

LITERATURE REVIEWS

1. Persimmon

1.1 Classification, Harvesting and Storage

Persimmon most commonly refers to the edible fruit borne by some species of the genus *Diospyros* (Ullio, 2003). The Japanese persimmon (*Diospyros kaki*) is a species related to common persimmon, but is native to Asia (China, Japan) (Gilman and Watson, 1993). It has wide variation in size, shape, and color, and is broadly classified for horticultural purposes into two major groups: non-astringent and astringent. Each group can be further subdivided, based on their responses to pollination: *pollination constant* implies that no change in flesh color occurs after pollination; whereas *pollination variant* implies that the flesh is highly colored when seedless, and dark reddish brown when seeded. When pollination is poor and only one seed is formed, a dark area develops around the seed but the remaining flesh is light colored. Persimmon fruit should be harvested when it is well-developed and is of the characteristic color for the cultivar (Kitagawa and Glucina, 1984).

Fruit needs to be well developed and show the characteristic color for the cultivar before being harvested. Fruit of astringent cultivars is inedible at harvest and must be treated to remove astringency. The fruit of non-astringent cultivars have completely lost their astringency before harvest time. The best way to harvest persimmons is to clip it with small secateurs from the tree, leaving the calyx attached to the fruit. It is possible to snap the fruit from the tree but this practice is not recommended, as it may injure the fruit and adjoining shoot. The fruit must be handled very carefully to avoid bruising, likely to result in marking which becomes unsightly as the fruit ripens (Ullio, 2003).

Astringency in persimmon is caused by soluble tannins in the fruit flesh (Taira and Ono, 1997). At harvest, astringent varieties of persimmon fruit contain approximately 2% of soluble tannins. Soluble tannins are responsible for an astringent

taste, and contain catechin, catechin-3-gallate, gallic acid and gallic acid-3-gallate (Vidrih *et al.*, 1994). Astringent varieties of persimmon have a limited consumption; therefore, it is necessary to improve their features using some technological processes. Most research relating to persimmon has been on storage conditions such as cold and controlled atmosphere storage after harvest, and has been carried out to determine astringency, color and firmness (Kitagawa and Glucina, 1984; Pesis *et al.*, 1988).

The removal of astringency from persimmon fruits has been achieved by several methods, based on exposing the fruit to anaerobic conditions or to products of anaerobic respiration (Ben-Arie and Sonogo, 1993). Anaerobic conditions stimulate production of acetaldehyde and ethanol by the fruits; the mechanism involves soluble tannins in the fresh fruit becoming insoluble upon condensation or polymerization with acetaldehyde (Pesis *et al.*, 1988; Taira and Ono, 1997). A method commonly used is to enclose the fruit for 1–2 days in a CO₂-enriched atmosphere (>80% CO₂) (Ben-Arie and Sonogo, 1993; Pesis *et al.*, 1988). Pesis *et al.* (1988) indicated that astringency was removed more rapidly under CO₂ than under vacuum, and that the de-astringency process under N₂ was the slowest. Moreover, the de-astringency process was positively related to the level of acetaldehyde accumulation. The shelf-life of astringent persimmons is greatly reduced if the astringency is artificially removed. Furthermore, the shelf-life of treated astringent fruits is dependent on the method used to remove the astringency.

Kitagawa and Glucina (1984) summarized the shelf-life of some persimmon cultivars from each condition. Hiratanenashi persimmon fruit which are treated on the tree with ethanol have a shelf-life of 15 days or more. Fruit that is treated with CO₂ has 7-10 days of shelf-life. Treatment with alcohol, off the tree, causes early softening, and the fruit has a shelf-life of only 5-6 days. The optimum cold storage temperature for Fuyu persimmon is 0°C. At 0°C, Fuyu which has a long shelf-life can be stored for about 2 months.

Tarutani (1965) reported that polyethylene film is effective in controlling gas exchange. Furthermore, when individual fruit are placed in a sealed polyethylene-film bag of a certain thickness, the respiration of the fruit causes controlled atmosphere conditions to be formed within the bag. When Fuyu fruit is placed in a 0.06-mm thick, low-density, polyethylene film bag and kept at 0°C, both CO₂ and O₂ are maintained in the range of 5-8%, and the fruit can be stored for 4-5 months.

Ullio (2003) indicated that persimmon can be successfully stored for up to 3 months at 0°C and 90-95% relative humidity. The cultivar Fuyu can be stored up to 5-6 months using controlled atmosphere storage with 5-8% CO₂ and 2-3% O₂ at 0°C.

1.2 Persimmon Production in Thailand

Persimmon was once the most important fruit crops grown in the north of Thailand. Since persimmons have been cultivated for many years, they have gradually spread, and in recent years, have been become very familiar in markets around Thailand. Since 1969, the uses of the fruit have been extensively studied at Kasetsart University under the auspices of the Royal Project Foundation. Major growing areas in Thailand are Chiangmai, Chiangrai, Maehongson, Phayao and Petchabun (Sripapern, 2000).

Persimmon is seasonal, beginning in July until September. About ten main persimmon cultivars are grown in Thailand, but only few are of commercial importance. The most leading cultivar among them is Fuyu, non - astringent type cultivar and P2 astringent type cultivar (Sripapern, 2000; Tunwirun, 2001).

Fuyu, also called Fuyukaki, is the commercial cultivar classified as a pollination constant, non-astringent type. The fruit is large (average 220-240 g.), round to oblate and indistinctly four-sided. Its skin is tough and fairly glossy, orange-red, and covered with a heavy bloom. Although the quality is excellent, the fruit does not store well (Tunwirun, 2001).

P2, also called Xichu, is the most popular commercial cultivar classified as a pollination constant, astringent type. This variety originated in China. It is smaller than Fuyu, oblate and characteristically round to four-sided with four shallow grooves. The skin is tough and glossy, and orange-red; the flesh is pale yellow. Its overall quality is also excellent, productivity is high; and stores very well. It is therefore the most appropriate cultivar grown in Thailand (Tunwirun, 2001).

Persimmons have limited processing potential in Thailand. The main processing outlets are drying. There are two types of dried product: semi-dried and dried persimmon. The processing steps are similar, differing only in the final moisture content. However, the semi-dried variety cannot be stored for a long time (at the most 2-3 weeks). Cultivars which produce a good quality of dried fruits are P2, P3 and Nightingale. These are all pollination-constant, astringent type fruits in which the tannin cells are coagulated during drying and astringency is removed naturally (Sriparern, 2000; Tunwirun, 2001; Yuenyongputtakal, 2002).

The processing steps used is shown in Figure 1. Persimmons are harvested as 80% ripeness and ripened using calcium carbide at the concentration of 200 g/ 100 m² for 2 days. Calcium carbide reacts with water to generate ethylene gas which activates ripening. The ripe persimmon is washed, trimmed the sepal, hand peeled and then dried. Usually, the fruit is cured with sulphur dioxide 15 g/mm³ for 30 min before drying. The purpose of this treatment is to reduce growth of fungi and also prevent oxidation, resulting in better fruit coloration on drying. Drying of persimmon is carried out at 35-45 °C for 6 days. During drying, the fruit is kneaded with the fingers twice daily. Kneading is necessary to give uniform texture and improve flavor (Royal Project Foundation, 1999; Sriparern, 2000; Tunwirun, 2001).

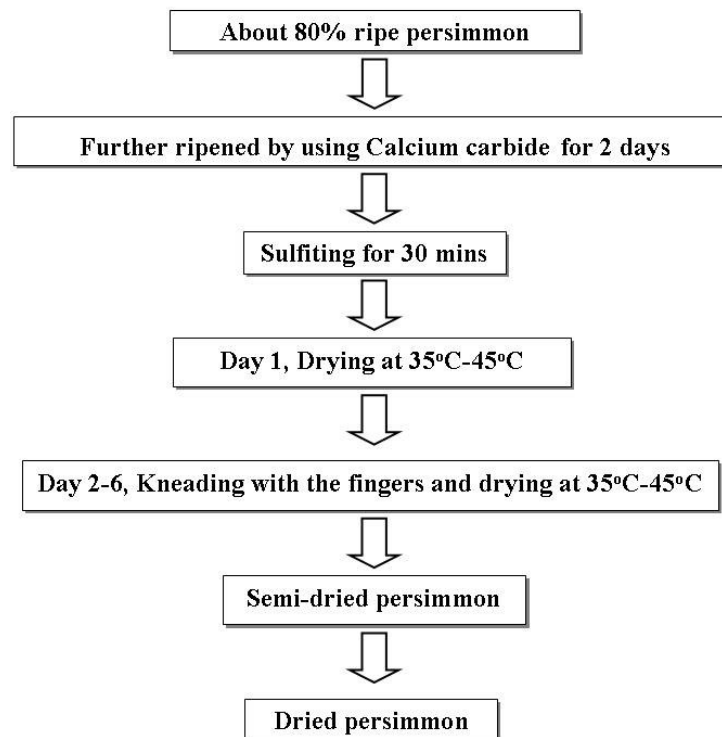


Figure 1 Semi-dried and dried persimmon

2. Using Osmotic as a Pre-treatment

If solutions of unequal concentration, or a solution and pure solvent, could be separated by a membrane which allowed solvent molecules to pass but was impermeable to solute molecules; only solvent molecules would diffuse from the solvent or dilute solution into the more concentrated solution. Such membranes are called semi permeable membranes. Osmosis is the name given to the diffusion of solvent through a semi-permeable membrane from a solvent into a solution or from a dilute solution into a more concentrated one. Thus, the process of osmosis can be used to remove water from a dilute solution contained within a semi-permeable membrane by surrounding the membrane with a more concentrated solution. Water diffuses through the membrane from the dilute to the concentrated solution until on equilibrium concentration is established. The solution can diffuse only very slowly

through the membrane, so that the major result of this process is transfer of water to the more concentrated solution.

Transfer of water by osmosis is applicable to fruit pieces by virtue of the fact that they contain sugars and other solutes in dilute solution, and their cellular surface structure acts as an effective semi-permeable membrane. By immersing fruit pieces in a concentrated solution of sugar, water can be removed to the extent of over 50% of the initial fruit weight. This method can be used as a means of partial dehydration of fruit.

2.1 Basic Theory of Osmotic Dehydration

Osmotic dehydration is a process where water rich foods are immersed in aqueous solutions which are normally concentrated salt or sugar solutions. There is a water outflow from the product and this transfer is replaced by the aqueous solution. During the process a small amount of the solutes from the product are lost to the aqueous solution. But the quantities of the solutes are negligible compared to the two main mass transfers that occur in the process. However this transfer cannot be disregarded as it is essential when looking at the final product composition (Dobie *et al.*, 1995).

Torreggiani (1993) discussed that an ideal osmotic dehydration situation would be for a semi-permeable membrane to be permeated by the molecules of the solvent but not by those of the solute. Osmotic dehydration is mainly carried out on fruits and vegetables and these products that have cell wall membranes which are alive, and can stretch and expand when the product grows or generates pressure from within. The cellular membranes will freely allow molecules of the solvent to pass through them, but they also allow a small amount of the solute molecules to pass through; this is shown in Figure 2. This type of membrane should be classified as permeable, as opposed to semi-permeable.

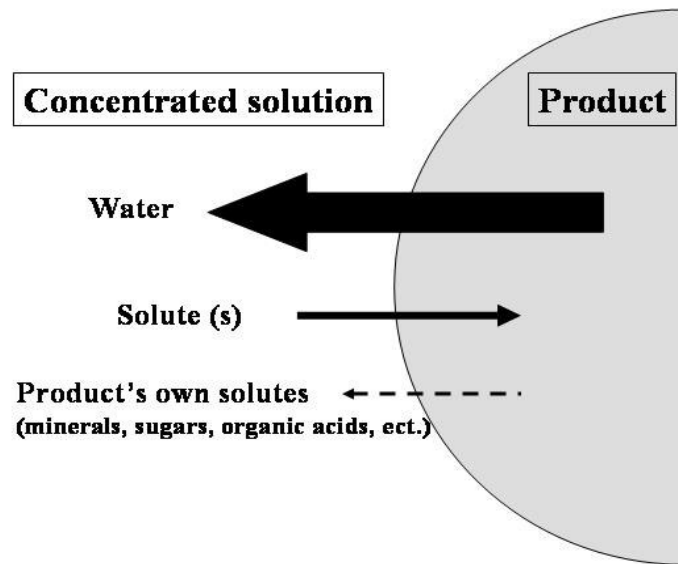


Figure 2 Mass transfers during the soaking process

Source: Raoult-Wack (1994)

The osmotic dehydration process gives rise to, at least, two major simultaneous counter-current flows: water diffusion out of the food into the solution and solute diffusion from solution into the food. There are both due to the water and solute activity gradients across cellular membranes. A driving force for water removal occurs from difference in osmotic pressure between food and its surrounding solution. The complex cellular structure of food acts as a semi-permeable membrane. Since the membrane responsible for osmotic transport is not perfectly selective, other solutes present in the cell can also be leached into the osmotic solution (Dixon and Jen, 1977; Lericci *et al.*, 1985; Giangiacomo *et al.*, 1987).

Osmotic dehydration incorporates a two-fold transformation of the product in its drying process. There is a decrease in water content as well as the incorporation of a solute, and this can result in overall weight loss by the product. Moreover, it is a useful technique for lowering water activity of fruit and vegetables.

During osmotic removal of water from foods, the dehydration front moves from the surface that is in contact with the osmotic solution to the center. The associated osmotic stress results in cell disintegration. The most likely cause of cell damage can be attributed to the reduction in size caused by water loss during osmotic treatment, resulting in the loss of contact between the outer cell membrane and the cell wall. Introducing a solute into the food material can alter the nutritional and functional properties of the food. Therefore a specific formulation could be achieved by using a specific solution. The direct altering of the formulation and the partial dehydration of the food product is what makes osmotic dehydration different to other dehydration techniques (Rastogi *et al.*, 2000).

2.2 Combined Processes

Osmotic dehydration has been seen as a preliminary stage before further processing, as the process is only capable of reducing a sample's moisture content to about 50%. It is used as a pre-treatment in many processes used to improve nutritional, sensorial and functional properties of food without changing its integrity, and acknowledged to be an energy efficient method of partial dehydration, since there is no need for a phase change. It can reduce the water activity of many food materials so that microbial growth will be inhibited. Since most foods contain large amounts of water, they are cost intensive to ship, pack and store. It generally precedes process such as freezing, freeze drying, vacuum drying, or air drying. It is effective around ambient temperatures, so heat damage to texture; color and flavor can be minimized (Torreggiani, 1993).

Compared to traditional drying processes, osmotic dehydration has reduced energy costs. The greatest energy consumption is in reconstituting the diluted osmotic solution and this could be achieved by concentration using multiple effect evaporators or by sugar addition. If evaporators are used the energy required for water removal is only approximately 25% of the energy required for conventional hot air drying (Torreggiani and Bertolo, 2001). They also reported that the differentiating feature of osmotic dehydration, compared to other dehydration

processes is the penetration of solutes into the food material. So it is possible, to a certain extent, to change the food system formulation, making it more suitable for further processing.

The commercial feasibility of using osmotic dehydration followed by vacuum drying for the processing of bananas was studied using semi-pilot plant scale operations and this process can be seen in Figure 3. The osmotically dried bananas retained more puffiness and crispness than samples which had only been treated by vacuum drying. The flavor also lasted for one year at ambient conditions compared to only two months for vacuum-dried samples. The natural banana flavor is better retained than even freeze-dried samples and the color remains vibrant with the reduced need for sulphur dioxide treatment (Torreggiani, 1993).

Osmotic dehydration as processing step prior to freezing has been proven as a useful tool for gentle processing of fruits. Talens *et al.* (2001) aimed to analyze changes in optical and mechanical properties of kiwi slices due to osmotic dehydration and subsequent to freezing thawing. The osmodehydrofreezing process improved color and mechanical parameters and resulted in reduced drip loss as compared to samples without pretreatment.

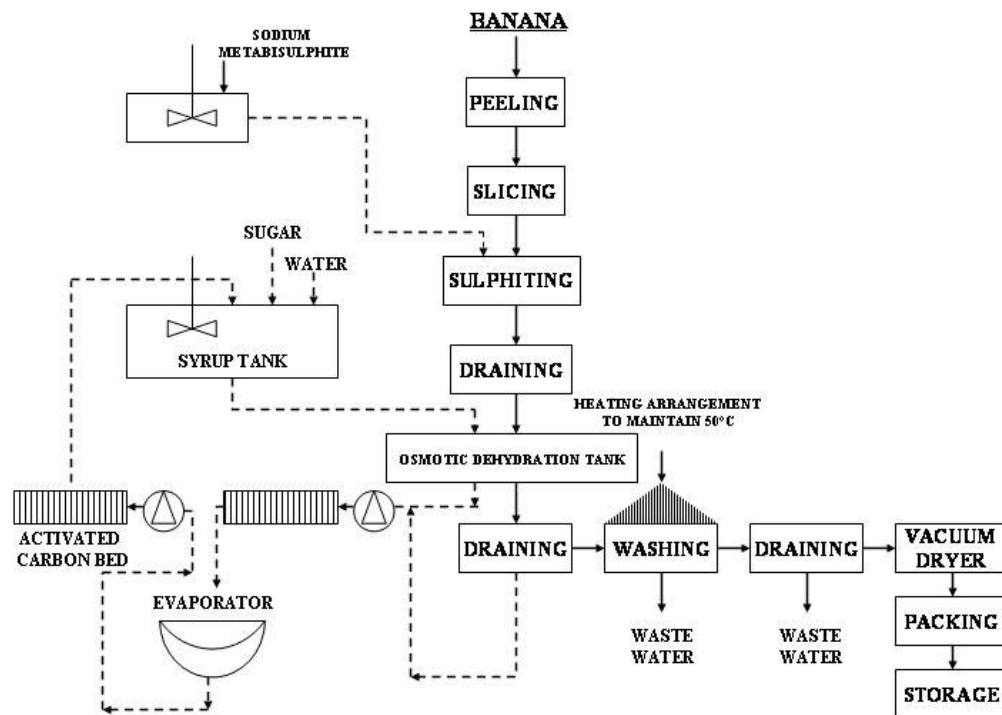


Figure 3 Flow diagrams for osmotic dehydration and vacuum drying of bananas

Source: Torreggiani, 1993

Maeslrelli *et al.* (2001) studied partial removal of water from muskmelon spheres before freezing by Dewatering–Impregnation–Soaking in concentrated solution (DIS) for 1 h, air dehydration and combined DIS-air dehydration to a final 50% weight reduction. All the pre-treatments caused the loss of desirable aroma compounds, while the undesirable aroma compounds increased in air dehydrated fruits and remained stable in the DIS-treated ones. Moreover, the sensory acceptability of the DIS-treated fruit was higher when compared with air dehydrated ones.

It has been observed that products which have first been treated by osmotic dehydration have reduced drying rates for the further drying processes, and these

processes have included solar drying, convective-air drying and vacuum drying (Torreggiani, 1993).

The effect of previous osmotic dehydration with glucose syrups before air drying of mango cubes (4 cm. x 4 cm. x 0.4 cm.) at 60°C was investigated. It was found that the osmotic pretreatment applied affected the course of drying. Osmotic dehydration adversely influenced drying rate, this effect increasing as glucose concentration in the impregnation solution increased. However, osmotic dehydration did not appear to change to any great extension the resistance of cell wall to water transport (Nieto *et al.*, 2001).

2.3 Advantages of Using Osmotic as a Pre-treatment

2.3.1 Quality improvement

Osmotic dehydration has the potential to improve the quality of the food. Studies have shown that osmotic dehydration improves the product quality in terms of color, flavor and texture (Ponting *et al.*, 1966; Rahman, 1992). Torreggiani (1993) and Raoult-Wack (1994) reviewed the merits of osmotic dehydration for product quality improvement and process efficiency. Heat damage to color and flavor are minimized, as products are not subject to a high temperature over an extended period of time. Loss of fresh fruit flavor commonly found with ordinary an air or vacuum drying method is prevented by the use of sugar or syrup as the osmotic drying agent. Bignardi *et al.*(2000) observed that muskmelon spheres pre-dehydrated by osmotic dehydration were significantly more accepted than those pre-air dehydrated, confirming the suitability of osmotic dehydration as a pre-treatment in the production of innovative high quality frozen products.

2.3.2 Energy Efficiency

It is an efficient form of drying because it is carried out at ambient temperature and pressure therefore saving energy and money. Lenart and Lewicki

(1987) observed that energy consumption in osmotic dehydration at 40 °C with syrup re-concentration by evaporation was at least two times lower than convection air drying at 70 °C. The high level of solute in osmotically treated products decreases water activity and preserves them and thus energy intensive drying process is avoided. In effect, osmotic dehydration reduces water removal load in a subsequent drying step which otherwise consumes a lot of energy.

In the frozen food industry, high energy levels are used for freezing due to the large quantity of water present in fresh foods. Huxsoll (1982) reported that a substantial proportion of energy was saved when foods were osmotically dehydrated before freezing.

2.3.3 Elimination of Chemical Treatment step

Chemical treatment to reduce enzymatic browning can be avoided by the osmotic process. The high concentration of sugar surrounding the fruit pieces prevents discoloration by enzymatic oxidative browning. Thus, good color retention prevails without the use of an additive such as SO₂. There are two effects of sugar in producing high quality product: first, effective inhibition of polyphenoloxidase, the enzyme which catalyses oxidative browning of many cut fruits and vegetables, and second, prevention of the loss of volatile flavor compounds during further air or vacuum drying (Ponting *et al.*, 1966).

2.3.4 Product Stability

The product obtained by osmotic process is more stable than untreated fruit and vegetables during storage due to low water activity caused by solute gain and water loss. At low water activity, reduced chemical reaction and the growth of toxin-producing micro-organisms in the food are low. Moreover, the use of osmodehydrofrozen apricot and peach cubes in yoghurt improved consistency and reduced whey separation of yoghurt (Giangiacomo *et al.*, 1994).

2.4 Limitation of using Osmotic dehydration as a Pre-treatment step

2.4.1 Process Design

Fruit and vegetables tend to float on the osmotic solution due to the higher density of the osmotic solution. Moreover, the viscosity of the osmotic solution exerts considerable mass transfer resistance, causing difficulty in agitation, and adherence of the solution to the surface of the food material. However, breakage of the fruit or vegetable pieces may occur by mechanical agitation (Rahman, 1992).

In terms of osmotic solution management, the amount of osmotic solution required for large-scale could produce large quantities of concentrated waste solutions. There are difficulties with scale-up these will need to be treated before disposal (Raoult-Wack, 1994).

2.4.2 Product Sensory Quality

Product saltiness or sweetness may increase during the osmotic process or the acidity may decrease, which is not desirable in some cases. This can be avoided by controlling the solute diffusion and optimizing the process to improve the sensory properties of the product.

2.5 Factors Affecting Osmotic Pre-treatment

2.5.1 Osmotic solution

2.5.1.1 Type of Osmotic Agent

The specific effect of the osmotic solution is of great importance when choosing the solution. The solute cost, organoleptic compatibility with the end product and additional preservation action by the solute are factors considered in selecting osmotic agents (Torreggiani, 1995). Several solutes, alone or

in combinations, have been used in hypertonic solutions for osmotic dehydration (Le Maguer, 1988).

Ternary sucrose and NaCl solution, multi-components salt-sugar aqueous solutions have been studied to increase the driving force of the process. Mixture of salt and sucrose in different proportion can be used for materials of plant and animal origin to obtain higher weight loss to solid gain ratios ($WL: SL$) than with individual solutes in binary solution; this also reduces impregnation (Sacchetti *et al.*, 2001; Ade-Omowaye *et al.*, 2002).

Lerici *et al.* (1985) have found that the addition of a small amount of NaCl (2% max. w/w) to different sucrose solutions during apple dehydration led to higher rates of water loss without increasing solids gain significantly.

Qi *et al.* (1988) have pointed out the effectiveness in combining NaCl and sucrose solutes to obtain a maximum water loss with low solids gain by the product, without significantly affecting product taste, for carrots dehydrated using 44% sucrose and 7% NaCl solutions (w/w).

Osmotic dehydration of apples cut into a cylinder shape were carried out in binary aqueous solution of sucrose (40-50%) and NaCl (15-26.5%) with different concentrations and temperatures, as well as in ternary solutions of 30/10, 40/10, 50/10, 20/15, 30/15, 40/15 % of sucrose and NaCl, respectively. The ratio of water loss to solids gain (WL/SG) for each osmotic treatment was particularly high in the case of salt solutions, due to a low solids gain. In the case of ternary mixed solutions, intermediate values for WL/SG are obtained. (Sereno *et al.*, 2001)

Osmotic dehydration of red paprika was studied using a combined sucrose and NaCl solution. It was found that the optimum conditions for sucrose concentration and NaCl concentration are 21.86g/10g and 2.02 g/100g, respectively for the appropriate criteria are achieved (Ade-Omowaye *et al.*, 2002).

Sucrose and NaCl solutions proved to be the best choices based on effectiveness, convenience and flavor. For apple sticks dehydrated using ternary sucrose and NaCl solutions, the addition of NaCl may help to attenuate the excessive sweetness of product processed with high sucrose concentration. It was also found that addition of NaCl at levels up to 1% did not have a detrimental effect on product acceptability when added to sucrose solutions having concentrations lower than 55% (Sacchetti *et al.*, 2001).

2.5.1.2 Concentration of the Osmotic Solution

Increase in osmotic solution concentration resulted in corresponding increases in water loss to equilibrium level and drying rate (Conway *et al.*, 1983; Hawkes and Flink, 1978; Lenart, 1992). Therefore, increased osmotic solution concentrations lead to increased weight reductions. This was attributed to the water activity of the osmotic solution which decreases with the increase in solute concentration in the osmotic solution (Biswal and Le Maguer, 1989; Biswal *et al.*, 1991; Rahman and Lamb, 1990). According to Ravindran (1987) an increase in 10°Brix corresponds to an increase of 5% of the final water loss percentage. Lazarides (1994) studied on the osmotic dehydration of apples using 45 and 65 ° Brix of sucrose solution. It was found that a higher sucrose concentration (65° Brix) a faster water loss (ca.30% increase). However, there was a much greater solid uptake (ca. 80% increase). He concluded that under increased osmotic solution concentration favored solid uptake and resulted in lower water loss to solids gain ratio. On the contrary, low concentration sucrose solution can cause minimal water loss which resulted in lower water loss to solid gain ratio (Karathanos *et al.*, 1995).

2.5.1.3 Physico-chemical Properties of Osmotic Solution

A number of authors have observed that the molecular weight, ionic state and solubility of the solute in water cause differences in the behavior of the osmotic solute (Hawkes and Flink, 1978; Lenart and Lewicki, 1987; Lenart, 1992; Lericci *et al.*, 1985). Furthermore, molecular size of the osmotic solute

has a significant effect on the water loss to solids gain ratio. The smaller the solute, the higher and the extent of solute penetration. For example, high dextrose equivalent (D.E.) corn syrup solids favoured sugar uptake and resulted in lower water loss to sugar gain ratio (Lazarides, 1994). Lower dextrose equivalent (large size) corn syrup solids gave negative solid gain values, indicating that solute uptake was lower than the leaching of natural tissue solid.

Osmotic dehydration is also affected by the pH of the osmotic solution. Moy *et al.* (1978) observed that acidification of osmotic solution increases the rate of water removal by changing in the tissue's properties and subsequently the texture of fruits and vegetables. Tanafranca *et al.* (1986) noted that the texture and color of the osmosed jackfruit were improved by adding citric acid 0.2% of the original fruit weight in the osmotic solution. At this condition the firmness of jackfruit pieces was maintained and the enzymatic browning can be avoided by the use of citric acid as anti-browning agent.

Effect of preservatives is also important to extend the shelf life of the osmosed products. Tanafranca *et al.* (1986) studied the effect of sodium metabisulfite on flavor and taste of the finished product. Sodium metabisulfite proved to be effective for preventing discoloration of dehydrated jackfruit. The ideal concentration seemed to be 0.1% by weight of the original fruit.

2.5.1.4 Osmotic Solution and Food Mass Ratio

Ponting *et al.* (1966) and Flink (1979) reported that an increase of osmotic solution to sample mass ratio resulted in an increase in both the solid gain and water loss in osmotic dehydration. To avoid significant dilution of the medium and subsequent decrease in the (osmotic) driving force during the process, a high ratio (at least 30:1) was used by most workers whereas some investigators used a much lower solution to product ratio (4:1 or 3:1) in order to monitor mass transfer by following the changes of the sugar solution concentration (Conway *et al.*, 1983).

2.5.2 Food Material

2.5.2.1 Physico-chemical Properties of Food Material

The chemical composition (protein, carbohydrate, fat and salt), physical structure (porosity, arrangement of cells, fibre orientation and skin) and pre-treatments may affect the kinetics of osmosis of food (Islam and Flink, 1982). In their studies the authors observed that steam blanching of the fresh potatoes slice for four minutes before osmosis gave lower water loss and higher solid gain. They concluded that the loss of membrane integrity due to heating was the cause of the poor mass transfer during osmotic dehydration.

Different species, different varieties of the same species, even different maturity levels of the same variety have been found to give substantially different responses to osmotic dehydration (Hartel, 1967). Species, variety and maturity level all have a significant effect on the natural tissue structure in terms of cell membrane structure, protopectin to soluble pectin ratio, amount of insoluble solids, intercellular spaces, tissue compactness and entrapped air. These structural differences substantially affect diffusional mass exchange between the product and osmotic medium

2.5.2.2 Geometry of Food Material

The geometry of sample pieces affects the behavior of the osmotic concentration due to the variation of the surface area per unit mass and diffusion length of water and solutes involved in mass transfer (Lerici *et al.*, 1985). According to Lerici *et al.* (1985) higher surface area sample shape (such as rings) gave higher water loss and sugar gain value compared to lower surface area samples (such as slices and stick). However, the small thickness associated with high surface area resulted in high sugar gain but low water loss. A reduction in water diffusion was due to the short diffusion length.

2.5.3 Operation

2.5.3.1 Immersion Time

The immersion time is significant factor affecting the osmotic dehydration. In general, rapidly rate of mass transfer in the early stages of the osmotic process after which the gradually slow down with time towards equilibrium end point has been reported (Conway *et al*, 1983; Lazarides, 1994; Uddin *et al.*, 2004). The condition defining the equilibrium state between product and osmotic solution was approached in long period immersion time. Lenart and Flink (1984) found that mass transport data were not significantly changed in the period between 4 and 20 hrs. It has been observed that the initial period of osmotic process is the most important one, since the mass transfer phenomena are fast and they have a dramatic impact on further evolution of the osmotic process. Lazarides (1994) reported that there was a considerably changed in mass transfer parameters during the early period of osmotic dehydration of apple slices. It was found that within the first hour the rate of water loss was about 50% and within 3 hours it more than doubled its initial total solids. Thus an efficient way to limit mass transfer value such as minimized solute uptake and obtained high water loss is early interruption of osmotic process.

2.5.3.2 Operating Temperature

Temperature is also a very important factor because it affects the drying rate and the quality of the osmosed product. According to Conway *et al.* (1983) it can be concluded that every 10° C increase in temperature correspond to 5% increase in final water loss percentage. Beristain *et al.* (1990) stated that increase in temperature of osmotic solution results in increases in water lose, whereas solid gain is less affected by temperature. Rahman and Lamb (1990) observed that at high temperature solute does not diffuse as easily as water through the cell membrane and thus the approach to osmotic equilibrium is achieved primarily by flow of water from the cell resulting in a lower solute gain by the food material. Higher process temperatures seem to promote faster water loss through swelling and

plasticizing of the cell membranes, faster water diffusion within the product, and better mass transfer characteristics at the product surface due to lower viscosity of the osmotic medium. At the same time solids diffusion within the product is also promoted by higher temperatures, only at different rates, mainly dictated by the size of the solute and concentration of the osmotic solution. However, Lazarides (1994) reported substantial higher sugar gains (up to ca.55%) compared to room temperature conditions during osmotic dehydration of apples at process temperature between 30 and 50° C.

2.5.3.3 Operating Agitation

Agitation prevents the formation of a low concentration area around the fruit due to migration of water from the fruit to the medium (Pointing, 1973). Without agitation, the water loss is decreased and the sugar gain is increased (Wack and Guilbert, 1990). Lenart and Flink (1984) reported that osmotic dehydration is enhanced by agitation or circulation of the osmotic solution around the sample. Agitation insures a continuous contact of the sample surface with concentrated osmotic solution, securing a large gradient at the product/solution interface. Therefore agitation has a tremendous impact on weight loss, whenever water removal is characterized by large external mass transfer resistance.

3. Mass Transfer during Osmotic Pre-treatment

Mass transfer rates during osmotic pre-treatment (dehydration) are influenced by several factors such as temperature and concentration of osmotic solution, the size and geometry of the material, the solution to material mass ratio, and the level of agitation of solution. The effect of the concentration and temperature of the osmotic solution has been studied in considerable detail and it has been shown that the rate of osmotic dehydration increases with both the parameters. The rate of dehydration also increases as the level of agitation is increased. Agitation is indeed one of the key factors and an adequate level of agitation ensures minimization or elimination of

liquid-side mass transfer effects. If the solid is bigger in size, it will dehydrate more slowly because the length of the diffusion path is greater. Smaller pieces on the other hand dehydrate more rapidly. The shape of the solid material is another important factor (Torreggiani and Bertolo, 2001; Park *et al.*, 2002).

Diffusion is physical process that involves mass transfer. The uptake or loss of solutes from solids is partly controlled by diffusion and is an important component in unit operations. Movement of food additives such as sodium chloride, calcium chloride, sorbic acid, sugar and combinations thereof have been examined due to their effects on food quality characteristics (texture, flavor, color, microbiological qualities, and pH) (Barnard and Quintero-Romos, 1998).

Mass transfer in foods has traditionally been approximated by models based on Fick's law, which is based on concentration gradients (Crank, 1975), thus allowing estimation of effective diffusion coefficients for water and solutes. During diffusion, solid and liquid come into contact and transfers occurs from liquid to solid (infusion) or from solid to liquid (leaching), depending on relative concentration of solute (Barnard and Quintero-Romos, 1998; Rastogi *et al.*, 2002).

Quantitative measurement of the rate at which a diffusion process occurs is usually expressed in terms of diffusivity (D , also called the "diffusion coefficient"). The estimation of diffusion coefficients for moisture and solute transport during osmotic dehydration is based on the solution of Fick's second law as applied to the situation under consideration. Fick's second law for unidirectional unsteady state diffusion is given by:

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} \quad (1)$$

For an infinite slab, effective diffusion coefficients of water as well as solute were estimated using the solution of Fick's second law (Eq. (1)) for a well-agitated unlimited volume of osmotic solution as given by Eq. (2) and (3) (Rastogi and

Raghavarao, 1997), and for well agitated limited volume of osmotic solution Eq. (4) and Eq. (5)

$$MR = \frac{M_t - M_e}{M_o - M_e} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[- \left(n + \frac{1}{2} \right)^2 \pi^2 F_{ow} \right] \quad (2)$$

$$SR = \frac{S_t - S_e}{S_o - S_e} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[- \left(n + \frac{1}{2} \right)^2 \pi^2 F_{os} \right] \quad (3)$$

$$MR = \frac{M_t - M_e}{M_o - M_e} = \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp \left[- q_n^2 \cdot F_{ow} \right] \quad (4)$$

$$SR = \frac{S_t - S_e}{S_o - S_e} = \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp \left[- q_n^2 \cdot F_{os} \right] \quad (5)$$

where MR and SR are moisture ratio and solid ratio of the slab at any time t ; M and S are the moisture and solute content; the subscripts o , e and t represent the relevant concentrations initially, at equilibrium, and at any time, respectively. F_{ow} and F_{os} are the Fourier number for moisture and solid diffusion, and are defined as $D_{ew} t/l^2$ and $D_{es} t/l^2$, respectively, where D_{ew} and D_{es} are the effective diffusion coefficients for water and solute; t is the immersion time and l is the half thickness; q_n 's are the non-zero positive roots of the equation $\tan q_n = -\alpha q_n$ and α is the ratio of the volume of solution to that of each piece. The values of F_{ow} and F_{os} can be obtained as a function of MR and SR from the above equations. These values can then be plotted against the corresponding values of t and the D_{ew} and D_{es} values were estimated from the slopes of these plots.

Ade-Omowaye *et al.* (2003) evaluated the effective moisture diffusivity of flat disc sample during partial osmotic dehydration using the analytical solution based on Fick's second law for unsteady state diffusion given by the Eq.(6).

$$\frac{M_t - M_e}{M_o - M_e} = \frac{8}{\pi^2} \left[\sum_{n=0}^{n=\infty} \frac{1}{(2n+1)^2} \exp\left[-(2n+1)^2 D_e (\pi / 2l)^2 t\right] \right] \quad (6)$$

where M_t , M_e and M_o stand for average moisture content (dry basis) at any time, t , at equilibrium, and at the initial moisture content, respectively, kg/kg; D_e is the effective diffusion coefficient, m^2/s ; t is the time from start to falling rate period, s; and l is the one half thickness of the solid layer through which diffusion occur, m. However, l is total thickness, when evaporation is from only one side. Eq.(6) assumes that D_e is constant and shrinkage of sample is negligible. For long drying times, the term in the above infinite series are expected to converge rapidly and may be approximated by first term, thus simplifies to Eq.(7). The effective moisture diffusivity, D_e was determined from slope ($D_e \pi^2 / 4l^2$) of the plot of $\ln(MR)$ against time, t .

$$MR = \frac{M_t - M_e}{M_o - M_e} = \frac{8}{\pi^2} \exp\left(\frac{-D_e \pi^2 t}{4l^2}\right) \quad (7)$$

For an osmotic dehydration process the diffusivity of the solute entering the sample can be measured as well as the diffusivity of the water being removed from the sample. It has been shown by Lazarides *et al.* (1995) that the effective diffusivities behave differently with increasing temperature. This is due to a stronger dependence on temperature of the solute diffusivity than the water diffusivity, and this may reflect the different mechanisms of transport for sugars and water within the cell. It was also shown that the cell membrane is a more effective barrier for sugar solutions than water. However, the result shows that by increasing the solution concentrations, the solute diffusivity is lowered. Tissue damage causes a dramatic decrease in the efficiency of the dehydration process, due to increased solute diffusivities and decreased water diffusivities.

4. Optimization Study using Response Surface Methodology

Response surface methodology (RSM) is an important tool in process and product development. RSM is a collection of experimental design and optimization techniques that enables the experimenter to determine the relationship between the response and the independent variables. RSM is typically used for mapping a response surface over a particular region of interest, optimizing the response, or for selecting operating conditions to achieve target specifications or customer requirements (Khuri and Cornell, 1996; Myers and Montgomery, 1995).

RSM consists of a group of mathematical and statistical techniques that can be used to define the relationships between the response and the independent variables. RSM defines the effect of the independent variables, alone or in combination, on the processes. In addition to analyzing the effects of the independent variables, this experimental methodology also generates a mathematical model. The relationship between the response and the input is given in Eq.(8):

$$\eta = f(x_1, x_2, \dots, x_n) + \varepsilon \quad (8)$$

where η is the response, f is the unknown function of response, x_1, x_2, \dots, x_n denote the independent variables, also called natural variables, n is the number of the independent variables and finally ε is the statistical error that represents other sources of variability not accounted for by f . These sources include the effects such as the measurement error. It is generally assumed that ε has a normal distribution with mean zero and variance (Neddermeijer and Oortmarssen, 2000; Baş and Boyacı, 2006).

An optimization study using RSM in process and product development can be divided into three stages. The first stage is the preliminary work in which the determination of the independent parameters and their levels are carried out. The second stage is the selection of the experimental design and the prediction and verification of the model equation. After the regression coefficients were obtained, the estimated response could be easily calculated using model equation. Usually the behavior of the system is unknown so one must check whether the model fits well to

the experimental data. For verification of the model adequacy, several techniques are carried out. Some of these techniques are residual analysis, scaling residuals, prediction error sum of squares (PRESS) residuals, and testing of the lack of fit. The overall predictive capability of the model is commonly explained by the coefficient of determination (R^2). The last one is obtaining the response surface plot and contour plot of the response as a function of the independent parameters and determination of optimum points. The visualization of the predicted model equation can be obtained by the response surface plot and contour plot. The response surface plot is the theoretical three-dimensional plot showing the relationship between the response and the independent variables. The two-dimensional display of the surface plot is called contour plot and in the contour plot, lines of constant response are drawn in the plane of the independent variables. The contour plots help to visualize the shape of a response surface. When the contour plot displays ellipses or circles, the center of the system refers to a point of maximum or minimum response (Myers and Montgomery, 1995; Baş and Boyacı, 2006).

There is a body of research relating to the optimization of osmotic dehydration process which uses response surface methodology with different approaches.

Ade-Omowaye *et al.* (2002) studied on osmotic dehydration behavior of red paprika by using response surface methodology technique. The effect of sucrose and NaCl and their complex interaction on water and solute diffusion coefficients as well as on equilibrium moisture content and solid contents were studied using central composite design of experiment. It was found that the optimum solute mix for the osmotic dehydration of red paprika was established. The concentration of sucrose and NaCl were 21.86 g/100g and 2.02 g/100 g, respectively. The following criteria were achieved: water diffusion coefficient $\geq 0.80 \times 10^{-9}$ m²/s, solid diffusion coefficient $\geq 0.82 \times 10^{-9}$ m²/s, equilibrium moisture content ≤ 6.85 kg/kg, and equilibrium solid content ≤ 2.00 kg/kg.

Osmotic dehydration of cantaloupe has been optimized using desired function methodology by Corzo and Gomez (2004). The effects of three independent parameters (temperature, concentration, and time) on three responses (mass loss,

water loss, and Brix increase) have been investigated by means of a five level central composite design. The response variables were fitted to predictive models applying multiple linear regressions. Applying the method of the desired function, the dehydration was optimized in 37.95 °C, 41.6 °Brix and 132.30 min in order to obtain weight loss equal to 0.11 g/g, water loss equal to 0.33 g/g and °Brix increase equal to 12.3 °Brix/g.

Uddin *et al.* (2004) reported that the regression equations obtained from osmotic dehydration of carrot can be used to find optimum conditions for the desired sensory and physical properties. Water and sucrose transfer were quantitatively investigated during osmotic dehydration of carrot slices using response surface methodology with the sucrose concentration (40–60%, w/w), temperature of sucrose solution (40–60 °C) and immersion time (0.5–6.0 h) being the independent process variables. Quadratic regression equations describing the effects of independent process variables on the water loss and sucrose gain were developed. It was found that immersion time and concentration of sucrose solution were the most significant factors affecting the water loss during osmotic dehydration of carrots followed by temperature. Effect of temperature and time were more pronounced for solid gain than the concentration of sucrose solution.

Response surface methodology was used for quantitative investigation of water and solids transfer during osmotic dehydration of sugar beet cossettes in combined aqueous solutions of sucrose and sodium chloride. Effects of immersion time (30–240 min), sucrose concentration (30–70%, w/w), sodium chloride concentration (0–8%, w/w), and temperature of the osmotic solution (30–50 °C) were estimated. Quadratic regression equations describing the effects of these factors on the water loss and solids gain were developed. It was found that effects of immersion time and sucrose concentrations were more significant on the water loss than the effects of sodium chloride concentration and temperature. As for solids gain immersion time and sodium chloride concentration were the most significant factors (Jokić *et al.*, 2005).

Response surface methodology was also used to determine the optimum processing conditions that yield maximum water loss and weight reduction and minimum solid gain and water activity during osmotic dehydration of potatoes. Temperature (20–60 °C), processing time (0.5–8 h), sucrose (40–60% w/w) and salt (0–15% w/w) concentrations were the factors investigated with respect to water loss, solid gain, weight reduction and water activity. Experiments were designed according to central composite rotatable design with these four factors each at five different levels, including central and axial points. With respect to water loss, solid gain, weight reduction and water activity, both linear and quadratic effects of four variables were found to be significant. The response surfaces and contour maps showing the interaction of process variables were constructed. Applying desirability function method, optimum operating conditions were found to be temperature of 22 °C, sucrose concentration of 54.5%, salt concentration of 14% and treatment time of 329 min. At this optimum point, water loss, solid gain, weight reduction and water activity were found to be 59.1 (g/100 g initial sample), 6.0 (g/100 g initial sample), 52.9 (g/100 g initial sample) and 0.785, respectively (Eren and Kaymak-Ertekin, 2006).

El-Aouar *et al.* (2006) studied on the osmotic dehydration of papaya slices. The study was carried out using two factorial experimental designs (sucrose and corn syrup), with three independent variables whose levels varied from 44% to 56% w/w for concentration, from 34 to 46 °C for temperature and from 120 to 210 min for immersion time. The results showed that, considering the same osmotic pressure for both osmotic agents, the values obtained for weight reduction, water loss and solid gain for dehydration in sucrose solutions were higher than those obtained in corn syrup solutions, due to their high viscosity and polysaccharide content. The opposite behavior was observed for water activity.

In order to develop a high quality product and add value to persimmon, it is necessary to process the fruit further, especially the astringent cultivars. The best way of achieving this objective is to use osmotic dehydration as a pretreatment step. This literature review has demonstrated that there is very little information on osmotic

dehydration characteristics of persimmon. A better understanding of mass transfer behavior during osmotic treatment which includes modeling aspects is necessary. This will allow the identification of best possible processing combinations which will result in a product quality with high acceptance after further processing. The following chapter of this thesis explains the materials and methods in detail. This is followed by the results and discussion and finally conclusion.