 3.1. Fluid bed freezer.

3.1.2. Freezing by Indirect Contact Method

The working principle of this method is to freeze the packaged products placed between two internally cooled plates as a result of contact with the plate. Since there is a plate between the frozen product and the refrigerant that performs the cooling, this method is called freezing by indirect contact method. Freezing of some foods in the freezer compartment of the refrigerators at home can be seen as a plate freezing method acting from one side.

The only condition for freezing foods by indirect contact method is that the product to be frozen is in a rectangular prism shaped package. The freezing rate of a packaged mass without surface contact decreases in this system. Because it is very important in terms of freezing time that the package touches the plate with a smooth surface. Accordingly, when the packages of the same shape and the same thickness are placed side by side on the plate and the other plate is seated from the top, a fast freezing can be achieved in two directions. The plates consist of four corners, hollow aluminum shelves, and there are cooling channels, namely refrigerant evaporator units.

The most common plate freezers are the "Birdseye Multiplate" freezer type. In these, in a well-insulated cabinet, many plates in the form of shelves are located one above the other. One end of each plate is connected to the refrigerant main supply line with a rubber pipe, and the other end to the refrigerant main return line with a rubber pipe. Thus, up and down movement of the plates with rubber pipe connections is realized. As a matter of fact, the bottom two plates are opened with a hydraulic arrangement. The packaged foodstuff is lined up here in a single row. Then, the other plates are frozen upwards in the same way. Finally, the rack array is compressed slowly with a low pressure (0.05 - 0.1 bar) in a hydraulic arrangement. This compress is of great importance as the effectiveness of plate freezers depends on the degree of contact between the plate and the food. For the same reason, the packages are filled a little more so that no gaps are left in the packages, and as a result of the compression, the content is well settled and the heat conduction accelerates [96].

This is the reason why products such as meat and fish that form a whole mass in the package freeze faster than vegetables and fruits in the form of particles with a gap between them. However, the packaging should not burst when the plates are compressed. To achieve this, wooden barriers are placed on both sides between the plates. Since the thickness of these is slightly less than the thickness of the packaging, compression occurs only up to the thickness of the wood pieces. The compression stream of wood particles is limited [98]. After the plates are frozen, the cabin doors are closed, and the cooler is operated at the desired temperature. The product is left here until its temperature reaches -18 ° C. The freezing time depends on the contact degree of the package and the plate, the type and thickness of the packaging material, the type of the frozen product, the temperature and the thickness of the whole packaged food. With this method, packaged masses of 5 cm thickness freeze in 90-120 minutes. A schematic illustration of a plate freezing system is given in Figure 3.2.

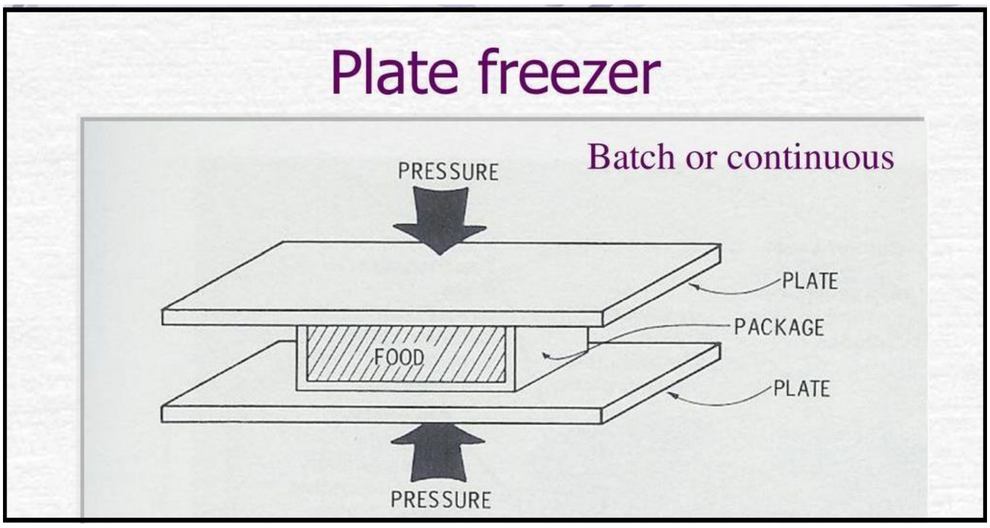


Figure 3.2. Schematic illustration of a plate freezing system.

There are also continuous working plate freezers. In one of these layouts there is a series of pairs of "shelf-plates". When the pair of shelves is uncovered in front of the freezer, the packaged products that are transported by the tape are automatically filled here. As this stacked rack enters the freezer and moves upward, a new placement on the idle rack begins. Each shelf (or it can be called a station) makes a cycle in the freezer and freezing is completed, and each station that has been frozen is emptied in turn. A continuous plate freezer is given in Figure 3.3.

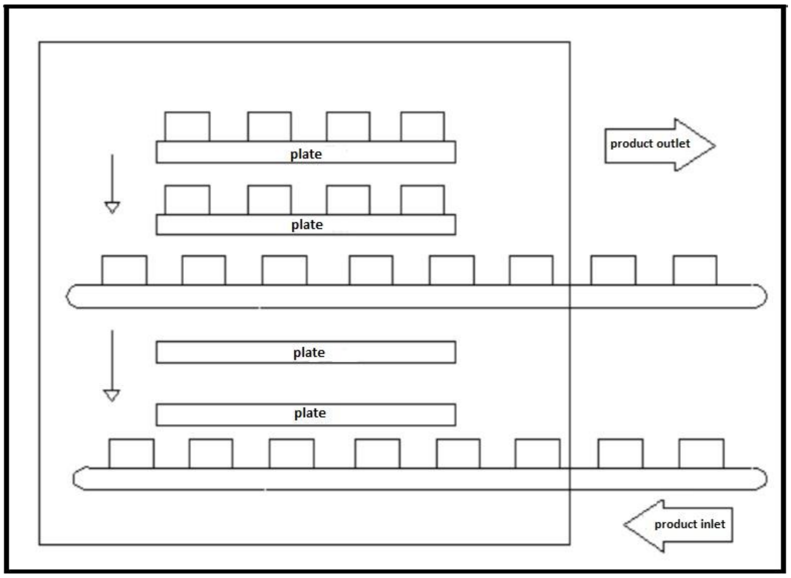


Figure 3.3. A continuous plate freezer.

In another plate freezing system operating with continuous loading, freezing is completed by sliding the packages between two plates, one fixed and the other movable, on the fixed plate with the help of a moving plate. Although the indirect contact method is suitable only for smooth-surfaced packaged products, it is also widely used in the rapid freezing of liquid foods. However, the principle of the devices used for this purpose is different. The plates used for this purpose are cylindrical and the outer part is insulated. There is very little space between the axial shaft (Mutator) of these devices called tubular scraper coolers and the inner surface of the cooling cylinder. There are scrapers on the shaft that almost scrape the inner surface of the cylinder. The liquid or semi-liquid product supplied to the cooler forms a very thin film in the space between the inner surface of the cylinder and the shaft. Meanwhile, while the freezing occurs, the scrapers on the shaft scrape the surface of the cylinder by the rotation of the shaft. In this way, the freezing surface is cleaned from the ice layer that prevents the heat conduction, and the rapid mixing of the frozen product during this time accelerates the freezing. Freezing only takes a few seconds.

The product, which is given to the freezer in liquid or puree form, is in the form of a liquid-snow mixture while leaving it. In fact, further freezing is neither correct nor possible in such a system. Otherwise, the cooler will remain blocked and remain in the form of a block, after this mass in the form of a mixture of liquids is packaged, it is stored by freezing to the desired degree in cold air freezers as the second stage [96].

3.1.3. Dip Freezing

It is the fast-freezing process by immersing the products in a non-water based refrigerant. In the first immersion freezing process, R-12 and other halocarbons were used as refrigerants, which increased the emissions of these substances in the atmosphere. Today, liquid nitrogen has completely replaced these types of refrigerants. The terrible boiling property of liquid nitrogen causes turbulence, thus allowing the separation of products and obtaining a very large surface heat transfer coefficient. With the fast freezing method applied with this method, minimum moisture loss, good odor storage, prevention of excessive freezing and liquid nitrogen emission in gas form at approximately room temperature are ensured to minimize the consumption of liquid nitrogen [99].

3.1.4. Freezing by Cryogenic Liquids Method

Immersing the products directly in liquid nitrogen can damage the products. By spraying liquid nitrogen on the products, the risk of damage to the products is reduced. Therefore, designs of freezers working with the principle of spraying liquid nitrogen to products passing through conveyor belts after 1960 have been made [100].

Liquid nitrogen and liquid carbon dioxide are the most commonly used cryogenic liquids in freezing foods. With strawberries and some berries, some delicate foods such as sliced tomatoes and mushrooms, a perfect product can be obtained with a very fast freezing. Cryogenic freezing method has also been developed mainly for this type and its application is still limited to these products [96].

Spiral spray cryogenic freezers and spray cryogenic freezing tunnel freezers work with this method. As small liquid nitrogen droplets evaporate on the products, it rapidly cools and freezes the product. Small liquid nitrogen droplets used in this type of freezer have a high evaporation surface heat transfer coefficient. The reason for this is that the liquid-solid contact takes place very well. Generally, there are three parts in cryogenic freezing tunnel freezers. Pre-cooling is applied to the products entering in the first part by moving the nitrogen gas formed by evaporation in the tunnel by means of fans. In the second part, the freezing process is carried out by spraying liquid nitrogen on the products on the belt. In the last part, the temperature of the product is balanced and taken out from the end of the tunnel [101].

3.1.5. Cryomechanical Freezing

In cryomechanical freezing systems, the product is pre-cooled in cryogenic immersed freezers before mechanical freezers such as spiral and fluidized beds. Fluid bed mechanical freezers seem to be the most suitable for freezing grapefruits. When a cryogenic immersion freezer is used, a shell is formed on the outside of the product within a few seconds with the help of liquid nitrogen. The shell formed in the product coming out of the cryogenic freezer is thick enough to withstand the environment of the mechanical freezer, which is warmer compared to this freezer. This layer prevents the product from being damaged due to the movement that occurs during the freezing of the product in the mechanical freezer and allows the products to preserve their shape [102].

3.2. FOOD DRYING TECHNIQUES AND STORAGE METHODS

Drying is one of the oldest recognized means of foodstuffs preservation [103]. Drying can be defined as the process of removing water in a product which is basically composed of water and dry matter by various methods [22]. The methods applied for drying vegetables and fruits are based on the principle of removing the water contained in the product to be dried by evaporating it from the environment by applying heat and mass transfer at the same time [104]. In technical drying, external intervention is made to the drying process and the moisture contained in the material is removed by different methods. For this reason, drying is defined as bringing the moisture of the product to be dried to the desired dryness values. The whole unit of units (heating, dehumidification, hydration, etc.), which provides the product to reach drying values in a certain period, is called the "drying system". The drying process is widely used in many branches of industry (food, paper, cement, timber and chemical industries) [105].

Drying applied to foodstuffs has many purposes, and perhaps the most obvious of these is to prevent spoilage of the product during long-term storage. At the end of the drying process, the product can be stored for a long time without spoiling, by reducing the humidity of the product to a sufficient level to limit microbial growth or other reactions. In addition, by reducing the moisture content of the product, quality features such as aroma and nutritional value are preserved. At the same time, by reducing the product volume at the end of the drying process, it increases efficiency in transport and storage of foodstuffs [106]. There are many methods used in drying foods. These methods are divided into two groups. These are, respectively:

- Natural drying (sun drying),
- Artificial drying.

3.2.1. Natural Drying (Sun Drying)

The substance is dried under sunlight without any technological interference. This is the approach that has been used for a long time. Temperature is the most critical thing. Since the moisture in the component is discharged into the air with the influence of heat without deforming the product. The product is spread on cardboard, nylon and linen on the ground or concrete floor and dried (Figure 3.4).

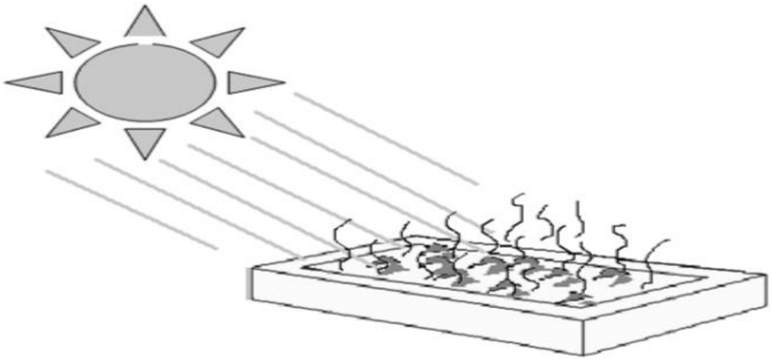


Figure 3.4. Natural drying (sun drying).

3.2.2. Artificial Drying

Artificial drying methods have been developed to reduce drying time, improve the quality and shield the product from the effects of sunlight. Compared to natural drying, the biggest benefit is that it offers a controlled drying environment and provides a superior product than natural drying in appearance [107]. Some of the artificial drying techniques are described below.

3.2.2.1. Ultraviolet Radiation Drying

Electromagnetic radiation is used in ultraviolet drying. Monomer structured coatings and dyestuffs are processed by drying under UV radiation. The biggest problem in the application of ultraviolet drying is the high investment cost [108].

3.2.2.2. Drying by Conduction

Examples of conduction drying include drying cylinders or balls (Figure 3.5), flat surfaces, open boilers and immersion heaters. The material to be dried must be in contact with the heating surface. In these systems, the amount of moisture prevents overheating. Conveyance drying systems are generally used for drying paper products. In conduction drying; high drying speed, constant heat and mass transfer conditions cannot be provided, the system cannot be controlled as desired, its operation is generally expensive, undesirable working conditions occur around the machine [109].

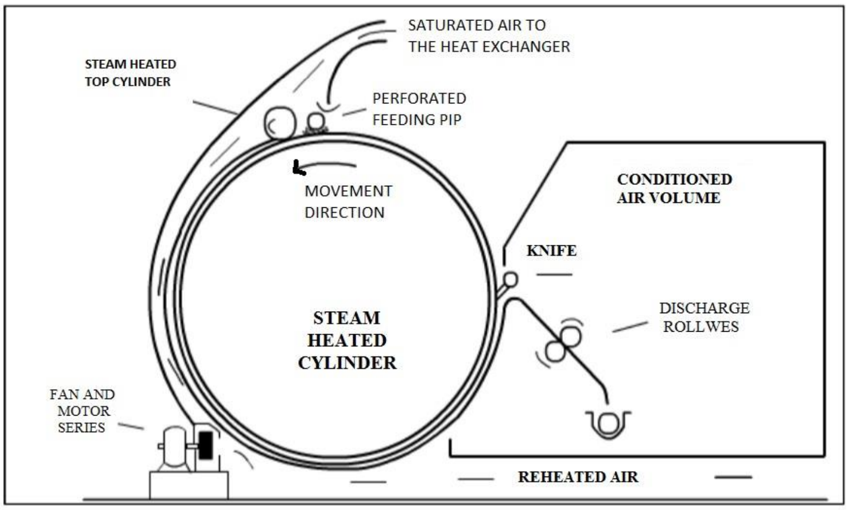


Figure 3.5. Transmission drying system.

3.2.2.3. Infrared Radiation Drying

Drying is provided by thermal radiation, infrared lamps, steam heating sources, gas heated incandescent reflectors and electrically heated surfaces. Infrared is only effective on the surface of the material and its areas close to the surface. Therefore, it is suitable for drying thin layers. Infrared heating is used for drying materials such as paper and textiles. If the material to be dried is flammable, the product should not be kept close to the heat source [108,109].

3.2.2.4. Vacuum Drying

In these dryers, drying takes place under vacuum at low temperatures. This method is applied in drying heat sensitive products or in products whose moisture content needs to be reduced to low levels [110].

3.2.2.5. Mixed Bed Drying

By using a vibrating rack or conveyor, a homogeneous drying is obtained as a result of the material vibrating continuously and at certain intervals. The same result is obtained by fluidizing some of the bed on the perforated rack or conveyor. It is suitable for drying grain [108].

3.2.2.6. Fluidized-Bed Drying

The working principle of this type of dryers is based on delivering the hot drying air to the solid particles to be dried at a certain speed from the bottom. This speed level is chosen so that the particles are suspended in the air. The function of the heated air is to create the anti-gravity effect necessary for both drying and fluidization. This type of dryer can be designed to dry the product in bulk. Temperature can be up to 100° C in fluid bed dryers. Some types also have vibration units to move the material to be dried. Drying air is passed through the granular materials in the fluidized bed. Air velocity should be adjusted very carefully. Since the contact between the powder or granular dryers' material and the fluidizing gas is very good, heat transfer between the drying air and the particles also takes place effectively. With this mechanism, it is possible to dry the materials without the risk of large temperature differences. The most important advantage of this system, in which automatic loading and unloading is possible, is that the drying process is completed in a short time. This type of dryer is suitable for drying coal, limestone, phosphate, plastic and medicine tablets [96,108,109]. Figure 3.6 shows the structure of the fluidized-bed dryer [22].

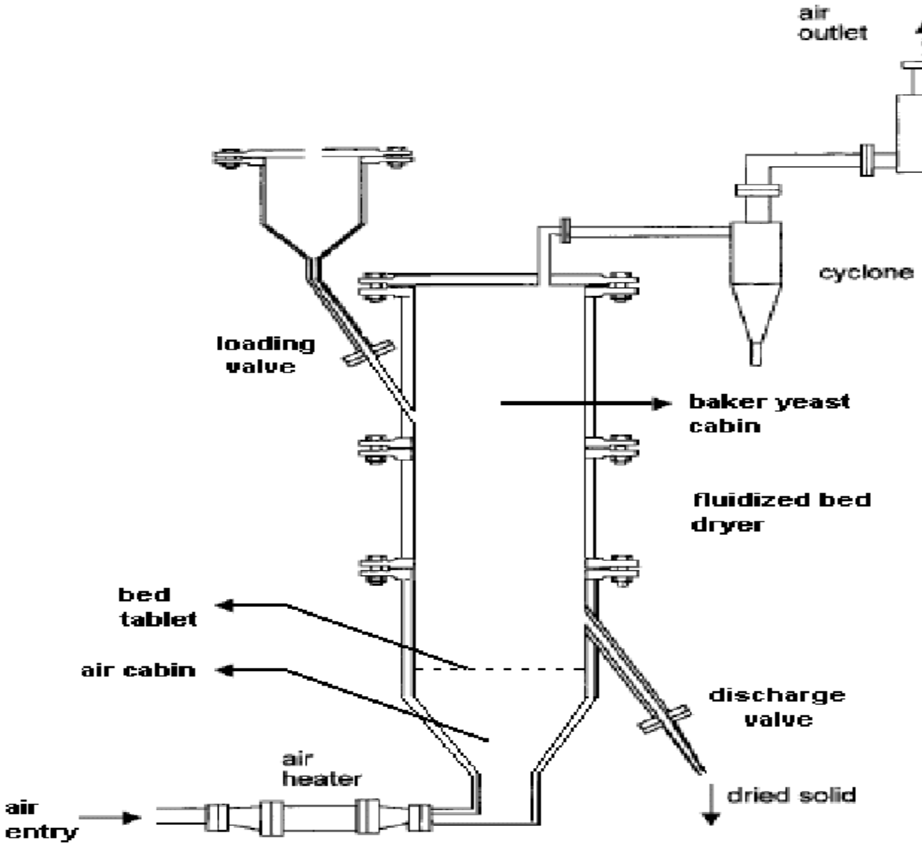


Figure 3.6. Fluidized-bed dryer.

3.2.2.7. Drying in Hot Steam Environment

In the process of drying in the superheated steam environment, the evaporated solvent (water or organic liquid) during the drying process with air or another gas should be dispersed into the static gas film to reach the bulk gas stream. The gas film, its resistance to mass transfer and the amount of drying vary depending on the rate of release of the solvent vapor. The thermal efficiency of this method is high, and the solvent is easy to recover into the system. In addition, excessive drying and oxidation caused by air and other chemical reactions are not observed [109].

3.2.2.8. Flash Drying

Evenly divided solid particles in flash drying systems can be quickly and properly dried by spreading into the hot gas stream [109]. There are application examples in pigment, synthetic, resin, food products, paper production [108].

3.2.2.9. Tunnel Dryer

If the amount of product to be dried is high and the general properties of the product are identical with the degree of dryness, it would be more appropriate to use continuous type dryers. The substance to be dried is placed in trays on the wagons and passed through the long tunnel. This process is arranged either in the form of continuous wagons or in such a way that when one wagon leaves the tunnel, another wagon loaded into the tunnel enters the tunnel. In various types of tunnel dryers, the directions of movement of air and product with respect to each other are different. If the wagons and hot air move in the same direction, this type of tunnel is called a "parallel flow tunnel". In this type of tunnel dryers, the drying air first encounters the new product. While the drying air cools and increases its humidity in the process, it comes into contact with the further dried product. This situation causes the dried product to absorb moisture again, even if a little. The diagram of a parallel flow tunnel dryer is given in Figure 3.7.

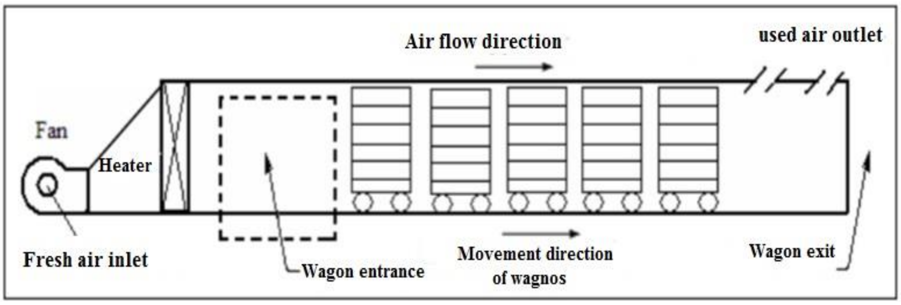


Figure 3.7. Parallel flow tunnel dryer.

If the drying air and the movement of the wagons are in opposite directions, this type of tunnel is called "opposite flow tunnel". In this type of tunnels, hot and dry air first comes into contact with the most dried product, then with the product with high humidity, while the humidity increases gradually by cooling. Figure 3.8 shows the diagram of the counter flow tunnel dryer.

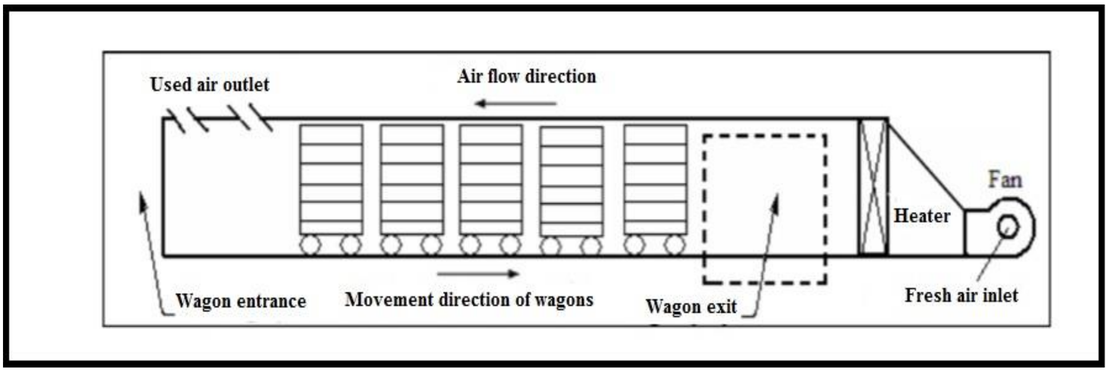


Figure 3.8. Counter flow tunnel dryer.

The most common systems for drying fruit and vegetables are parallel or counter flow tunnels. The drying characteristics of the counter flow tunnel and the parallel flow tunnel are different. In parallel flow tunnels, the initial drying rate is very high. Since the surface of the product dries very quickly, there is little shrinkage or wrinkling in the product. However, voids and cracks occur in granular products. Since the drying air is relatively cold and very humid at the end of the drying tunnel, the final stage of drying takes place very slowly. In counter flow tunnels, the material encounters more favorable drying conditions as it dries. The first stage of drying takes place with cooler and more humid drying air, and since the difference in moisture distribution is not much in the dried product, there is a complete and unimpeded wrinkling. The counter flow tunnel is particularly suitable for soft fruits such as plums. Otherwise, in the first stage of drying, the sap water flows out. Besides, it is used in cross flow tunnels [111].

3.2.2.10. Spray Dryers

Spray dryers are used in the production of milk powder, coffee, soap and detergent. Because the dried material has the same structure as the droplet or particle structure and the drying time is very short. Liquid materials can be dried in large quantities when dried in spray dryers. Spray dryers can be in the form of two fluid nozzles, high pressure nozzles or rotating discs. While the air temperature varies between 93 - 760 ° C, special construction materials are used for high temperatures. The higher the air temperature, the higher the thermal efficiency, so higher temperatures are preferred. Even temperature sensitive products can be dried thanks to the low drying time. The rotating type spray dryer is given in Figure 3.9 [109].

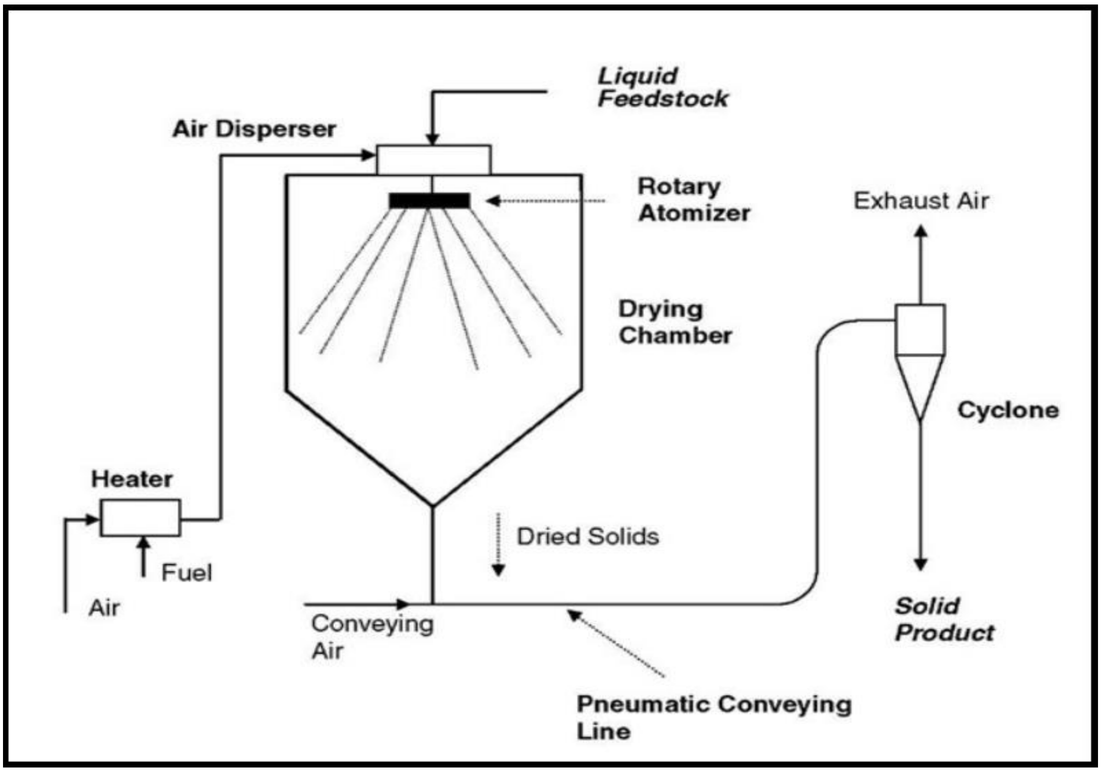


Figure 3.9. Rotating spray dryer.

3.2.2.11. Rotary Dryers

The products to be dried in rotary dryers should be in granular or crystalline form and dry enough to be transported by one of the generally applied transportation methods before drying. In addition, the product should have little to no adherence to cause buildup on the dryer walls. All rotary dryers with axes horizontal have a cylindrical body set up to make a small angle and placed on wheels that will rotate themselves around their axes. The product to be dried is fed to the dryer from the higher end of the dryer, moves slowly towards the lower end of the dryer with the help of the rotational movement of the dryer and is discharged from there. The progress of the product to be dried in the dryer, its mixing and better contact with the drying air is provided by the shelves and wings inside the dryer [111]. The scheme of the rotary dryer is shown in Figure 3.10.

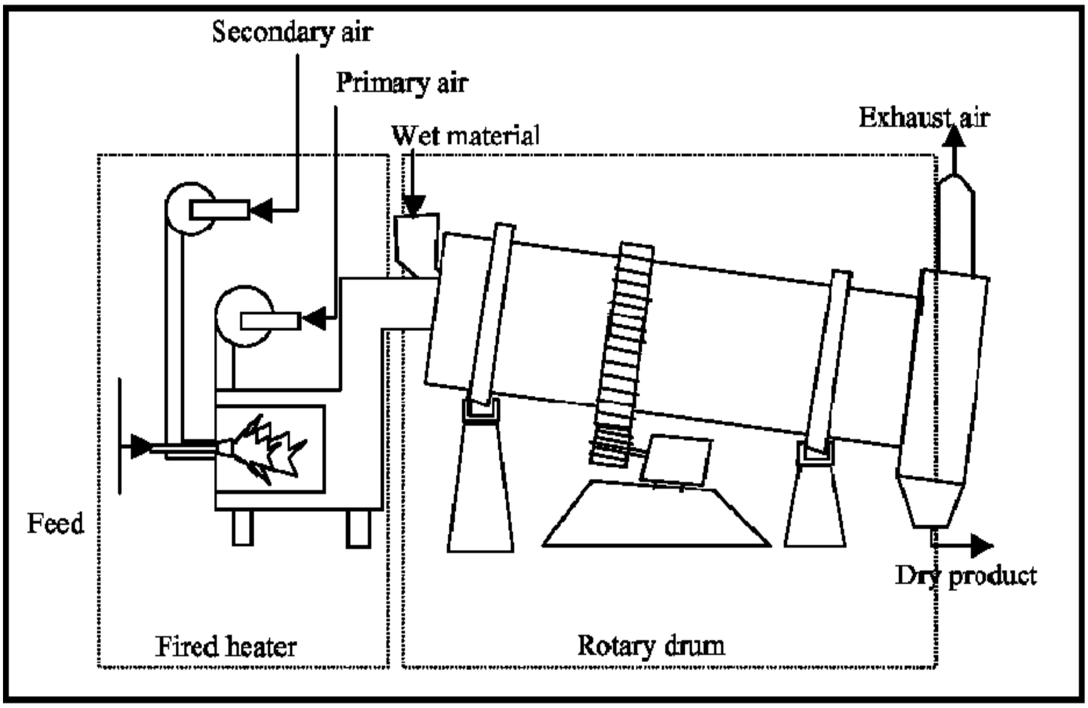


Figure 3.10. Rotary dryer.

3.2.2.12. Cabinet and Sectional Dryers

There are many models such as cabinet dryers, heated ceiling systems (these systems only provide natural convection and generally a weak and irregular drying), forced convection and more complex systems with specially designed compartments. In this type of dryers, the drying process is done by laying in trays to increase the surface area of the material to be dried. In Figure 3.11, the cabinet dryer used in the drying of the products is given [109].

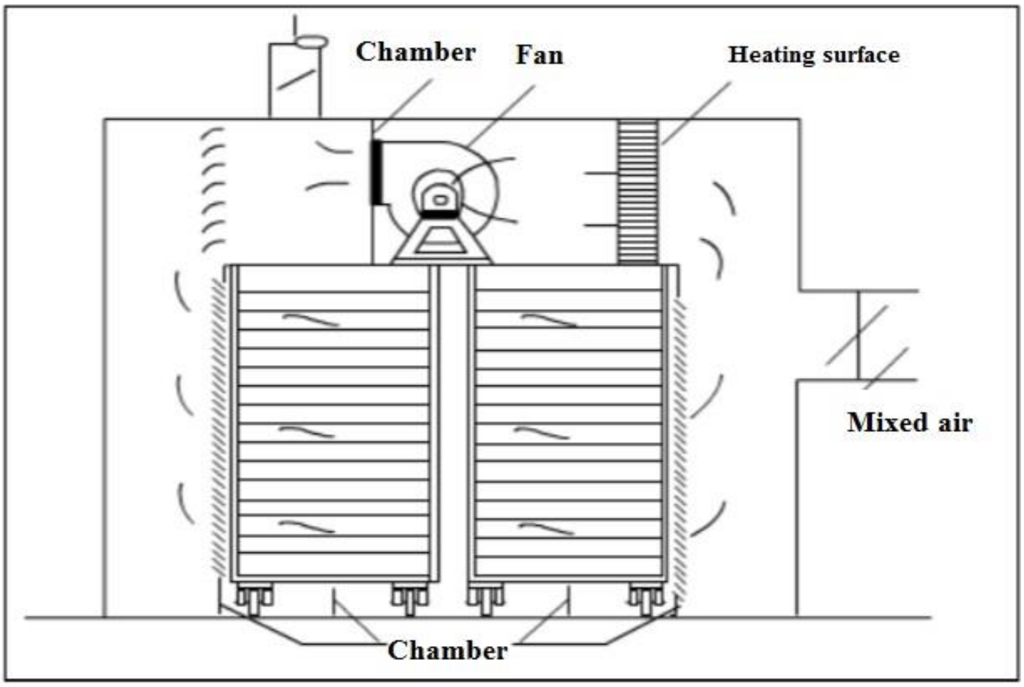


Figure 3.11. Cabinet dryer.

3.2.2.13. Dielectric Drying

In this type of drying, thermal energy is generated inside the material placed in an electromagnetic field with a very high frequency in the radio frequency or microwave region. Heat generated as a result of molecular friction due to rapid changes in the direction of the electromagnetic field alters the flow of the pole. Since the dielectric constant of liquid water is much higher than that of many solid materials, heat is generated in the water-containing part of the material. This event is removed from the material by evaporating water [112].

3.2.2.14. Microwave Drying

A very high frequency (900 to 5000 Mhz) power supply is used in microwave drying. It can be described as a form of dielectric heating since it is applied to heating non-conductive materials. Microwave drying is applied to thin materials in the form of strips. The protective measures required to be taken at the entrance and exit of the system make it difficult to work continuously. The safety measures required to operate the system make microwave drying more expensive than dielectric drying [108].

3.2.2.15. Sterilization

Foodstuffs are sterilized for 10 to 15 minutes at 110 ° C to 115 ° C in hermetically sealed containers. In particular, this method is used to process infant formula, dietetic food and fruit nectars [107].

3.2.2.16. Freeze Drying

Freeze drying is based on sublimation. Sublimation is the process of evaporation of water from the frozen product in a closed environment below the triple point, i.e., 0.6113 kPa pressure and a temperature of 0.01 ° C [113,114]. Since the water does not become liquid during this process, the product does not deteriorate. The water crystals in the frozen product evaporate in the pores of the product and do not damage the cell wall in the product. This process does not spoil the color, structure and appearance of the product and also makes the product look fresh [72,115].

Freeze drying is used for drying very sensitive materials that are sensitive to heat. Freeze drying is primarily used in the drying of serum, bacteria, and virus cultures, in the pharmaceutical industry and in the drying of foods (coffee, milk powder etc.) [78,116]. The material to be dried is first frozen between -20 ° and -40 ° C according to its properties. This freezing process can be carried out in any conventional freezing arrangement. It is then quickly taken to the drying cell. The drying cell is vacuumed with the help of a vacuum pump and the ice in the frozen material is sublimated and the drying process of the material takes place. The advantages of freeze drying are that when water is added to the dried material again, it reaches a structure that is very close to its pre-drying structure, the shelf life of the dried material is extended, its weight is reduced, storage space is saved, and it is stored at room temperature [74,117].

PART 4

FREEZE DRYING

4.1. INTRODUCTION TO FREEZE DRYING

Freeze drying, also known as lyophilization, is a decomposition process widely used in biotechnological products, some sensitive chemicals, and the pharmaceutical industry [65,78,118–121]. Freeze drying method is a process to remove the bound water (desorption) by sublimation of the solvent (free water) from frozen material or frozen solutions under very low pressure [113,114]. Freeze drying is slow and expensive [116,122,123]. However, at the end of drying, the highest quality product is obtained compared to other drying techniques [72,115]. When water is added to the freeze-dried material again, it reaches a structure that is very close to its pre-drying structure by taking water (rehydration) thanks to its shrunken and porous structure [74,117]. The product has advantages such as extended shelf life, reduced weight, saving on storage space, and storage at room temperature without the need for cold storage [80,124].

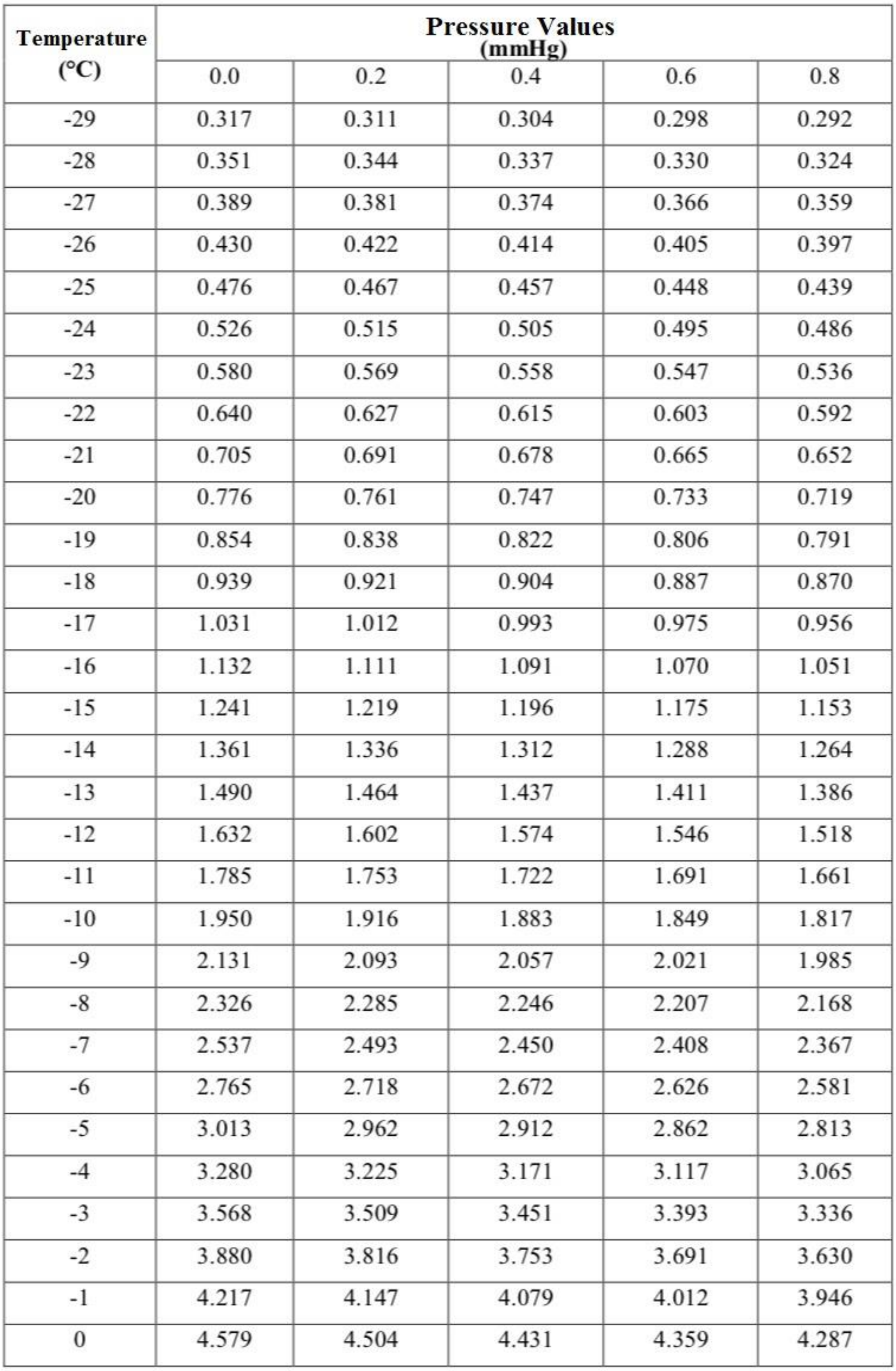
4.2. SUBLIMATION THEORY

The free-drying process is based on sublimation. The sublimation process in freeze-drying is the process where the frozen water in the substance goes directly into the vapor phase without melting [125]. In some cases, the three phases of matter (solid-liquid-gas) can coexist. These equilibrium states together form the triple point [126].
The pure substance will include different volume and same pressure and temperature. The conditions of the triple point for water are 0.01 ° C and 0.6113 kPa. Water can only be found at triple point under these conditions. No substance can remain in equilibrium in the liquid phase at a pressure below the triple point pressure. Same argument is valid for temperature in terms of substances whose volume shrinks when

frozen. However, high pressure substances can present in liquid phase under the triple stage temperature. Water cannot be as a liquid under atmospheric pressure, but as a liquid at -20 ° C at 200 MPa pressure. A substance may pass from the solid phase to the vapor phase in two ways. In the first way, it first passes to the liquid phase and then to the vapor phase. In the second way, solid matter passes directly into the vapor phase. Direct transition can only occur at pressures below the triple point. Because it is not possible for the substance to be in a liquid state below this pressure point. The transition from the solid phase to the direct vapor phase is named sublimation. Substances with triple point pressure greater than atmospheric pressure, including dry ice (solid carbon dioxide), sublimation is the only method to transition to the vapor phase under atmospheric pressure. Sublimation circumstances for each sublimable substance are different [127].

For example, frozen water undergoes sublimation at normal pressure at room temperature, while at the minimum conditions of ice sublimation, the temperature is 0 ° C, the pressure is 4.579 mm Hg (0.610 kPa). Ice can sublimate when the pressure is 4,579 mm Hg or less, at 0 ° C or below. With a more comprehensive definition, sublimation of ice is possible with the water vapor pressure higher than the water vapor pressure of the surrounding environment. The ice vapor pressure depends on its temperature. For example, while the vapor pressure of ice at 0 ° C is 4,579 mm Hg, the vapor pressure of ice at -15 ° C is 1,241 mm Hg (Table 4.1).

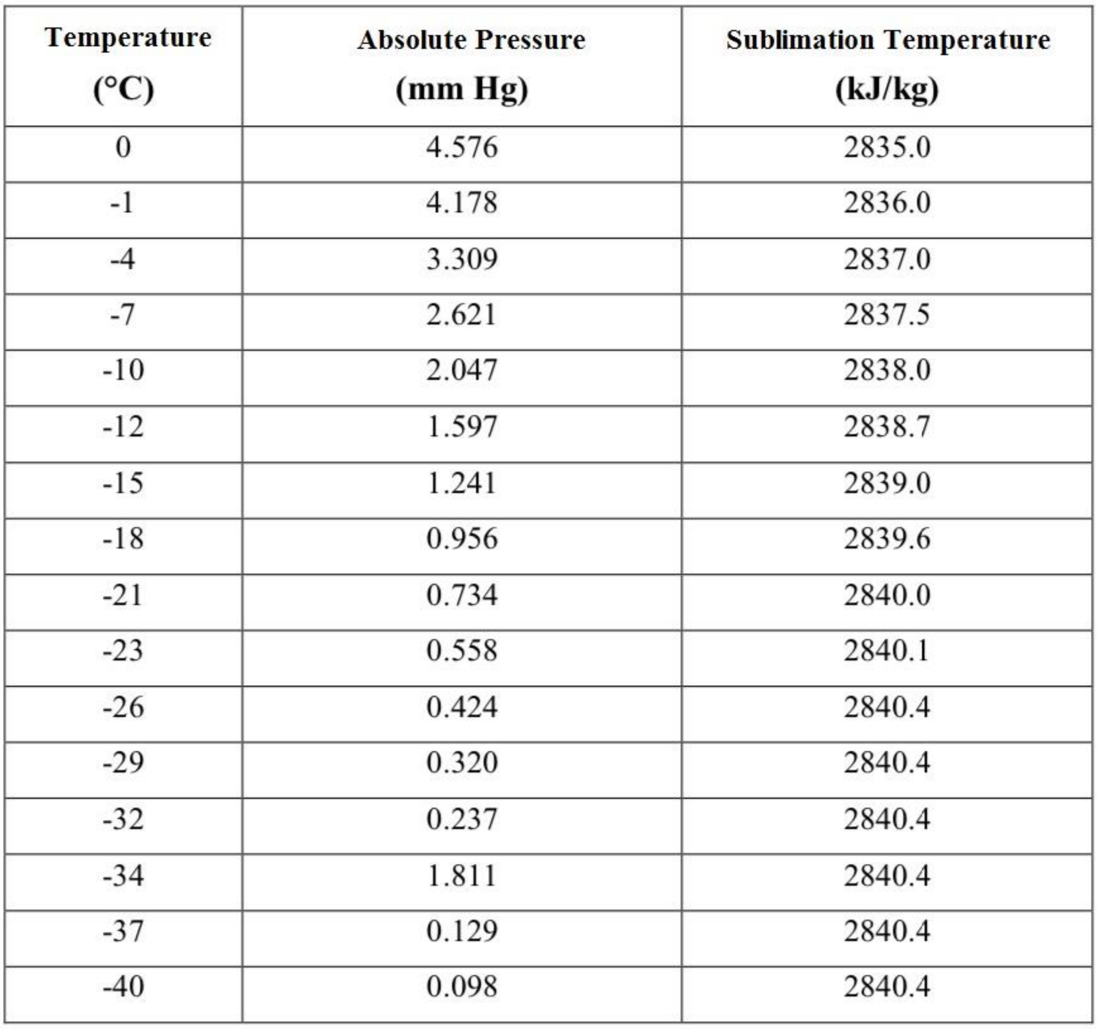
Table 4.1. The vapor pressure of ice at different temperatures.



Temperature (°C)	Pressure Values (mmHg)				
	0.0	0.2	0.4	0.6	0.8
-29	0.317	0.311	0.304	0.298	0.292
-28	0.351	0.344	0.337	0.330	0.324
-27	0.389	0.381	0.374	0.366	0.359
-26	0.430	0.422	0.414	0.405	0.397
-25	0.476	0.467	0.457	0.448	0.439
-24	0.526	0.515	0.505	0.495	0.486
-23	0.580	0.569	0.558	0.547	0.536
-22	0.640	0.627	0.615	0.603	0.592
-21	0.705	0.691	0.678	0.665	0.652
-20	0.776	0.761	0.747	0.733	0.719
-19	0.854	0.838	0.822	0.806	0.791
-18	0.939	0.921	0.904	0.887	0.870
-17	1.031	1.012	0.993	0.975	0.956
-16	1.132	1.111	1.091	1.070	1.051
-15	1.241	1.219	1.196	1.175	1.153
-14	1.361	1.336	1.312	1.288	1.264
-13	1.490	1.464	1.437	1.411	1.386
-12	1.632	1.602	1.574	1.546	1.518
-11	1.785	1.753	1.722	1.691	1.661
-10	1.950	1.916	1.883	1.849	1.817
-9	2.131	2.093	2.057	2.021	1.985
-8	2.326	2.285	2.246	2.207	2.168
-7	2.537	2.493	2.450	2.408	2.367
-6	2.765	2.718	2.672	2.626	2.581
-5	3.013	2.962	2.912	2.862	2.813
-4	3.280	3.225	3.171	3.117	3.065
-3	3.568	3.509	3.451	3.393	3.336
-2	3.880	3.816	3.753	3.691	3.630
-1	4.217	4.147	4.079	4.012	3.946
0	4.579	4.504	4.431	4.359	4.287

As it is known, "freezing latent heat" of 335 kJ / kg is released when water at 0 °C turns into ice at 0 ° C. While water at 0 ° C turns into vapor at 0 ° C, it absorbs 2500 kJ / kg of vaporization latent heat. Ice at 0 ° C absorbs 2835 kJ / kg (335 + 2500 = 2835 kJ / kg) while transforming into vapor at 0 ° C. This heat, which is the sum of the latent heat of freezing and evaporation, is called the “sublimation latent heat.” If the heat required for sublimation of ice is taken from the ice, the temperature of the ice drops. , product temperature decreases gradually [96]. Table 4.2 shows sublimation latent heat, vapor pressure and temperature in ice vapor system.

Table 4.2. Sublimation latent heat and vapor pressure change based on temperature in ice steam system.



Temperature (°C)	**Absolute Pressure (mm Hg)**	**Sublimation Temperature (kJ/kg)**
0	4.576	2835.0
-1	4.178	2836.0
-4	3.309	2837.0
-7	2.621	2837.5
-10	2.047	2838.0
-12	1.597	2838.7
-15	1.241	2839.0
-18	0.956	2839.6
-21	0.734	2840.0
-23	0.558	2840.1
-26	0.424	2840.4
-29	0.320	2840.4
-32	0.237	2840.4
-34	1.811	2840.4
-37	0.129	2840.4
-40	0.098	2840.4

4.3. THERMODYNAMICS OF SUBLIMATION

It is necessary to look to the equilibrium phase diagram of water when determining the sublimation circumstances. The equilibrium phase diagram (triple point) displays the pressure and temperature where the different phases are in equilibrium in a single component system of water. This diagram can be used to determine the required temperature and pressure ranges in the event of sublimation of water. Figure 4.1 shows the pressure-temperature phase equilibrium diagram of a substance such as water which increases with freezing.

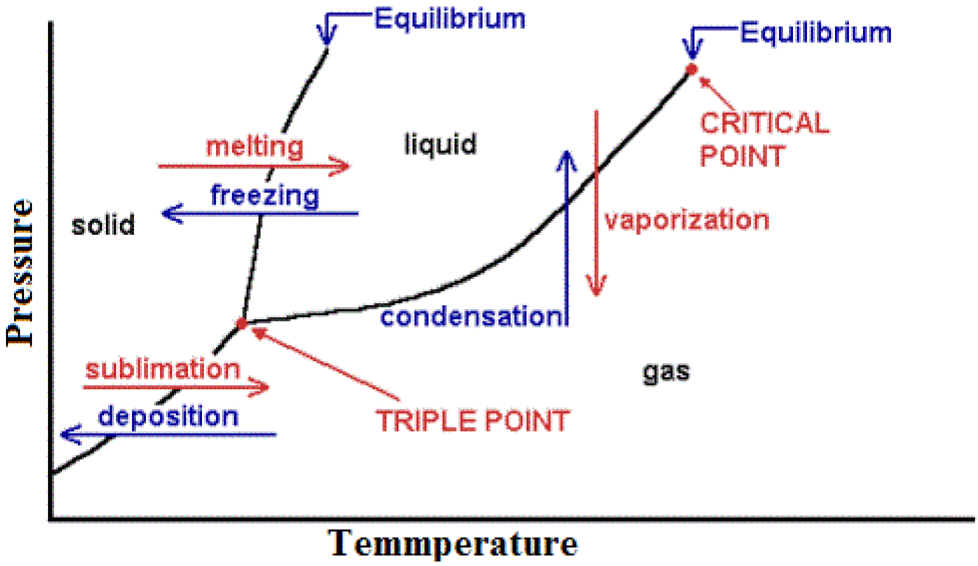


Figure 4.1. Equilibrium phase diagram (triple point).

As it can be understood from the figure 4.1, the transition of the substance from the solid state to the liquid state is melting, the transition from the liquid state to the solid state, as is freezing, the transition from the liquid state to the gas state is evaporation, the transition from the gas state to the liquid state is condensation. The important thing in freeze drying process is sublimation from solid state to gaseous state, and vice versa, transition from gas to solid state is deposition (collapse) [124,125]. Figure 4.2 shows the saturation curve between the gas phase and solid phase of water. As can be seen in the figure, for ice sublimation, it is seen that the triple point temperature of the ice should be 0 ° C and the vapor pressure must be 0.61 kPa under the triple point pressure.

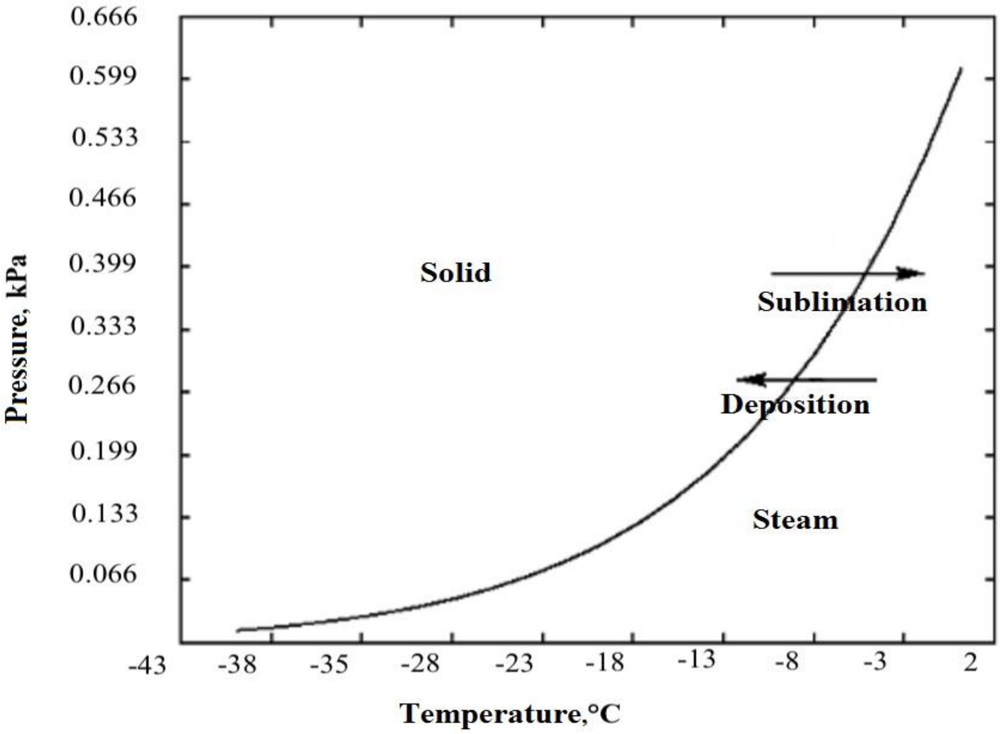


Figure 4.2. Saturation curve between solid phase of water and gas phase [61].

In order to get sustainable sublimation process, the gas and ice in the sublimation range must not be in equilibrium. In a two-phase system, when the Gibbs energy of one phase is equal to the Gibbs energy of the other phase, the phases are in equilibrium for specified temperature and pressure.

Gibbs energy, G, can be calculated with the following equation:

$$G = H - T_k . S \tag{4.1}$$

Here [125,128];

H: Enthalpy, (kJ)
T_k: Temperature, (K)
S: Entropy, (kJ / K)

In sublimation case, the phase change stops when the G of gas equals to the G of ice. Figure 4.2 shows this equilibrium circumstance with saturation curve. One of the phases will not be shown when the difference (ΔG) between the gibbs energies of the two phases is not zero. The G of the steam must be lower than the G of ice in order to show the sublimation. It is possible to achieve this situation by increasing the ice temperature or remove the gas from equilibrium status by reducing the pressure [125]. When the sublimation process occurs at equilibrium conditions or very close to it, the relationship between the pressure and temperature can be explained by the Clausius-Claperyon equation.

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{sub}}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \tag{4.2}$$

Here, P (pressure) is saturated vapor pressure depending on the temperature T (absolute temperature), ΔH_{sub} is the hidden sublimation heat, R is the gas constant [125,129]. As well as, the Clausius-Claperyon equation assumes that the hidden sublimation temperature is constant over the sub-range from the first to the second state. This equation is used to determine the vapor pressure in the sublimation interface when the temperature of the ice is given at the interface. Nevertheless, since hidden heat is a temperature function, it is more appropriate to determine the temperature function on the curve in Figure 4.2 and use it instead in the Clausiu-Claperyon equation [125].

4.4. STAGES OF THE FREEZE-DRYING PROCESS

Freeze drying process consists of three important stages. These are, respectively [63]:

1. Freezing Phase,
2. First Drying Phase,
3. Second Drying Phase.

4.4.1. Freezing Phase

The freezing shall be performed in accordance with the material to be dried. Water in foods cannot be found in pure form. The eutectic value changes according to the nature and concentration of the substance in the water. For biological tissues, this temperature is usually -21.6 ° C, which is the eutectic value of NaCl. Tissues are frozen at temperatures below this value [74,117,124].

If the product is large, the solvent on the outside of the product will freeze, but the inside may remain unfrozen. For this, all of the solvent and solid matter contained in the product must be frozen. It is very important that the solvent becomes crystalline. Conversion from liquid to glassy solid (glassy formation) can occur without ice crystal formation [74,124]. It is difficult to get water from this structure. If the tissue is frozen at temperatures above the eutectic value, crystallization will not be achieved and drying of the tissue will be very difficult.

There is a relationship between the size of the ice crystals and the porous structure formed in the material. When the crystals pass into the vapor phase, they free up space as much as they occupy. Small crystals form few and small pores in the structure. When the ice crystal is small, less porous structure is formed. The larger the ice diameter, the more porous it grows. In the fast-freezing process, small ice crystals are formed. Small ice crystals are difficult to freeze-dry, but their sublimation is less damaging to the structure of the material. In the slow freezing process large ice crystals are formed. Large ice crystals are easier to freeze-dry than small ice crystals. But it causes more damage to the structure of the material [124]. At the end of the freezing process, 65-90% of the water in the system initially is frozen, the remaining 10-35% is bound water (non-frozen water). Freezing the material can be done either in a freeze-drying device or in another freezer.

4.4.2. First Drying Phase

Sublimation is the transformation of the solvent (usually water) from a solid state under low pressure into a gaseous state from frozen materials. The gaseous removal of water from the frozen layer occurs with the vapor concentration difference. The water vapor removed from the material by sublimation spreads to the drying cell [124]. The water vapor is continuously transported from the drying cell to the condenser by means of vacuum in order to create unbalanced conditions that ensure the continuous removal of water vapor from the material. Thus, the vapor pressure of the drying cell is kept low to ensure sublimation of the solvent.

While water molecules sublimate, it takes very high sublimation heat (2840 kJ / kg) from the material to be dried and the temperature of the frozen layer drops further [74]. If the temperature is not supplied to the system from any heat source, the water vapor in the product comes into balance with its partial pressure and the decomposition of the water from the product by sublimation stops. In order for sublimation to continue, heat must be given to the system from any heat source. The material to be dried is given heat, conduction, convection or radiation. The heating of the product with conduction is provided by heating the plates under the container where the product is located [74,130]. The heat supplied to the system is not increased randomly. The maximum heat of the freeze-dried layer should be chosen in such a way that it does not lose bioactivity, does not change color, and does not cause chemical and biochemical reactions [74,124].

Sublimation rate increases rapidly in a short time. An interface is formed between the layer that dries as a result of sublimation and is still frozen. Pores in the drying area create resistance to steam flow. This resistance decreases the sublimation rate and approaches "0" over time. With the complete sublimation of the free water, the first drying period that is known a mass transfer limited process ends [55]. When the first drying period is over, the moisture content is 7-8% [124].

4.4.3. Second Drying Phase

The second drying stage, the last stage of the freeze drying process that is known a heat transfer limited process [55], involves the removal of unfrozen (bound) water. In the second drying stage, physical adsorption is the process of desorption of bound water, which is present as chemical adsorption and crystallization water [116]. In an ideal freeze-drying process, the second drying phase begins immediately at the end of the first drying phase. In the well-designed freeze-drying process, it represents the removal of only the frozen water by sublimation during the first drying phase and the removal of only the bound water during the second drying phase. But in reality, in freeze-drying systems, a small amount of bound water is removed from the material to be dried during the first drying phase. In freeze drying systems, the moment when all the frozen solvent in the substance to be dried is removed by sublimation (the end of the first drying stage) is considered the beginning of the second stage. Thus, only bound water is removed from the substance to be dried during the second drying stage. 65-90% of the total water in the material is water in Free State, and it is removed by sublimation during the first drying phase. 10-35% of the total water is bound water. The removal of bound water affects the drying rate and total drying time. The time required for removal of bound water may be equal to or longer than the time required for free water removal. The bound water in the material to be dried is removed by applying heat to the material under vacuum. As in the first drying phase, the heat given to the material during drying is not increased indiscriminately in the second drying phase. During the second drying phase of this temperature, the moisture content of the product varies greatly according to the temperature and time. Temperatures between 10-35 °C are generally preferred for temperature dependent products, and 50 °C and above for less temperature dependent products [74].

4.5. FREEZE DRYING SYSTEM ELEMENTS

Figure 4.3 shows the working principle of a freeze-drying system with the main units. Freeze drying system; it consists of four parts: cooling system, drying cell, vacuum pump, and heating unit.

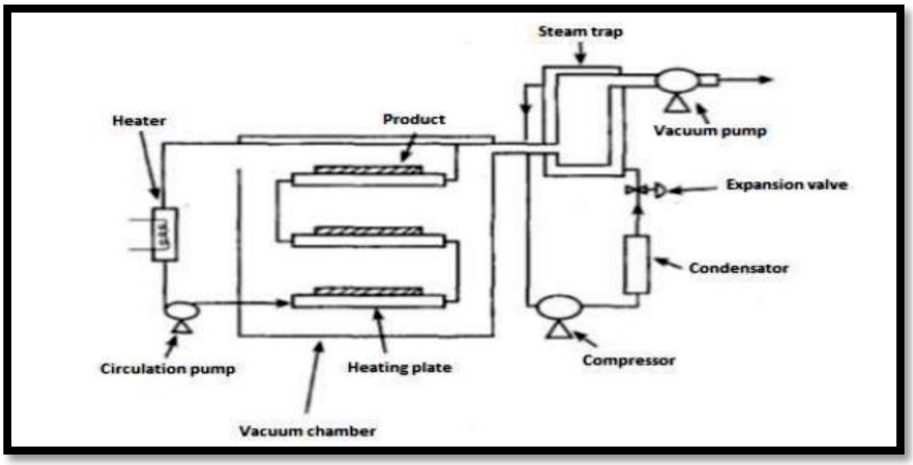


Figure 4.3. Freeze drying system scheme.

4.5.1. Cooling System

The vapor compression refrigeration cycle can be used as a cooling system in the freeze-drying system. The vapor compression refrigeration system is the cooling system by changing the physical state of the refrigerant circulated in a closed circuit, that is, from liquid to gas, from gas to liquid [94]. The vapor compression refrigeration system is the most widely known and widely used system of cooling systems. In the vapor compression refrigeration system, the refrigerant transforms from vapor to liquid, from liquid to vapor. This transformation continues throughout the system runtime. The basic components of a vapor compression cooling system are given in Figure 4.4. Basic elements of the vapor compression refrigeration system including evaporator, expansion valve or capillary tube, compressor and condenser [131,132].

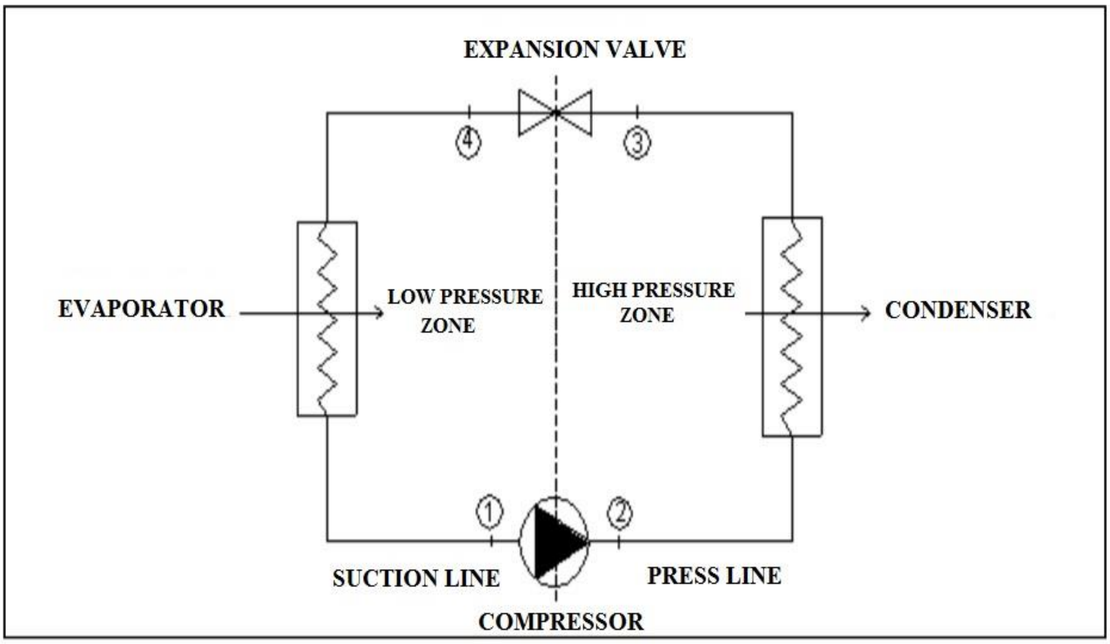


Figure 4.4. Elements of the vapor compression refrigeration system.

In the system, the compressor increases the pressure and temperature by compressing the refrigerant in the form of saturated vapor, which was at low pressure coming from the evaporator [133]. The refrigerant exiting the compressor at high pressure comes to the condenser, where it condenses by throwing heat (condensation latent heat) to the environment. The refrigerant, which comes out as a liquid from the condenser, is passed through an expansion valve or capillary tube to reduce its pressure. The fluid entering the evaporator at low pressure evaporates here. While evaporation takes place, heat (vaporization latent heat) is drawn from the cooled environment and thus the cooling event takes place. The vapor phase refrigerant leaving the evaporator enters the compressor at low pressure and the cycle continues. According to the figures on Figure 4.4 of the ideal vapor compression refrigeration cycle, the logP-h diagram is given in Figure 4.5.

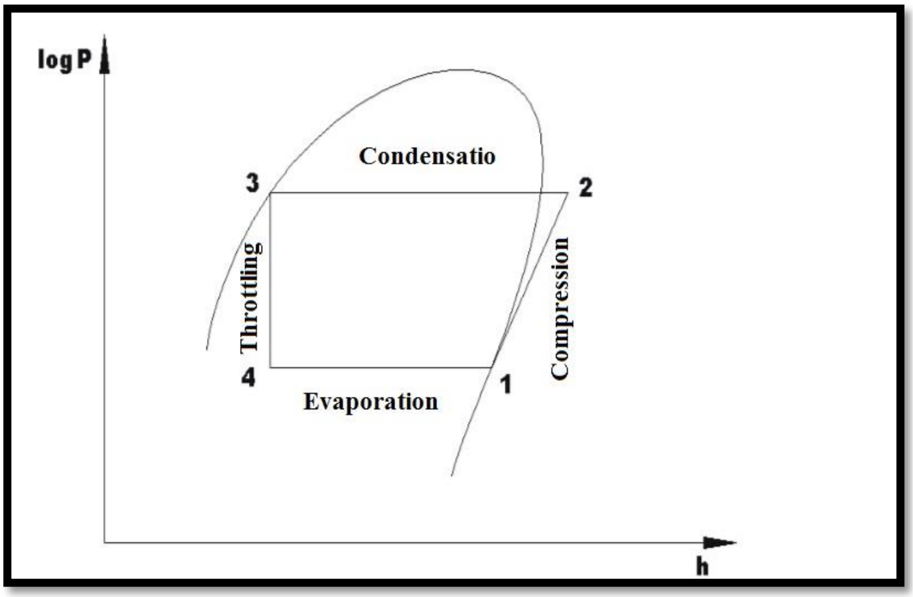


Figure 4.5. logP-h diagram of the ideal refrigeration cycle with vapor compression.

In the logP-h diagram in Figure 4.5, the phases of the refrigerant in the vapor compression refrigeration cycle during the cycle are described below with the help of the numbers indicated on the diagram.

1-2 : Compression of saturated steam from evaporation pressure to condensation pressure with the help of a compressor (Reversible adiabatic compression).

2-3 : Discharge of the heat by expelling it at constant pressure (until it becomes saturated liquid).

3-4 : Reducing the pressure of the liquid from the condensation pressure to the vapor pressure (irreversible expansion at constant enthalpy) (throttling) by passing an expansion through a throttling element that resists the flow, without heat and work exchange.

4-1 : Evaporation (Reversible heat withdrawal) by withdrawing heat from the environment at constant pressure [34,92,134].

The heat absorbed by the evaporator from the cooled environment (Q_L) is equal to the cooling load.

$$QL = QE \tag{4.3}$$

- The capacity of the evaporator

$$QE = m\,(h1 - h4) \qquad (4.4.)$$

$\dot{m}$: Mass flow rate of the refrigerant, (kg / s).
QE : Evaporator capacity, (kW).
$h1$: Specific enthalpy of the refrigerant at the compressor inlet, (kJ / kg).
$h4$: Specific enthalpy of the refrigerant at the evaporator inlet, (kJ / kg).
This equality is found in [135].

- Mass flow rate of the refrigerant

By substituting in equation 4.3 for the value of Q_E from equation 4.4, the mass flow rate of the refrigerant circulating in the vapor compression refrigeration system is found. Condenser and compressor capacities are found by replacing the refrigerant flow in Equation 4.6 and Equation 4.7. The mass flow rate of the refrigerant circulating in the vapor compression refrigeration system:

$$m = \frac{Q_L}{h_1 - h_4} \tag{4.5}$$

This equality is found in [136].

- Condenser capacity

$$QC = m\,(h2 - h3) \tag{4.6}$$

QC : Condenser capacity, (kW).
$h2$: Specific enthalpy of the refrigerant at the compressor outlet, (kJ / kg).
$h3$: Specific enthalpy of the refrigerant at the condenser outlet, (kJ / kg).

This equality is found in [137].

- Required work for the compressor:

$$Wc = m\,(h2 - h1) \tag{4.7}$$

Wc: Compressor power, (kW).

This equality is found in [132].

4.5.2. Drying Cell

In the freeze-drying process, it is the unit where the drying of the product is carried out. The drying cell is vacuumed from the air to create a low pressure during the drying process. In the drying cell, there is a tray where the product to be dried will be placed and a heating unit that provides the heat required for the sublimation process to take place. Drying cell should be made of stainless and not affected by external pressure. In addition, there should be a sight glass to observe the drying process.

4.5.3. Vacuum Pump

It is the element that provides the necessary vacuum in the drying cell for the ice in the frozen material to evaporate (sublimation) without liquefying. The vacuum pump creates a low pressure in the drying chamber by vacuuming the air in the drying chamber where the product is located. At this low pressure, there must be a lower pressure than the pressure of the water in what we call triple phase, so that the water in the product should evaporate before it becomes liquefied.

- The volumetric speed of the vacuum pump:

The volumetric velocity of the vacuum pump is calculated according to Equation 4.8.

$$\boldsymbol{S_v} = \eta \, \frac{V_f}{t_{ev}} \ln\left[\frac{P_{atm}}{P_{ev}}\right] \tag{3.8}$$

S_v : Vacuum pump speed, (m / s).

η : Vacuum pump efficiency.

V_f : free volume of the drying cell, (m^3).

t_{ev} : Evaporation time, (s).

P_{atm}: Atmospheric pressure, (Pa).

P_{ev} : Evaporation pressure, (Pa).

- Vacuum pump flow rate

$$m = S_v \, \rho_a \tag{4.9}$$

m : Mass flow rate of the vacuum pump, (kg / s).

ρ_a: The density of the air in the drying cell, (kg / m).

It is calculated by equation:

$$\rho_a = \frac{P_a \, . \, M_a}{R \, . \, T_{k.vc}} \tag{4.10}$$

P_a : Air pressure in the drying cell, (Pa).

M_a : Molecular weight of air in the drying cell, (kg / mol).

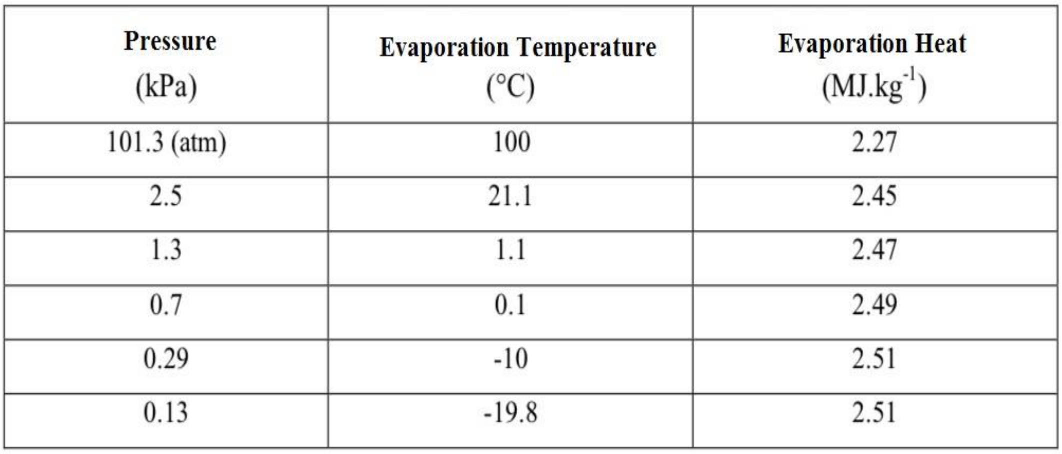
R : Gas constant (8.31472 J/mol.K).

$T_{k.vc}$: Absolute temperature (k) of the vacuum chamber (drying cell) [138,139].

4.5.4. Heating Unit

During drying, the heat taken from the product by sublimation is continuously given to the product by a heating system. Food dries from the outside to the inside. When the last ice in the center is sublimated, the product is completely dried. Due to the development of drying in this way, it is seen that it is very difficult to deliver heat to the deep ice layer in freeze drying. It is very difficult for the heat to exceed this dried insulating layer. For this reason, the drying speed slows down after a while in the freeze-drying method. For better heating, radiation sources such as infrared or microwave, which have deep penetration properties, are used rather than conduction heating [96]. Sublimation heat amounts that should be given according to pressure and temperature values are given in Table 4.3.

Table 4.3. Sublimation latent heat in the ice-steam system and its variation depending on the steam pressure and temperature.



Pressure (kPa)	**Evaporation Temperature** (°C)	**Evaporation Heat** ($MJ.kg^{-1}$)
101.3 (atm)	100	2.27
2.5	21.1	2.45
1.3	1.1	2.47
0.7	0.1	2.49
0.29	-10	2.51
0.13	-19.8	2.51

4.6. WORKING PRINCIPLE OF THE FREEZE-DRYING SYSTEM

In the freeze-drying method, the material to be dried is frozen first; thus, the water in it is bound as ice and then this ice is evaporated under suitable conditions (vacuum). The freeze-drying process consists of two stages as "freezing" and "drying". The first stage freezing process can be carried out in any conventional freezing apparatus. The speed of freezing applied and the reconstitution properties of the dried product are extremely effective. The faster the freezing process, the smaller and more ice crystals will form, the more pores appear in the dried product. Thus, the rehydration rate of the product is high, and the rehydration is complete. Rehydration is when the dried product is re-hydrated, the product can return to its pre-drying state. However, products to be dried after preliminary preparations are generally frozen at a rate of 0.5-3.0 cm / h down to -20 ° C and -30 ° C. One of the most important problems in freeze-drying is to give heat to the product to be dried. The temperature of the dried product must always be kept higher than the condenser temperature. However, under this condition, a steam flow from the dried product to the condenser can be achieved. The product dried in freeze-drying must be continuously heated. Figure 4.6 shows the heating of a freeze-dried product with plate heaters during drying [96].

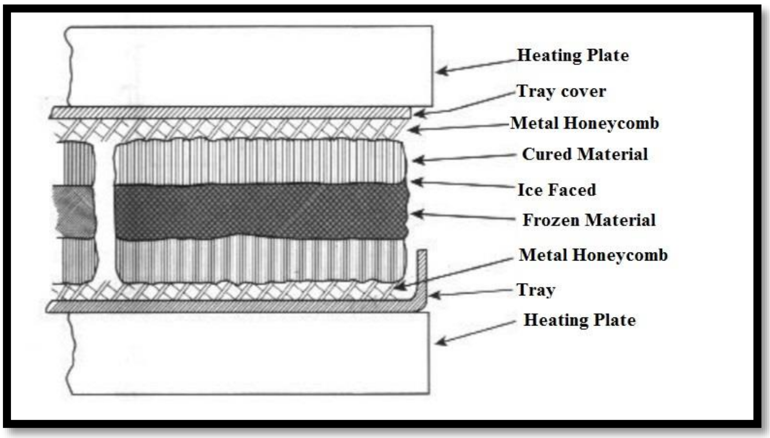


Figure 4.6. Conduction heating of food in freeze drying.

In conduction heating, as in plate heating, the heated food is not placed directly on the plate, so as not to block the outlet of sublimated steam. Between the food and the plate, there is always a honeycomb made of metal that conducts heat but does not prevent the movement of steam. Sublimation occurs first on the surface. In this way, with the drying of the surface, the ice layer gradually recedes inwards (Figure 4.7).

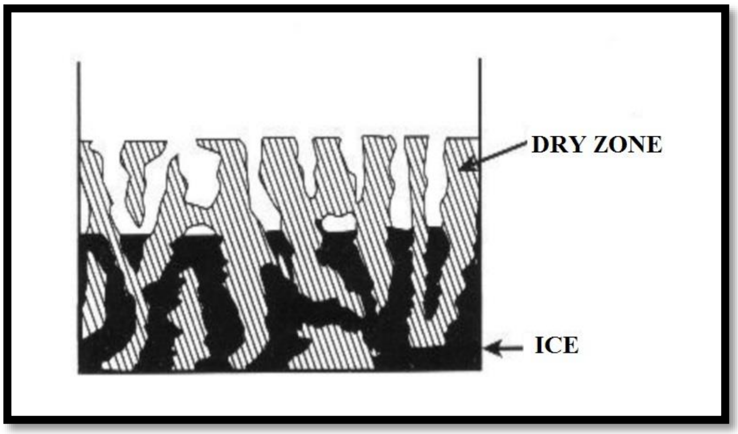


Figure 4.7. Porous structure formation in freeze-drying.

In some freeze-drying devices, heating plates are made with studs. Thus, drying is accelerated by providing a better heat transfer with these nails that reach deep into the dried material [74,96].

4.7. APPLICATION AREAS OF FREEZE DRYING

Some food items such as coffee, onion, soup, some seafood, and fruit, which are difficult to dry with traditional drying methods, are dried by freeze drying [83]. Freeze drying method is also used in the pharmaceutical industry. Some drugs may deteriorate over time while in solution. Drugs that are prone to spoilage are freeze-dried after production to stabilize their molecules, thus preserving their bioactivity [116]. Inert materials such as ceramics, superconductors and historical documents can also be freeze dried. Another example is freeze drying of nuclear waste. In this case, the common activity is added chemicals suitable for nuclear wastes in the form of dry powder, melted into glass bricks and poured and cheap storage is provided [74,124], [140].

Storage of biological materials for a long time is easier with this method. Blood plasma, serum, hormone solutions, organ or tissue to be transplanted, artificial skin are biological materials that can be stored for a long time with this method. This method is also used in the storage of living cells such as yeast, virus, and bacteria [74,124].

Freeze drying process is used to prepare tissue samples for microscopic imaging in histological studies, and to prepare samples for chemical and biochemical analysis. In addition, freeze-drying is used to store bone grafts at room temperature [124,141].

4.8. ADVANTAGES OF FREEZING DRYING

The quality of freeze-dried products cannot be achieved by any drying method. For this reason, freeze drying can be applied commercially in drying many valuable and heat sensitive biological products. On the other hand, the aroma and nutritional values of freeze-dried products are preserved at a very high level [55]. When water is added to the freeze-dried material again, it regains its structure before drying by taking water (rehydration). By lowering the temperature, the formation of microorganisms and bacteria is reduced, preventing the foodstuff from spoiling. With the crystallization of the water in the product, the decrease in the amount of water in the system prevents microbial growth or bacteria formation [74,117].

One of the advantages of freeze drying is that the temperature is very low, the relative humidity is low and the local water loss is very fast, minimizing enzymatic reactions and protein degradation compared to other conventional drying methods. In addition, the material to be dried can be stored at room temperature without the need for cold storage [74,80, 96,124].

PART 5

MATERIAL AND METHOD

5.1. MATERIEL

5.1.1. Plant materials (Hawthorn)

Hawthorn (Crataegus) belongs to the Rosette plant family (also called Rosaceae), and it exists in North America, Europe, and Asia [142]. Mature hawthorn fruits can be green, yellow or dark purple as seen in Figure 5.1, and it is commonly available in Turkey. It ripens during mid-autumn [143].

Figure 5.1. Hawthorn.

According to studies, hawthorn protects people against hypercholesterolemia, hypotension, and cardiovascular issues [144]; so, it has been used as a medicine for improving cardiovascular function [145]. and reducing blood cholesterol [146]. The wild variety found in Turkey has substantial quantities of calcium, potassium, magnesium, and sodium when it was analyzed using an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) [143]. Other nutrients of hawthorn include vitamins, lipids, proteins, carbohydrates [77,147], micronutrients, antioxidants, and bioactive compounds [148].

5.1.2. Measuring Devices

5.1.2.1. Freeze Drying Device

The freeze dryer used in the experiments is the labogene brand Scanvac Coolsafe model freeze-drying device. This device can achieve drying effectively with condenser temperature down. The CoolSafe range of Freeze Dryers CoolSafe 4-15 L is an outstanding and versatile range of advanced bench-top freeze dryers. They are the product of more than 40 years of experience and expertise and are the ideal choice for research, process development and small-scale production. Available in 3 different capacities: 4 liters and 9 liters and 15 liters. All come with a choice of condenser temperatures and a wide range of high-quality chambers and accessories. All models offer both simplicity of operation and the highest performance characteristics to meet the demands of today’s research and development laboratories. The schematic appearance of the freeze dryer used in the experiments is shown in Figure 5.2.

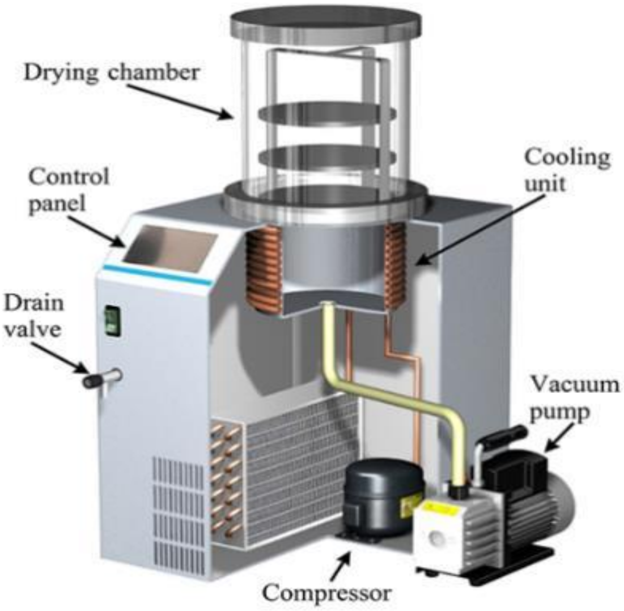


Figure 5.2. Schematic diagram of the freeze-drying device.

- Device features

1	Material trays	4pcs
2	Material tray size	Dia.200mm
3	Condenser capacity	4L
4	Condenser Temp	-55C/-80C
5	Vacuum pressure	<5Pa
6	Vacuum pump power with	4×10^{-4} mbar
7	Defrosting	Natural
8	Control Type	Touch Screen
9	Power Install	1340W(-55C)/1520W(-80C)
10	Voltage	110V/60Hz/1P,220V/50-60Hz/1P
11	Machine Size (Without Drying chamber)	615*450*370 mm (-55C),850*680*410 mm (-80C)

5.1.2.2. Precision Balance

Precision scales of the METTLER TOLEDO MS303S brand were used to measure the weight of the samples used in the experiment as well as the continuous weight shift during the drying process (Figure 5.3). The technical characteristics of this scale are shown below.

Figure 5.3. Precision balance from Mettler Toledo.

- Device features

1	Max. capacity	320 g
2	Legibility	0.001 g
3	Repeatability (sd)	0.001 g
4	Linearity	0.002 g
5	Fixed fixation time	1.5 s
6	Fixed fixation time	IP54
7	Height storage area	165 mm
8	Weighing area dimensions	127x127 mm
9	Scale dimension LxWxH	347x204x280 mm

5.1.2.3. Refrigerator

We froze the hawthorn to sublimate the moisture inside. Sublimation is the process of transferring moisture from the solid to the vapor phase. To do this, we first freeze the moisture in the hawthorn using a refrigerator and then move the frozen moisture directly to the vapor phase using a freeze drier device. The refrigerator that has been used in the study is shown in Figure 5.4.

Figure 5.4. Refrigerator.

5.1.2.4. Oven

The oven is a device used for drying, germ breeding, and disinfection or sterilization by achieving a certain temperature in it. The oven device is made of two layers of sheet metal and has an airtight cover. In addition to physical processes such as drying and dehumidification, ovens are also used to obtain the high temperatures required for some chemical reactions. In the thesis study, the purpose of using the oven is to extract moisture content from the product even though the freeze-drying process has been completed. The precise and precious measurement of the moisture ratio in the substance can be done in this manner. The oven used is BINDER brand KB53 series shown in Figure 5.5 and its technical specifications are presented below.

Figure 5.5. Binder brand oven.

- Device features

1. Electronically controlled preheating cabin technology.
2. Temperature adjustment range from -10 ° C to 100 ° C.
3. Time setting for real-time weekly scheduling multifunctional.
4. Digital temperature regulation with an accuracy of 1 ° C

5. Adjustable ramp functions with the help of the program editor
6. Adjustable fan speed (0-100%)
7. With remaining time indicator
8. Independently adjustable temperature safety system, with sound and light with alarm system
9. With an interior glass door
10. Providing a connection to APT-Com Data Control system optional RS422 output or to be connected to a printer RS232 output.

5.2. METHOD

5.2.1. Supply of Hawthorn Fruit

As is known, hawthorn fruits are commonly available in Turkey. Ripe hawthorn fruits can be green, yellow or dark purple. It also ripens during mid-autumn. Therefore, the hawthorn fruits required for experiments were supplied from the Turkish market during the autumn season and were carefully selected and brought to the university's laboratory to be prepared for experiments, as shown in Figure 5.6.

Figure 5.6. Hawthorn.

5.2.2. Preparing Hawthorn Samples for Freeze Drying

For this experimental study, we used 100g hawthorn samples, and repeated the experiment for seven times. The fruit was in the form of 5mm thick slices and it was placed in the containers, as Figure 5.7 shows. One day before the experiments, all 7 sliced hawthorn samples were placed in a deep freezer to obtain frozen samples.

Figure 5.7. Hawthorn samples.

5.2.3. Freeze-drying Experiments of Hawthorn

The basic freeze-drying process takes place through sublimation process and depends on increasing temperature of frozen product under lower pressure. Vacuum pumps are used to reduce the drying cell pressure and compressor balances the internal temperature of the freezing chamber too. Many control panel adjustments are performed before running the freeze-drying device, and the required values of time, pressure and temperature are entered. Each sample is freeze-dried for 14 hours. Figure 5.8 shows values of time and temperature.

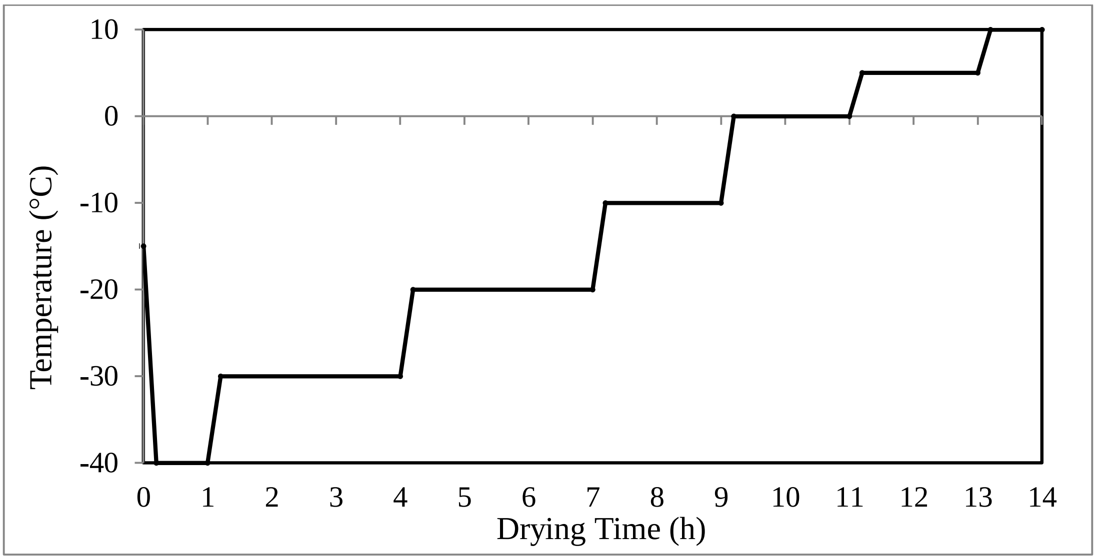


Figure 5.8. Temperature values as a function of drying time.

Before placing in the freeze-drier, all the samples were frozen overnight in a deep freezer. Their temperature was -15°C. The samples were placed in a freeze-drying chamber as shown in the figure 5.9. During the initial 1 hour, the process continued at -40°C temperature and 0.01kPa pressure. After that, the temperature was set at -30°C for 3hrs, -20°C for 3hrs, -10°C for 2hrs, 0°C for 2hrs, 5°C for 2hrs, and 10°C for 1hr, respectively, while the pressure was kept constant; so, freeze-drying finished after 14 hours.

Figure 5.9. Freeze drying of the hawthorn by scanvac coolsafe device.

We prepared 7 different samples for this study for measuring weight loss after every couple of hours. Therefore, after placing the sample on the device, the device is turned on and the sample is removed after 2 hours. At the end of the two hours, the sample weight is measured by weighing it on a precision scale with 0.001 g resolution, as shown in the figure 5.10, the shape of the sample after the first two hours drying. The second sample is placed on the device and the device is turned on according to the same drying setting. This time, the sample is removed from the device after four hours and the weight loss is calculated at the end of the fourth hours. This process can be applied on other hawthorn samples and at the end of the 6th, 8th, 10th, 12th and 14th hours, the samples are taken and placed in an oven for about 60 minutes. Later, the sample is removed from the drying oven and placed in a curved glass that includes more plenty of silica gel for about 15 minutes. Finally, the hawthorn which is taken from the dryer is weighed on a precision scale and the result is registered. The purpose of this method is to extract moisture content from the product even though the freeze-drying process has been completed. The precise and precious measurement of the moisture ration in the substance can be done in this manner.

Figure 5.10. The shape of the sample after the first two hours drying.

PART 6

RESULTS AND DISCUSSION

6.1. MOISTURE CONTENT ANALYSIS

The moisture content was determined through measuring the time-dependent mass loss using a sensitive weight scale. The 100g product had 74.676g moisture while the remaining part was 25.324g, which is the product’s dry part. Table 6.1 shows hawthorn samples’ weight loss after two-hour intervals of total 14 hours freeze-drying and Figure 6.1 depicts this hawthorn samples’ weight loss as a curve with the freeze-drying time. Figure 6.2 is a pie chart that shows moisture content and dry content as a percentage of the product mass.

Table 6.1. Weight loss of hawthorn by freeze-drying over time.

Time	**5 mm**
Hour	**Weight (grm)**
0	100
2	48.704
4	39.661
6	36.207
8	32.675
10	30.159
12	27.518
14	25.559
Stable	25.324

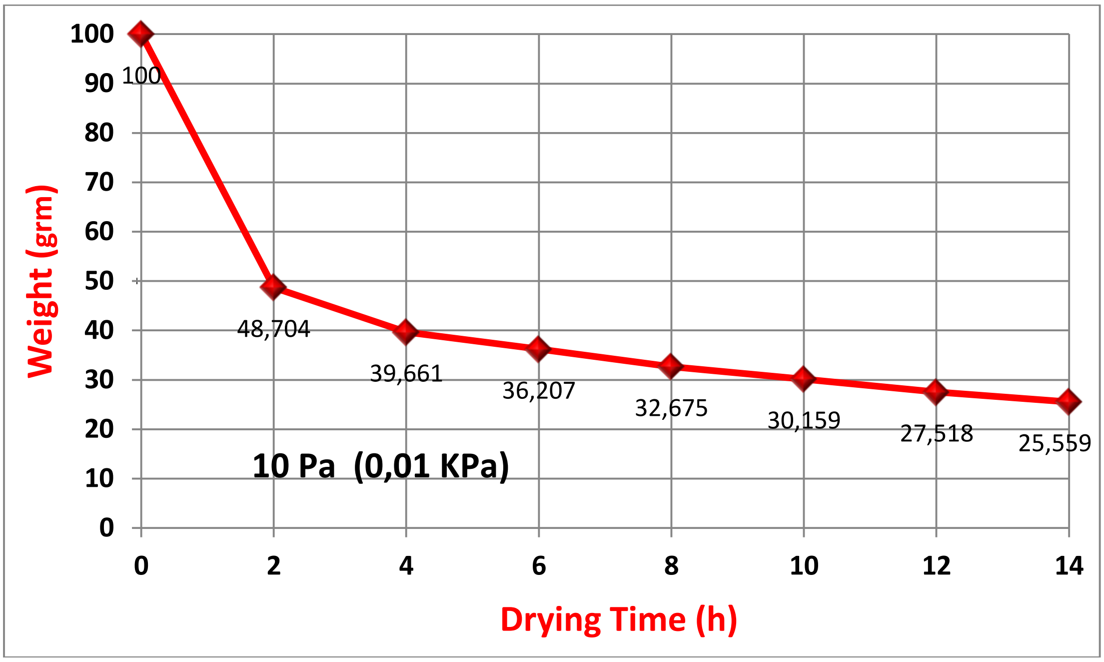


Figure 6.1. Weight loss of hawthorn over time.

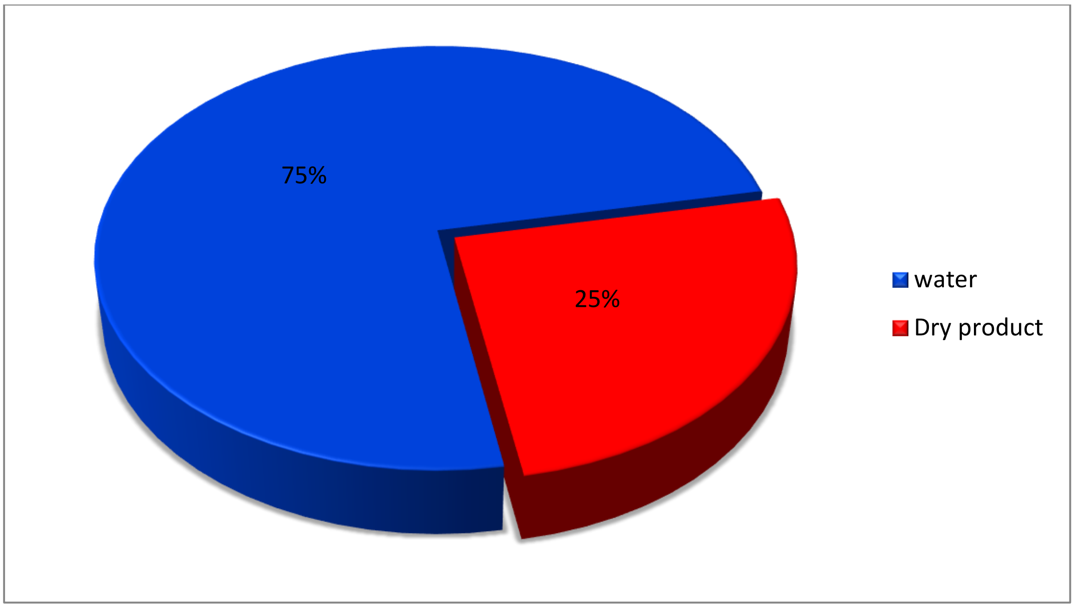


Figure 6.2. Percentage of moisture content and the dry product.

In numerous conditions and for different materials, empirical models can be applied but their use is reduced because their equations have many parameters and complicated structures. Moreover, the use of semi-empirical models has also become limited because their parameters are just linked to relevant products. Complex equations are not needed for identifying the drying ratio. Constructed equations are just valid for experimental specimens under the specific experimental conditions. We know that the logarithmic drying equation is appropriate and generally, it is used in semi-empirical models [79].

The hawthorn sample changes with time, so moisture ratio *(MR)* is a time-based and non-dimensional function, which is calculated using Equation 6.1.

$$MR = \frac{M_t - M_d}{M_0 - M_d} \tag{6.1}$$

Here M_0, M_t, and M_d, are primary, intermediate time (t), and final equilibrium moisture contents while Equation 6.1 is simplified for M_t / M_0 to make it practical [149]. Moisture Ratio (*MR*) is shown in the left side of Equation 6.1 at several t moments. We can compute the drying ratio (*DR*) using the following equation:

$$DR = \frac{M_{\mathrm{t+dt}} - M_{\mathrm{t}}}{dt} \tag{6.2}$$

In this equation, DR, M_{t}, and $M_{\mathrm{t+dt}}$ represent the drying ratio, moisture content at t time period, and moisture content for time t+dt, respectively [55,149]. Figure 6.3 shows the experimental results of 14-hour freeze-drying, and the curve shows variation in the hawthorn samples' moisture ratio with respect to drying time.

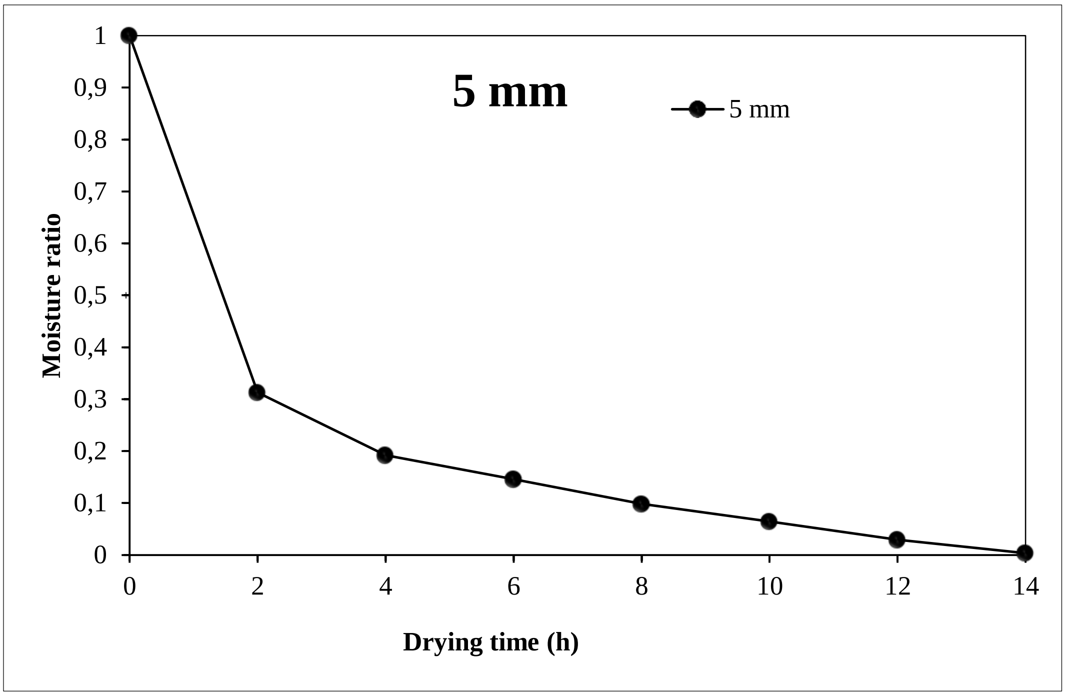


Figure 6.3. Moisture ratio variation curve for hawthorn samples during 14-hour drying time.

6.2. DRYING CHARACTERISTICS

Figure 6.4 shows the moisture content curve for hawthorn samples with respect to drying time. In this curve, moisture content is the ratio between the water content to the dry matter. During the initial 2 hours, the moisture content significantly reduces but later it slows down.

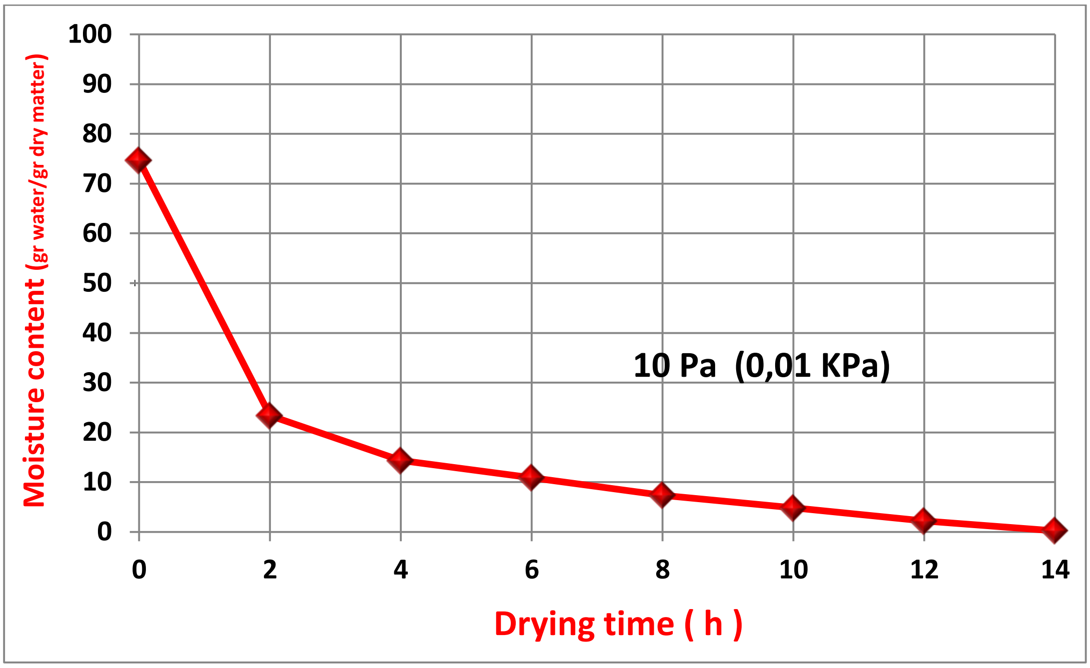


Figure 6.4. Moisture content curve of hawthorn slices with respect to drying time.

Figure 6.5 shows the drying rate of frozen hawthorn slices. During the first 2-hour period of freeze-drying, drying rate is significantly high because the samples have high surface moisture but later, the drying rate sharply declines during the next 2-hour period, since the freeze dryer’s plate temperature is quite low (−30°C) and the surface moisture content (MC) dries up quickly but later, the drying rate further slows down during the third 2-hour period. Then, during the fourth 2-hour period, a drying rate rises a little because the freeze dryer’s plate temperature increases. Later, the drying rate gradually decline until the end of freeze-drying process. Figure. 6.4 and 6.5 show how drying rate declines when there is low moisture content in the sample.

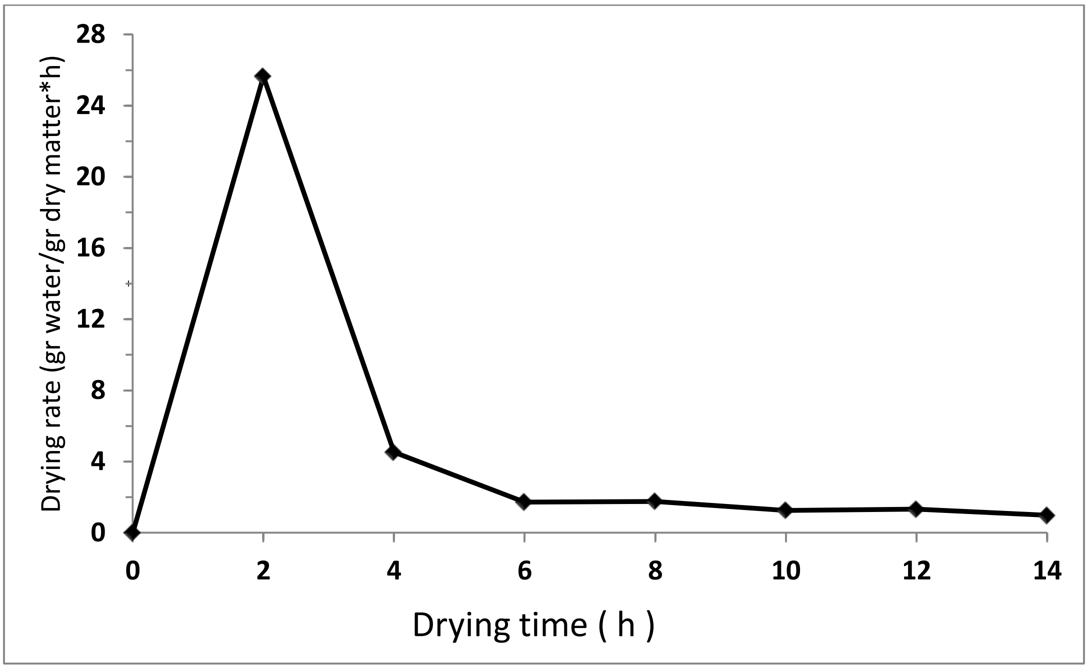


Figure 6.5. The drying rate curve of hawthorn slices as a function of drying time.

Figure 6.5 shows deviation that is because of the freeze dryer's different plate temperatures when freeze-drying takes place. Fig. 5.8 shows that the freezer dryer plates' temperature was initially set at −40ºC, and then, it gradually increased to 10°C for preventing the hawthorn samples from getting scorched. If we analyze Fig. 8, it clearly indicates that the drying rate slowed down because of increasing drying time and reducing the samples' moisture content. It implies that no constant rate period exists when freeze-drying of hawthorn is in progress. For mass transfer during the falling-rate period, diffusion is a prevailing process. Water vapors at the interface appear as a consequence of sublimation are transferred to the sample surface with the help of a dried region capillary. Such water vapors are extracted through a freeze dryer's condenser because the water vapors' partial pressure at the condenser surface is substantially lower as compared to the partial water vapor pressure at the sample surface.

6.3. EVALUATION OF THE MODELS

When the moisture content of a substance is evaluated and time-dependent mass losses were calculated, we constructed their mathematical model-dependent graphs for eight different drying kinetic models. MATLAB simulation was used for executing such operations. Total eight separate drying kinetic models have shown the evaluated moisture ratio (MR), which is used in MATLAB, as Table 6.1 indicates.

Table 6.2. Empirical and semiempirical equations for drying kinetics models.

Model no.	**Model name**	**Model**	**References**
1	Newton	$MR = exp(-kt)$	[149]
2	Page	$MR = exp(-kt^n)$	[150]
3	Modified Page I	$MR = exp[-(kt)^n]$	[78]
4	Henderson and Pabis	$MR = a.exp(-kt)$	[79]
5	Logarithmic	$MR = a.\exp(-kt) + c$	[122]
6	Two-term exponential	$MR = a.exp(-kt) + (1 - a)\ exp\ (-kat)$	[151]
7	Wang and Singh	$MR = 1 + at + bt^2$	[152]
8	Diffusion approach	$MR = a.exp(-kt) + (1 - a)\ exp\ (-kbt)$	[153]

The key parameters for proving the agreement between the moisture ratios of the sample produced by the experiments and calculated by the kinetic models using a statistical approach are the diminished chi-square (X^2), the root mean square error (RMSE) and the coefficient of determination (R^2). By solving equations 6.3, 6.4, and 6.5, we can compute the mentioned parameters:

$$X^2 = \frac{\sum_{i=1}^{n}\left(MR_{exp} - MR_{pre}\right)^2}{N - z} \tag{6.3}$$

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{n}\left(MR_{pre,i} - MR_{exp,i}\right)^2\right]^{1/2} \tag{6.4}$$

$$R^2 = 1 - \left[\frac{\sum(\mathrm{MR_{exp}} - \mathrm{MR_{pre}})^2}{\sum(\mathrm{MR_{pre}})^2} \right] \tag{6.5}$$

where $MR_{pre,i}$ is the i^{th} predicted MR, $MR_{exp,i}$ is the i^{th} experimental MR,, N is the number of observations and z is the number of drying constants in the model [55]. Equation 6.3 shows strong alignment between kinetic and experimental model values, which increase when the chi-square (X^2) reduces. Equation 6.4 displays the root mean square error (RMSE) that determines the model equations' appropriateness and represents the difference between the predicted values obtained for the model and the experimental values. Additionally, large coefficient of determination (R^2) values exist in Equation 6.5, and their proximity to 1 shows the kinetic model's applicability. A multi-regression model is used to calculate the coefficients contained in the most fitting model [150,154].

Both experimental findings and findings of eight different kinetic drying models were used to determine the most effective and suitable drying model among the eight applied models based on the values of R^2, X^2, and RMSE, which were obtained from the models. Table 6.2 displays the R^2, X^2, and RMSE values for all eight kinetic drying models. Based on the values R^2 and X^2, the Diffusion Approach Model is the most appropriate and effective drying model because its R^2 value is 0.9987, which is closest to 1. The X^2 value of the Diffusion Approach Model is 1.959×10^{-4} and that is closest to 0. This model is also suitable because its root means square error (RMSE) value is 0.011063, which is also the closest RMSE value to 0.

Table 6.3. Results obtained using eight kinetic drying models.

Model Name	**Model parameters**	**R^2**	**X^2**	**RMSE**
Newton	k = 0.4537	0.9676	3.45 x 10^{-3}	0.054952
Page	k = 0.7658 n = 0.5603	0.9973	3.392 x 10^{-4}	0.01595
Modified Page I	k = 0.6636 n = 0.5277	0.997	3.717 x 10^{-4}	0.016697
Henderson and Pabis	a = 0.9755 k = 0.442	0.9683	9.26 x 10^{-4}	0.026355
Logarithmic	a = 0.9321 c = 0.05988 k = 0.5721	0.9845	2.315 x 10^{-3}	0.038038
Two-term exponential	a = 0.2949 k = 1.152	0.9824	2.178 x 10^{-3}	0.040424
Wang and Singh	a = -0.2115 b = 0.01061	0.7936	2.561 x 10^{-2}	0.138602
Diffusion approach	a = 0.5405 b = 0.09891 k = 2.08	0.9987	1.959 x 10^{-4}	0.011063

Figure 6.6 best shows this concurrence, which also shows that the Diffusion Approach Model is used to find the experimental and expected MR values. It is clear that there is a strong concurrence between the expected and experimental MR values. It also means that the data points exist in the vicinity of the 45° straight line on the plots, and it further establishes the model’s suitability to predict hawthorn’s drying characteristics.

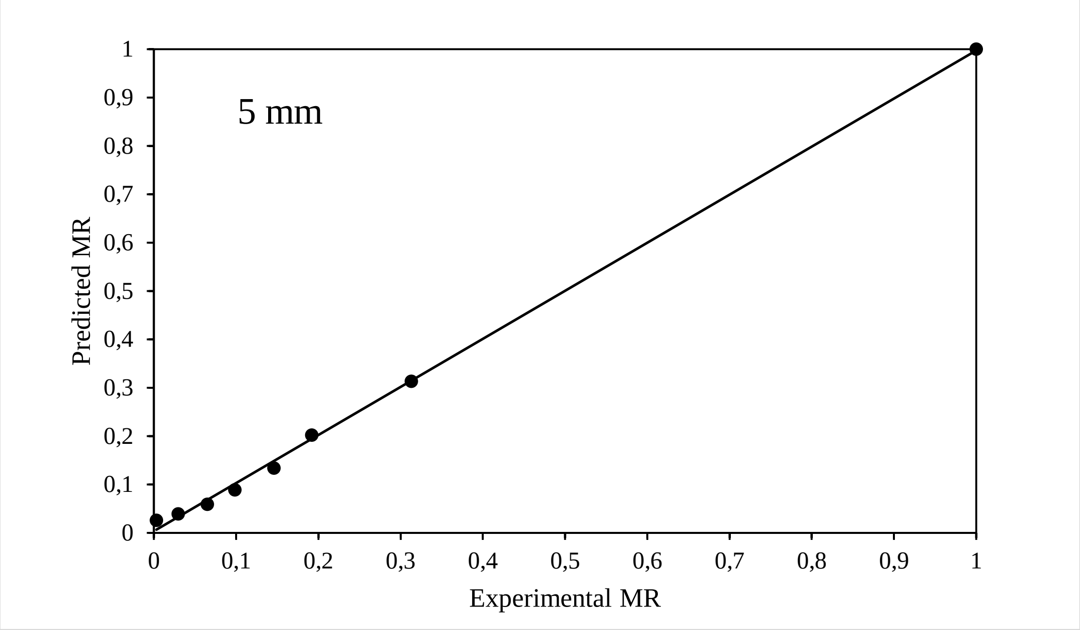


Figure 6.6. Comparison between experimental and predicted moisture ratio values applying the Diffusion Approach Model.

6.4. DETERMINATION OF EFFECTIVE DIFFUSIVITY

For food and material drying efficient diffusivity is an important transport characteristic that depends on the moisture content and temperature of a material. Fick's diffusion equation has a second law, which makes it a mass-diffusion equation for drying agricultural products in a fall-rate phase. The drying processes' theoretical model can be determined by its solution, which is shown in the equation given below:

$$\frac{\partial M}{\partial t} = D_{eff}\, \nabla^2\, M \qquad (6.6.)$$

Diffusion equation solution (Eq. 6.6) for slab geometry was first used by Crank (1975). He assumed that there is a negligible exterior resistance, uniform initial moisture distribution, negligible shrinkage, and constant diffusivity [155]:

$$MR = \frac{8}{\pi^2}\begin{bmatrix} exp\left(-\frac{\pi^2 D_{eff}\, t}{4L^2}\right) + \frac{1}{9} exp\left(-9\frac{\pi^2 D_{eff}\, t}{4L^2}\right) \\ + \frac{1}{25} exp\left(-25\frac{\pi^2 D_{eff}\, t}{4L^2}\right) + \frac{1}{49} exp\left(-49\frac{\pi^2 D_{eff}\, t}{4L^2}\right) \ldots \end{bmatrix} \qquad (6.7)$$

Here t defines drying time (s), D_{eff} shows effective diffusivity (m^2/s), n presents a positive integer, and L shows half-thickness of the samples (m). Keeping in view long drying duration with steady diffusion coefficient in a Cartesian coordinate system, we simplified Eq. 6.7 to a limiting form of diffusion equation, as Equation 6.8 shows [55]:

$$MR = \frac{8}{\pi^2} exp\left(\frac{\pi^2 D_{eff}\, t}{4\, L^2}\right) \tag{6.8}$$

After plotting the experimental drying data for ln (MR) versus time, we determined effective diffusivity *(D_{eff})* values, as Figure 6.7 shows.

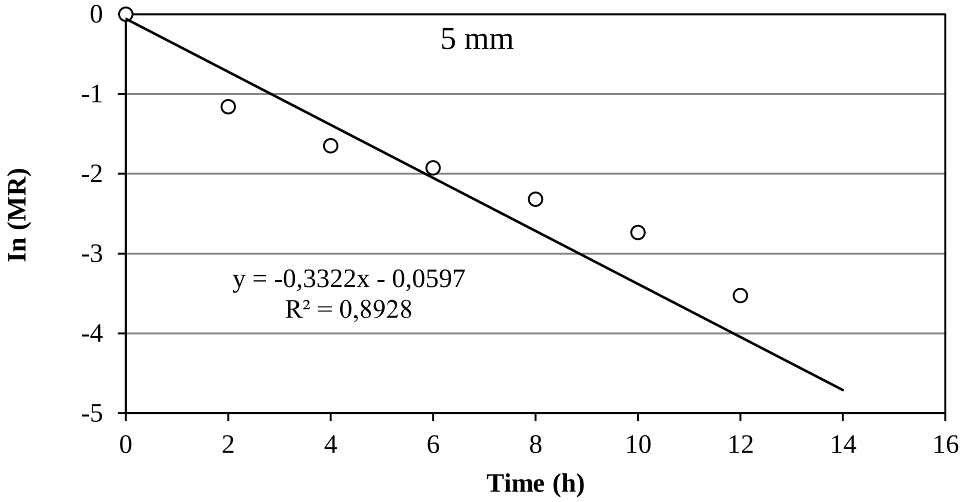


Figure 6.7. ln (MR) versus freeze-drying time for Hawthorn samples.

Equation 6.8 shows that in ln (MR) plot versus drying time should be in a straight line with slope *K*:

$$K = \frac{\pi^2 D_{eff}}{4L^2} \tag{6.9}$$

In Figure 6.7, we found slope (K) from the graph. For 5mm thick hawthorn slices, effective diffusion value (D_{eff}) was determined using Equation 6.9, and its value was $2.33742 \times 10^{-10} m^2/s$. From this research, the effective diffusion value was found within the reference range $10^{-12} – 10^{-8} m^2/s$ for drying food materials [156]. According to the literature, no research has been performed so far to establish hawthorn's kinetic model, and no attempt has been made to quantify its effective diffusivity or moisture content in freeze-drying process. We conclude that hawthorn's effective diffusivity has good agreement with the general effective diffusivity range for drying food materials.

PART 7

CONCLUSION AND RECOMMENDATIONS

7.1. CONCLUSION

After conducting our experiments, we summarized our findings pertaining to the freeze-drying process, which is one of the easiest and efficient ways to remove water from a food product because it preserves both flavor and quality of food that ultimately helps maintaining their market value. On the other hand, this method has high investment needs and operational costs as compared to the traditional drying processes. This experiment was conducted to preserve the slices of hawthorn by using freeze-drying technique with 100g average weight. This process was conducted using a device (SCANVAC COOLSAFE) for 14 hours. It is given that the sliced samples of hawthorn fruit had 5mm thickness and 74.67% water. Moreover, we selected a suitable kinetic drying model out of the total eight models based on the calculated MR and DR values, and we measured mass losses after every two hours. We found that the Diffusion Approach Model is the best because its R^2 value is closest to 1, which was 0.9987 while the X^2 and RMSE values are closest to 0, which were $1.95\ 9x\ 10^{-4}$ and 0.011063, respectively. In addition, we found the effective diffusivity value, which was $2.33742 \times 10^{-10} m^2/s$ for the mentioned hawthorn slices. It was confirmed that the calculated effective diffusivity value was within the reference range mentioned in the literature ($10^{-12} – 10^{-8}\ m^2/s$) for food products.

7.2. SUGGESTIONS

In light of the experimental results and insights obtained as a result of the thesis review, the following recommendations were considered necessary.

- As weight losses are required to be taken during freeze-drying, the product is put in the device and measured at the desired moment, a new product with the same weight is placed in the device for the next cycle and this time is taken at a different time from the previous time, and this procedure is replicated for each time. This method is a massive waste of time, necessitates vast amounts of product and extends the device's running time. During the drying time, any weight loss can be viewed on the digital screen using a sensitive weight meter mounted inside the device.
- The operating system of the device must be able to turn itself off when the desired weight is met using the weight loss measuring mechanism described above, which has placed in the freeze-drying device, and that it can provide automatic control by adjusting the internal pressure to suit the ambient conditions.
- After being frozen in the refrigerator, the substance to be dried in the manufactured freeze-drying machine is transported to the drying chamber. The drying chamber may also be used to freeze the product.
- For the sublimation process, radiation sources such as ultraviolet or microwaves, which have the potential to penetrate deeper while supplying greater warmth than conduction heating, may be used in the drying process. Furthermore, it will reduce the long drying time and high energy consumption. To reduce quality issues, freeze-drying technique (FD) may be used as a single operation as well as in conjunction with other techniques.

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RESUME

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