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Review

A review of osmodehydration for food industry

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As a cost saving drying technology, osmotic dehydration is not receiving much attention in the food industry due to the poor understanding of the counter current flow phenomena associated with it. Therefore, it is very important to investigate the underlying principles of the counter current flow to improve industrial implementation of the technology. Osmotic dehydration experiments had been reported plant and animal materials. Minimal improvement on amount and rate of water loss and corresponding solid gain had been reported in the presence of sodium chloride and agitation especially for the first thirty minutes of osmotic dehydration. Simulation of cell membrane using artificial cell had showed that the presence of starch in food materials retards the diffusion of water. A multilinear regression (MLR) model had been developed for water loss and solid gain during osmotic dehydration of the plant and animal materials. These models took into account the effect of temperature, concentration, time of immersion, sample size, sample type and agitation. Temperature was the most important factor whereas agitation was the least. Artificial neural networks (ANNs) (using the radial basis function (RBF) network with a Gaussian function) had been used successfully to model osmotic dehydration. When predictions of experimental data from MRL and ANN were compared, better agreement was found for ANN models than MLR models. A new method, thermocalorimetry, was developed to study osmotic dehydration. Scanning Electron Microscopy (SEM) micrographs revealed that osmotic treatment has a significant effect on the structural properties (cell wall and middle lamella) for the different plant materials. These successfully reports buttress the need for employment of osmotic dehydration in food industries.

Key words: Osmodehydration, multilinear regression, Artificial neural networks, radial basis function, scanning electron microscopy, Visking osmometer

INTRODUCTION

In Sub-Saharan Africa, preservation of fruits by drying provides livelihood opportunities for people in rural, peri-urban and urban areas, including producers of raw materials, commodity traders, food processors, vendors and exporters. In Ghana, dried fruits and vegetables are increasingly a large proportion of the export products from the country. The total export worth from dried fruits and vegetables in 1995 was $124,678 of which 21% was from fruits and in 1998 exports of dried fruits and vegetables had increased to $3,600,600, of which 42% was from fruits (Ghana export promotion council, 2000). In spite of developments in new food manufacturing processes and designs, the potential for sustainable increases in income is jeopardised by market constraints related to perceived problems of product safety and quality. This calls for the implementation of improved drying technologies and food management safety systems such as hazard analysis critical control point (HACCP) programmes designed to identify, categorise and eliminate food safety hazards by the implementation of proper process controls. However, only through an adequate understanding of the process involved in food processing that the necessary improvements and controls can be realised.

Most fruits and vegetables have a definite harvesting time and a limited shelf-life. Most harvested fruits quickly deteriorate due to microbial and biochemical activity. However, different preservation methods are used to extend the shelf-life by a few weeks, one year or more. The methods include canning, bottling, freezing, drying, fermentation, pasteurisation, chemical additives, packaging and irradiation (Burrows, 1996). The most notable preservation methods employed on an industrial scale are canning, freezing and drying (McMinn and Magee,

1999). The choice of preservation method most often depends on the raw material. Jayaraman and Das Gupta (1992) observed that the increasing rejection of chemicals for food preservation and the demand to provide a comprehensive range of products has generated renewed interest in drying operations. The diversity of products has led to the introduction of numerous drying methods to remove moisture from the wide variety of produce in the food processing industry. The drying process can take many forms and utilises different types of dryer, with each developed to suit a given operation or product. Drying processes applied to fruits and vegetables can be classified into four generations: solar drying, atmospheric drying, sub-atmospheric drying and novel drying technologies (Jayaraman and Das Gupta, 1995). Solar drying includes sun or natural dryers, solar dryers-direct, solar dryers-indirect and hybrid or mixed systems. Atmospheric drying is either continuous or batch. Continuous drying utilises spray dryer, fluidised bed dryer, belt dryer, rotary dryer, tunnel dryer and drum dryer whereas batch drying involves kiln dryer, cabinet or compartmental dryer and tower dryer. Sub-atmospheric drying includes vacuum shelf dryer, continuous vacuum dryer and freeze dryer. Novel drying technologies are microwave drying, infra-red radiation drying, electric or magnetic field drying, superheated steam drying, explosion puffing, foam mat drying, acoustic drying and osmotic dehydration (Jayaraman and Das Gupta, 1995).

Since ancient time, dehydration has been one of the most common natural and reliable methods for food preservation. Although reaction rates are generally reduced by dehydration, undesirable changes due to reactions such as enzymatic browning may result in quality changes (Acker, 1969; Kouassi and Roos, 2001). Sugar, honey and salt have been used as aids in the drying of fruits and vegetables at various times in the past (Goldblith, 1972; Woodroof, 1986). However, sugar was used to preserve the quality of the dried product, usually in small amounts, rather than as a means of removing water.

Osmotic dehydration is the process of water removal by immersion of water-containing cellular solid in a concentrated aqueous solution (Ponting, 1973). The fundamental purpose of food dehydration is to lower the water content in order to minimise rates of chemical reactions and to facilitate distribution and storage. In osmotic dehydration, foods are immersed or soaked in a saline or sugar solution. This results in three types of counter mass transfer phenomenon (Ponting, 1973). First, water outflow from the food tissue to the osmotic solution, second, a solute transfer from the osmotic solution to the food tissue, third, a leaching out of the food tissue's own solutes (sugars, organic acids, minerals, vitamins) into the osmotic solution. The third transfer is quantitatively negligible compared with the first two types of transfer, but essential with regard to the composition of the product. Its driving force is the difference in the osmotic pressure of solutions on both sides of the semi-permeable cell membranes. Selective and low-molecular cell sap components such as sugars and organic acids to diffuse into the surrounding solution of higher osmotic pressure. Other cell components, only to a small extent, pass outside of the membrane. The diffusion of water and low-molecular weight substances from the tissue structure during the osmotic dehydration is accompanied by the counter-current diffusion of osmo-active substances. For this reason, osmotic dehydration as opposed to conventional drying is characterised by the complex movement of water, substances dissolved in cell sap and osmo-active substances. This significantly influences the process itself and its final effect with respect to preservation, nutrition and organoleptic properties (Lenart, 1992). The process of water removal and increase in osmo-active substances lowers the water activity in the cell (Lewicki and Lenart, 1992). Thus, through the process, de-watering and direct formulation of a product is possible by introducing the desired amount of an active principle, a preservative agent, any solute of nutritional interest, or a sensory quality improver into the food tissue (Ponting, 1973; Raoult-Wack, 1994). Food tissues are normally immersed in concentrated solution of osmo-active substances such as sucrose, fructose, glucose, glycerol, starch syrup and sodium chloride at moderate temperatures thereby reducing heat damage to texture, colour and flavour of food (Torreggiani, 1993). The food materials are therefore exposed to minimal thermal stress. Two major characteristics separate osmotic dehydration from conventional drying. First, the immersion results in both are de-watering and formulation effect. Second, the immersion results in generally less stable (e.g. relatively short shelf-life) products as a result of de-watering. Thus, osmotic dehydration as a pre-treatment to many processes improves nutritional, sensorial and functional properties of the food without changing its integrity. It is often applied as a pre-processing step before foods are subjected to further processing techniques such as air drying (Nanjundaswamy et al., 1978), vacuum drying (Dixon and Jen, 1977), freezing (Ponting, 1973), freeze drying (Hawks and Flink, 1978), sun drying, pasteurising or acidification and coating by edible surface layers (Flink, 1979). Much of the initial water content can be removed in this way from the tissue to ensure storage stability of the final product to prevent spoilage. The process has generally been applied to fruits and vegetables (Raoult-Wack, 1994; Spiess and Behsnilian, 1998; Torreggiani, 1993) and more recently, meats and fish (Collignan et al., 2001) and gel materials such as agar and protein (Bohuon et al., 1998). Interest in using low temperature osmotic dehydration for processing animal products has been on the increase (Collignan and Raoult-Wack, 1992). Le Maguer (1988) listed fruits and vegetables that have been osmotically dehydrated (Table

Table 1. Osmotic dehydrated fruits.

Raw material	Osmotic substances	Concentration of solute (%)
Pineapples	Saccharose	65
Bananas	Saccharose	65
	Saccharose	67 - 70
Blueberries	Saccharose	-
Pears	Glucose – Fructose syrup	60
	Starch syrup/Saccharose	70
Apples	Saccharose	59
	Fructose	60
	Glucose	51
	Starch syrup	70
	Fructose syrup	70
Berries	Saccharose	50
Mangoes	Sodium chloride	25
Apricots	Starch syrup/ Saccharose	70
Plums	Saccharic syrup	-
Cherries	Starch syrup / Saccharose	70
	Glucose / Saccharose	70

Table 2. Osmotic dehydrated vegetables.

Raw material	Osmotic substances	Concentration of solute (%)
Onion	Saccharose / sodium chloride	54 / 10
Carrot	Sodium chloride	10
	Saccharose	5 - 60
	Sodium chloride	10
	Glucose	50
	Sodium chloride and ethanol	
	Saccharose / sodium chloride	45 / 15
	Starch syrup	70
Tomatoes	Sodium chloride	10
Potatoes	Saccharose / sodium chloride	45 / 15
Agar gel	Saccharose	60
Pumpkin	Saccharose	61

1 and 2).

Fruits in general contain more than 70% water and spoil quickly, if not stored properly. Even proper storage fails to properties of cell membranes make it possible for water preserve the fruits for a longer period unless they are dehydrated. Transfer of water by osmosis is applicable to fruit pieces, since they contain sugars and other solutes in dilute solutions and their cellular surface structure acts as an effective semi-permeable membrane.

Studies by Ponting et al. (1966) on partial dehydration of fruit pieces in concentrated sugar solution showed that water can be removed to the extent of 50% of the initial

weight of fruit such as bananas, papaya, mangoes and apples.

ADVANTAGES OF OSMOTIC DEHYDRATION PROCESS

Although the principle of osmosis as a means of water removal has been available for quite some time, application of osmotic treatments to food can be considered among the new or improved techniques with a potential to substantially improve the quality of dried fruits and vegetables at a substantial saving in energy cost. The recent increase in osmotic treatments observed by Spiess and Behsnilian (1998) arises primarily from the need for quality improvement and from economic factors. The authors stated that water removal without stress and the entry of solutes during osmotic dehydration improves the quality of the food material. The process can enhance natural flavour, colour retention and softer textures in fruit products when the correct choice of solutes controlled and equilibrated ratio of water removal and impregnation are maintained thereby avoiding additives such as antioxidants. As a result food ingredients can be designed for particular uses. The economic interest relates to the reduced energy consumption (lower temperatures) for water removal without phase change, as compared to conventional drying as well as the possible reduction of the refrigeration load by partial concentration prior to freezing of fruit and vegetables.

Studies by a number of authors have shown that the process of osmotic dehydration in a high concentration of solute has several advantages: quality improvement in terms of colour, flavour and texture, energy efficiency, cost reduction in packaging and distribution, no chemical treatment required, product stability and retention of nutrients during storage.

Quality improvement

The process of an initial osmotic treatment before convection drying is particularly advantageous as far as the quality of the given food product is concerned. Studies have shown that osmotic dehydration improves the product quality in terms of colour, flavour 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 colour and flavour are minimised, as products are not subject to a high temperature over an extended period of time. Loss of fresh fruit flavour commonly found with ordinary air or vacuum drying methods is prevented by the use of sugar or syrup as the osmotic drying agent.

Discoloration of the fruit by enzymatic oxidative browning is prevented by the high concentration of sugar surrounding the fruit pieces. The process achieves sweeter products compared with conventionally dried products. Fruits and vegetables osmotically dehydrated become very attractive for direct use due to their chem.-ical composition and physico-chemical properties. Lenart and Lewicki (1988) reported much higher retention of taste and flavour substances in osmo-convection drying as compared with those dried by convection. Ponting et al. (1966) observed that osmotic-vacuum-dried product has more fruit flavour than the same freeze-dried fruit.

However, the fundamental understanding about the mechanism of flavour entrapment in the food matrix, colour retention and physics of textural improvement are not well illustrated in the literature.

According to Chirife et al. (1973), Chirife and Karel (1973), Flink and Karel (1970a,b), Flink and Labuza (1972), Solms et al. (1973) and Voilley and Simatos (1979) the phenomena that may occur to maintain aroma are: adsorption of volatiles onto the infused solute matrix, colour retention and physico-chemical interaction between volatiles and other substances and micro-regional encapsulation in which volatile compounds are immobilised in “cages” formed with the association of dissolved solids. 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.

Energy efficiency

Osmotic dehydration can be conducted at low temperatures and therefore is a less energy intensive process than air or vacuum drying. Lenart and Lewicki (1988) 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.

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 a substantial proportion of energy saved when foods were osmotically dehydrated before freezing. Refrigeration load during freezing can reduce when there is a reduction in the moisture content of food by osmotic dehydration. Torreggiani (1995) reviewed the usefulness of partial water removal prior to freezing referring to numerous species of fruits. Most often, convective air drying is used for partial dehydration.

However, Forni et al. (1990) observed that heat modifications affected the colour of some fruits such as kiwifruit, under any form of drying technique. For such fruits, osmotic dehydration, which is effective at room temperature and operates away from oxygen, could replace air drying.

The high level of solute in osmotically treated products

decreases water activity and preserves them, 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. The resultant osmotic solution can be used in juice or beverage industries as a product, improving process economy, or it may be re-concentrated for further drying.

Packaging and distribution cost reduction

A considerable cost reduction occurs in packaging and distribution of osmotically dehydrated product due to the simple nature (reduction in product weight and volume) of osmotically dehydrated products resulting in easier handling and transportation to market. Additionally, all types of fruits and vegetables could be made available throughout the year addressing the problem of fruit glut seasons. Biswal et al. (1991) stated that osmotic dehydrated fruit and vegetables prior to freezing saves packing and distribution costs. The product quality is comparable with that of conventional products. The process is referred to as “dehydrofreezing”.

Chemical treatment not required

Commercial canning of fresh apple is not practised due to inherent problems associated with the gas volume in apple tissue, difficulty of its removal during exhausting (removal of air and entrapped gases from the can before closing), less drained weight and mushy texture (Sharma et al., 1991). Calcium chloride, a firming agent, has been used in attempts to preserve apple slices in can in order to improve texture (Dang et al., 1976). However, using osmotically treated apple pieces in the canning process result in firmer texture and improved quality of the product (Sharma et al., 1991). This process is known as “osmo-canning”. Chemical treatment to reduce enzymatic browning can be avoided by the osmotic process (Ponting et al., 1966). 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 flavour compounds during further air or vacuum drying (Wientjes, 1968). However if the final product after air-drying contains 10 - 20% moisture, enzymic and non-enzymic browning causes slow deterioration of colour and flavour (Ponting, 1973). Ponting (1973) suggested adding a blanching step after the osmotic process and using sulphur dioxide during or after the osmotic step if final moisture content of the fruit and vegetables is more than 20%.

Product stability during storage

The product obtained by osmotic process is more stable than untreated fruit and vegetables during storage due to low water activity 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. In the case of canning using high moisture fresh fruit and vegetable, water flow from the product to the syrup brine causes dilution and reduced flavour. This is prevented by using the osmo-canning process to improve product stability (Sharma et al., 1991). Similarly the use of osmo-dehydrofrozen apricot and peach cubes in yoghurt improved consistency and reduced whey separation of yoghurt (Giangiacomo et al., 1994).

LIMITATIONS OF OSMOTIC DEHYDRATION PROCESS

Yao and Le Maguer (1996) observed that although osmotic dehydration seems very promising, the food industry is not implementing it as widely as expected. They attributed such low interest to the poor understanding of the mass transfer phenomena associated with it due to the diversity of the underlying mechanisms involved in osmotic dehydration. Unresolved is the principle behind the mass transfer of water from the tissues to the osmotic solution and conversely uptake of solutes from the osmotic solution into the tissues.

Another major constraint for implementation by industry is the problem of the resulting syrup management (Rahman and Perera, 1999). It is expected that the composition of the osmotic solution will change due to the water outflow from the food and the uptake of solute originating from the food material. In order to achieve satisfactory control of the process variables we need a better understanding of the mechanisms involved.

Osmotic dehydration has some limitation according to Ponting et al. (1966). The decrease in acidity may be a disadvantage in certain products which is corrected by adding a fruit acid to the osmotic solution. Normally a residue of the sugar is left on the fruit after drying and although this is usually only a thin film on the surface it may be undesirable. This is reduced by a quick rinse in water after the osmotic dehydration step. The cost of osmotic drying, coupled with air or vacuum drying is more expensive than the latter alone, but is much less expensive than freeze-drying (Torreggiani and Bertolo, 2001). The preliminary treatment of fruits and vegetables influences the chemical composition and physical properties of dried products. According to Lenart and Lewicki (1987) osmotic dehydration narrows the range of other applied methods of inactivating enzymes, such as sulphiting of fruits or blanching of vegetables. By both blanching and freezing, the raw material structure is damaged and cell membranes are destroyed causing a greater shrinkage of the dried material. Sulphiting does not cause such a change on the physico-chemical properties of dried products, but nevertheless it is

considered undesirable due to the toxicity of sulphur compounds (Lenart and Lewicki, 1987).

FACTORS AFFECTING OSMOTIC DEHYDRATION PROCESS

Several factors affect the mass transfer during osmotic dehydration. These are the temperature of the osmotic solution, concentration of the osmotic solution (such as solute molecular weight and nature, presence of ions), type of osmotic agent, agitation of the osmotic solution, time duration, geometry (size) of the food material, variety of the food material, osmotic solution and the food mass ratio, physico-chemical properties of the food materials and operating pressure. Hawkes and Flink (1978) investigated the influence of the temperature and the duration of the osmotic process on osmotic dehydration while Ertekin and Cakaloz (1996) investigated the influence of the solutes used. A number of recent publications have described the influence of these variables on the mass transfer rates (Raoult-Wack et al., 1992; Raoult-Wack, 1994; Rastogi and Raghavarao, 1994, 1995, 1997a). Since mass transfer rates are slow, a number of approaches have also been used to improve the rate. These include: the application of partial vacuum (Fito, 1994; Fito and Pastor, 1994; Fito et al., 1996; Rastogi and Raghavarao, 1996), ultrasound during treatment (Simal et al., 1999), ultra high hydrostatic pressure (Rastogi and Niranjan, 1998) and high intensity electric field pulses (Rastogi et al., 1999) to the material prior to osmotic dehydration.

Temperature of osmotic solution

The most important variable affecting the kinetics of mass transfer during osmotic dehydration is temperature. 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 (water) 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. The higher uptake values of treatments above 20°C were probably due to the membrane swelling and plasticizing effect, which improved the cell membrane permeability to sugar molecules.

Concentration of the osmotic solution

Conway et al. (1983), Hawkes and Flink (1978) and Lenart (1992) reported that increase in osmotic solution concentration resulted in corresponding increases in water loss to equilibrium level and drying rate. 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; Farkas and Lazar, 1969; Lenart and Flink, 1984a; Lerici et al., 1985; Magee et al., 1983; Marcotte and Maguer, 1991; Rahman and Lamb, 1990). Studies by Saurel et al. (1994a, b) showed a dense solute-barrier layer formed at the surface of the food material when the osmotic solution increased. This enhances the dewatering effect and reduced the loss of nutrients during the process. A similar solute-barrier is also formed in the case of osmotic solutions with higher molecular weight solutes even at low concentration. Studies by Lazarides (1994) on apples in a higher concentration sugar solution (65 vs. 45°Brix) for 3 hours, showed a faster water loss (ca.30% increase) at the same time, however, there was a severe loss from the osmotic solution in terms of a much greater uptake of sugar solids (ca. 80% increase). The authors concluded that short-term osmosis under increased concentration favoured solute uptake resulting in lower water loss and solids gain ratios. Results on the negative effect of osmosis by low concentration sucrose solution on fruits have also been reported by Karathanos et al. (1995). For example, low concentration sucrose solution causes minimal water loss culminating in lower water loss and solid gain ratios.

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 (Maguer, 1988). Sugar and salt solutions proved to be the best choices based on effectiveness, convenience and flavour.

Lenart and Flink (1984a) comparing various osmotic

solutions at constant solid concentration reported that mixed sucrose and salt solutions gave a greater decrease in product water activity compared to pure sucrose solutions, although water transport rates were similar. This was attributed to the extensive salt uptake. Further studies by the same workers on spatial distribution analysis revealed large differences between osmosis distribution curves for the dehydration taking place in sucrose or salt solutions (Lenart and Flink, 1984b). Their analysis showed that sucrose accumulated in the thin sub-surface layer resulting in surface tissue compacting (an extra mass transport barrier), salt was found to penetrate the osmosed tissue to a much greater depth. The presence of salt in the osmotic solution can hinder the formation of the compacted surface layer, allowing higher rates of water lose and solid gain. Finally, increasing salt concentration leads to a lower water activity solution with respectively increased driving (osmotic) force. In addition to fruits and vegetables, sugar and salt solutions have also been used successfully for dehydration of animal products. Collignan and Raoult-Wack (1992) working on fish and meat used concentrated sucrose and salt solutions to partially de-water meat and fish at low temperature (10°C). They observed that the presence of sugar promotes water loss and hinders salt uptake, an important factor in the meat and fish processing industry, since it leads to shorter processing times and better control of salt uptake. Extensive solids uptake is the major drawback against using sucrose, salt or mixed sucrose and salt solutions due to the above-mentioned negative impact on both product quality (nutritional and organoleptic) and on the rate of water removal.

Properties of solute used in osmosis

Studies show that the physico-chemical properties of the solute affect osmotic dehydration (Bolin et al., 1983; Hawkes and Flink, 1978; Lenart and Lewicki, 1987 and 1989; Lenart, 1992; Lerici et al., 1985). The authors observed that the molecular weight, ionic state and solubility of the solute in water cause differences in the behaviour of the osmotic solute. Further, molecular size of the osmotic solute has a significant effect on the water loss to solids gain ratio. The smaller the solute, the larger the depth and the extent of solute penetration. For example, large dextrose equivalent (D.E.) corn syrup solids favoured sugar uptake resulting in lower water loss to sugar gain ratios and vice versa (Lazarides, 1994). Lower dextrose equivalent (large size) corn syrup solids gave negative solid gain values, indicating that solute uptake was inferior to leaching (loss) of natural tissue solids.

Osmotic process is also affected by the pH of the osmotic solution. Moy et al. (1978) observed that acidification increases the rate of water removal by changes in the tissue's properties and subsequently in the texture of fruits and vegetables. Contreras and Smyrl (1981) found water removal to be maximal at pH 3 for apple rings using corn syrup. At pH 2 the apple rings became very soft, maybe due to hydrolysis and depolymerization of the pectin. However, firmness was maintained at pH values between 3 - 6.

Agitation of the osmotic solution

Contreras and Smyrl (1981), Hawkes and Flink (1978) and Lenart and Flink (1984a) 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 characterised by large external mass transfer resistance. This is the case when water leaving the particle surface hits a high viscosity, slow moving or immobile medium and accumulates in a progressively diluted contact zone.

Raoult-Wack et al. (1989) observed that agitation favours water loss, especially at lower temperatures (< 30°C), where viscosity is high and during the early stages of osmosis. The extent of water loss increased with agitation and reached a certain plateau. On the other hand, the rate of solid gain decreased with agitation. For short process periods agitation has no effect on the solids gain. For longer process period solids gain decreased drastically with agitation. The authors concluded that agitation has no direct impact on solid gain throughout the entire osmotic process, since external transfer of the osmotic solute is not limiting.

The agitation-induced decrease in the rate of solids gain for longer osmosis periods could be an indirect effect of higher water loss (due to agitation) altering the solute concentration gradient inside the food particle. Since diffusion of solutes into natural tissue is slow, most of the solute accumulates in a thin sub-surface layer. Lenart and Lewicki (1987) showed that solute penetration during osmotic dehydration in sucrose solution was only to a depth of about 2 - 3mm. However, Ponting et al. (1966) stated that in some cases it might be more beneficial if agitation is not used when consideration is given to equipment needs and the breaking of fruit.

Geometry of the material

The geometry of sample pieces affects the behaviour of the osmotic concentration due to the variation of the surface area per unit volume (or mass) and diffusion length of water and solutes involved in mass transport (Lerici et al., 1985). According to Lerici et al. (1985) up to

a certain total surface area/half thickness (A/L) ratio, higher specific 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). Exceeding this A/L limit, however, higher specific surface area samples (such as cubes) favoured sugar gain at the expense of lower water loss resulting in lower weight reduction. The lowest water loss association with the highest A/L ratio was explained as a result of reduced water diffusion due to the high sugar uptake.

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 of the (osmotic) driving force during the process a large 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 changes in the concentration of the sugar solution (Conway et al., 1983).

Physico-chemical properties of food materials

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 a steam blanching of the sample for four minutes before osmosis gave lower water loss and higher solid gain when applied to fresh potato slices. They concluded that the loss of membrane integrity due to heating was the cause of the poor osmotic concentration behaviour.

Operating pressure

Studies show that vacuum osmotic dehydration results in a change of behaviour of mass transfer in fruit-sugar solution systems (Fito, 1994; Fito and Pastor, 1994; Perera, 1990; Shi and Manupoey, 1994). Vacuum treatments intensify the capillary flow and increase water transfer, but have no influence on solute uptake (Fito, 1994). The total water transfer results from a combination of traditional diffusion and capillary flow and is affected by the porosity or void fraction of the fruit (Fito and Pastor, 1994; Shi and Manupoey, 1994).

Species, variety and maturity level

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. Hartel (1967) showed that under identical process conditions different potato varieties give substantially different (by ca 25%) weight reduction (water loss).

Process duration

The studies by Lenart and Flink (1984a) to determine the conditions defining the equilibrium state between product and osmotic solution show that equilibrium is characterised by an equality of water activity and soluble solids concentration in the product and solution. Whereas equilibrium was approached within 20 h, it was found that mass transport data (except for solids gain) were not significantly changed in the period between 4 and 20 h.

A period of 3 to 5 h osmotic process was recorded in most non-equilibrium studies (Biswal et al., 1991; Conway et al., 1983; Hawkes and Flink, 1978). It was observed that the first period of time is the most important one, since the transport phenomena are fast and they have a dramatic impact on further evolution of the osmotic process. Lazarides (1994) reported that within the first hour of osmotic dehydration of apple slices the rate of water loss dropped to about 50% of the initial rate and within 3 h the product has lost 50% of its initial moisture, while it more than doubled its initial total solids, picking up sugar. Thus an efficient way to limit solute uptake and obtain large water loss and solids gain ratios is early interruption of osmosis.

PROBLEMS ON APPLICATIONS OF OSMOTIC DEHYDRATION IN INDUSTRIES

Product sensory quality

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

Osmotic solution management

The microbial validation of osmotic dehydration for long-time operation and reuse of the syrup by recycling are important factors for industrial applications (Raoult-Wack,

1994). Microbial contamination increases with the number of times that the osmotic solution is re-cycled. The cost of the syrup is a key factor for the success of the process. The resulting osmotic solution management is an industrial challenge. These include solution composition and concentration, recycling, solute addition, re-use and waste disposal. The control of solute composition in recycling for single solute solutions is easier than mixed solute solutions. During the re-cycling process, the dilute solution can be re-concentrated by evaporation or reverse osmosis.

Process control and design

Inadequate information and data arising from past research has precluded more effective design and control of osmotic dehydration by the food industry. Further studies are necessary to get a clear understanding of the variation of equilibrium and rate constants with process variables and characteristics of the food materials. Most of the osmotic studies have been concerned with the quantitative prediction of the processing factors, but more qualitative prediction of the processing is necessary for industrial use in process design and control. On-line measurements of concentration can provide continuous control of the process. 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 flow of osmotic solution in case of continuous flow process or by mechanical agitation in the case of batch processing. The equilibrium is the end point of osmosis, but for practical purpose a number of other factors should be considered to ensure the quality of the final product. These include damage to the cells and development of off-flavour due to longer processing time and re-use of the osmotic solution (Rahman, 1992). Finally, adequate packaging systems are necessary to ensure quality products for consumers.

Enzymatic browning of fruits and vegetables

Minimally-processed fruits and vegetables form a large proportion of the produce purchased by consumers who are choosing convenient and ready-to-use fruits and vegetables, with a fresh-like quality and containing only natural ingredients (Ahvenainen, 1996). Wound-induced biochemical and physiological changes associated with water loss, respiration and cut-surface browning accompanied by microbial spoilage is the main culprits of deterioration in minimally-processed fruit and vegetables (Rolle and Chism, 1987). The extent of browning after processing of a fruit or vegetable is often dependent upon which particular cultivar is used, as shown with apples (Kim et al., 1993) and potatoes (Sapers et al., 1989). There are about five causes of browning in process and stored fruit and vegetables: enzymatic browning of the phenols, Maillard reaction, ascorbic acid oxidation, caramelization and formation of ‘browned’ polymers by oxidized lipids. The oxidation of the o-diphenols to o-quinones by polyphenoloxidase is the most important cause of the change in colour as the o-quinones quickly polymerize and produce brown pigments (Mayer and Harel, 1979; Vamos-Vigyazo, 1981). There is also a loss in the nutritional value through oxidation of ascorbic acid during enzymatic browning. In the food industry, enzymatic browning can be avoided by using thermal inactivation of polyphenoloxidase instead of blanching and the use of sulphites as anti-browning compounds although the latter has been banned by the USA food and drug administration for most fresh applications (FDA, 1986). Bisulphites were found to be dangerous to human health, especially in asthmatic patients (Taylor and Bush, 1986). The chemical action of the bisulphites is to react with the o-quinones to form colourless complex compounds (Embs and Markakis, 1965; Valle, 1952; Wedzicha, 1984). A number of natural ingredients and additives are used to control enzymatic browning (Table 3).

DEVELOPMENT OF PREDICTIVE MODEL

Most research carried out to model the mass transfer in osmotic dehydration is mainly based on simplified semi-empirical models (Yao and Maguer, 1996).

Morphology of plant storage tissues and fluxes

Parenchymatous cells are the main cell types involved in the osmotic dehydration process. The cells consist of three parts: intercellular volume, extracellular volume and a cell membrane in between the two volumes. The extracellular volume contains cell wall and free space between the individual cells. The intercellular volume includes cytoplasm and a vacuole (Figure 1).

According to Crapiste and Rotstein (1982) the cell membrane is mostly considered volume-less, but they combine the resistance of tonoplast, plasmalemma and cytoplasm into cell membrane resistance. The plant cells develop a turgor pressure inside the cell, because water flows into the cell without comparable loss of solutes and the inelastic cell wall, which supports the membrane and restricts the expansion of the cells. During osmotic dehydration processing, the solute diffuses into the extracellular volume. Depending on the geometry of the solute it may or not penetrate the cell membrane and enter the intracellular volume. As the solute penetrates

Table 3. Enzymatic browning control activities.

References	Natural ingredients and additives	Storage	Fruit/vegetable
Buta et al. (1999)	Calcium propionate + 4 hexylresorcinol, Isoascorbic acid, N-acetylcysteine	None	Apple
Buta and Moline (2001)	Calcium propionate, Calcium chloride 4-hexylresorcinol, Isoascorbic acid, N-acetylcysteine,Ascorbic acid, reduced glutathione, Cysteine, S- carbamylcysteine, Phosphoric acid, Sodium acid pyrophosphate	None	Potato
De Poix et al. (1980)	Sodium chloride + Calcium Chloride	None	Apple
Gonzalez- Aguilar et al. (2001)	4-hexylresorcinol, D-isoascorbic acid, N-acetylcysteine, Potassium sorbate	None	Radish
Gorny et al. (1998)	Calcium chloride	MA*	Pear
Gunes and Lee (1997)	Amino acid (with cysteine) + Citric acid	MA	Potato
Langdon (1987)	Citric acid + Ascorbic acid	None	Potato Puree
Laurila et al. (1998)	Citric acid + Ascorbic acid	MA	Potato
McEvily et al. (1992)	4-hexylresorcinol + Isoascorbic acid + Ascorbic acid	None	Potato Pear
Moline et al. (1999)	Citric acid + N-acetylcysteine	None	Banana
Molnar-Perl and Friedman (1990)	N-acetylcysteine	MA	Potato
Monsalve-Gonzalez et al. (1995)	4-hexylresorcinol, D-isoascorbic acid,	None None	Apple Pear
Sapers and Douglas (1987)	Citric acid monohydrate + Ascorbic acid	None	Apple
Ponting et al. (1972)	Ascorbic acid + Calcium Chloride	None	Apple
Santerre et al. (1988)	Citric acid + Ascorbic acid + Erythorbic acid	None	Apple
Sapers et al. (1989)	Ascorbic acid-2-phosphate; Ascorbic acid-2-triphosphate	None	Apple
Sapers et al. (1990)	Sodium ascorbate/erythorbate + Calcium chloride	None	Apple
Sapers and Miller (1993)	Sodium pyrophosphate + Calcium chloride + Citric acid + Isoascorbic acid	MA	Potato

*Modified atmosphere (low O_2 + high CO_2).

the tissue it creates a chemical potential difference across the cell membrane and draws the water out into the extracellular volume. As Ponting (1973) stated, there are at least two major simultaneous, counter current flows in osmotic process the solute flow from the concentrated solution into the tissue and the water out flow from the tissue into the osmotic solution and then a third flow of the tissue's own solutes into the osmotic solution. These flows interact with each other the diffusive and convective flows in the extracellular volume are in a dynamic balance with a solute front moving from the tissue surface towards the centre (Fito, 1994). Most models are based on the assumption that mass transfer is described by a simplified unsteady state Fickian diffusion model (Conway et al., 1983; Hawkes and Flink, 1978). According to the authors effective diffusivities are calculated by regression analysis of specific mass transport data. However, the uses of such models are largely limited to the specific experimental set up (Lazarides, 1994). Raoult-Wack (1994) reported that the fundamental knowledge for the prediction of the mass transport is still a grey area although considerable efforts have been made to improve the understanding of mass transfer in osmotic dehydration. Normally, two methods are used to determine the kinetics of osmotic dehydration. First, a continuous method that involves the measurement of weight loss of a single sample and its final moisture content at the end of the process (Azuara et al., 1998). This is rather recent but promises a lot of improvements over the second method, the discontinuous

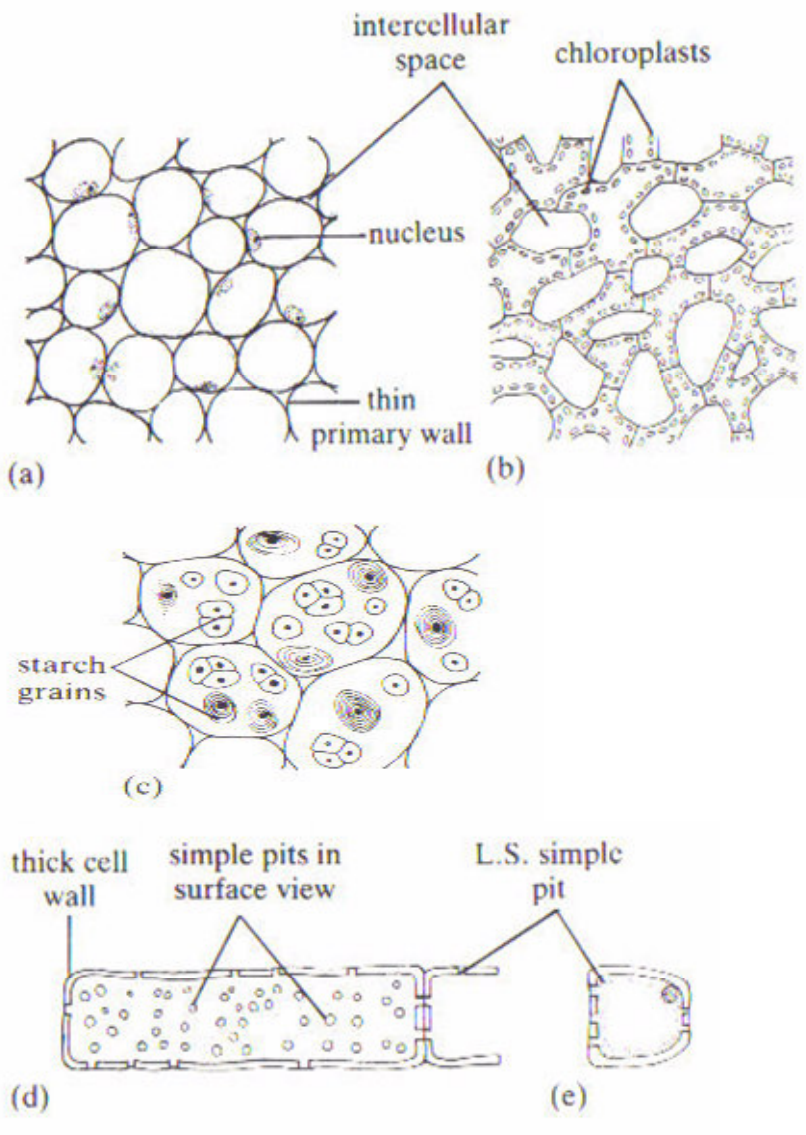

Figure 1. Parenchyma. (a) Spherical (isodiametric) parenchyma typical of the pith of many plants. (b) 'Armed' parenchyma from spongy mesophyll of *Ficus* leaf. Note the abundance of chloroplasts and intercellular spaces. (c) Parenchyma from storage root of sweet potato (*Ipomoea batatas*). The cellular inclusions are starch grains, some of which are compound grains. (d) and (e) Xylem parenchyma in L.S and T.S (the protoplasts omitted in L.S) note simple pits (Loveless, 1983, p.30).

method where measurements of water loss and solid gain are carried out on separate samples supposed to be the same in terms of geometry and dimensions, weight, volume and initial moisture content. The continuous method allows a more precise determination of experimental points and also helps in the prediction of the variations of the moisture content with respect to time.

Magee et al. (1983) used a rate parameter to model osmotic dehydration of apple slices as a function of the concentration and temperature of the osmotic solution. This parameter was calculated from the slope of the straight line obtained from apple sugar concentration versus square root of time. However this model was limited in the information that can be derived from it. Biswal et al. (1991) used a similar empirical model for osmotic dehydration of sweet beans. Conway et al. (1983) developed a model working on apple slices by considering the apple slices to be infinite slices, yet experimentally these were rings 1cm thick, 2.5cm internal diameter and 6.8cm external diameter, which hardly conforms to the theoretical geometry. This probably contributed to the apparent high diffusion coefficients produced by the model as compared to published works in literature for similar systems (Garrote et al., 1984;

Hough et al., 1990; Liley and Gambell, 1973; Selman et al., 1983). Conway et al. (1983) found diffusion coefficients of water ranging from 15 x 10^{-9} to 60 x 10^{-9} m^2s^{-1} depending on the initial sucrose concentration (50 - 70°Brix) and operating temperature (30 -50°C). In similar studies on pineapple (Beristain et al., 1990) the diffusion coefficient reported varied between 0.6 x 10^{-9} and 2.5 x 10^{-9} m^2s^{-1}. The difference was attributed to the diversity of these products and differences in the model. Another assumption of the Conway et al. (1983) model was that the sugars diffuse rapidly in the early stages of dehydration into the apples but the concentration then remains constant until the end of the dehydration period. However, Hough et al. (1993) did not use this assumption. Instead, the sugar diffuses slowly and continuously into the apples due to the semi- permeable nature of the cell membrane. This probably contributed to the high value of apparent diffusion coefficient water concentration decreases due to water leaving the fruit and sugar entering. In this model only water is considered as diffusing. Lerici et al. (1985) stated that to characterise osmotic treatments it is important to take into account not only the weight reduction and the water loss but also the solids gain.

Studies by Toupin (1986), Toupin et al. (1989) and Toupin and Maguer (1989) on cell membrane during osmotic dehydration used a simplified geometrical analogue of the actual cellular matrix to study the influence of the various cellular and tissue properties on the dynamics of the mass transport phenomena taking place in plant storage tissues. These authors presented a rather complicated model for the stimulation of water and solute fluxes in cellular tissues. However, Marcotte et al. (1991) used thermodynamic description of the forces involved in the osmosis process to modify the model proposed by Toupin (1986). Subsequent studies by Marcotte and Maguer (1991) using computer simulations showed good agreement between predicted and experimental values, supporting the validity of the proposed model.

In studies on coconut by Rastogi and Raghavarao (1995) the authors assumed an exponential approach to equilibrium to estimate the effective diffusion coefficient of water in coconut tissue by determining the rate constants. The diffusion coefficient conformed to an Arrhenius-type equation with respect to temperature. Such determination was made possible for foodstuffs of any particular geometry such as slab, cylinder and sphere by using the relationship between kinetics of dehydration and Fick's second law (Azuara et al., 1992). Salvatori et al. (1998) working on apples proposed an advancing disturbance front to describe the mass transfer. The rate of advancement of the front was slightly dependent on temperature. The authors conducted a structural investigation using a cryoscanning electron microscopy and found a close relation between front advancement and cellular alteration and collapse. As a result of water loss, cell shrinkage occurred and the ratio between the intracellular volume and the intercellular spaces decreased considerably.

Studies on osmotic dehydration of foods have been diverse. All the models developed by the authors aimed at obtaining a better understanding of the mass transfer phenomenon and how it is influenced by various cell and tissue properties. These studies established that the mass transfer in natural tissues is not simply a diffusion phenomenon and that cell membrane represents the major resistance to the mass transfer in such systems (Lazarides, 1994). These models depended on a large number of biophysical properties, such as elastic modulus of the cell wall, cell wall void fraction, cell wall tortuosity, membrane permeabilities and others. However the authors recognise the difficulty to measure these properties and in some cases their values need adjusting to fit experimental data. According to Flink (1975), Hartal (1967) and Ponting (1973) differences in specific cellular and tissue properties of products resulted in discrepancies between the results of several products. These discrepancies are accounted for by variation in tissue 'compactness' (Giangiacomo et al., 1987), percentage of insoluble material (Lenart and Flink, 1984b), intercellular space and volume and presence of air in the tissues (Rotstein, 1988). Therefore osmotic dehydration under vacuum favours mass transfer as reported by Dalla Rosa et al. (1982), Fito and Pastor (1994), Hawkes and Flink (1978) and Zozulevich and D'Yachenko (1969). In addition, other tissue parameters include the ratio of pecto-cellulosic complexes to free pectins (Forni et al., 1996), degree of gelling of pectins (Moy et al., 1978) and enzymatic activity and the nature of any soluble substances present (Giangiacomo et al., 1987). Generally, according to Islam and Flink (1982), Karel (1975), Nur (1976), Ponting (1973) and Saurel (1995) anything likely to cause structural damage to the plant tissue (overripe fruit, thermal, chemical or enzymatic treatments) favours solute gain at the expense of water loss. Two resistances are identified as opposing mass transfer during osmotic dehydration of products, one internal and the other external (Spiazzi and Mascheroni, 1997). The external resistance is determined by the fluid dynamics of the solid-fluid interface whereas the internal, much more complex, resistance is influenced by cell tissue structure, cellular membrane permeability, deformation of fruit/vegetable pieces and the interaction between the different mass fluxes. Under the usual treatment conditions, the external resistance is negligible compared to the internal one.

Bolin et al. (1983), Hawkes and Flink (1978) and Marcotte (1988) observed that solute penetration is confined to extracellular spaces. This was confirmed by Isse and Schubert (1991) and Saurel (1995). The authors observed that sucrose passes through the cell wall and accumulates between the cell wall and the cellular membrane where it forms a hypertonic solution leading to

water out flux through the cellular membrane. Other authors (Bolin et al., 1983; Geurst et al., 1974; Karel, 1975) suggested that water loss is greater than solute gain only because of the differences between the diffusion coefficient of water and solute in the product.

Benefits of predictive modelling

A model is simply an equation relating a dependent variable to an independent variable. Generating models for describing the effect of processing on constituents in foods is appealing and necessary for several reasons. First, with process models it is possible to explore the potential for improving existing processes without performing numerous, often expensive experiments. Improvements through modelling could include increasing the retention of nutrients, reducing the energy demand of the process and reducing the toxicological impact of the process. Secondly, development of process models generally leads to insights into possible mechanisms of changes in the foods, which in turn leads to new products/process development. Thirdly, with kinetic models for changes in foods, it is possible to predict shelf-life of foods as influenced by conditions during storage. The potential for improving food quality through modelling is tremendous but limited by the lack of quantitative data and predictive models.

Engineers require quantitative models to design and optimize processes (Arabshahi and Lund, 1985). Water loss modelling provides a useful tool for understanding the osmotic dehydration process. Description of this process as internal diffusion controlled is quite common and therefore the application of Fick's first law is widely used (Azuara et al., 1992; Lazarides et al., 1995; Monsalve-Gonzalez et al., 1993).

TECHNIQUES FOR OSMOTIC DEHYDRATION ANALYSIS

A number of approaches have been used to study the mass transfer in osmotically dehydrated foods. These are gravimetric, scanning electron microscopy/cryo-SEM, artificial neural networks (ANN) and artificial cells (Raoult-Wack, 1994; Torregiani, 1993). In spite of the wide range of applications, none have involved microcalorimetry.

Gravimetric method

The gravimetric method has been used extensively to analyse osmotically dehydrated foods. In general the time evolution of osmotic dehydration is quantified by measuring weight reduction (WR) and total solids contents (TS). From these values are calculated the water loss (WL), defined as grams of water removed per initial sample mass and solid gain (SG) expressed as grams of solute incorporated into the initial mass of sample. The concentration of soluble solids is also sometimes used to analyse the process as it allows water concentration to be estimated in both the product and the external solution. In addition there is the volume reduction, another complementing variable that is not always measured. In studies conducted by Azuara et al. (1998) on golden delicious apples osmotically dehydrated at 30°C in 500 g of sucrose/kg solution monitored for five hours, variables were calculated as follows:

$$WFL = (S_1 t * WFL_\infty) / 1 + S_1 t \quad (1)$$

$$SG = (S_2 t * SG_\infty) / 1 + S_2 t \quad (2)$$

$$ML = WFL - SG \quad (3)$$

where t = time, S_1 = a constant related to water loss, S_2 = a constant related to solid gain, WFL = amount of water loss by the sample at time t (fraction, percent, g or kg), SG = amount of solids gain by the sample at time t (fraction, percent, g, kg), WFL_∞ = amount of water loss at equilibrium, SG_∞ = amount of solids gain at equilibrium, ML = mass loss.

Sereno et al. (2001) working on golden delicious apple at 5 - 6°C in 40 - 60%w/w sucrose and 15 - 26.5%w/w sodium chloride studied at four hours calculated the weight reduction (WR), water loss (WL) and solids gain (SG) as follows:

$$WR = (w - w_o) / s_o \quad (4)$$

$$SG = (s - s_o) / s_o \quad (5)$$

$$WL = SG - WR \quad (6)$$

Where w, w_o are the present (that is after 4 h) and initial sample masses and s, s_o are the present and initial masses of solids in the sample, respectively.

Shi et al. (1995) in their investigations on apricots, strawberries and pineapples osmotically dehydrated at 30 - 50°C in 65°Brix sucrose solutions under normal pressure, vacuum and pulsed vacuum treatments for 15 - 240 min, calculated variables as follows:

$$\cong M = (M_o - M_t) / M_o \quad (7)$$

$$\cong M_w = (M_o * X_{wo} - M_t * X_{wt}) / M_o \quad (8)$$

$$\cong M_s = (M_t * X_{st} - M_o * X_{s0}) / M_0 \quad (9)$$

$$\cong M = \cong M_w - \cong M_s \quad (10)$$

where ≅M = weight reduction, ≅M_w = water loss, ≅M_s = solids gain, M_o = initial mass of sample (kg), M_t = mass of osmosed sample at time t (kg), X_{so} = initial soluble solid content of the sample (°Brix), X_{st} = total soluble solid content of osmosed sample at time t (°Brix), X_{wo} = initial water content of fruit sample (kg/kg), X_{wt} = water content of osmosed sample at time t (kg/kg).

Isothermal heat conduction microcalorimetry

Calorimeters form a broad and heterogeneous group of scientific instruments that are used to study small heat changes (Forrest, 1972). The first calorimetric instruments were described more than 200 years ago and since then large number of calorimetric designs and experimental procedures based on different measurement principles have been reported (Armstrong, 1964). Calorimetry is a sensitive indicator of the energy changes in biological systems, giving information about the rate and extent of reactions, no matter how complex the process is occurring.

The application of heat conduction isothermal microcalorimetry has been proposed for some time as a rapid and general technique for the determination of both thermodynamic and kinetic parameters of chemical reactions (Beezer et al., 1998; Beezer et al., 1999; Beezer, 2000; Gaisford et al., 1999; Willson, 1995; Willson et al., 1995; Willson et al., 1996; Willson et al., 1999). This is further confirmed in studies by Selzer et al. (1998 and 1999) when isothermal heat conduction microcalorimetry was employed as an analytical tool to determine both kinetic and thermodynamic parameters of reacting systems. All chemical and physical changes are accompanied by changes in heat content or enthalpy, thus all chemical reactions including the solid state, solution phase, gas-phase and biological phase can be studied in microcalorimeters. According to Willson et al. (1995) the output of a heat conduction isothermal microcalorimeter is power (in watts) against time hence is capable of analysis to produce not only thermodynamic data but also kinetic data. The isothermal microcalorimeter (for example the TAM, Thermometric, Sweden) has previously been shown capable of detecting the reaction of a compound that has a first order reaction rate constant of $1 \times 10^{-11} s^{-1}$ (Willson et al., 1995).

Some of the advantages using isothermal microcalorimetry include direct observation on the sample whatever its form, non-destructive and non-invasive methods, and experimental simplicity (Willson et al., 1995). Samples can be loaded into the calorimeter in any state and the reaction that occurs can be studied under controlled temperature, pressure, humidity, gas partial pressure, and addition of scavengers. However, the disadvantage is that it requires iterative procedures to determine the target parameters (n, the order of the reaction; k, the rate constant; and $\Delta_R H$, the reaction enthalpy change) (Beezer et al., 2000; Willson et al., 1995). From Selzer et al. (1998 and 1999) the calorimetric output Φo at time t = 0 is generally $\Phi o = kHA_T^n$ for the n^{th} order of reaction and the first order case by $\Phi o = kHA_T$, where A_T = load placed into the calorimeter. Therefore A_T = A (reacting amount of sample) + (A_T – A) (non-reacting amount of sample). The plot of Ln Φo against Ln A_T is linear with a slope equal to the order of reaction n. Plotting Ln Φo against t will be linear for the first order reaction and the slope –k, the first-order rate constant. A_T is therefore appropriate to be identified as the sample quantity loaded into the calorimeter or the total mass of the quantitatively uncharacterised sample placed in the calorimeter (Beezer et al., 2000).

Kinetics

Calorimetry is the measurement of heat. The total amount of heat evolved is a measure of the extent of the process and can be related to thermodynamics. The calorimeter measures heat flow. The rate of heat change is a measure of the intensity (the rate) of the process and can be related to kinetics (Hemminger and Höhne, 1984). The rate of a reaction may be described by the Arrhenius equation, which describes the temperature dependence of the rate constant, k.

$$\text{Ln}(K) = \text{Ln}(A) - E_a / RT \qquad 11$$

where A = pre-exponential factor, E_a = activation energy, R = gas constant, T = absolute temperature.

Thermodynamics

The transformation of energy in a system is called thermodynamics. Different substances have different amounts of energy. The total energy of the products of a reaction will differ from the total energy of the reactants. This process is accompanied by an absorption or liberation of energy in the form of heat. Calorimetry is concerned with the measurement of such changes. The first law of thermodynamics in its application to calorimetry is frequently called the Law of Hess: energy cannot be created nor destroyed. The energy of an isolated system is therefore, constant. The internal energy, ≅AU, is the summation of the enthalpy change (the heat of combustion at constant pressure), ≅H, and the work of expansion against the atmosphere, P≅V. Hence

$$\cong U = \cong H - PV \qquad 12$$

The enthalpy is a measure of the heat content for a system of constant pressure. Biological systems' reactions

can be considered both at constant pressure and at constant volume and the change in energy (enthalpy) content accompanying a reaction corresponds to the experimentally measured heat of evolution, Q. When heat is absorbed or produced, the reaction is endothermic or exothermic, respectively. The amount of heat evolved is proportional to the number of moles of the reaction, n, which takes place.

$$Q = n \cong H \quad 13$$

Calorimetry is therefore a sensitive indicator of the energy changes in biological systems, giving information about the rates and the extent of reactions, no matter how complex the process is occurring.

Artificial neural networks (ANN)

Artificial neural networks (ANN) have been the focus of interest in many diverse fields of science and technology. ANN is basically a computer model that simulates the very basic ability of the brain. It consists of an association of elementary cells or 'neurones' grouped into distinct layers and interconnected according to a given architecture (Bishop, 1994). Neural networks are recognised as good tools for dynamic modelling (Rumelhart and Zipner, 1985). The advantages of ANN are the ability to model without any assumptions about the nature of the underlying mechanisms and their ability to take into account non-linearities and interactions between variables (Bishop, 1994). Most importantly is the unique capability of learning from exemplar training data sets and consequently, an ability to adapt to the changing environment (Hertz et al., 1991; Jansson, 1991).

ANN is also able to deal with uncertainties and with noisy and approximate data. They are rapidly becoming an interesting, novel method in the estimation, prediction and control of dynamic bioprocesses (Linko and Zhu, 1991; 1992a, c, d). According to Linko et al. (1992) the application of the ANN models to food processing systems is very novel. Trelea et al. (1997) stated that in the field of food process engineering, it is a good alternative to the conventional empirical modelling based on polynomial and linear regressions. ANN modelling performances to the conventional empirical modelling have been recognized and confirmed by many research reports (Baughman and Liu, 1995; Eerikainen et al., 1993). Neuralware (1996) provides a wide overview of potential applications of the neural network as classification, prediction, data association and optimisation. ANN applications in food and agriculture included fermentation (Latrille et al., 1993), extrusion (Linko et al., 1992), filtration (Dornier et al., 1995), drying (Huang and Mujumdar, 1993), psychrometry (Sreekanth et al., 1998), thermal processing (Sablani et al., 1995), rheology (Ruan et al., 1995) and sensory science (Park et al., 1995).

Scanning electron microscopy (SEM)

Driving force and structure are the two major factors in the understanding and control of the mass transport phenomena occurring in food processing, in general and in osmotic processing in particular. According to Gekas (1992) the type of food structure at a cellular level determines the pathways of both water and nutrient transport. Therefore, they affect rates of mass transfer from or to cells, thus influencing the final quality of stored or processed foods. Knowledge of the properties of the physical structure is needed for modelling of the mass and heat transfer operations. Micro structural features such as shape and size changes in cell and intercellular spaces, cell wall deformations-relaxation changes are captured by microscopic techniques (Aguilera and Lillford, 1996; Alzamora et al., 1996).

Scanning electron microscopy (SEM) has previously been used to study food tissues during processing (Aguilera et al., 2001; Fedec et al., 1977; Huang et al., 1990; Marle et al., 1992; Moledina et al., 1978).

Visking osmometer (Artificial cell method)

Most natural (and some man–made) membranes are partially permeable allowing some substances to pass but not others, depending on the relative particle sizes or solubility properties. One such artificial membrane is Visking tubing. Visking tubing is a form of processed cellulose or cellophane which is semipermeable that allows small molecules like water, glucose and iodine to pass through but does not allow larger molecules like sucrose and starch. If solutions of different concentration are on either side of the Visking membrane, water molecules will pass through and tend to dilute the more concentrated solution. This tubing is used to simulate a cell membrane. Visking tubing has been used to study the diffusion of substances across membranes in both plants and animals (Huang et al., 2000; Shavit et al., 1995; Wijmans, 2004).

CONCLUSION

The last few decades has seen much research work to improve the quality of food products. This is attributed to the increased demand for healthy, natural and tasty processed foods. For example, semi-dried fruit ingredients are included in a wide range of complex foods such as ice-creams, cereals, dairy, confectionery and baking products. There are a number of processing technologies to produce dried products. To obtain better quality of food products osmotic dehydration is recommended as a

processing method. However, the food industry uptake of osmotic dehydration of foods has not been extensive as expected due to the poor understanding of the counter current flow phenomena associated with it. However, these flows are in a dynamic equilibrium with each other and significantly influence the final product in terms of preservation, nutrition and organoleptic properties.

Traditional methods of studying the osmotic dehydration have used gravimetric methods and fairly simplified semi-empirical models. This approach is useful as the complexity of the osmotic process in food materials is such that only models can accurately predict moisture levels. However, previous research work, which has only used gravimetric methods, has not compared similarly shaped materials with different tissues characteristics (e.g. high and low starch) and has only used semi-empirical models (no training and testing of model equations). Most models developed considered factors such temperature, concentration and diffusivity, not considering other factors such as material type and agitation of the osmotic solution.

Therefore, present research work should develop new empirical models and compare these to artificial neural networks with a capability of integrating large numbers of independent variables (e.g. fruit sample physical state, initial moisture content of the sample, temperature and concentration of the osmotic solution) in such a way that the value of the dependent variable(s) (e.g. final target moisture content of the semi-dried product) can be predicted with a high degree of accuracy. These is beneficial for improved understanding of the underlying principles of the counter current flow in a range of plant tissues during the osmotic dehydration and subsequently develop better predictive models of the process. As well as comparing with the use of the thermocalorimetry to measure the energy changes in the system as a simpler means of studying mass transfer compared to the time-consuming gravimetric methods.

A microstructural observation enables the differences in the cellular responses to osmotic dehydration between the different plant materials to be captured. Incorporation of the stereo imaging programmes distinctively supported observations on water loss often reported for gravimetric studies. In the multilinear regression models (MLR), in cases where the developed model had good predictions dependent on temperature, osmotic solution concentration, duration of immersion and sample size.

However the inadequacy of the MLR models for water loss and solid gain are improved when artificial neural networks were utilised. This is due to the flexibility of ANN and especially the employed radial basis function to model linear and non-linear parameters successfully.

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