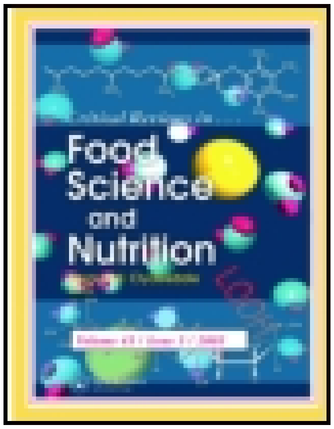

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State of Polyphenols in the Drying Process of Fruits and Vegetables

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State of Polyphenols in the Drying Process of Fruits and Vegetables

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Introduction

Over the past decade consumers have been seeking out healthier and more nutritious food. Furthermore consumers have been increasing their intake of fruit and vegetables (Morris and Brady, 2003). Fruits and vegetables have higher water contents, which limits their shelf life and limits wider distribution. This has lead to an increase in the production of processed fruits and vegetables, including dehydrated fruits and vegetables. Dehydrated products have low water contents, which prevents the development of microorganisms that deteriorate fresh fruit and vegetables. However, these drying processes can have a negative effect on the nutrients within the food product.

Drying of food is a frequently used preservation method and prevents microbial activity that can lead to undesirable changes. For millennia, humans have dried foods. There are examples of sun drying dating back as early as 20,000 BC in Russia and the American Indians were able to make dried mashed potatoes in 3500 BC. In Ancient Egypt, fruit was first sun dried including apples, grapes and apricots. Drying continued through the years, including being used by the Colonies in North America. In 1650 AD, the Colonies dried boiled Indian corn using fires.

The first patent on vegetable drying was issued in America and consisted of boiling vegetables in salt water and drying them for 20-30 hours. Technological developments in the drying process increased in the 20th century and the first spray drier was patented in 1901. During the First World War, troops were given dried vegetables and fruits, and this lead to an expansion in vegetable drying especially in Europe. Cabinet, tunnel and conveyor driers were all utilized and research on vacuum drying was initiated. World War II also lead to an increase in drying facilities and the processes included drum-dried soup mixes, vacuum dried fruits and air-dried garlic and onion. In the 1950s research into freeze drying began in the United Kingdom and led to development of the accelerated freeze drying method. This was followed by the introduction of fluidized bed driers and the spouted bed drier. Along with the production of new drying techniques, the understanding of drying mechanics also increased (Hayashi, 1989, Morris and Brady, 2003). Furthermore studies have been done to investigate how drying affects the nutritional components in a food, including polyphenols.

Polyphenols are compounds found throughout the plant kingdom and can be divided into several different classes. The classes include phenolic acids, lignans, anthocyanins and flavonoids (Manach et al., 2004). Phenolic acids can then be divided into two classes, those that are derived from benzoic acid and others that are derived from cinnamic acid. These compounds are usually part of a complex structure or are present in bound form (Kähkönen et al, 1999). They are found in many fruits including cherries, apples, strawberries and mangoes. Phenolic acids contribute to the taste and colour of the food and also offer nutritional benefits. Lignans are found as minor components in fruits and vegetables such as pears, prunes, asparagus and carrots. Lignans are then metabolized to enterodiol and enterolactone in the intestine by microflora (Thompson et al., 1991). Flavonoids are present in plant as glycosides and can be divided into six different subclasses. The subclasses are flavonols, flavones, isoflavones, flavanones, anthocyanidins and flavanols. Flavonoids are the colour componds in plants and can be found in a wide variety of fruits, flowers and leaves (Kähkönen et al., 2004). Anthocyanins are major polyphenol pigments in plant and are a highly reactive species. Anthocyanins have been reported to contribute more to the antioxidant activity of fruits than flavonols or phenolic acids (Jakobek et al., 2009). The different classes and applications of polyphenols are detailed in the review by El Gharras (2009).

There are many health benefits derived from eating foods that contain polyphenols. Polyphenols can act in an antioxidant and act as radical scavengers or chain breakers depending on their chemical structure (Rice-Evans 2001). It has been shown that many polyphenol rich vegetables and fruits are effective in protecting against colon cancer (Martinez 2005). Regular consumption of polyphenol rich food may help to decrease the incidence of cardiovascular diseases (Arts et al., 2001). Specifically, studies have shown that intakes of flavonols, flavones and flavanals have helped to reduce the risk of cardiovascular disease and anthocyanin intake has helped to reduce the number of deaths attributed to cardiovascular disease (Arts and Hollman, 2005). Risk of neurodegenerative disorders including Alzheimer’s and Parkinson’s disease, that usually affect humans as they age, is decreased by intake of polyphenols. Regular dietary intake of flavonoid rich foods has been shown to preserve the cognitive action, delay the onset of

Alzheimer's disease and reduce the risk of developing Parkinson's disease (Mink et al, 2007). All the nutritional benefits of polyphenols are discussed in the review by Vanzour et al., (2006).

Due to the nutritional benefits offered by polyphenols when ingested, this review presents how the drying processes utilized to dehydrate fruit and vegetables affects these compounds. This review will first discuss how polyphenols are degraded and what attributes affect their retention. It will look at degradation mechanisms proposed in literature, along with models that are applied to describe how polyphenols degrade within food products. The next section will discuss studies in which the polyphenol content was investigated during drying. There are too many polyphenols to be named individually, so the overall polyphenol content and the classes discussed above will be considered in these studies. However, if large amount of a polyphenol in the food is affected drastically, it will be discussed in more detail. Methods to preserve polyphenols will also be presented.

Degradation of Polyphenols

Polyphenols are compounds that have structures that are very easily oxidized and this can lead to degradation of antioxidant capacities. There are two main ways polyphenols are degraded, enzymatic and non-enzymatic methods. Enzymatic degradation includes enzymes like polyphenol oxidase, lipoxygenase and peroxidase. Non-enzymatic degradation includes Maillard reactions, which leads to phenol oxidation (Vanzour et al, 2010). The three enzymes mentioned above will be examined in this section, along with the Maillard reaction. However they are not only ways that polyphenols can be destroyed; these are just the major reactions that take place within food.

Polyphenol oxidase (PPO) is also known as tyrosinase and is a copper containing enzyme that is able to catalyze two different reactions with the use of oxygen. The two reactions are the hydroxylation of monophenols to o-diphenols and then the subsequent oxidation of these o-diphenols to o-quinones. The o-quinones can react with other compounds like amino acids and produce melanins, which are brown in colour (Lopez-Nicholas and Garcia-Carmona, 2010). Due to its binuclear copper active site, it can exist in three different forms during the reaction; which include met, oxy and deoxy states (Cabanes et al., 2007). When a fruit or vegetable is wounded, the PPO is able to interact with the polyphenols within the food (Lopez-Nicholas and Garcia-Carmona 2010, Sanchez-Ferrer et al, 1995). Polyphenol oxidase has been found in wheat, tea, potatoes, cucumbers, artichokes, lettuce, pears, papayas, grapes, peaches, mangos, apples and even cocoa (Gando-Herrero et al., 2003). PPO activity can be prevented by chelating agents such as Ethylene diamine tetraacetic acid (EDTA) or citric acid. Furthermore, compounds like troplolone, kojic acid and recorcinols, which are structurally analogous to phenolic substrates, and reducing agents such as sulfites or ascorbic acid, also are able to inhibit PPO activity (Sanchez-Ferrer et al., 1995).

Lipoxygenase (LOX) can be found in many plants and is particularly abundant in beans, peas and potato tubers (Martinez and Whitaker 1995). LOX contains one atom of iron, which is in the Fe (II) state and is oxidized to the Fe (III) state before it can act as an oxidation catalyst. The iron is oxidized either by hydroperoxides or hydrogen peroxide (Baysal and Demirdoven 2007, Casey et al., 1998). This reaction is the rate-limiting step and causes a lag period while the enzyme extracts hydrogen from a polyunsaturated fatty acid (Casey et al., 1998). This enzyme is able to catalyse oxygenation at points along the carbon chain and it usually reacts with linoleic

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and linolenic acid, which are the major polyunsaturated fatty acids found in plant tissues. This reaction can have negative effects on colour, flavour and antioxidant status of plant based foods (Vanzour et al., 2010). For instance, in fruits and vegetables, carontenoids are the natural colourants, and if they appear bleached, it is likely that LOX caused this change in appearance (Weber et al, 1974). LOX has an optimum pH of 6.8 and it may be involved in the ripening process of some fruits, including strawberries (Veldink et al, 1998, Lopez-Nicolas et al., 2001). Blanching of fruits and vegetables inactivate LOX and improve colour and texture of food product (Sharma et al., 2006). Minimizing exposure to lipids, light and air can also help to prevent LOX activity in fruits and vegetables (Murcia et al., 1999).

Peroxidase (POD) is an oxidative enzyme and degrades polyphenols within food products. It is a heme protein and it reacts non-selectively using hydrogen peroxide as the electron acceptor to oxidize the ferrous ion. By oxidizing the ferrous ion, it creates a Fe(IV)-O species. This reacts with the reducing substrate and produces a oxidized product and the ferric ion is regenerated (Vanzour et al., 2010). POD can participate in a large number of oxidative reactions, which change the colour and texture of a food, degrade chlorophyll, and oxidize phenols. During storage POD can work to create undesirable odours and loss of flavour (Sanchez-Ferrer et al., 1995, Eskin et al., 1977). POD is a heat stable enzyme and due to its large number of isoenzymes, it cannot be totally deactivated by heat treatments (Eskin et al., 1977). However POD activity can be limited by the availability of hydrogen peroxide, as well as other electron acceptors like superoxide radicals and lipid peroxides (Valderrama and Clemente 2004, Mdiuli 2005). POD activity has also been shown to be decreased by the combined use of ascorbic acid and ultrasound treatment (Chisari et al., 2007).

The Maillard reaction is a chemical reaction between amino groups and a reducing sugar and it forms coloured or uncoloured products. Some of the resulting products have antioxidant activity and are able to scavenge oxygen radicals or chelate metals (Jang and Moon 2011). This antioxidant activity is usually attributed to a chain breaking mechanism (Jang and Moon 2011, Mogol et al., 2010). The first stage of the reaction consists of a reaction between the carbonyl group of the sugar with the amino group of an amino acid to form a Schiff's base, which then rearranges to an amino ketose. The intermediate step is the degradation of the amino ketose and produces a variety of different reactive compounds. These compounds then react further in the last stage, which is a condensation to produce melanoidins, brown pigments (Wojidylo et al, 2009). This reaction is favoured at high pH values and the reactivity is higher with pentoses than hexoses (Bittner 2006, Muratore et al., 2008). It is more likely to occur during thermal processing and in low moisture systems. Low moisture systems have higher solids content and this leads to an interaction between reducing sugars and amino acids in fruits and vegetables. The reaction results in degradation of nutrients such as sugars, essential amino acids and ascorbic acid (Billaud et al., 2005). It can reduce the amino acids by 50% (Wojidylo et al, 2009). The reaction also decreases the protein digestibility and inhibits digestive enzymes. Sulphite has been shown to reduce the effect of the Maillard reaction by reacting with intermediates and producing colourless pigments (Billaud et al., 2005).

Drying Methods

There are many different drying methods that have been applied to fruits and vegetables, from the most basic technique such as solar/sun drying to more expensive methods like freeze or microwave drying. In recent years, to produce dried foods with higher nutritional and sensorial attributes, non-conventional drying methods have been employed, such as pulsed electric field and combinations of drying methods (Ling et al., 2005). This part of the review will present studies that incorporate different drying methods and discuss how the polyphenol content is affected by these techniques.

Drying fruits and vegetables reduces the amount of water that is available for reactions. The drying medium utilized determines the mass transfer phenomena that occur. In the solid to gas mass transfer mechanism, usually experienced during hot air drying or sun drying, part of the volatile content can be transferred to gas. In a liquid to solid system, for instance osmotic dehydration, the food is immersed in a hypertonic solution, usually a sugar solution. The counter current transport mechanisms are employed and the water is transferred from the food to the solution and the solute (sugar) is transported from the solution to the food. Internal and external resistance depicts mass transfer in both systems. Internal resistance depends on the food's properties and temperature of the drying process, while the external resistance is dependent upon the boundary layer thickness of the food. Drying kinetics tend to be slow since the mass transport resistance in food is usually quite high (Santos and Silva 2006, Mulet et al., 2003).

Models used to describe the transport mechanisms explain two drying periods. The first period shows a constant rate of drying and usually refers to the free water at the surface of the food and can lead to a moisture gradient being created. This moisture gradient results in the second phase of drying which has a falling rate of moisture reduction (Rossello et al., 1997). There are two transfer mechanisms, which have been used to describe the movement of water in

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food during dehydration (Mulet 1994). The first is the diffusion model formulated by Lewis in 1921 and further developed by Sherwood in 1929. The second model is called capillary transport model formulated by Luikov in 1966. The diversity of materials in foods makes it very difficult to make generalizations when it comes to drying of foods. The principles for freeze-drying varies slightly from those mentioned above, but they will be explored more in the freeze-drying section.

Solar/Sun Drying

Open-sun drying has been used for many centuries to dry fruits and vegetables, as well as other products (Togrul and Pehlivan 2004). It is still practiced widely in many tropical and subtropical countries around the world. Solar energy is an important alternative source of energy and it is abundant, inexhaustible and non-polluting (Doymaz 2004). However it does have many inherent limitations, like high losses of product from inadequate drying, fungal attacks, insects, birds, rodents and unexpected downpour of rain (Tarhan 2006). It is also a slow process that includes high labour costs and requires a large area (Togrul and Pehlivan 2004, Doymaz 2004). Open sun drying usually occurs at temperatures less than 55 °C , which leads to a slow drying rate (Tarhan 2006). To increase the drying rate of the fruit or vegetable, the surface resistance of the product can be removed by chemical pretreatments such as ethyl oleate, potassium carbonate or sodium hydroxide (Doymaz 2006).

Due to the disadvantages of open sun dryers, solar driers have been developed. Solar driers consist of a greenhouse like chamber and have been shown to shorten the drying period (Li et al., 2005). Solar energy is either used as the sole source of the required heat or can be used as a supplemental source. Air flow can be generated either by natural or forced convection

(Ekechukwu and Norton 1999). Use of visqueen-covered and polyethylene- covered solar driers has been shown to reduce the loss of vitamin C, beta-carotene and phytochemicals during dehyrdration (Ndawula et al., 2004). The use of solar driers prevents the food from regaining moisture at night or during rainy days (Li et al., 2005).

Sun/solar drying have both negative and positive effects on the polyphenol content of fruits and vegetables. In dates, the amount of anthocyanins decreased such that they could not be detected in the dried product. Only 15% of anthocyanins were detected after the dates had been dried for one hour. The destruction of the anthocyanins is due to the heat and light involved in the solar drying. The total phenolic content of the sun dried dates was significantly higher than the fresh dates. Tannins are degraded during the dehydration process by temperature and maturation enzymes and leads to a release of phenolic compounds (Al- Farsi et al., 2005). Raisins also have increased phenolic content after drying, due to the hydrolysis of tannins, lignins and oligmers (Serratosa et al., 2008). These phenolic compounds are lower in molecular weight and can become free or bound phenolics. The amount of hydrocinnamic acids decreased by 96% and this is expected because hydrocinnamic acids are well known substrates for oxidative enzymes (Al- Farsi et al., 2005, Serratosa et al., 2008). Overall, in raisins and dates some polyphenols appear to be lost, but the total polyphenol content remain relatively unchanged due to the production of many smaller phenolic acids (Al- Farsi et al., 2005, Williamson and Carugho 2010). In contrast, Portugal pears after sun drying only contained 32% of the original polyphenol content found in the pulp of fresh pears. The polyphenol content decreased significantly due to enzymatic degradation and coupled oxidative reactions that irreversibly bound polyphenols (Ferreira et al., 2002). Some pre-treatments have been used to prevent the loss of polyphenols during sun drying. Golden raisins have higher polyphenol content due to the raisins being treated with hot water and sulfur dioxide. This pre-treatment inactivates the polyphenol oxidase and the raisin is able to retain most of the flavonols and phenolic acids found in fresh grapes (Williamson and Carugho 2010). However, the use of sulphite prevents the production of oxidized cinnamics during the dehydration process (Karadentz et al., 2000). Apricots in Turkey are traditionally pretreated with sulphite and then sun dried. As mentioned before this is a slow process, so the use of microwave finish drying has been suggested to decrease the drying period. The use of microwave finish drying would decrease the amount of sulphite used and increases the amount polyphenols retained. The faster drying period decreases the amount of time that the heat, temperature and enzymes can degrade the polyphenols (Koc and Alpasian 2003).

Hot Air Drying

Hot Air Drying is a process that has been around for many years and it is used to remove the moisture from a substance by exposing it to a continuous flow of hot air that causes the moisture to evaporate (Ratti 2001). The moisture is transferred out of the food to the atmosphere by diffusion or capillary mechanism. The concentration gradient is the driving force of this process and the diffusion can occur in the form of liquid or vapour (Rahman 2007). The evaporation of water at elevated temperatures can cause chemical, physical and biological changes in foods. Furthermore it increases the concentration of the soluble components in the remaining portion of the food, after the removal of moisture. This increased concentration of the soluble components can promote chemical and enzymatic reactions due to higher concentrations of reagents and catalysts. Changes in pH, redox potential and solubility can also occur and affect the polyphenols within the fruit or vegetable (Lewicki 2006).

Cabinet and bed dryers are usually used for hot air drying and they utilize very simple drying techniques. The fruit or vegetable is placed in an enclosed, heated chamber and hot air is allowed to pass over the product, usually done in a continuous process. The rate of drying is affected by many factors including temperature, humidity, air velocity, air exchange, product geometry and product thickness. In general, the hotter the air is, the faster the drying rate and similarly, the lower the humidity, the higher the drying rate is; however both these factors also affect the total phenolic content of the product (Rahman 2007).

Chang et al. (2006), reported that tomatoes that were air dried have a higher total phenolic content than fresh or freeze dried tomatoes, while Dewanto et al. (2002), reported that hot air drying did not change the total phenolic content of tomatoes. However, in tomatoes dried at 42 °C a decrease in the total phenolic content was observed, which is in contrast to the other studies (Kerkhops et al., 2005). The difference in the results in can be attributed to the lower temperature that was used in the study conducted by Kerkhofs et al, (2005). The lower temperature used in this study allowed the phenolic oxidizing enzymes to degrade the phenols within the tomato (Kerkhops et al., 2005). The total phenolic content was higher in the studies conducted by Dewanto et al. (2002), and Chang et al. (2006), because the thermal processing was done at a higher temperature which liberated some of the phenolic compounds from the matrix. Phenolic acids occur in tomato as metabolic intermediates and they accumulate in the vacoules. The hot air drying breaks down the cellular constituents and is able to release the bound phenolics. The disruption of cell walls will also release the oxidative and hydrolytic enzymes that can degrade polyphenols, but the high temperature of hot air drying is able to inactivate the enzymes or slow the enzyme activity (Chang et al., 2006, Dewanto et al., 2002). Furthermore, it is possible that a higher temperature is required to release the bound phenolics. In the study conducted by Kerkhofs et al. (2005), increasing the drying temperature briefly to release phenolics and denature enzymes and then return to the lower drying temperature increased the phenolic content.

In fruits like peaches and apples, dehydration at 60°C increased their total phenolic contents (Rababan et al., 2005). Persimmon was also dehydrated and the total phenolic content increased as the dehydration time increased (Akyildiz et al., 2008). Corn (Dewanto et al., 2002) and pumpkin flour (Que et al., 2008) were also reported to have increased total phenolic content after hot air drying. The reasons these fruits and vegetables had increased total phenolic content could be because as stated above, the bound phenolics were liberated and it could also be due to interconversion between phenolic molecules (Chang et al.,2006, Dewanto et al., 2002, Que et al., 2008). In fruits there are many precursors of phenolic molecules and by non enzymatic browning, like Maillard reactions, they are able to generate and accumulate phenolic substances that will increase the overall phenolic content of the foods (Que et al., 2008).

Plums were dried to prunes at both 60°C and 85°C. At both temperatures the total phenolic content in prunes was below that of the fresh plums. However the antioxidant activity was higher in prunes than plums due to polyphenols created through the Maillard reaction that have a higher antioxidant power (Piga et al., 2003). Total phenolic content decreased in raspberries (Mejia-Meza et al., 2010), strawberries and marionberries (Asami et al., 2003). This decrease in phenolics in these berries can be attributed to high amount of anthocyanins and anthocyanins are thermo-liable and undergo oxidative condensation (Asami et al., 2003). Hot air drying decreased the total phenolic content in asparagus (Nindo et al., 2003), yams (Chung et al., 2008, Ahmed et al., 2010), corn (Asami et al., 2003), and peppers (Vega-Galvez et al., 2009). These vegetables decreased in phenolic content due to their exposure to the heated air that lead to the oxidation of the phenolics (Nindo et al., 2003, Chung et al., 2008, Ahmed et al., 2010). Orange peel and pulp was studied to see how hot air drying at different temperature and for different amount of times affect total phenolic content. They found that high temperatures and longer drying times destroy the phenolic compounds (Carme-Garau et al., 2007).

Anthocyanins are found in plums but not in prunes or are present in very small amounts. The high temperature and exposure to oxygen that are encountered in hot air drying leads to a rapid degradation of anthocyanins (Piga et al., 2003, Donovan et al., 1998). Plums also contain chlorogenic acid, which can act as an intermediary in polyphenol oxidase reactions that degrade anthocyanins (Piga et al., 2003). The degradation of anthocyanins can also be seen in raspberries (Mejia-Meza et al., 2010), grapes (Frangipane et al., 2007), blackberries (Wu et al., 2010) and blueberries (Mejia- Meza et al., 2008). This disappearance of anthocyanins can frequently lead to a change in colour of the dehydrated fruit (Mejia- Meza et al., 2008). Flavonoids are negatively affected by hot air drying. Blueberries (Mejia- Meza et al., 2008), apricots (Madrau et al., 2009), plums (Piga et al., 2003, Donovan et al.,1998) all contained flavonoids and after hot air drying they decreased significantly. Flavanoids are degraded proportionally to an increase in the temperature (Piga et al., 2003, Madrua et al., 2009). Flavonoids are poor substrates for oxidases and therefore are not related to enzyme activity (Madrua et al., 2009).

Amount of hydrocinnamic acids, overall, usually stayed the same or increased after hot air drying. Plums contain a high amount of chlorogenic acid and if they are dried at high temperature the chlorogenic acid content will be maintained because the oxidase enzymes are deactivated. If the drying temperature is lower the oxidases, along with the presence of air, are able to degrade chlorogenic acid (Piga et al., 2003). During the drying process of plums to prunes, cinnamates are created and help to retain the amount of hydrocinnamic acids that was found in the fresh plum (Donovan et al., 1998). Hydroxycinnamic acids are also found in apricots, and like plums, when they are dried at higher temperatures, they have a higher hydroxycinnamic acid content due to the deactivation of oxidases and the creation of new cinnamates (Madrau et al., 2009).

Microwave Drying

Microwave drying is a rapid drying technique that is used to dehydrate fruits and vegetables. There are many advantages to utilizing this technique, including shorter drying time, improved product quality and can be used for a variety of different products (Ling et al., 2005, Zhang et al., 2006). However, it is a very complicated technology and has high start up costs. Microwave drying is used in combination with other drying techniques, such as hot air drying or vacuum drying and can be used as a pre-treatment and also to help finish drying a product or as a post-treatment (Koc and Alpasian 2003, Zhang et al., 2006). A complete microwave drying process consists of three drying phases. A heating up period is the first phase, in which the microwave energy is converted into thermal energy within the moist portions of the food. Gradually the temperature of the food increases and when the temperature is above that of the environment the food begins to lose moisture at a slow rate. The second phase then begins and is called the rapid drying period. The thermal energy that was created from the microwave energy is used to vapourize the moisture in foods. The reduced drying period is the last phase and if the energy needed for moisture vapourization is below the amount of thermal energy created, it can result in overheating or charring (Zhang et al., 2006). Microwave drying has some disadvantages including textural damage, uneven heating and microwave energy is unable to penetrate into some foods (Zhang et al., 2006, Maskan 2000). As was mentioned before, other drying methods can be combined with microwave drying to overcome these obstacles and examples of which will be explored in this section.

Microwave drying has been used in mashed apples to increase the phenolic content and decrease the amount of browning that occurs (Vadivambal and Jayas 2007, Gerard and Roberts 2004). Sweet potatoes have also been dehydrated with microwave energy and the microwave-dried samples had a total phenolic content that was three times higher than in fresh sweet potato. However, the samples were steam blanched before being dehydrated and this pretreatment may have contributed to this increase in total phenolic content. Steam ruptures the cell structure, which results in more polyphenol components being extracted (Yang et al., 2010). Onion slices dried using microwave energy had increased total phenolic content after dehydration (Arsian and Ozcan 2010). These fruits and vegetables had increased total phenolic content, likely due to the temperature of microwave drying that released bound phenolics from the breakdown of cellular constituents. Furthermore, microwave drying takes less time than hot air drying and therefore there is less exposure to oxygen and the high temperature helps to prevent the oxidative enzyme activities (Yang et al., 2010, Arsian and Ozcan 2010).

Malkeet et al. also studied the effects of microwave drying of sweet potato without the pretreatment of steam blanching. They found that microwave drying decreased the total phenolic content, but not as severely as hot air drying (Padda and Picha 2008). Longan, an exotic fruit popular in Southeast Asia, was also dehydrated by microwave energy and the total phenolic content decreased (Yang et al., 2007). The reason for the decrease in the phenolics could be attributed to the temperature or time of the microwave drying which both have a negative effect on the phenolics if the temperature is too high or the drying period is too long (Padda and Picha 2008, Yang et al., 2007).

As stated before microwave drying can also be used as a pretreatment or as a finishing drying step. Apples slices were osmotically dehydrated and then pretreated with various degrees of microwave energy before being hot air dried. They found that the best treatment was 300W of energy for five minutes. If the microwave energy was increased, it increased the temperature too much, such that the polyphenols were decomposed. But the 300W power was enough to inactivate oxidative enzymes and to release the bound polyphenols within the apples (Tarko et al., 2009). Microwave drying was used as a pretreatment along with blanching for the dehydration of purple carrots. They found that the purple carrots that were microwave dried had a lower amount of anthocyanins than those that were just hot air dried. The temperature created by the microwave energy may have been too high and destroyed the thermo-liable anthocyanins (Uyan et al., 2004). Microwave drying was used to finish drying citrus pomace after it had been sun dried. The microwave drying was able to cleave and liberate the phenolic compounds in the citrus pomace at 250 W, however, if the energy increased then the total phenolic content began to decrease as the thermo-liable polyphenols were destroyed (Hayat et al., 2010).

Microwave drying has also been used in combination with other drying methods to produce better quality products. Asparagus contain flavonoids and when dehydrated using a combination of microwave energy and spouted bed, was able retain a higher amount of flavonoids than those that were hot air dried. This is likely due to a shorter drying time, which did not allow for as much degradation (Nindo et al., 2003). The spouted bed system is good to be used in combination with a microwave drying because it allows for an uniformly dried product (Nindo et al., 2003, St. George et al., 2004). Another combination drying technique is the vacuum microwave drying technique (MIVAC). Strawberries dried with the MIVAC retained a higher amount of polyphenols compared to hot air drying (Wu et al., 2010). The same was found in MIVAC drying of cranberries (Leusink et al., 2010), blueberries (Mejia-Meza et al., 2008), raspberries (Mejia- Meza et al., 2010) and Saskatoon berries (Kwok et al., 2004). The total phenolic content increased in these berries due to reduced time and temperature it takes to dehydrate them and thus prevents the degradation of polyphenols (Madrau et al., 2009). The vacuum also helps to prevent oxidative enzyme activities in the berries due to lack of oxygen in the system (Madrau et al., 2009, Brennan 1996). However the temperature of MIVAC is enough to degrade anthocyanins and decreased amounts of anthocyanins was seen in all studies mentioned above (Mejia-Meza et al., 2010, Wu et al., 2010, Madrau et al., 2009, Leusink et al., 2010, Kwok et al., 2004). This indicates that the MIVAC procedure is also liberating bound phenolic within the berries (Wu et al., 2010). The MIVAC system can also be used as a

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finishing drying step after hot air drying to remove the last remaining water in the fruit at a faster rate and has shown to retain more polyphenols and anthocyanins than just using hot air drying (Mejia-Meza et al., 2010, Madrau et al., 2009).

Freeze Drying

Freeze drying is a method of drying where the fruit or vegetables are frozen and then the ice is caused to sublime to produce a dried product (Marques et al., 2006). Complete drying takes place in three stages. The first stage is the freezing stage and during this stage the water is withdrawn from the hydrated components of the food. This leads to the formation of ice crystals. The second stage is the sublimation stage and the majority of the water is removed from the food at this stage. The water is removed by sublimation of the ice crystals and during this stage there is no movement of liquid and therefore the soluble components are not redistributed throughout the food. The third and final stage is when the water that is strongly bound to the solid is removed. This can be done in the freeze drier or using other equipment like microwave or hot air drying (Brennan 1996).

Little to no shrinkage takes place in the food during drying and the food is able to retain its shape and size. The structure is also very porous, which allows it to rehydrate quickly. The entrapment of volatiles within the solid allows the food to retain its odour and taste. Freeze drying food helps to maintain its nutritional quality (Marques et al., 2006, Krokida et al., 1998). Not all foods can be freeze dried though; foods where their structure is susceptible to damage during freezing, will have a poor structure upon rehydration (Krokida et al., 1998). Furthermore, proteins can be denatured due to the concentration of solutes during the freezing stage of drying.

Once foods are freeze-dried, they are prone to oxidation during storage, as well as being brittle and susceptible to mechanical damage. Due to this attribute, expensive packaging may be required or an additives may be added before the dehydration process (Kirleis and Stine 1978). One last problem with freeze drying is that it is a relatively expensive process when compared to other process of drying (Marques et al., 2006, Brennan 1996).

Grape skins, which are left over after the production of wine are a very high source of polyphenols (Larrauri et al., 1997). In two separate studies freeze drying was able to retain a higher amount of polyphenols than those grape skins dehydrated using other methods like oven drying (Larrauri et al., 1997, De Torres et al., 2010). Freeze drying was also found to retain a higher amount of polyphenols in blueberries (Mejia-Meza et al., 2008), raspberries (Michalczyki et al., 2008), bilberries (Michalczyki et al., 2008) and strawberries (Mogol et al., 2010). Freeze drying is able to preserve the polyphenol content due to the low temperature, as well as the vacuum pressure (Mogol et al., 2010, Madrau et al., 2009). This is able to prevent the thermal and oxidative degradation of the polyphenols (Mogol et al., 2010). The enzymatic reactions that degrade polyphenols will be limited due to the freezing step (Hammami and Rene 1997). Freeze drying was able to retain the anthocyanin content in raspberries (Mejia-Meza et al., 2010), blueberries (Mejia-Meza et al., 2008) and strawberries (Mogol et al., 2010), likely due to the low temperature of freeze drying (Mejia-Meza et al., 2010). Freeze drying is able to retain a higher amount of polyphenols than all other forms of drying mentioned in this review, but due to expense associated with it and long length of processing it can not be used for all products. It is usually just used for high value products like coffee, some herbs, crispy fruits and vegetables, and ingredients incorporated into ready-to-eat foods (Pan et al., 2008).

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Conclusion

There are many different methods and combinations of methods that can be applied to the drying of foods. Fruits and vegetables have very unique characteristics that affect their drying behaviour and the final quality of the food. Lately efforts have been made to improve traditional drying methods or create new techniques that maintain attributes like flavour, nutrition, volatiles and colour of the finished dehydrated product. This review presented many different dehydration methods and how they affect the overall polyphenol contents, along with certain important certain polyphenols that were drastically affected. Several variables affect the polyphenol content during drying including different environment variables, the composition and physical structure of the fruit or vegetable. Furthermore, the composition and physical structure change as the drying process proceeds. It is important to note that other pretreatment methods, like washing and peeling, and post treatment processes, like storage conditions, can also affect the overall polyphenol content of the food.

The environmental variables including time, temperature and concentration of oxygen in the atmosphere are the most important parameters that affect the polyphenol content. Polyphenols are susceptible to heat and oxidation, therefore the combination of these parameters usually determines the final polyphenol content. The food composition also contributes to the polyphenol content found after drying. The water activity, enzymes, pH and variety of polyphenols in the food, can change the reactions that occur during dehydration. More investigation is needed to provide a better understanding of how polyphenols are degraded during drying processes since different fruit and vegetables consist of different physical and chemical characteristics. Furthermore, improvements to traditional drying methods should always be investigated to see how they affect the nutritional content of the food.

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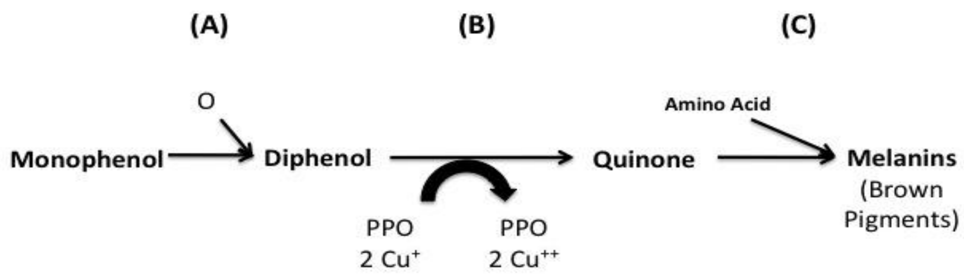

Figure 1- A hydroxylation (A) and then an oxidation (B). The quinone reacts further to produce a brown pigment (C). (Adapted from Queiroz et al., 2008).

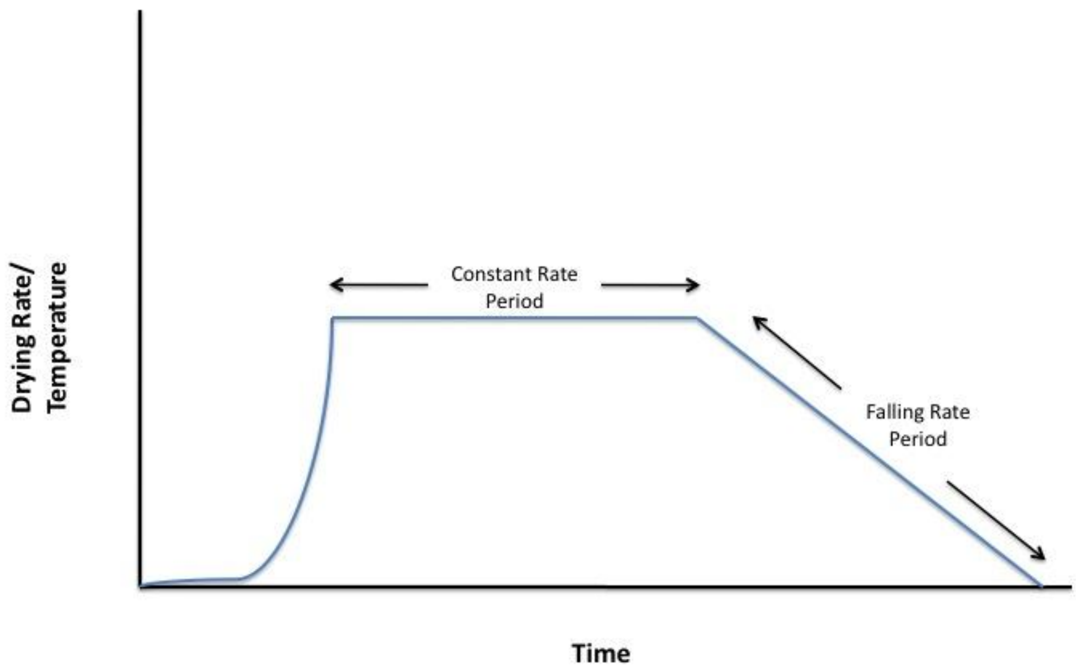

Figure 2- A typical drying curve that includes 2 different periods of drying (constant and falling rate).

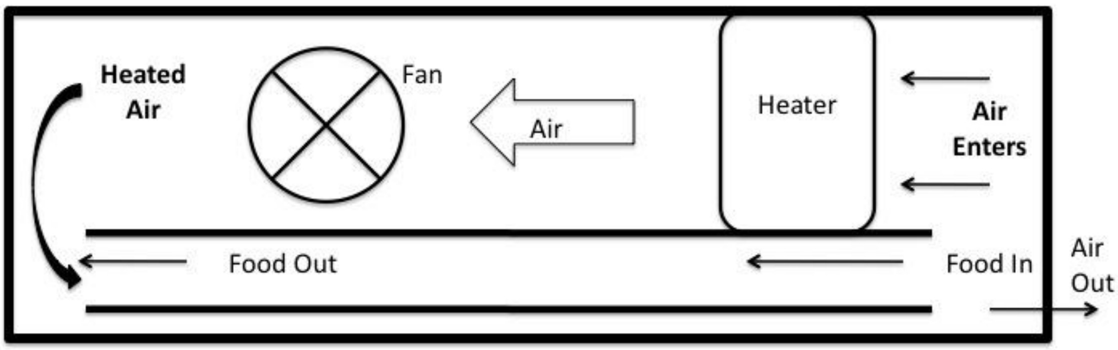

Figure 3- An example of a typical continuous flow dryer (using a counter flow system).

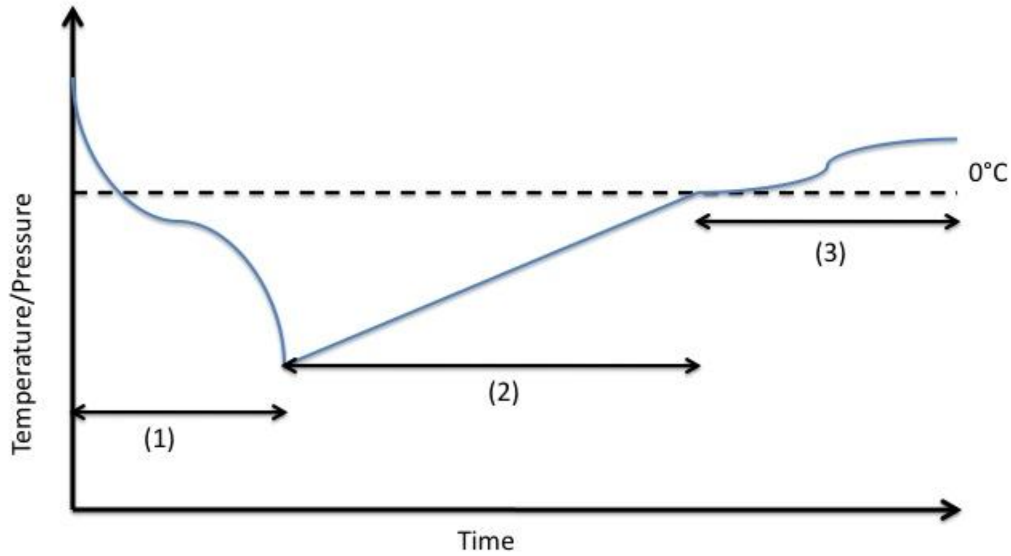

Figure 4- The three stages of freeze drying: freezing (1), sublimation (2) and bound water removal (3).