Food preservation technologies



Sebnem Tavman¹, Semih Otles¹, Selale Glaue² and Nihan Gogus² ¹Food Engineering Department, Ege University, İzmir, Turkey, ²Efes Vocational School, Dokuz Eylul University, İzmir, Turkey

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4.1 Introduction

According to the United Nations Economic and Social Affairs Department, the world's population was 7.3 billion in 2015 and will reach 8.5 billion by 2030, 9.7 billion by 2050, and 11.2 billion in 2100. Global action against hunger predicts that we must increase food production by 70% to feed this rapidly growing world population. However, increasing farming practices will not be enough to solve global food demand. The development and global implementation of more efficient, energy- and resource-saving technologies helps the industry respond to increasing food demand while reducing environmental impact and providing sustainability. Reducing food waste must also represent an important part of the equation. The reports of the United Nations estimate that 30%–50% of the globally produced food—about 2 billion tons—is lost or wasted. Food may be lost due to some

inadequacies during production and processing, as well as market and consumer trends. They range from poor storage and inadequate transportation logistics to customer purchases of extra products. The establishment of efficient, sustainable food preservation technologies also plays a vital role in preventing wastage associated with food spoilage. The rapidly increasing world population necessitates that the amount of food wasted due to spoilage is kept to a minimum. Food production is only one part of the process to ensure continuous, diverse, safe, food supplies to meet the consumer demands. Lack of food safety systems costs the food industry millions of dollars annually through waste, reprocessing, recalls, and the resulting loss of sales. Foodborne diseases are no longer limited to developing countries. Unsafe food is not fit for human consumption and therefore is wasted. Failure to comply with minimum food safety standards can cause food losses. Several factors can lead to food being unsafe, such as naturally occurring toxins in food itself, microorganisms, contaminated water, unsafe use of pesticides, and veterinary drug residues. Poor and unhygienic handling and storage conditions, and lack of adequate temperature control, can also cause unsafe food and should be prevented by a food preservation technique (FAO, 2011). In the food supply chain of developing and developed countries consumers are responsible for most of the food waste where a recent European food waste program has defined consumer food waste as a major problem. The amount of consumer food waste has attracted the attention of The COST Network, EU network on food waste evaluation, in terms of solving this challenge through technological and political prevention. A safer global food system minimizing all food losses is important, where it also shows us how consumers can reduce food waste in their houses. At this point food preservation methods play an important role in waste reduction by ensuring safer food usage with minimizing food loss (Martindale and Schibel, 2017).

Since ancient times preservation of food has played an important role in human life. The first preservation methods used by early humans were sun drying, salting, and fermentation, which were used to provide food in periods when fresh foods were not available. The need of greater quantities and better quality of processed food increased and continued to increase with the development of civilization. Therefore, this caused increasing interest to the large food preservation industry, which attempts to supply food that is economical, nutritious, and satisfying (Karel and Lund, 2003a). Moreover, food preservation decreases food degradation and enhances the utilization of food by several conventional and innovative preservation methods, which in turn minimizes waste production, saves food, and promotes a sustainable food industry (Martindale and Schiebel, 2017; Chemat et al., 2017). The global value of food lost or wasted is estimated at US\$1 trillion per year by the FAO ("Global Initiative on Food Loss and Waste Reduction," 2015), representing a loss of economic value. Therefore, food technology under severe or nonclassical conditions is a currently developing area in applied research and industry to preserve foods and reduce waste. Innovative processing, preservation, and extraction procedures may improve production efficiency and contribute to environmental preservation by reducing the use of water and solvents, fossil energy, prevention of wastewater, and production of hazardous substances (Chemat et al., 2017).

Thermal processing of foods, which is also known as the conventional preservation technique, forms the large part of this food processing industry. Also, autoxidation in food and biological systems is responsible for many adverse effects and implications in food stability and preservation as well as human health. Human health is now assumed to be affected by oxidative damage of foods, which causes the occurrence of some important diseases such as cardiovascular diseases, diabetes, hypertension, metabolic syndrome, cancers, etc. in humans. Therefore, it is essential to preserve foods in terms of waste reduction and human health maintenance by using different commercial and innovative preservation techniques or their combination.

4.2 Thermal food preservation

Food preservation by thermal treatment is one of the most often used and known methods for the inactivation of microorganisms and enzymes, both to prevent a risk to public health and to achieve a commercially reliable shelf life for foods. By using thermal food preservation, long shelf-life foods that do not require refrigeration can be produced. It is also easy to control process conditions during the treatment. Other advantages are the destruction of some antinutritional items that may be present in the food (e.g., destruction of trypsin inhibitor in some legumes) and the ease of digestion and absorption of some of the food items found in the food (e.g., facilitation of digestion of proteins, gelatinization of starch) (Awuahet al., 2007; Augusto et al., 2018).

Thermal processing is based on the use of thermal energy (heat) where the food is heated by a hot fluid to a specific temperature, kept for a certain time that has been previously calculated to optimize the product characteristics, called processing time, and then cooled by a cold fluid to interrupt the thermal actions (Augusto et al., 2018; Karel and Lund, 2003b).

However, temperature speeds up degradation reactions, so that heat treatments adversely affect nutritional compounds and sensorial properties. Therefore, the thermal process should be designed to balance the needs of commercial sterility with the commercial demand to submit a high-quality product. New technologies in food processing operations aim to reduce damage to nutrients and sensory elements by reducing heating times and optimizing heating temperatures. Besides inactivation of pathogens, thermal treatment can also form some other desirable changes, such as protein coagulation, texture softening, and formation of aromatic components.

Thermal processing effectiveness is affected by the characteristics of the product and microorganisms, and by the processing conditions. Fat level, composition, pH, size and shape, used preservatives, and water activity are the product characteristics that influence thermal processing. The microorganism characteristics include the strain, growth conditions, and resistance to stress such as acid and/or heat. The processing conditions are the heating source, heating rate, processing type, and environmental conditions during processing (Osaili, 2012). The thermal processing is designed according to the process target. It can be a vegetative cell, a microbial spore, or an enzyme that must be chosen to ensure safety and quality of the processed food (Augusto et al., 2018; Karel and Lund, 2003b).

Thermal destruction of microorganisms is a time/temperature process. It can be explained by two notions: decimal reduction time (D value) and thermal resistance constant (z value). The D value is the heating time required to kill 90% of a certain number of microorganisms at a given temperature. It indicates the tolerance of the microorganism to the increase in heating time at a given temperature. As D value increases, thermal resistance of microorganisms increases. D value is calculated at each temperature from the linear regression model between \log_{10} of the bacterial survivors and heating time. The D value is the negative inverse slope of the survivor curve and can be expressed mathematically as follows:

$$D = \frac{t_2 - t_1}{\log_{10}(A) - \log_{10}(B)}$$
(4.1)

where A and B represent the survivor counts following heating for times t_1 and t_2 minutes.

The z value is the temperature difference required for the thermal inactivation curve to cause a 1 \log_{10} reduction. It indicates the tolerance of a specific pathogen to the temperature changes in the product. The greater the z value, the less the microorganisms are affected by the temperature rise. The z value is calculated by determining the linear regression between \log_{10} of D values and their corresponding temperature. The z value is the negative inverse slope of the thermal resistance curve and can be expressed mathematically as follows:

$$z = \frac{T_2 - T_1}{\log_{10}(D_1) - \log_{10}(D_2)}$$
(4.2)

where D_1 and D_2 are D values at temperatures T_1 and T_2 , respectively (Osaili, 2012).

The major conventional thermal processes applied in food preservation are sterilization and pasteurization. Cooling and freezing are also basic methods that are often used. Recently, electroheating technologies such as microwave heating, ohmic heating, and radio frequency (RF) have emerged to resolve the problems with conventional preservation processes. These technologies have been used to inactivate microorganisms in different types of food (Osaili, 2012).

4.2.1 Pasteurization

Pasteurization is the most important preservation method and is essential for food safety. It kills all the disease-causing and most other bacteria that might cause deterioration with minimal changes in sensory and nutritional properties. It is the milder



Figure 4.1 Types of pasteurization.

thermal process and generally used to extend the shelf life of food varying from few days (low-acid products with high a_w) up to months (high-acid products and/or with low a_w) at low temperatures, usually at 4°C (Ramesh, 2007a; Augusto et al., 2018).

The intensity of the heat treatment is specified mostly by the pH value of the food. At pH values greater than 4.5 (low-acid food) extermination of pathogenic bacteria, whereas below 4.5 extermination of spoilage microorganisms or inactivation of enzyme is significant. In high-acid foods (pH < 3.9) generally non-sporeforming bacteria, yeast, and molds cause spoilage, while in acidic foods (pH 4.0-4.4) yeasts, molds, and both thermophilic and mesophilic bacteria grow. High-acid fruits also have enzymes such as catalase, peroxidase, polyphenol oxidase, pectin esterase, etc. that must additionally be inactivated (Ramesh, 2007a). Pasteurization is generally applied under atmospheric pressure at temperatures about $60^{\circ}C-100^{\circ}C$ for adequate time to preserve foods like milks, fruit juices, beer, and fermented drinks. This method needs to be used with another preservation method to assure stability because pasteurized products have low stability and variable shelf-life (Augusto et al., 2018).

There are four types of pasteurization as seen at Fig. 4.1 (Ramesh, 2007a):

4.2.2 Sterilization

Sterilization is another thermal process used in food preservation. This is an intensive heat treatment applied at temperatures above 100° C (generally 115° C -130° C) for inactivation of microorganisms. The final product should have no viable organisms. It destroys molds, yeasts, vegetative bacteria, and spores. It enables the stability of the product at ambient temperatures and extends the shelf life. It is applied to

low-acid foods (pH > 4.6) that may be contaminated with *Clostridium botulinum* spores during storage and therefore should be treated at least 121.1° C for 3 minutes. to achieve a 12*D* reduction of microorganism. All the process conditions should be designed according to the "cold point", which is the slowest heating part of the product. If this point is sterilized, the rest of the product is sterilized.

During sterilization, first the product is heated up a temperature of $110^{\circ}C-125^{\circ}C$. Then, the product needs a few minutes to equilibrate and reduce the temperature gradient between the surface and center. After the equilibrium, the product should stay at this temperature for a certain time to ensure the sterilization value, which is determined by F_o value. (If the sterilization temperature is $121^{\circ}C$ and the *z* value is $10^{\circ}C$, the sterilization time required for this temperature is indicated as the F_o value.) Finally, the product should be cooled.

There are two types of sterilization. The first is complete sterilization, which means there should not be any living microorganisms. But this type of sterilization leads to reduced quality and nutritional value. The other type is commercial sterilization, which is intended to destroy all pathogens and the microorganisms that may degrade food under normal storage conditions. Some microorganisms that do not deteriorate and have high thermal resistance may survive. The purpose here is to protect the food quality (Ramesh, 2007b).

The target microorganism at sterilization is *C. botulinum*, which is known to be the most resistant pathogen in low-acidity foods. It is mesophilic anaerobic bacteria and has very heat resistant spores. Botulinum toxins are the most potent biological toxins known.

There are two food sterilization methods: thermal and nonthermal processing. Thermal processing is also divided into in-container sterilization (bulk canning) and aseptic sterilization (processing) (Ramesh, 2007b).

4.3 Developments in cooling and freezing technology

4.3.1 Cooling/chilling

Cooling can be described as the storage of food products at temperatures above freezing and below 15°C, keeping the water in liquid phase. It is widely used for short-term preservation and prolongs shelf life with less damage to sensory and nutritional properties. It slows the growth of microorganisms and retards the chemical reactions like enzyme-catalyzed oxidative browning or oxidation, chemical changes that cause color degradation, moisture loss, postharvest and postslaughter metabolic activities of plant and animal tissues. Except raw materials it is generally used with other preservation processes because the physicochemical, microbiological, and biochemical reactions continue to occur at these temperatures (Augusto et al., 2018; Karel and Lund, 2003b).

The reduction in most reaction rates can be explained by the Q_{10} notion (Eq. (4.3)). It can be defined as the variation in the rate of the reactions by changing the temperature at 10°C, describing an exponential reduction in the reactions with decreasing temperature (Fig. 4.2).



Figure 4.2 Q_{10} concept to define the rate of reaction as a function of temperature.



Figure 4.3 Enzymatic activity in relation to temperature.

Generally, for the food products Q_{10} value changes between 2 and 5, which means reducing the temperature by 10°C, reducing the rate of the reactions approximately 2 and 5 times. The longer shelf life of refrigerated products is explained by this notion:

$$Q_{10} = \frac{\text{Reaction rate in } T = T_i + 10^{\circ} C}{\text{Reaction rate in } T = T_i}$$
(4.3)

However, the actions of enzymatic and microbial reactions are more complicated and cannot be expressed only by the Q_{10} concept.

Fig. 4.3 shows the activity of an enzyme as a function of temperature. Even though the phenomenon of Q_{10} may explain its activity in a certain temperature

range, the denaturation occurs due to maintenance at higher temperatures than the optimum result in reduced enzymatic activity (Augusto et al., 2018).

Parallel activity can be seen for microbial growth with one important difference: the minimum development temperature of each microorganism, below which it remains in a latent state. The minimum and optimum growth temperature ranges of four main types of microorganisms are as follows, respectively: psychrophiles $(0^{\circ}C-5^{\circ}C)$, $(12^{\circ}C-18^{\circ}C)$; psychrotrophs $(0^{\circ}C-5^{\circ}C)$, $(20^{\circ}C-30^{\circ}C)$; mesophiles $(5^{\circ}C-10^{\circ}C)$, $(30^{\circ}C-40^{\circ}C)$; and thermophiles $(30^{\circ}C-40^{\circ}C)$, $(55^{\circ}C-65^{\circ}C)$.

Consequently, cooling can reduce the microbial growth and inhibit the growth of microorganisms but does not ensure microbial inactivation. Therefore, it must be used with another preservation method (Augusto et al., 2018).

4.3.2 Freezing

Freezing is one of the best ways to extend shelf-life even though several new preservation techniques are acquiring popularity and importance. Freezing is a conventional and simply applied method with a major advantage being its capability to achieve stability without loss of initial quality (Karel and Lund, 2003b).

Freezing influences the physical condition of the substance due to the transformation of water into ice. This occurs when the energy is removed as cooling under the freezing temperature. The general practice for freezing requires a temperature drop to the storage level of around -18° C. All the freezing processes like precooling, supercooling, freezing, tempering, eutectic, ice nucleation, and glass transition points of the products can be clearly demonstrated using freezing or cooling curves and phase diagrams (Tavman and Tuncay, 2018; Rahman and Velez-Ruiz, 2007; Cheng et al., 2017).

Freezing has three stages. First is the cooling of the product to its freezing point (precooling or chilling stage). Here, only sensible heat is removed, and temperature is reduced to simplify ice crystallization of free water. Second stage is moving away the latent heat of crystallization (phase transition stage). This stage comprises the conversion of the water into ice during the crystallization process. So, it is the fundamental step that determines the quality of the frozen product and freezing efficiency. The final stage is cooling the product to the final storage temperature (tempering stage) (Kiani and Sun, 2011).

The breakdown of food by biochemical and physicochemical reactions slows down by freezing but does not stop. The most important factors that prevent quality losses in frozen products are storage temperature, time, and thawing procedures. At temperatures below -18° C, all the microbial activity stops, but enzymatic and non-enzymatic reactions continue slowly during frozen storage. Freezing also inhibits random motion of water molecules.

It is crucial to form small ice crystals in freezing to get the least tissue damage and drip loss in thawing. In general, freezing is faster than thawing and during thawing, damage occurs by microorganisms, chemical, and physical changes (Li and Sun, 2002). By controlling the freezing process together with storage and preparation conditions, the quality of the frozen food can be increased. Usually, fast freezing is preferred rather than slow freezing. Whereas, some products can be damaged if they are submitted directly to extremely low temperature for a long time. Volume expansion and contraction expansion can express this freeze cracking damage and volume expansion occurs during ice formation. Ice crystal structure has a great importance to protect the quality of frozen products. It is desirable to form fine ice crystals distributed inside and outside the cell to obtain better quality and better-preserved foods, because of less damage to the tissue. On the other hand, large crystals are more acceptable in processes like freeze-drying and freeze concentration. So, control of the water crystallization during the freezing process is very important and recently, new fast freezing technologies to control the crystallization of water have been applied (Kiani and Sun, 2011).

When compared with canning and drying, freezing is the cheapest method of food preservation. The crucial point of freezing is the starting temperature. The material should begin at a temperature near to the freezing point to have preferable crystallization (Tavman and Tuncay, 2018).

The freezing method should be selected according to the type of product, sanitation requirements, reliability, and economic reasons. The common methods used in the food industry include plate contact, air blast, fluidized bed, immersion, and cryogenic freezing.

In the plate freezing method, the product is compressed between metal plates with pressure for good contact pressure. This method can only be used for regular shaped materials. After freezing is completed, hot liquid is used to dissolve the ice.

In immersion freezing, product is immersed in a brine at low temperature to obtain rapid temperature drop by direct heat exchange.

In the air-blast freezing method, food is subjected to cold air flowing at a high speed (2.5-5 m/s) in a tray. At this method velocity selection is important. If the speed is low, the product will freeze slowly, which is not desirable. Even if it is fast, unit-freezing costs increase. The types of air-blast freezing are fluidized bed freezing, belt freezing, spiral freezing, and tunnel freezing.

In cryogenic freezing, food is contacted with liquid gases (liquid nitrogen, liquid carbon dioxide, or their vapor) where the temperatures are below -60° C. This freezing method is very fast, can be used for lots of products, capital cost is low, and high-quality products can be obtained.

4.3.2.1 New freezing technologies

The new freezing technologies include high pressure freezing, ice nucleating proteins, antifreeze proteins, ultrasound-assisted freezing, magnetic resonance freezing, and microwave assisted freezing (Rahman and Velez-Ruiz, 2007).

4.3.2.1.1 High pressure freezing

When the water is frozen at atmospheric pressure, the resulting ice will damage the tissue by increasing the volume. But under high pressure, different kinds of ices are

formed and during phase transition, they do not increase volume and they do not harm tissue. As a result, high pressure helps the freezing process and improves product quality.

We can change the physical state of food by using external temperature or pressure. Under high pressure, the freezing point of liquid water can be reduced to below 0° C. When pressure is released, a high supercooling can be obtained, and as a result the ice-nucleation rate is greatly increased.

The use of high pressure simplifies supercooling and it is convenient where uniform and small sized ice crystal distribution is required (Cheng et al., 2017; Li and Sun, 2002).

4.3.2.1.2 Dehydrofreezing

At this type of freezing, food is first dehydrated to a desired moisture and then frozen. Dehydrofreezing ensures the preservation of fruits and vegetables by removing part of the water from food materials prior to freezing. This dehydration process, by removing a part of cellular water, decreases freezing point and freezing time. Thus, as an advantage, improved food quality can be achieved. Also, low energy consumption, as well as low packaging, distribution, and storage costs are the other advantages (Cheng et al., 2017; Li and Sun, 2002).

4.3.2.1.3 Antifreeze protein and nucleation protein

Antifreeze protein and ice-nucleation protein are inserted directly to the food and interact with ice. They are two opposite groups of protein and have different functions. They affect the ice crystal size and crystal structure in food.

The function of the antifreeze protein is to lower the freezing temperature and to restrict the ice formation and change the ice nature by suppressing the growth of ice nuclei. It also delays the recrystallization on frozen storage. Ice nucleating proteins increase ice nucleating temperatures and reduce the degree of supercooling (Li and Sun, 2002).

4.3.2.1.4 Ultrasound-assisted freezing

The application of power ultrasound in food freezing has various aspects, which include initiation of nucleation control of size of ice crystals, speeding up the freezing rate, and improvement of quality of frozen foods (Cheng et al., 2015).

In addition to its traditional application in accelerating the ice-nucleation process, it can also be applied to freeze concentration and freeze-drying processes to control crystal size distribution in the frozen products. If it is applied to the process of freezing fresh foodstuffs, ultrasound can not only increase the freezing rate, but also improve the quality of the frozen products. The ability of power ultrasound in performing these functions is affected by a variety of parameters, such as the duration, intensity, or frequency of ultrasonic waves, etc. (Zheng and Sun, 2006).

Among these effects, cavitation is the most important, which can lead not only to the production of cavitation bubbles but also to the occurrence of microstreaming. The former can act as ice nuclei and increase ice-nucleation rate, while the latter can enhance the heat and mass transfer during the freezing process. Moreover, large ice crystals will fracture into smaller size crystals when subjected to the alternating acoustic stress. Resulting from these acoustic effects, power ultrasound has proved itself an effective tool to initiate the nucleation of ice crystals, control the size and shape of ice crystals, accelerate the rate of freezing, and improve the quality of frozen foods (Zheng and Sun, 2006).

The final main step for the safe consumption of frozen foods is the method of thawing. When the food is thawed from outside to inside, before its center is efficiently defrosted, the temperatures and conditions can cause microbial growth. Therefore, using refrigerated containers, microwave ovens, or water currents during the finalizing of the thawing to minimize the microbial growth is crucial (Augusto et al., 2018).

4.4 Ohmic heating

Ohmic heating is a thermal method that reduces energy input to food, thus reducing thermal damage and positively affecting quality of the food (Butz and Tauscher, 2002). Ohmic heating is a process in which electric current passes through the food product and due to the electrical resistance of the food, heating occurs as a result of the movement of ions. It is also called Joule heating, electric resistance heating, direct electric resistance heating, electroheating, and electroconductive heating (Barba et al., 2018; Lima, 2007). Ohmic heating can be used to produce heat within the product if materials contain sufficient water and electrolytes to allow the passage of electric current (Knirsch et al., 2010).

As opposed to conventional heating's time-consuming convection and conduction heat transfers, ohmic heating is volumetric and has reduced heat transfer time. The electrical conductivity of the food or food mixture is the most significant parameter in ohmic heating. For the solid—liquid mixtures, as an ideal situation, they are required to have equal electrical conductivities, thus heat at the same rate. Density and specific heat of the product also influences the temperature distribution. Besides, viscosity of the fluid is important at ohmic heating, as higher viscosity fluids cause faster ohmic heating than lower viscosity fluids.

It is a green technology because it is a very rapid process, therefore heat losses from the product are very small and environmental losses are minimized. Also, energy losses are significantly reduced due to direct application of electrical energy to the product (Lyng and McKenna, 2011).

Ohmic heating has various advantages like liquid-particle mixtures can be heated uniformly, ultra-high temperature processing temperatures can be reached quickly, product damage is less because there are no hot surfaces for heat transfer, and it has high energy conversion yields and low capital cost.

Ohmic heating can be used as a continuous in-line heating method of pumpable foods for cooking and sterilization of viscous liquids and mixtures containing particulate food products (Baysal and Icier, 2010). It can be used in several food processes, such as cooking, blanching, pasteurization, sterilization, fermentation, dehydration, evaporation, and extraction, specifically in highly viscous or particulate foods. It can be applied to liquids, solids, and liquid-solid mixture foods like liquid egg, whole fruits such as strawberry, juices, sauces, stews, meats, seafood, pasta, and soups (Knirsch et al., 2010; Lima, 2007; Baysal and Icier, 2010).

Naturally, microbial inactivation in ohmic heating is thermal but due to the existence of electric field, slight nonthermal cell wall damage can be observed. As a main outcome of this effect, the D value observed for the microbial inactivation under ohmic heating is reduced when compared with traditional heating methods (Knirsch et al., 2010).

4.5 Microwaves

Microwave heating is being used in household and industrial food preparation and processing. It is preferred because of its volumetric origin, fast temperature increase, controllable heat deposition, and simple sanitation conditions.

The process is rapid and the come-up time required to reach the desired temperature is minimum. Therefore, microwave heating is preferred for pasteurization and sterilization. Also, the High Temperature Short Time (HTST) process is a conventional method and is not convenient for solid foods due to slow heat conduction, which overheats the surface of the solid. Microwave heating can accomplish this slow thermal diffusion of conventional heating (Ahmed and Ramaswamy, 2007).

Microwaves are electromagnetic waves that have frequencies between 300 MHz and 300 GHz and wavelengths from 1 to 0.001 m. Microwave heating influences the polar molecules of the material. In this way, electromagnetic field energy transforms into thermal energy. In conventional heating, heat diffuses in from the surface of the material and heat transfer takes place first by convention and then conduction, which requires a longer time. Whereas, microwave heating generates volumetric heat, which means that materials can absorb microwave energy internally and convert it into heat (Vadivambal and Jayas, 2010).

This volumetric heat can significantly decrease the total heating time and so the high temperatures needed for commercial sterilization to destroy the microorganisms are enhanced and thermal degradation of the desired components is reduced (Ahmed and Ramaswamy, 2007).

For industrial, scientific, and medical use, only limited frequencies (915 or 2450 MHz) are authorized to prevent interference with radio frequencies used for telecommunication (Barba et al., 2018; Ahmed and Ramaswamy, 2007).

Microwave heating in foods emerges when the electrical energy of an electromagnetic field in a microwave cavity is coupled with food and due to subsequent distribution in the food product. This causes a rapid increase in temperature within the product. Molecular interaction with the electromagnetic field provides microwave energy at the molecular level. This situation occurs especially through the dipole shift of polar solvents and molecular friction resulting from the conductive migration of dissolved ions. Therefore, dipole rotation and ionic polarization are the main mechanisms. Because of this internal molecular friction, heat is produced quickly (Ahmed and Ramaswamy, 2007).

Processes in which microwave energy can be used are pasteurization, sterilization, drying, cooking, baking, thawing, tempering, blanching, reheating, and even combined with freezing (Barba et al., 2018; Osaili, 2012). Microwave has several more advantages. It diffuses inside the food materials with reduced processing time and energy. Because the heat transfer is rapid, the flavors, sensory qualities, and color of the foods are well preserved as well as the nutritional and vitamin content. It has higher heating efficiency and suitable sanitation conditions. The system maintenance is cost-effective, suitable for heat-sensitive fluids, quiet, and without any gas outlet.

The disadvantages of microwave heating are usually related to nonuniform heating, which may produce hot and cold spots within the same food item. Main problems are low quality end product, overheating, and inability to ensure the microbial safety. But the major inconvenience is the presence of hot spots in various regions resulting from product geometry (Vadivambal and Jayas, 2010).

The industrial applications of microwave can be listed as follows: tempering of fish, meat, and poultry; precooking of bacon; sausage cooking; baking; drying; blanching of vegetables; concentration; puffing; and foaming.

4.6 Radio frequency

The RF, which is at higher frequencies than microwaves, occupies a region between 1 and 300 MHz in the spectrum of electromagnetic fields although the main frequencies used for industrial heating lie in the range 10-50 MHz. Like microwaves, only selected frequencies (namely 13.56 ± 0.00678 , 27.12 ± 0.16272 , and 40.68 ± 0.02034 MHz) are permitted for industrial, scientific, and medical applications (Marra et al., 2009). RF heating is also called high frequency dielectric heating.

RF heating enables associated rapid and uniform heat distribution, large penetration depth, and lower energy consumption, which makes this technology promising for food applications. RF heating can be used for drying, baking, and thawing of frozen meat and in meat processing. However, its use in continuous pasteurization and sterilization of foods is rather limited. During RF heating, applied alternating electric field causes the molecules and ions to oscillate, which results in molecular friction. Thus, heat is generated inside the product. When all the other conditions are kept constant, RF heating is affected mainly by the dielectric properties of the product (Piyasena et al., 2003).

RF heating of foods is clearly affected by dielectric properties. On the other hand, dielectric properties are influenced by several factors like frequency level, temperature, and properties of food, such as viscosity, water content, and chemical composition. Therefore, these properties should be considered when creating the heating system.

In contrast to conventional systems having large temperature gradients because of the transfer of heat from hot medium to cooler product, RF heating transfers the electromagnetic energy directly into the product and starts the frictional interaction between molecules causing volumetric heating (i.e., heat is generated within the product) (Piyasena et al., 2003).

Application areas of RF heating are cooking processed meat, heating bread and dehydrating vegetables, thawing of frozen products, postbaking (final drying) of cookies and crackers, sausage emulsion pasteurization, sterilization, and continuous flow aseptic processing and packaging systems (Piyasena et al., 2003). RF can be used to reduce microbial contamination and improve food safety and quality. There are studies on the reduction of microbial contamination of fresh carrots, meat, apple juice, milk, apple cider, and pork meat products by RF (Osaili, 2012).

As seen from the literature, RF heating has also been utilized for the pasteurization of dairy and pasta products, for the sterilization of low-acid foods, microbial inactivation of salmon caviar, ground beef pathogens, and other food materials (Barba et al., 2018).

4.7 Inhibition of oxidation in foods

Oxygen affects preserved foods and beverages in different ways such as rancidity of unsaturated fats, browning and loss of vitamin C (ascorbic acid) of fruits and vegetables, deterioration of bakery products, discoloration of fresh meat, and deterioration of flavor of beverages. The quality loss or spoilage of food products caused by oxygen strongly influences the consumer acceptance of products, which in turn causes significant amount of food loss or waste, which means the loss of economic value. Therefore, it is essential to understand and inhibit oxidation in food systems.

A free radical chain reaction that is responsible for the mechanism of lipid oxidation can be separated into three phases: initiation, propagation, and termination.

Initiation phase starts with the formation of free radicals by hydrogen abstraction reactions through metal ions, light, radiation, or other agents. If there is oxygen in the environment, it reacts with these highly reactive carbon-centered free radicals generating hydroperoxyl radicals.

In the propagation phase these hydroperoxyl radicals can abstract a hydrogen from a lipid, generating peroxy radical being very reactive. Peroxy radical abstracts a hydrogen from another polyunsaturated fatty acid molecule and forms hydroperoxide and alkyl free radical. Hydroperoxide can become the source of additional reactive radicals under the action of metal ions and causes the formation of free peroxy and alkoxy radical. This chain reaction sequence can be repeated many times. Hydroperoxides also undergo a variety of decomposition reactions generating off, rancid, stale flavor, or aroma-forming compounds.

In the termination phase free radicals in the medium interact with each other and form some nonradical compounds. The oxidation process is interrupted as substrates become depleted and radical recombination reactions begin to dominate. Nonlipid food materials can also undergo oxidative changes such as pigment degradation, oxidative vitamin loss, and protein oxidation (Pokorny, 2007; Berdahl et al., 2010).

4.7.1 Types of antioxidants

Antioxidants are the substances that can protect materials against autoxidation by delaying the start or slowing the rate of oxidation. There are many compounds both natural and synthetic that possess antioxidant activity. Generally, lipid-soluble antioxidants such as monohydric or polyhydric phenols with different ring structures are used in food systems. Antioxidants have mainly six groups, as seen in Fig. 4.4.

Maximum performance is achieved when the primary antioxidants are used in combination with different metal chelating agents or other phenolic antioxidants; this is the synergistic effect (Nawar, 1996; Berdahl et al., 2010). Major types of the inhibitors can be listed as singlet oxygen quenchers, chelating agent, synergists, hydroperoxide deactivators, and antioxidants (Fig. 4.5). Singlet oxygen quenchers such as carotenes convert singlet oxygen into triplet oxygen, chelating agents such as citric acid bind heavy metals into inactive complexes, synergists such as ascorbyl palmitate regenerate antioxidants, hydroperoxide deactivators such as cystein react with hydroperoxides, and antioxidants such as tocopherols react with free radicals (Pokorny, 2007).

Synthetic antioxidants such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG), and tertbutylhydroquinone (TBHQ) are the ones that are widely used in foods. However, there are some studies indicating that high concentrations of certain synthetic antioxidants such as BHA and BHT may cause weak carcinogenic effects in some animals. Even the use of TBHQ is restricted in Japan. Fortunately, natural antioxidants such as tocopherols, ascorbic acid, erythrobic acid, or their salts and derivatives such as ascorbyl palmitate, as well as extracts of rosemary and sage, have found prevalent applications in the food industry (Shahidi and Zhong, 2010).

The fat-containing foods can be stored for only a limited period of time during slow oxidation where the food decomposition has not started yet. In the beginning of storage the oxidation rate is very slow, therefore this stage is called the induction period, where the shelf life of the food product can be extended by addition of antioxidants. However, antioxidants are not able to eliminate the oxidation reactions



Figure 4.4 Types of antioxidants.



Figure 4.5 Major types of inhibitors.

although they are active during extended storage time. Some of the specific effects of oxidation-induced degradation in foods can be listed as follows:

- 1. Rancid taste and aroma formation in fats and fat-containing foods
- 2. Discoloring in pigments
- 3. Formation of toxic oxidation products
- 4. Taste and aroma loss and disorders in product
- 5. Changes in texture
- **6.** Decrease in nutritional value due to destruction of vitamins (A, D, and E) and essential fatty acids (especially linoleic acid)

Reagents that cause or accelerate oxidation are primarily oxygen and also metal ions such as iron and copper, light, temperature, some pigments, and the rate of unsaturation.

Oxidation of food products is inhibited in four ways:

- Minimizing the influence of the physical factors during processing and storage such as air, light, and high temperature by modern packaging methods.
- Inhibiting the autoxidation of lipids, which is initiated by free radicals. Autoxidation process can be hindered by antioxidants, which are chain-breaking inhibitors, or by preventive inhibitors.
- Inhibiting the photosensitized oxidation. Physical quenchers such as tocopherol and carotenoids prevent single electron transfer reaction of the primary excited molecule.
- Enzymes such as lipoxygenase can be inhibited by flavonoids, phenolic acids, and gallates and also by heating. As heating also causes nonenzymatic oxidation it may cause oxidation to increase.

Antioxidants are the most effective substances in the food industry that inhibit the degradation and rancidity of food for a certain time by delaying the effect of atmospheric oxygen under normal temperature conditions during production, storage, transport, and marketing of various foodstuffs. They do not increase the quality of the food and do not change the flavor and smell. The desired quality can only be achieved by providing good raw material, correct production technique, and proper packaging and storage conditions. For proper and effective use of antioxidants, it is necessary to know the mechanism of oxidation, the functions of the antioxidant used, and to add antioxidant to the food before the oxidation starts (Çakmakçı and Gökalp, 1992; Yanishlieva-Maslarova, 2001; Cichello, 2015; Pokorny, 2007).

4.7.2 Use of antioxidants in food

Various antioxidants perform at different effectiveness when used in oils and fatcontaining foods owing to the differences in their molecular structure. Factors that affect the potential application of antioxidant in a food system can be summarized as convenience of association with food, performance characteristics, pH sensitivity, discoloring or off flavor tendency, cost, and availability. Moreover, the presence of prooxidants and antioxidants present in the food itself or formed during processing has to be considered while predicting the functionality of the added antioxidant in food. Thus, selecting the appropriate antioxidant or combination of antioxidants for a food product is very complicated. Also, the hydrophilic–lipophilic properties of antioxidants influence their effectiveness in food applications. Vegetable origin food products are rarely stabilized by antioxidant addition compared with animal origin food products, which might be due to the presence of natural antioxidants such as tocopherols, carotenoids, or flavonoids in vegetable origin foods. Oxidation is catalyzed by a group of enzymes and lipoxygenases in vegetable origin foods.

Synthetic antioxidants are generally effective in fish oils, vegetable oils, animal fats and oils, and low-fat snack foods. However, in the last decade or two natural antioxidants have received increasing interest due to consumer preferences (Nawar, 1996; Yanishlieva-Maslarova, 2001).

4.7.2.1 Protection of fats and oils

The stability of animal fats such as milk fat or beef fat against oxidation is low despite the relatively low degree of unsaturation due to the presence of natural antioxidants in very low quantities. On the other hand both synthetic and natural antioxidants are very active in the stabilization of animal fats. Mixtures of antioxidants and synergists are used for stabilization. Lipid-soluble antioxidants give good results, but polar antioxidants can also be used. BHA is less effective in animal fats and shortenings when used alone than BHT or gallates, but its effectiveness increases with added synergists.

It is very difficult to stabilize vegetable oils due to unsaturated fatty acids; however the presence of natural antioxidants, mainly tocopherols in edible oils, is their advantage. Tocopherols as natural antioxidants exert their maximum antioxidant activity at relatively low levels almost equal to their concentration in vegetable oils. The addition of phenolic antioxidants to vegetable oils generally has limited efficacy, but the addition of synergists is beneficial. Useful inhibitors in vegetable oils are mainly ascorbyl palmitate, phospholipids, or organic polyvalent acids. BHA and BHT are more effective in animal fats than they are in vegetable oils and they have no significant effect on the stability of margarine. The efficacy of the antioxidants of TBHQ is equal to BHA but both have greater efficacy than BHT. Among the synthetic antioxidants PG has also been widely used in fats and oils, meat products, confectionery, nuts, milk products, fish products, margarine, and baked goods at levels between 0.001% and 0.04%. Before the deodorization of edible oils citric acid is often added and its decomposition products are also efficient as synergists of tocopherols (Pokorny, 2007; Berdahl et al., 2010; Pokorny, 2003, Pokorny and Trojakova, 2001).

4.7.2.2 Protection of nuts and oil seeds

Protection of peanuts that are roasted is difficult except for the application of spices on their surfaces. However, it is better to store them in a vacuum or in an inert atmosphere. After the roasting process in hot oil, about 2%-3% oil remains on the surface of the peanut. Addition of antioxidants into frying oils such as rice bran oil containing natural antioxidants improves the shelf life of nuts roasted in soybean or rapeseed oils. Moreover, a mixture of salt and TBHQ can be used for the stabilization. For the crushed or ground seeds used to produce a paste, like peanut butter, addition of antioxidants such as Tocomix D (a mixture of a- and d-tocopherols, citrate esters of monoacylglycerols) and Embanox 10 (a mixture of BHT and BHA) may be useful to improve stability during storage. Also, rosemary oleoresins were actively used for the stabilization of nuts (Pokorny and Trojakova, 2001).

4.7.2.3 Protection of cereal products

Cereal products such as peeled rice, white flour, or grits do not need to be stabilized. But to increase shelf life of whole grain flours enzymes have to be inactivated. Antioxidants such as rice bran, aqueous extracts from other whole grains or brans, tea extracts, and fruit extracts may be added to breakfast cereals with good results. Also, natural amino acids methionine and cysteine, phospholipids, and uric acid were also active as antioxidants in breakfast cereals. Antioxidants are mostly added to the extruded products with flour and other additives to the extruder barrel for homogeneous distribution. Extruded snack products' natural coloration is stabilized generally by an oil-soluble liquid rosemary extract (4942 Rosmanox) and its mixture with tocopherols (4993 Rosmanox E). BHA and TBHQ are also used in some of the snacks containing cottonseed oil and corn flour.

Some cereal products such as cookies, crackers, and cakes contain added fat. They should be stabilized by antioxidants to extend the shelf life. Sugar-snap cookies may be stabilized by BHA, but natural antioxidants are preferable by the consumers. Ferulic acid and sodium phytate, casein, whey proteins, or Maillard reaction products may be used instead of BHA in cookies. Caffeic acid and roasted coffee bean powder or extract being more active than tocopherol and chlorogenic acid, which are the components of coffee bean, have been added to cookies. Synergists like ascorbic and erythorbic acids, citric acid, and its isopropyl ester are also used with tocopherols. On the other hand, flavoring spices such as lemongrass extracts, clove leaves, black pepper leaves, and turmeric also increase the shelf life of cakes. Addition of spearmint, peppermint, and basil or their diethyl ether extracts gives better antioxidant effect than BHA at specific concentrations in cracker biscuits (Pokorny and Trojakova, 2001; Shahidi and Chandrasekara, 2015).

4.7.2.4 Protection of fruits and vegetables

As the lipid content in fruits and vegetables is very low the subject is not the lipid oxidation. The shelf life of fruits and vegetables is limited by factors like enzymatic browning, which affects the sensory properties. Therefore, to prevent oxidation of polyphenols, which are formed during enzymatic browning, antioxidants are added to fruits and mushrooms. Enzymes responsible for the oxidation of polyunsaturated fatty acids such as lipoxygenases are deactivated by blanching and then natural anti-oxidants, generally flavonoids, are added to protect lipid oxidation to achieve the best stabilization. Moreover, essential oils present in fruits show antioxidants. For example, orange juice is stabilized with the combination of ascorbic acid, phenolic acids, and pasteurization. For the stability of mashed potatoes, ascorbyl palmitate or a mixture of rosemary, thyme, and marjoram are used more efficiently than α -tocopherol or TBHQ (Pokorny and Trojakova, 2001; Shahidi and Chandrasekara, 2015).

4.7.2.5 Protection of meat products

The application of antioxidants for animal products is very useful due to the lack of natural antioxidants in their structure. Only small amounts of antioxidants are efficient because the oxidation sensitive polyunsaturated fatty acids are relatively low in fats of land mammals.

There is an oxidative stability difference between animal species and muscle types within a species due to some endogenous factors that control the oxidation such as the presence of active antioxidants, oxygen deactivating enzymes, and on the other hand prooxidants like iron and ascorbic acid. Stability of the products is dependent on the balance between these factors. For example, the difference between the stability of meat species is that the most stable one is beef, followed by pork, chicken, turkey, and finally fish. Additionally, within a species such as poultry, the white meat is more durable against oxidation than the dark meat.

Ground rosemary leaves or rosemary oleoresin are widely used natural antioxidants in meat products. As an example, rosemary antioxidant was found to be effective for the stability of cooked minced pork or frozen pork sausage during storage. Also, rosemary oleoresin was efficiently used in reconstituted raw or cooked pork steaks or in reconstituted chicken nuggets as tripolyphosphate was used as a metal chelating agent in both of the meat products. Besides meat lipids were efficiently stabilized by green tea catechins. Stability of beef patties stored at 4°C is provided by tocopherols at the defined concentration.

Since ancient times, smoke has been traditionally used for the preservation of meat products. Ash and beech wood, which are phenolic-rich smoke sources, may extend the stability of lard or pork meat during storage, which is important in smoked meat production. During the curing process sodium nitrite addition prevents pork meat oxidation. Treatment of nitrite during cold storage increases the antioxidant activity of pork and beef. Maillard products in sausages and soy sauce in pork

patties also protect them against oxidative degradation. Widely used antioxidants in meat products are either lipid soluble (tocopherols and carotenoids) or watersoluble (ascorbic acid, dipeptides, and plant phenolics or polyphenolics; raw meat will also contain antioxidant enzymes). Fish oils contain fatty acids with four to six double bonds, therefore they are susceptible to oxidation and it is very difficult to stabilize them against rancidification. The most widely used natural antioxidants for fish product preservation are tocopherols (Pokorny, 2003; Cuppett, 2001).

4.7.2.6 Protection of packaged foods

For distribution of some foods, packaging is needed. Therefore, the packaging material is very important for the preservation of these foods. Antioxidants may be added to the package to inhibit the oxygen diffusion, if the material is permeable to oxygen. The added antioxidants may migrate to the food, especially high-fat foods, from the package. Thus, the antioxidants that can be used in packaging should also be those that are allowed in foods, and their usage amounts in the material should be such that their quantities in foods do not exceed the legal limits. Even if the food manufacturer does not want to preserve the food in this way, packaging materials can be protected against oxidation by adding antioxidants already in the plant during the production.

On the other hand, antioxidants such as β -carotene, BHA, tocopherols, and ascorbic acid that are used in foods to prevent the oxygen degradation of food molecules such as lipids cannot absorb the oxygen in the void space of the packaging or between food particles. Oxygen interceptors are compounds that prevent oxygen from reaching the food product and they can be used both in the food product and package materials against autooxidation. Oxygen absorbers (scavengers) are materials that remove the oxygen from void space around the food particles and are generally used within a satchel that is added to modified atmosphere packaging. Their working mechanism is that they react with oxygen and moisture through the oxidation of a salt such as iron carbonate. Oxygen absorbers are applied to a wide variety of food types for preservation including bread and biscuits, fruit and vegetables, nut products, fish and seafood products, and meat products (Pokorny, 2007; Cichello 2015).

Water content of the foods has a significant effect on the efficiency of antioxidants in foods. Dry foods such as dried soups, dried milk, dried meats, etc. are susceptible to oxidation, because air oxygen can freely reach to the lipid film on nonlipidic particles through the tiny channels that occurred after the removal of water. Thus, autoxidation reaction initiation rate is very high and the antioxidants can be decomposed during processing and storage, which in turn makes the food stabilization less effective. Water-containing foods are protected from the oxygen by carbohydrates or a layer of hydrated proteins due to the more stable lipid fraction. Nonpolar antioxidants are more effective than the polar antioxidants because polar antioxidants may pass to the aqueous phase causing an activity loss. Other food components like proteins also have protective action and they may act as synergists of the inhibitors, which improves the antioxidant effect. Protein amine groups contribute to the protection of foods against oxidation by reacting with lipid peroxides and thus decreasing the level of free radicals. Chelating agents and heavy metals like heme derivatives in animal products are often present in food products as natural components, as well. Therefore, it is necessary to optimize the mixture of inhibitors and test the antioxidants to stabilize any kind of food product due to the complex structure of foods. (Pokorny, 2007).

4.8 Hurdle concept

Nowadays there is an increasing interest in food products with fewer chemical additives and physical injuries, which creates new opportunities for the hurdle technology concept of food preservation. Sensory and nutritive quality as well as the microbial safety and stability of the foodstuffs are based on the application of combined preservation methods, called hurdles. Widely used important hurdle factors in food preservation are water activity (a_w), temperature (high or low), redox potential (E_h), acidity (pH), competitive microorganisms (e.g., lactic acid bacteria), and preservatives (e.g., nitrite, sorbate, sulfite, antioxidants).

The hurdle concept is mainly based on the fact that many inhibitory factors (hurdles) can be effective when combined, although they are not able to prevent microbial growth individually. Unfortunately, the use of severe preservation methods may cause undesirable changes in food quality such as loss of nutrients, loss of flavor and aroma compounds, changes in texture, nonenzymatic browning, and protein denaturation, which may be limiting factor. Therefore, when two or more preservation methods are combined, due to their increased effect that is being summed, intensity of each method may be reduced. If a food is preserved only by high salt or low acidity it may be organoleptically unacceptable by the consumers, but when low salt is combined with low acidity then the consumer acceptability level will be higher.

To give an example, fruit jams and jellies would be appropriate that are produced from the similar concentrations of fruit and sugar to about 65–72 Brix. The main reason for their conservation is the low water activity of the product; however, preservation is achieved by a sum of methods such as low a_w , low pH for the formation of pectin gel, and thermal processing during evaporation for the concentration. Another good example of the hurdle concept is frozen concentrated orange juice preserved by the sum of thermal processing (pasteurization), water activity reduction by concentration, and freezing. Among meat products, sausage is an example of pasteurized product that still needs to be stored refrigerated, although it contains antimicrobial agents like nitrates and nitrites. Additionally, it will have longer shelf life when packed under vacuum (lower E_h). Over the last 20 years, hurdle technology has become more widespread and wisely applied as important conservation factors (e.g., temperature, pH, a_w , E_h , competitive microorganisms, preservatives) and their interactions have become better known (Augusto et al., 2018; Hamad, 2012; Leistner, 2000).

4.9 Conclusion

To preserve foods the application of heat is a very important process. Existing commercial thermal processing technology needs to be developed and improved in terms of final product safety and quality with the optimization of process efficiency. So far, the innovative electroheating technologies such as RF heating, microwave heating, and ohmic heating have substituted for the widely used commercial preservation processes. These technologies have been used to inactivate microorganisms in different types of food. In terms of oxidation inhibition in food products, there is an increasing focus on the determination of new, effective, and natural antioxidants. Another progress in this field is to reduce the concentration of added antioxidants to foods, which can be provided with the combination of phenolic substances, which are known as primary antioxidant with synergists (Generally Recognized as Safe status). Another way of removing oxygen is the addition of oxygen scavengers such as a combination of D-glucose and glucose oxidase to the packaging material. Finally there is an increasing tendency to more natural preservation techniques with the addition of fewer additives including antioxidants.

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