PHYSICOCHEMICAL PROPERTIES OF ENCAPSULATED RED RASPBERRY (*Rubus idaeus*) POWDER: INFLUENCE OF HIGH PRESSURE HOMOGENIZATION

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ABSTRACT

Encapsulated red raspberry (*Rubus idaeus*) powders with gum Arabic were produced using spray drying method. The raspberry puree samples were treated with and without high pressure homogenizers prior to spray drying. Physiochemical properties of spray dried raspberry powders were analyzed. The median particle size (X_{50}) of raspberry powder produced with high pressure homogenized puree (14.6 µm) was smaller than raspberry powder produced without high pressure homogenization applied to puree (18.3 µm). Glass transition temperatures and water contents of encapsulated raspberry powders were not significantly different ($p > 0.05$) at equivalent water activities. High pressure homogenization of puree resulted in greater apparent density and porosity for encapsulated raspberry powder. Greater particle size resulted in higher hygroscopicity and water solubility index (WSI) for encapsulated raspberry powder produced without high pressure homogenization of puree. Anthocyanins concentration was greater in raspberry powder pretreated with high pressure homogenization although powder exhibited lesser brightness, redness and yellowness.

Keywords: Anthocyanins, gum Arabic, particle size, phenolics, water solubility index,

INTRODUCTION

Consumer demand for antioxidant rich fruits has been increasing for the past few years because of their potential health benefits. Studies reported that berries, including red raspberries are rich in various antioxidant compounds such as anthocyanins (1,2). The role of anthocyanins in cancer treatments (3), biological activity (4) and human nutrition (5) has been well documented. The common anthocyanins found in raspberry are cyanidin-3-sophoroside-5-glucoside and cyanidin-3-glucoside with minor amounts of pelargonidin-3-glucosides and pelargonidin-3-rutinosides (6).

Washington State produces around 60% of the red raspberries in the United States, and more than 90% of that production is processed or frozen immediately since raspberries are highly perishable (7). A major portion of processed/frozen raspberries are dried in order to satisfy the demand for diversified food products. Dried raspberries are used as ingredients in many food formulations, including dairy and bakery products.

Among drying technologies, spray drying is one of the widely used methods to produce encapsulated fruit powders. Claussen et al. (8) reported that spray dried potato protein concentrates were lighter and more appealing than vacuum freeze-dried and atmospheric freeze-dried concentrates. Several studies on spray drying of variety of foods such as cashew apple juice (9), lime juice (10), Gac (11), potato protein concentrate (8), anthocyanin from kokum (12), and cactus pear juice (13) have been reported. Fruit powders are highly hygroscopic and thermoplastic in nature, causing adhesion on dryer walls (10), along with difficulty in handling and caking. Sticking of the powders onto the dryer walls is due to the presence of low molar mass sugars (i.e. fructose, glucose and sucrose) and acids in the fruit pulp (14-17). In addition, the low glass transition (T_g) and sticky point temperatures (the temperature at which a powdery material will start caking and sticking on the walls of the container) of fruit powders make it challenging to produce powders from fruit juices (18, 19). High molar mass carbohydrates, such as maltodextrins and gum Arabic, are generally added to fruit juices to reduce the hygroscopicity and stickiness of fruit powders after spray drying (15-16, 20-21). Further, these high molar mass compounds act as encapsulating agents, which entrap and retain the flavor constituents and protect the bioactive and antioxidant compounds, such as anthocyanins and polyphenols, in food powders during drying and storage. (22-24). Jafari et al. (25) reviewed properties of encapsulating agents used in spray drying. Gum Arabic is one of the most popular, has good emulsifying capacity, high solubility and low viscosity in aqueous solution, which aids the drying process. Gum Arabic also retains volatile substances and provides protection against oxidation due to its excellent surface active qualities (25-28).

In order to produce food emulsions with smaller, more uniform-sized, dispersed particles, homogenization is carried out before spray drying (29). The type of homogenization technique used prior to spray drying may have an impact on the particle size distribution of the final product. High pressure homogenization (pressure levels of 50-350 MPa) can be used before spray drying to produce micro- and nano-meter sized particles, which may help in protecting and delivering bioactive and antioxidant compounds in food products (29,30). Furthermore, the particle size distribution may influence the bioavailability of bioactive antioxidant compounds and the physicochemical properties of the encapsulated food powders. Amidon et al. (31) reported that the bioavailability of bioactive compounds was greater when the particle size was less than 150 nm due to their increased absorption in the gastrointestinal track. High pressure homogenization may also help improve the emulsifying and encapsulating properties of high molar mass encapsulating compounds such as gum Arabic (32). Therefore, the objective of this study was to investigate the effect of high pressure homogenization on physiochemical properties of red raspberry powders encapsulated using gum Arabic.

2. MATERIALS AND METHODS

Fresh red raspberries (*Rubus idaeus* L.) were purchased from local grocery store (Safeway Inc., Pullman, WA). Immediately after receiving the raspberries they were stored at −35°C for maximum 2 days until further experiments were carried out. For puree preparation, raspberries were thawed at 4°C for 2 h. The thawed raspberries were crushed in a beaker (200 ml) and the seeds were separated using cheese cloth. The de-seeded raspberry puree was homogenized for 5 min using an Omni mixer homogenizer (Model No. 17105, Omni International, Waterbury, CT, USA) and filtered through cheese cloth. Gum Arabic (10% w/w [wet basis]) (TIC Pretested® gum Arabic FT powder, TIC Gums, Belcamp, MD) was used as an encapsulating agent by blending it with raspberry puree for 5 min. The gum Arabic was previously dissolved in water before mixing it with raspberry puree. The raspberry puree was further homogenized for 15 min in the Omni mixer homogenizer.

A high pressure homogenizer microfluidizer (Microfluidics M110P with an H10Z interaction chamber, Microfluidics, Newton, MA, U.S.A.) at 207 MPa pressure with five passes through 250 µm auxiliary chamber was used to prepare the raspberry puree into smaller particle size (33). The high pressure homogenizer coil was cooled using ice to avoid possible degradation of anthocyanins in the puree. Both regular and high pressure homogenized purees were stored in plastic bottles at 4°C for maximum 1 h.

Raspberry puree with gum Arabic (10% w/w) was fed into the spray dryer (SI Anhydro Attleboro Falls Mass, Copenhagen, Denmark). The feed/pump rate was 30 ml/min with spray drying air temperature at 160-162°C and outlet air temperature at 85-87°C. The spray dried, encapsulated raspberry powders were collected in Ziplock plastic bags and kept inside glass sealed chambers wrapped with aluminum foil. The encapsulated raspberry powders were stored at −18°C until further analyses were performed. The protocol used for producing encapsulated raspberry powders with and without high pressure homogenization and analyzing their physicochemical properties is presented (Figure 1).

2.4 Measurements of Physiochemical properties

Morphological analysis and particle size determination of encapsulated raspberry powders pretreated with and without homogenization before spray drying were conducted using an environmental scanning electron microscope (ESEM) (Quanta 200 ESEM, FEI Co., Hillsboro, OR). The samples were kept under low vacuum mode of 200 Pa and voltage of 20 kV in the ESEM.

The particle size of red raspberry powders was determined using a particle size analyzer (HELOS KR, Sympatec GmbH, Clausthal-Zellerfeld, Germany). The measurement of powder particle size was conducted using a 5 mW He-Ne laser, parallel Fourier optics, and a 31 element semicircular detector. The particle size determination was based on the Fraunhofer theory of laser diffraction. Powder particles were dispersed using a RODOS dry powder disperser powered by air pressure at 300 kPa. Calculations were performed using Sympatec Windox V 5.6. The median particle size (X_{50}) was determined as the equivalent particle size corresponding to 50% of the cumulative distribution function of the sample.

The encapsulated raspberry powders were equilibrated for two weeks with saturated LiCl solution to achieve a uniform water activity of 0.113. Water contents of red raspberry powders were measured using a vacuum oven as per the method described by the AOAC 984.25 at 70°C for 24 h (34). Raspberry powder (2 g) was used to measure water content in triplicate. The glass transition temperatures of the equilibrated raspberry powders were conducted using a differential scanning calorimeter (DSC, Q2000, TA Instruments, New Castle, DE). The instrument was calibrated at standard temperatures and enthalpies of fusion of indium and sapphire. An empty, sealed aluminum pan was used as a reference while testing both samples. Ten to 20 mg of each powder was sealed in aluminum pans (volume 30 μL) and cooled from room temperature (23°C) to -50°C at 5°C/min and then equilibrated for 10 min. Powders were scanned from -50°C to 150°C while warmed at a rate of 5°C/min. The glass transition temperature (T_g) is identified as a vertical shift in the heat flow curve of the thermogram. TA Instruments Universal analysis software was used to analyze the onset, mid and end points of the glass transition. Duplicate samples of encapsulated red raspberry powder were used to determine the glass transition temperatures. The water activity of encapsulated raspberry powders was determined using a water activity meter (AquaLab, Decagon Devices, Pullman, WA).

Bulk density for red raspberry powders was determined using the method described by Haugaard et al. (35) and Pisecky et al. (36). To determine the bulk density of encapsulated raspberry powders, 10 g raspberry powder was placed in a 25 ml measuring cylinder. The cylinder was gently tapped 100 times to settle the powder and remove the air gap between the particles. Volume of the settled raspberry powder was calculated using the inner diameter of the measuring cylinder and powder height after tapping. Then bulk density (ρ_b) was determined using the following equation:

$$\rho_b = \frac{m_s}{V_t} \qquad (1)$$

where ρ_b is the bulk density, m_s and V_t are the mass of powder and total volume of the powder after tapping, respectively.

The apparent density of the raspberry powders was calculated using a pycnometer method. Encapsulated raspberry powders (2 to 4 g) were immersed in a known volume of toluene (C_7H_8) placed in a 25 ml pycnometer and the displaced volumes were measured. Toluene was used instead of water to avoid absorption of the sample during measurement. Apparent density was calculated from the duplicate samples.

$$\rho_a = \frac{m_s}{V_s} \tag{2}$$

where ρ_a is the apparent density, m_s and V_s are the mass of powder and displaced volume, respectively.

Bulk porosity (ε) of the encapsulated raspberry powders was calculated from the apparent density and bulk density (37).

$$\varepsilon = 1 - \frac{\rho_b}{\rho_a} \tag{3}$$

Where ε is the bulk porosity, ρ_b and ρ_a are the bulk density and apparent density of red raspberry powder.

For hygroscopicity determination, 1 g each of the regular and high pressure homogenized red raspberry powders were kept in 10 ml beakers sealed inside a glass jar maintained at a relative humidity of 79.5 % using a saturated salt solution of potassium nitrate at room temperature (23°C). After 1 week when the equilibrium was reached, the samples were weighed and the hygroscopicity of the powders was calculated using the following equation (19):

$$\text{Hygroscopicity (\%)} = \frac{\frac{b}{a_h} + W_i}{1 + \frac{b}{a_h}} \tag{4}$$

where b is the increase in weight of raspberry powder in grams, a_h is the amount of powder used for measurement in grams and W_i (% wet basis) is the water content of the powder before exposing the powder to a humid air environment (34). The analysis was conducted in triplicate.

The water solubility index (WSI) of the raspberry powders was measured using the method described by Anderson et al. (38). Two and one-half grams of the raspberry power was mixed thoroughly for 5 min in 30 ml distilled water in a 50 ml centrifuge tube. The centrifuge tube was incubated at 37°C in a water bath (HAAKE DL 30, Thermo Electron Corp., Germany) for 35 min. The solution was then centrifuged at 17,640×g for 20 min at 4°C. The supernatant was collected in a pre-weighted 80 ml beaker and vacuum dried in an oven at 105°C.

$$\text{WSI} = \frac{\text{Weight of dried supernatant}}{\text{Weight of original sample}} \times 100 \tag{5}$$

The color of the red raspberry powders was determined using Minolta Spectrophotometer (CM-2002, Minolta Camera Co., Ltd, Osaka, Japan), calibrated with a glossy, white standard tile. The powders were spread uniformly and evenly to a depth of 3 mm in a plastic Petri dish to minimize the influence of surface heterogeneity and bulk density on the color measurements. Results were expressed as values L^*, a^* and b^* on the Hunter color scale (REF), where L^* denotes lightness, a^* redness and greenness, and b^* yellowness and blueness. An L^* value of 0 is black and 100 is white. An a^* value of -120 is green and +120 is red. Hunter values of each sample were measured in triplicate.

For total anthocyanin determination, 50 mg of dried raspberry powder or 100 mg fresh fruit tissue was extracted in 1 mL 1% (v/v) HCl-methanol in microcentrifuge tubes. After storage for 24 h at -20°C, sample tubes were centrifuged at 20817 × g for 10 min at 4°C and the supernatant decanted into 15 mL plastic tubes. The pellet remaining in each sample tube was extracted twice more, with supernatants decanted into the 15 mL plastic tubes. The accumulated supernatants for each sample were made up to 3-mL volumes with HCl-methanol on the fourth day. Total anthocyanins were determined by the pH-differential absorbance method, using molar extinction coefficient of 37150 $M^{-1}cm^{-1}$ at 524 nm for cyanidin-3-sophoroside-5-glucoside in raspberries (39). Each extract was measured in triplicate and the total anthocyanin concentration was expressed in mg cyanidin-3-sophoroside-5-glucoside per g dry weight.

Total phenolic compounds in the raspberry powders were quantified using Folin-Ciocalteu (F-C) phenol reagent (2 N) by revised methods described by Singleton et al. (40). Specifically, 50 mg fruit powder or 100 mg fresh fruit tissue was extracted with 1 mL 80% (v/v) methanol in microcentrifuge tubes. Samples were vortexed, allowed to extract for 1 h at room temperature and then overnight at -20°C followed by centrifugation at 20817 × g for 20 min at 4°C. The supernatants were decanted into 15 mL plastic tubes. The pellet remaining in each sample tube was extracted twice more, decanted supernatants decanted into the 15 mL plastic tubes. The accumulated supernatants for each sample were made up to 4 mL with 80% (v/v) methanol after the final extraction. The assay was performed by adding 300 µL sample extract into two, 15-mL tubes containing 600 µL 80% (v/v) methanol, 5 mL 10% (v/v) F-C reagent, and either 4 mL saturated Na_2CO_3 (75 g L^{-1}) or 4 mL water. The tubes were mixed thoroughly and incubated at room temperature for 2 h. Aliquots (1 mL) from the sample tubes containing Na_2CO_3 or water were added to 1.5 mL plastic cuvettes and the absorbance of each was measured at 760 nm in a UV-visible spectrophotometer (Model HP8453, Hewlett-Packard Co., Palo Alto, CA). The concentration of phenolic compounds was determined by subtracting absorbance of samples containing Na_2CO_3 from that of samples containing water and expressed as gallic acid (3,4,5-trihydroxybenzoic acid) equivalents.

For total antioxidant activity determination, the end-point 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS)/hydrogen peroxide (H_2O_2)/peroxidase (horseradish peroxidase, HRP type VI-A) method of Cano et al. (41) was used with modifications to measure the antioxidant activity of hydrophilic and lipophilic fractions (42). Specifically, 50 mg raspberry powder or 200 mg fresh fruit tissue was extracted in 700 mL of 50 mM 2-(*N*-morpholino)ethanesulfonic acid (MES, pH 6.0) and 700 mL of ethyl acetate in microcentrifuge tubes. The tubes were vortexed for 30 s, and centrifuged at 17949 × g for 10 min at 4°C. The organic (top) and aqueous (bottom) phases were separated with a pipette for measurement of hydrophilic and lipophilic antioxidant activities (HAA and LAA, respectively). For both fractions, 40 µL of 1 mM H_2O_2, 100 µL of 15 mM ABTS, and 10 µL of 3.3 U μL^{-1} HRP were placed in glass cuvettes and gently shaken for 10 s, after which 50 mM phosphate buffer (pH 7.4) was added to the samples and mixed with a stir paddle. The absorbance at 734 nm was monitored in a UV-visible spectrophotometer until stable (<10 sec). Later, 5 µL (for HAA) or 40 µL (for LAA) extract was added for a total reaction volume of 1 mL, mixed with a stir paddle, and monitored at 734 nm until absorbance reached a minimum. HAA and LAA were calculated from the absorbance difference and expressed on the basis of Trolox equivalents from standard curves of 5 mM Trolox diluted in 50 mM MES buffer (pH 6.0) or 100% (v/v) ethyl acetate, respectively, and measured as described for the samples. HAA and TAA were summed to estimate total antioxidant activity (TAA).

Statistical analysis was conducted using SAS®9.1 (SAS Institute Inc., Cary, NC). Analysis of variance (ANOVA) was used to determine significant differences between treatment means at the 95% confidence interval.

3. RESULT AND DISCUSSION

3.1. Particle Size distribution and Morphology

Morphological analysis of the encapsulated raspberry powders by ESEM indicates no substantial difference in particle morphology between encapsulated raspberry powders produced with and without high-pressure homogenization before spray drying (Figures 2a&b). Generally, the encapsulated raspberry powders were round in shape with some concavities on the surface. Communian et al. (43) also reported concavities on the surface of spray dried chlorophyllide microspheres. The concavities on the microspheres may be attributed to particle shrinkage due to water evaporation during spray drying as reported by Rosenburg et al. (28).

Encapsulated raspberry powders exhibited unimodal particle size distribution, showing the powders were homogeneous, with no caking or aggregation of particles (Figure 3). The encapsulated raspberry powder obtained after high-pressure homogenization exhibited a slightly smaller particle size (X_{50} = 14.6 µm) than that of encapsulated powder obtained after regular homogenization (X_{50} = 18.3 µm) (Table 1 and Figure 3). The smaller particle size of encapsulated, high-pressure powder is attributed to the reduced droplet size after high-pressure homogenization. The ice cooling of puree during high pressure homogenization may have prevented more accentuated droplet size reduction. However, ice cooling was necessary to reduce the temperature of raspberry puree to minimize possible degradation of anthocyanins due to high temperatures generated in raspberry puree during high pressure homogenization. It was reported that ultra-high pressure, and the resulting high temperature and shear stress, reduced droplet size of an emulsion after high-pressure homogenization (32). Rocha-Guzman et al. (30) reported high-pressure homogenized powder samples resulted in 50% smaller particle size in comparison to non-homogenized samples.

3.2 Water content, Water activity and Glass transition temperature

The water contents of encapsulated raspberry powders pretreated with and without high-pressure homogenization before spray drying were 0.049 and 0.033 kg water/kg powder sample, respectively. After equilibration at a_w of 0.113, the water contents of encapsulated raspberry powders pretreated with and without high pressure homogenization before spray drying did not differ significantly ($P \geq 0.05$) at 0.029 and 0.032 kg water/kg raspberry, respectively (Table 2). Kha et al. (11) reported the water content of spray dried Gac powder was 0.045 kg water/kg sample. No significant difference was observed in glass transition temperatures (T_{gi}, T_{gm}, and T_{ge}) of encapsulated raspberry powders pretreated with and without high-pressure homogenization before spray drying (Table 2). The similar glass transition temperature is attributed to the equivalent water contents and chemical composition of the raspberry powders. Initial glass transition temperatures (T_{gi}) of encapsulated raspberry powders (20-20.5^{o}C) were similar to room temperature (23^{o}C) (Table 2), and therefore, they can be stored at room temperature for an extended period of time without any significant loss of flavor and antioxidant compounds (17,44). The possible moisture transfer between storage environment and low water activity encapsulated raspberry powders should be avoided during storage by proper packaging to minimize quality changes. A small addition of gum Arabic (10% of total solids) with raspberry puree used in this study increased the T_g of the pure raspberry powder substantially (2.5-3^{o}C increase in T_{gi} and 6.9-7^{o}C in T_{gm}) (45). Further addition of gum Arabic (15-20% of total solids) could increase the T_{gi} above room temperature without considerable changes in physicochemical properties.

Molar mass of solid constituents in food matrices has a significant impact on their glass transition temperature. High molar mass food constituents, such as gum Arabic, exhibit high glass transition temperatures. The low shear stresses during regular homogenization may not be significant enough to cause structural changes of high molar mass compounds. While high-pressure homogenization may break the covalent bonds and degrade the structure of high molar mass compounds attributed to the increase in temperature by shear stress under high pressure (32). The structural changes may reduce the molar mass of compounds during high pressure homogenization which may alter their glass transition temperatures. However, our results indicated that the glass transition temperature of raspberry powders are dependent on the water content, suggesting no structural changes in powder after high pressure homogenization (Table 2) (46).

3.3 Density, Hygroscopicity and Water solubility index (WSI)

Bulk density is a packing property of a food material. Bulk density is dependent on size, shape and surface properties of powder particles. Powders with smooth and uniform surface have greater bulk density. Powders with smaller bulk density have greater volume of package for same amount of material. In general, bulk density increases with a decrease in particle size as more particles occupy a given volume, which allow less void spaces between particles (47). However, in the case of encapsulated raspberry powders, there was no significant difference ($P \geq 0.05$) between the bulk densities (550 kg/m^3) of high pressure and regular homogenized raspberry powders (Table 2). In case of spray dried Gac powder, the bulk density was 700 kg/m^3 (11), while for vacuum dried mango powder, the reported bulk density was 530 kg/m^3 (14). Apparent density represents the density including all the pores in a material. For food powders, apparent density ranges between 1000-1500 kg/m^3 (48). Apparent density of encapsulated raspberry powder pretreated with high-pressure homogenization (1300 kg/m^3) was slightly greater than that of regular homogenized raspberry powder (1200 kg/m^3) (Table 1). The greater value of bulk porosity of encapsulated raspberry powder pretreated with high-pressure homogenization was attributed to its higher apparent density (Eq 3.). Rodriguez-Hernandez et al. (13) reported the apparent density of cactus pear juice as 1052 kg/m^3.

The encapsulated raspberry powders pretreated with high-pressure homogenization were less hygroscopic (3.45%), indicating homogenization technique has an influence on hygroscopicity (Table 1). Better encapsulation as a resulted of high-pressure homogenization before spray drying may have contributed to the smaller hygroscopicity of raspberry powders. Rodriguez-Hernandez et al. (13) reported that inlet air pressure affected the hygroscopicity of powders after spray drying. Less hygroscopicity was observed when greater air pressure was applied, attributing to more compact powder constitution due to the higher pressures. Nayak and Rasogi (12) reported the hygroscopic water content of encapsulated kokum anthocyanins ranged from 4.38-5.8% depending on dextrose equivalent of maltodextrins used as encapsulating agents. Hygroscopic food powders exhibit stickiness and caking when exposed to moisture during storage and distribution. However, hygroscopicity is a favorable property considering solubility of a food powder during rehydration. Solubility is one of the important instant properties (wettability, dispersability, solubility) for encapsulated raspberry powder, since it may be subjected to rehydration when used as a food ingredient. Encapsulated raspberry powder pretreated with high-pressure homogenization exhibited a smaller water solubility index (WSI = 61.7%) than that of raspberry powders (WSI = 70.1%) not pretreated with high-pressure homogenization of the puree. The observed higher solubility of regular homogenized powder may be attributed to its greater particle size distribution. Abadio et al. (49) reported similar WSI (81.6 %) in pineapple juice powder.

3.4 Color

Color of encapsulated raspberry powder is an important attribute since it can be commercially used as an ingredient or coloring agent in food formulations. A significant difference in L^*, a^* and b^* values were observed between encapsulated raspberry powders pretreated with high-pressure homogenization and regular homogenization techniques (Table 3). A greater L^* value (47.6) for encapsulated powder pretreated with high-pressure homogenization indicates they were lighter in color than encapsulated raspberry powder pretreated with the regular homogenization technique (43.7). Also, a smaller a^* value (41.7) (red to green color) for encapsulated powder pretreated with high-pressure homogenization indicates less red color intensity, which may be attributed to better encapsulation by the carrier agent, gum Arabic. The lower b^* value (9.43) (blue to yellow color) for encapsulated raspberry powder pretreated with high-pressure homogenization represents greater yellowness. In general, regular homogenization pretreatment of encapsulated raspberry powder produced brighter powders with more redness and yellowness.

3.5 Phytochemicals content

The total anthocyanin concentration was significantly greater ($P \leq 0.05$) in encapsulated raspberry powder pretreated with high-pressure homogenization (6.47 mg/g DW) than without high pressure homogenization (4.85 mg/g DW) or the fresh raspberries from which the powders were derived (5.96 mg/g DW) (Table 4). The total anthocyanin concentration in freeze-dried raspberries ranged from 6.45-11.6 mg/g DW (Table 4) (50). The smaller retention of anthocyanins in spray-dried raspberries in comparison to the freeze-dried raspberries could be due to the higher temperatures used in spray drying compared to the lower temperatures and vacuum conditions inside the freeze-drying chamber. In addition, gum Arabic was used to encapsulate raspberry powders during spray drying while no encapsulation material was used during freeze-drying. The concentration of total phenolics in encapsulated raspberry powder pretreated with and without high-pressure homogenization were identical (5.33 mg gallic acid equivalents/g DW). The total phenolics concentration in spray dried raspberry powders were considerably less than that of fresh or freeze dried raspberries (14.4-25.2 mg gallic acid equivalents/g DW), which may be attributed to the destruction of some heat sensitive phenolic compounds during spray drying (Table 4) (50). The total antioxidant activity of encapsulated raspberry powder pretreated with high-pressure homogenization (56.9 mmol Trolox equivalents/g DW) was significantly greater than that of raspberry powder not pretreated with high-pressure homogenization (48.6 mmol Trolox equivalents/g DW). The total antioxidant activity of spray dried raspberry powder was less than that of freeze-dried raspberry powder (69.2-158 mmol Trolox equivalents/g DW).

The better retention of anthocyanins and greater antioxidant activity in encapsulated raspberry powder pretreated with high-pressure homogenization may be attributed to better coating and encapsulation of anthocyanins and other antioxidant bioactive compounds by the gum Arabic matrix at higher pressures (51). In addition, high pressure homogenization resulted in smaller particles, which are normally better coated and encapsulated than larger particles, leading to greater retention during drying (51). Retention of limonene was greater at higher homogenization pressures in a freeze-dried gum Arabic-gelatin-sucrose matrix (51). Rocha-Guzman et al. (30) reported high pressure retains a greater total polyphenolic content and this pattern could be associated with smaller particle size. The attractive red color of red raspberries is related to the concentration of anthocyanin molecules. Even though encapsulated raspberries pretreated with high-pressure homogenization retained more anthocyanins, they exhibited lighter and less red color intensity in comparison to the encapsulated raspberries pretreated with regular homogenization. This could be due to better encapsulation of anthocyanins and coating by gum Arabic at high pressures during homogenization, thereby masking the surface color of the raspberry powder. In addition, other molecules may be responsible for the color of red raspberries.

CONCLUSIONS

The encapsulated raspberry powders were spherical in shape with some concavities on the surface attributed to shrinkage during spray drying. Encapsulated raspberry powders were more uniform and less agglomerated as observed by scanning electron microscopy. Particle size and homogenization technique did not have an influence on glass transition temperature, which was dependent only on the water content. Water solubility index and hygroscopicity of encapsulated raspberry powders pretreated with high pressure homogenization were greater, indicating better physicochemical properties than those processed without high pressure homogenization. The higher hygroscopicity, however, may lead to stickiness during storage of food powders. High-pressure homogenization retained more anthocyanins in raspberry powders by providing better encapsulation and coating. High-pressure homogenization should be considered as a pretreatment before spray drying of encapsulated raspberry powders based on the application and physicochemical properties of interest. The findings of the current study are useful for raspberry and other fruit processing and ingredient industries in selecting appropriate homogenization techniques for producing encapsulated, highly colored, fruit powders.

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FIGURE CAPTIONS

Figure 1	Flow chart of the experimental methods used for producing encapsulated raspberry powders and analyzing their physicochemical properties
Figure 2	Environmental Scanning Electron Microscopy micrographs of encapsulated raspberry powders A). without and B). with high pressure homogenization
Figure 3	Cumulative distribution of particle size and identification of X_{50} in encapsulated raspberry powders pretreated with regular and high-pressure homogenization

Table 1. Physical properties of spray dried red raspberry powders

Encapsulated raspberry powder	Bulk Density (kg/m^3)	Apparent or Particle Density (kg/m^3)	Bulk Porosity	Hygroscopicity (%)	WSI (%)	Particle Size (µm)
Without high pressure homogenization	550^{a} (0)	1200^{c} (0.016)	0.53	3.46^{e} (0.002)	70.1^{g} (0.37)	18.3
With high pressure homogenization	550^{a} (0.012)	1300^{d} (0.015)	0.57	3.45^{f} (0.006)	61.7^{h} (0.33)	14.6

Same superscripts in column indicates that there is no significant difference in the values

Table 2. Water content, glass transition temperatures (T_{gi}, T_{gm} and T_{ge}) and water activity of spray dried red raspberry powders after equilibration at 0.113 a_w

Encapsulated raspberry powder	Water content (kg water/kg raspberry)	Glass Transition Temperature Range (°C)			Water activity, a_w
		T_{gi}	T_{gm}	T_{ge}	
Without high pressure homogenization	0.032^{d} (0.0005)	20.0^{a} (0.410)	26.2^{b} (0.495)	29.2^{c} (0.778)	0.113
With high Pressure homogenization	0.029^{d} (0.0008)	20.5^{a} (0.700)	26.1^{b} (0.707)	30.5^{c} (0.495)	0.113

Same superscripts in column indicates that there is no significant difference in the values

Table 3. Color indices (L^*, a^*, b^* values) in spray dried red raspberry powders

Encapsulated raspberry powder	L^*	a^*	b^*
Without high pressure homogenization	43.7[a] (0.270)	45.1[c] (0.520)	11.3[e] (0.370)
With high Pressure homogenization	47.6[b] (0.480)	41.7[d] (0.810)	9.43[f] (0.350)

Same superscripts in column indicates that there is no significant difference in the values

Table 4. Quantity of phytochemicals in fresh raspberries and spray dried red raspberry powders (DW: dry weight of solids)

Raspberry sample	Total Anthocyanins (mg Cyd-3-Soph-5-Glu equivalents/g DW)	Total Phenolics (mg gallic acid equivalents/g DW)	Total antioxidant activity after processing (mmol Trolox equivalents/g DW)
Fresh	5.96[a] (0.310)	11.3[d] (0.325)	51.7[fg] (5.15)
Without high pressure homogenization	4.85[b] (0.154)	5.33[e] (0.079)	48.6[f] (1.02)
With high Pressure homogenization	6.47[c] (0.126)	5.33[e] (0.283)	56.9[g] (5.63)
Freeze-dried raspberry powder (50)	6.45-11.6	14.4-25.2	69.2-158

Same superscripts in column indicates that there is no significant difference in the values

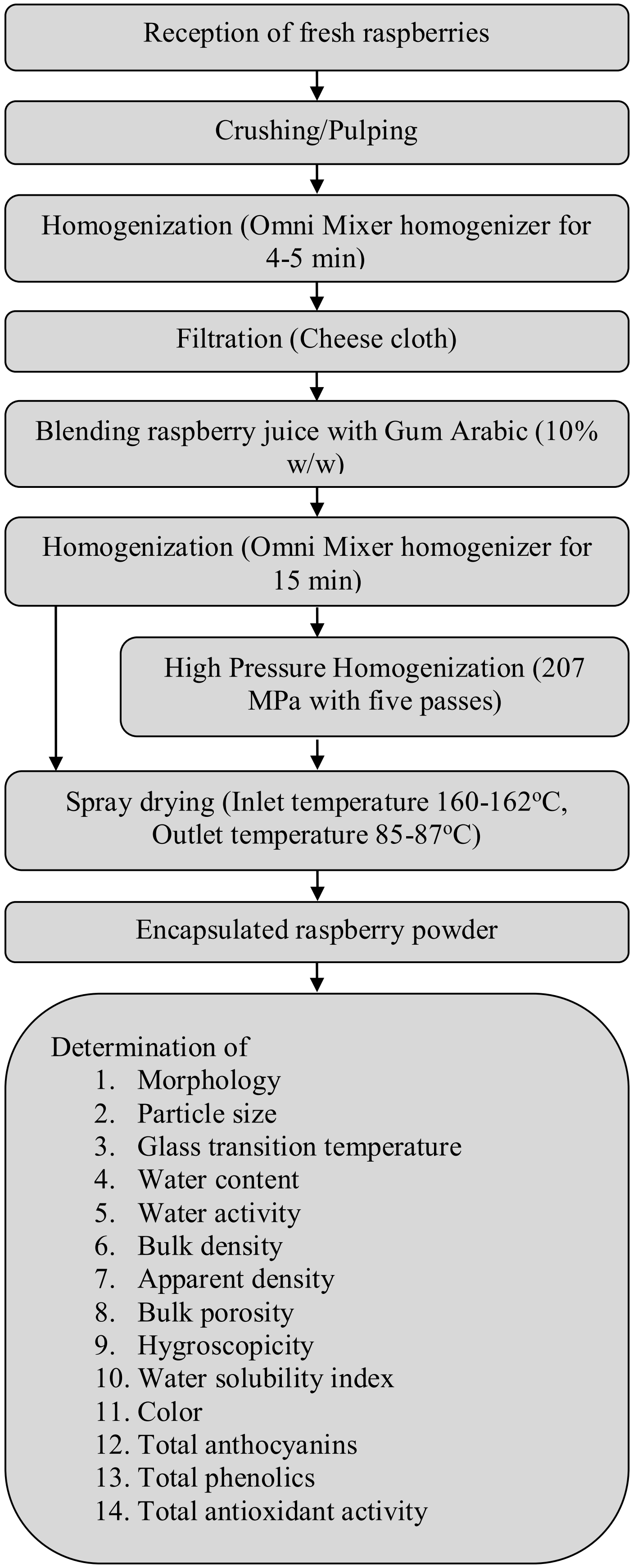

Reception of fresh raspberries
Crushing/Pulping
Homogenization (Omni Mixer homogenizer for 4-5 min)
Filtration (Cheese cloth)
Blending raspberry juice with Gum Arabic (10% w/w)
Homogenization (Omni Mixer homogenizer for 15 min)
High Pressure Homogenization (207 MPa with five passes)
Spray drying (Inlet temperature 160-162°C, Outlet temperature 85-87°C)
Encapsulated raspberry powder
Determination of
1. Morphology
2. Particle size
3. Glass transition temperature
4. Water content
5. Water activity
6. Bulk density
7. Apparent density
8. Bulk porosity
9. Hygroscopicity
10. Water solubility index
11. Color
12. Total anthocyanins
13. Total phenolics
14. Total antioxidant activity

Figure 1

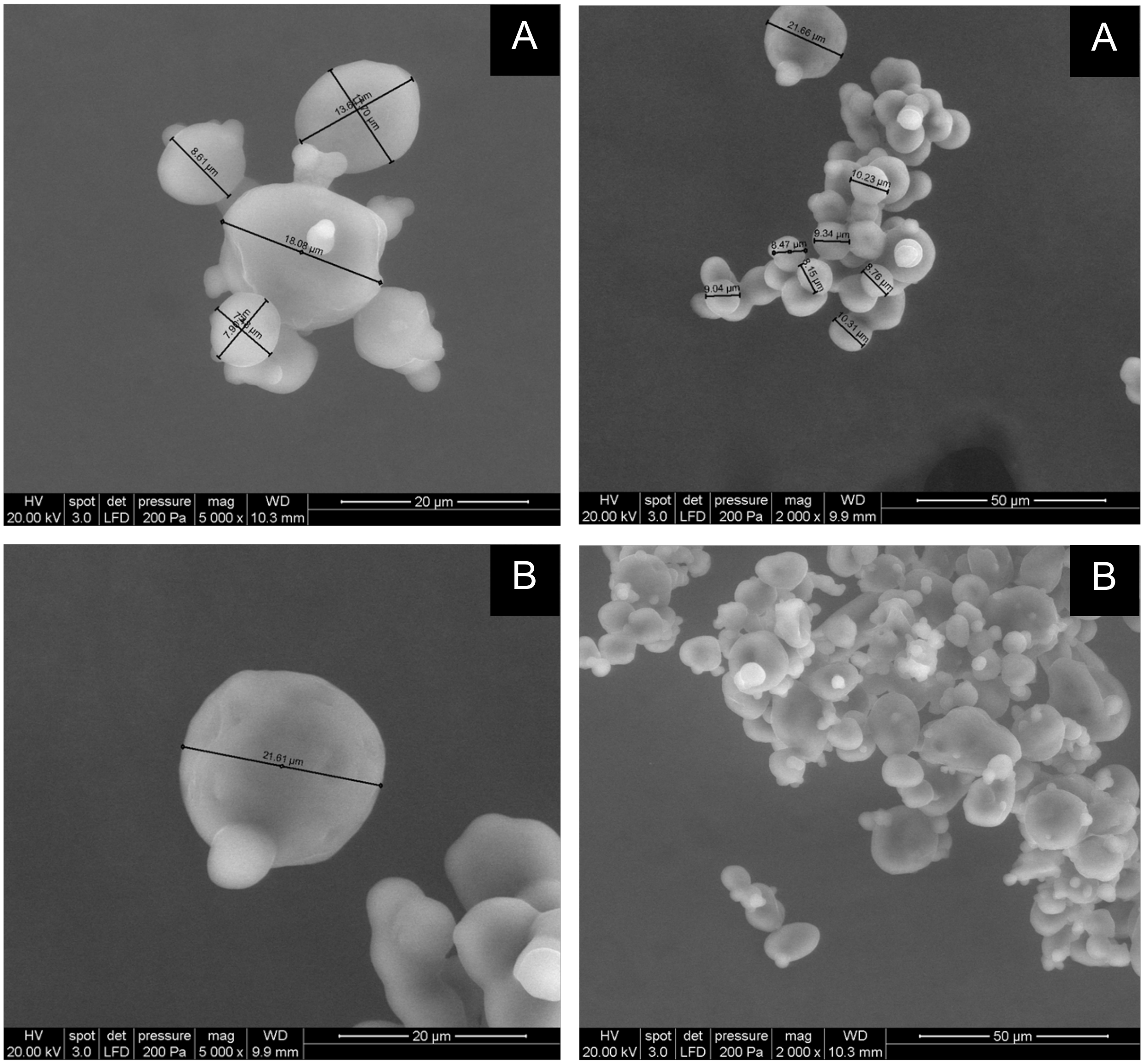
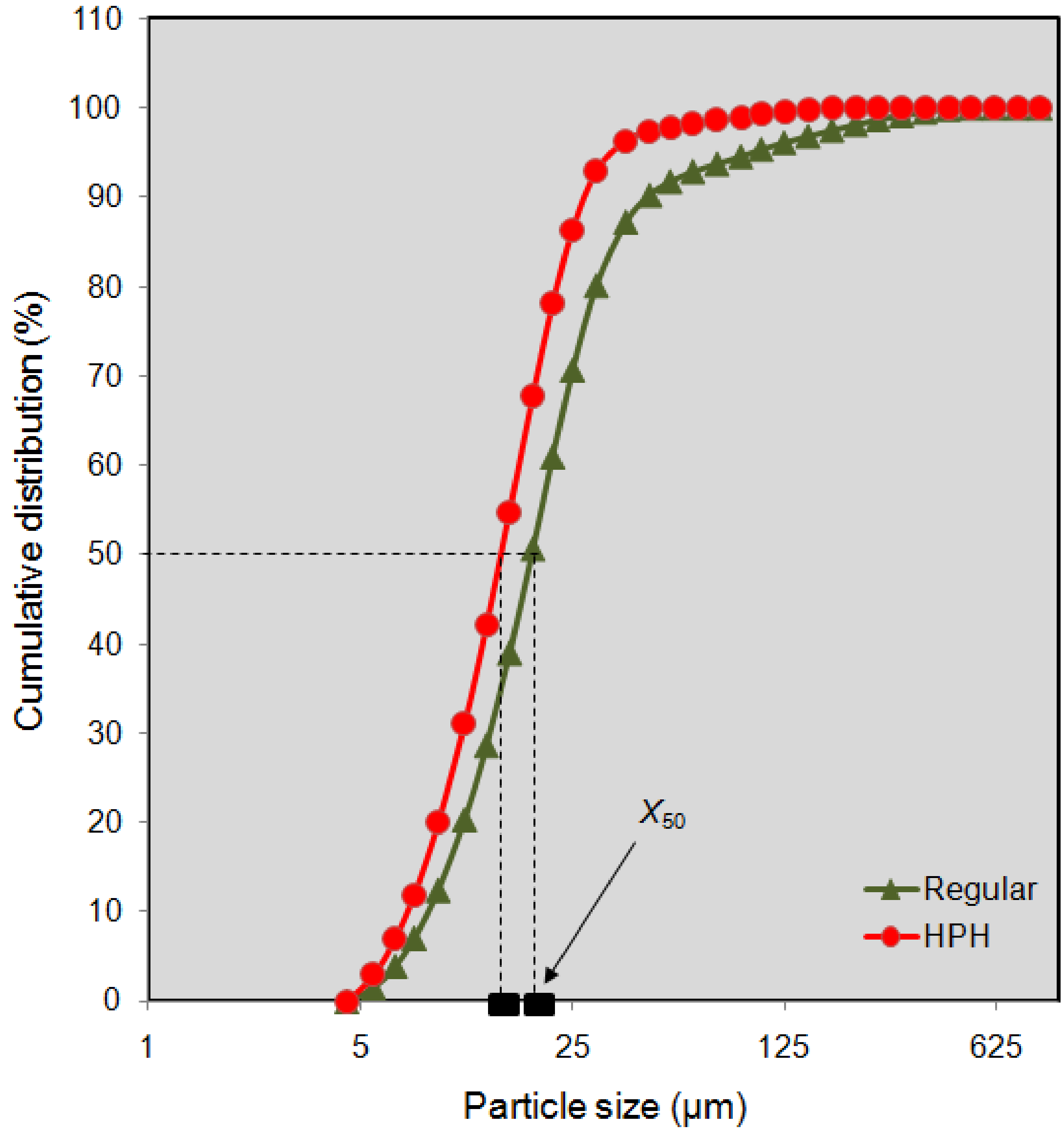

A
8.61 µm
18.08 µm
HV spot det pressure mag WD
20.00 kV 3.0 LFD 200 Pa 5 000 x 10.3 mm
20 µm
A
21.66 µm
10.23 µm
9.34 µm
8.47 µm
9.04 µm
8.15 µm
8.76 µm
10.31 µm
HV spot det pressure mag WD
20.00 kV 3.0 LFD 200 Pa 2 000 x 9.9 mm
50 µm
B
21.61 µm
HV spot det pressure mag WD
20.00 kV 3.0 LFD 200 Pa 5 000 x 9.9 mm
20 µm
B
HV spot det pressure mag WD
20.00 kV 3.0 LFD 200 Pa 2 000 x 10.3 mm
50 µm

Figure 2



Cumulative distribution (%)
110
100
90
80
70
60
50
40
30
20
10
0
1
5
25
125
625
Particle size (μm)
X50
Regular
HPH

Figure 3

REFERENCES

1. De Ancos, B.; Gonzalez, E.; Pilar Cano, M. Differentiation of raspberry varieties according to anthocyanin composition. European Food Research and Technology 1999, 208(1), 33–8
2. Zhang, Y.; Vareed, S. K.; Nair, M. G. Human tumor cell growth inhibition by nontoxic anthocyanidins, the pigments in fruits and vegetables. Life Science 2005, 76, 1465–1472.
3. Lule, S.U.; & Xia, W. Food phenolics, pros and cons: a review. Food Reviews International 2005, 21(4), 367−388.
4. Kong, J. M.; Chia, L. S.; Goh, N. K.; Chia, T. F.; & Brouillard, R. Analysis and biological activities of anthocyanins. Phytochemistry 2003, 64(5), 923−933.
5. Stintzing, F. C.; Carle, R. Functional properties of anthocyanins and betalains in plants, food and human nutrition. Trends in Food Science and Technology 2004, 15(1), 19−38.
6. Patras, A.; Brunton, N. P.; O'Donnell, C.; Tiwari, B. K. Effect of thermal processing on anthocyanin stability in foods; mechanisms and kinetics of degradation. Trends in Food Science and Technology 2010, 21(1), 3-11.
7. Washington Red Raspberry Commission, http://www.red-raspberry.org/ (Accessed: April 24, 2008).
8. Claussen, I. C.; Strommen, I.; Egelandsdal, B.; Straekvern, K. O. Effects of drying methods on functionality of a native potato protein concentrate. Drying Technology 2007, 25, 1101–1108.
9. Oliveira, M. A.; Maria, G. A.; De Figueiredo, R. W.; De Souza, A. C. R.; De Brito, E. s.; De Azeredo, H. M. C. Addition of cashew tree gum to maltodextrin-based carriers for

spray drying of cashew apple juice. International Journal of Food Science and Technology 2009, 44(3), 641−645.

10. Roustapour, O.R.; Hosseinalipour, M.; Ghobadian, B. An Experimental investigation of lime juice drying in a pilot plant spray dryer. Drying Technology 2006, 24, 181−188.

11. Kha, T. C.; Nguyen, M. H.; Roach, P. D. Effects of spray drying conditions on the physiochemical and antioxidant properties of the Gac (*Momordica cochinchinensis*) fruit aril powder. Journal of Food Engineering 2010, 98, 385−392.

12. Nayak, C. A.; Rastogi, N. K. Effect of selected additives on microencapsulation of anthocyanin by spray drying. Drying Technology 2010, 28, 1396–1404.

13. Rodriguez-Hernandez, G. R.; Gonzalez-Garcia, R., Grajales-Lagunes, A. Ruiz-Cabrera, M. A. Spray-drying of cactus pear juice (*Opuntia streptacantha*): Effect on the physicochemical properties of powder and reconstituted product. Drying Technology 2005, 23, 955–973

14. Jaya , S.; Das, H.; Mani, S. Optimization of maltodextrin and tricalcium phosphate for producing vacuum dried mango powder. International Journal of Food Science 2006, 9, 13−24.

15. Bhandari, B. R.; Datta, N.; & Howes, T. Problems associated with spray drying of sugar-rich foods. Drying Technology 1997, 15, 671−684.

16. Bhandari, B. R.; & Hartel, R. W. Phase transition during food powder production and powder stability. In Encapsulated and Powdered Foods; Onwulate, C., Eds.; Taylor & Francis.: Boca Raton, USA, 2005; 261−292.

17. Dolinsky, A.; Maletskaya, K.; & Snezhkin, Y. Fruit and vegetable powders production technology on the bases of spray and convective drying methods. Drying Technology 2000, 18, 747−758.

18. Roos, Y. H. Glass transition-related physiochemical changes in foods. Food Technology 1995, 49, 97−102.

19. Jaya, S. & Das, H. Effect of maltodextrin, glycerol monostearate and tricalcium phosphate on vacuum dried mango powder properties. Journal of Food Engineering 2004, 63, 125−134.

20. Silva, M. A.; Sobral, P. J. A.; & Kieckbusch, T. G. State diagram of freeze-dried camu-camu (Myrciaria dubia (HBK) Mc Vaugh) pulp with and without maltodextrin addition. Journal of Food Engineering 2006, 77, 426−432.

21. Sablani, S. S.; Shrestha, A. K.; Bhandari, B. R.. A new method of producing date powder granules: Physicochemical characteristics of powder. Journal of Food Engineering 2008, 87(3), 416-421

22. Champagne, C.P.; Fustier, P. Microencapsulation for the improved delivery of bioactive compounds into foods. Current Opinion in Biotechnology 2007, 18, 184−90.

23. Madene, A.; Jacquot, M.; Scher, J.; & Desobry, S. Flavour encapsulation and controlled release – a review. International Journal of Food Science & Technology 2006,41, 1−21.

24. Galmarini, M. V.; Zamora, M. V.; Baby, R..; Chirife, J. & Mesina, V. Aromatic profiles of spray-dried encapsulated orange flavors: influence of matrix composition on the aroma retention evaluated by sensory analysis and electronic nose techniques. International Journal of Food Science and Technology, 2008, 43, 1569−1576.

25. Jafari, S. M.; Assadpoor, E.; He, Y.; Bhandari, B. Encapsulation efficiency of food flavors and oils during spray drying. Drying Technology 2008, 26, 816–835.

26. Rennecius, G.A. Carbohydrates for flavor encapsulation. Food Technology 1991, 46(3), 144–152.

27. Righetto, A. M.; & Netto, F. M. Effect of encapsulating materials on water sorption, glass transition and stability of juice from immature acerola. International Journal of Food Properties 2005, 8, 337−346.

28. Rosemberg, M.; Kopelman, I. J.; Talmon, Y. Factors affecting retention in spray-drying microencapsulation of volatile materials. Journal of Agriculture and Food Chemistry 1990, 38, 1288−1294.

29. Dong, Y.; Feng, S. S. Poly(D,L-co-glycolide0 (PGLA) nanoparticles prepared by high pressure homogenization for paclitaxel chemotherapy. International Journal of Pharmaceutics 2007, 342, 208−14.

30. Rocha-Guzman, N. E.; Gallegos-Infante, J. A.; Fonzalez-Laredo, R. F.; Harte, F.; Medina-Torres, L.; Ochoa-Martinez, L. A.; & Soto-Garcia, M. Effect of high-pressure homogenization on the physical and antioxidant properties of Quercus resinosa infusions encapsulated by spray-drying. Journal of Food Science 2010, 75(5), N57-N61.

31. Amidon, G. L.; Lennernas, H.; Shah, V. P.; Crison, J. R. A theoretical basis for a biopharmaceutic drug classification: The correlation of *in vitro* drug product dissolution and *in vivo* bioavailability. Pharmaceutical Research 1995, 12, 413−20.

32. Floury, J.; Desrumaux, A.; Axelos, M. A. V.; Legrand, J. Degradation of methylcellulose during high pressure homogenisation. Food Hydrocolloids 2002, 16, 47–53

33. Sablani, S. S.; Dasse, F.; Bastarrachea, L.; Dhawan, S.; Hendrix, K.; Min, S. C. Apple peel-based edible film development using a high-pressure homogenization. Journal of Food Science 2009, 74(7), E372-E381

34. AOAC, Association of Official Analytical Chemists. Official Methods of Analysis (14th edn). Association of Official Analytical Chemists, Washington DC 1984.

35. Haugaard, I. S.; Krag, J.; Pisecky, J.; and Westergaard, V. Analytical methods for dry milk powders. 1978, Denmark: Niro Atomizer.

36. Pisecky, J.; Standards, specifications and test methods for dry milk products. In Concentration and drying of foods; Diarmuid, M. C., Ed.; Elsevier Science Publishing Inc.: New York, 1985; 203−220.

37. Krokida, M. K.; Karathanos, V. T.; Maroulis, Z. B. Effect of freeze-drying conditions on shrinkage and porosity of dehydrated agricultural products. Journal of Food Engineering 1998, 35(4), 369-380.

38. Anderson, R. A.; Conway, H. F.; Pfeifer, V. F.; and Griffin, E. L. Gelatinization o f corn grits by roll and extrusion cooking. Cereal Science 1969, 14, 4-7.

39. Wrolstad, R. E.; Acree, T. E.; Decker, E. A.; Penner, M. H.; Reid, D. H.; Schwartz, S. J.; Shoemaker, C. F.; and Sporns, P; Anthocyanins. In Handbook of Food Analytical Chemistry 2; John Wiley and Sons, Inc.: New Jersey, 2005; 19-31.

40. Singleton, V. L.; Orthofer, R.; Lameula-Raventos, R. M. Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin-Ciocalteu reagent. Methods in Enzymology 1999, 299, 152-179.

41. Cano, A.; Hernandez-Ruız, J.; Garcıa-Canovas, F.; Acosta, M.; and Arnao, M. B. An end-point method for estimation of the total antioxidant activity in plant material. Phytochemical Analysis 1998, 9, 196–202.

42. Arnao, M. B.; Cano, A.; Acosta, M. The hydrophilic and lipophilic contribution to total antioxidant activity. Food Chemistry 2001, 73, 239-244.

43. Communian, T. A.; Monterrey-Quintero, E. S.; Thomazini, M.; Balieiro, J. C. C.; Piccone, P.; Pittia, P.; Favaro-Trindade, C. S. Assessment of production efficiency, physicochemical properties and storage stability of spray-dried chlorophyllide, a natural food colorant, using gum Arabic, maltodextrin, and soy protein isolate-based carrier systems. International Journal of Food Science and Technology 2011, 46, 1259-1265.

44. Sablani, S. S.; Syamaladevi, R. M.; Swanson, B. G. A review of methods, data and applications of state diagrams of food systems. Food Engineering Reviews 2010, 2, 168–203.

45. Syamaladevi, R. M.; Sablani, S.S.; Tang, J.; Powers, J.; Swanson, B.G. State diagram and water adsorption isotherm of raspberry (*Rubus idaeus*). Journal of Food Engineering 2009, 91, 460–467.

46. Syamaladevi, R. M.; Sablani, S. S.; Tang, J.; Powers, J. R.; Swanson, B. G. Water sorption and glass transition temperatures in red raspberry (*Rubus idaeus*). Thermochimica Acta 2010, 503-504, 90-96.

47. Grabowski, J. A.; Truong, V. D.; Daubert, C. R. Spray-drying of amylase hydrolyzed sweetpotato puree and physicochemical properties of powder. Journal of Food Science 2006, 71(5), E209-E217.

48. Barbosa-Canovas, G. V.; Ortega-Rivas, E.; Juliano, P.; Yan, H. Food Powders: Physical Properties, Processing and Functionality; Kluwer Academic/Plenum Publishers; New York, 2005.

49. Abadio, F. D. B.; Domingues, A. M.; Borges, S. V.; Oliveira, V. M. Physical properties of powdered pineapple (Ananas comosus) juice: effect of maltodextrin concentration and atomization speed. Journal of Food Engineering 2004, 64 (3), 285−287.

50. Sablani, S. S.; Bastarrachea, L.; Andrews, P. K.; Davies, N. M.; Walters, T.; Saez, H. Effects of air and freeze drying on phytochemical content of conventional and organic berries. Drying Technology 2010, 29(2), 205-216.

51. Kaushik, V. and Roos, Y. H. Limonene encapsulation in freeze drying of gum Arabic-sucrose-gelatin systems. LWT-Food Science and Technology 2007, 40, 1381-1391.