1   Physicochemical properties of spray dried honey powder produced with

2   whey protein isolate and maltodextrin as carrier agents

3   Qilong Shi[a,b]，Zhongxiang Fang[c]，Bhesh Bhandari[a,*]

4   *a School of Agriculture and Food Sciences, The University of Queensland,*

5   *Brisbane, QLD 4072, Australia*

6   *b School of Agricultural Engineering and Food Science, Shandong University of Technology,*

7   *Zhang Zhou Road, Zibo, Shandong Province 255049, PR China*

8   c Food Science & Technology Program, School of Public Health, Curtin Health Innovation Research

9   Institute, International Institute of Agri-Food Security, Curtin University, Bentley, Western Australia,

10   6102, Australia

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12   **Abstract**

13   The efficiency of carrier agents of whey protein isolate (WPI) and maltodextrin (MD)

14   alone or with a combination on spray drying of honey was evaluated. No powder was

15   recovered when pure honey was spray dried. Honey powders were successfully obtained

16   (powder recovery>50%) by adding MD and WPI alone with Honey: MD = 40: 60or

17   Honey: WPI = 70: 30, respectively. The combination of WPI and MD as carrier agents

18   worked effectively for spray drying of honey. Powder recovery increased from 0 (Honey:

19   MD: WPI = 60: 40: 0) to 57.35±4.71% when MD was replaced by 0.5% WPI (Honey:

20   MD: WPI = 60: 39.5: 0.5). The mechanism of WPI on spray drying of honey is

*Corresponding author at: School of Agriculture and Food Sciences, The University of Queensland,

Brisbane, QLD 4072, Australia. Tel.: +61 7 33469192; Fax: +61 7 33651177.

E-mail address: b.bhandari@uq.edu.au(B.Bhandari); shiqilong2006@hotmail.com(Q.Shi).

1 attributed to the preferential migration of protein to the droplet/air interface together

2 with their excellent skin-forming properties upon drying. Powders moisture content,

3 water activity, hygroscopicity and colour parameters were negligibly influenced by

4 different carriers. Bulk density and particle size were positively affected by MD

5 concentration, which might be related to agglomeration process of particles.

6 *Keywords:* Honey; Spray drying; Physicochemical properties; Whey protein isolate;

7 Maltodextrin

1. Introduction

Honey in its liquid and natural state presents significant handling problems in mass production operations and consumption because of its viscosity and stickiness (Cui et al., 2008). The highly viscous sugar solution in honey is often supersaturated and susceptible of time dependent crystallization. The disadvantages of crystallization include: 1) difficulty in handling and pouring, 2) consumers' dislike because of changed appearance and homogeneity loss as a result of the formation and coexistence of two phases-crystalline and liquid, 3) water activity (a_w) increase up to levels which may be congruous with microbial fermentative processes (Tosi et al., 2004; Venir et al., 2010). Conversion of liquid honey into a solid state will potentially increase the stability of the product. Furthermore, honey powder can be easily blended with other dry ingredients or it can be directly added to seasonings or dry coatings. Other advantages of honey powder over the liquid form include easier transportation, decreased volume/weight, reduced storage space and reduced complexity of the cleaning operations (Samborska and Czelejewska, 2012).

Spray drying is a well-established and widely used method for transforming a wide range of liquid food products into powder form (Jayasundera et al., 2011a). However, conversion of liquid honey into powder form by spray drying may have the problems of stickiness and high hygroscopicity, which mainly due to the presence of a high proportion of low molecular weight sugars in honey (Adhikari et al., 2007). The sticky problem leads to considerable economic loss and operating problems during drying, and thereby, limits the application of spray drying for food and pharmaceutical

materials (Maa et al., 1998; Boonyai et al., 2004). The problem of the stickness of sugars has been related to their low glass transition temperature (T_g) of a given amorphous material (Roos, 1996). Honey contains high proportion (how much, %, references..) of inherent low molecular weight sugars, namely fructose and glucose, with the T_g of 16 $^{\circ}$C and 31 $^{\circ}$C, respectively. The quantifiable sticky behavior of an amorphous product is observed at temperatures about 10–20 $^{\circ}$C above T_g (Roos and Karel, 1991; Bhandari et al., 1997). Therefore, stickness is liable to occur for spray dried honey owing to the drying air outlet temperature (normally ranges from 60 to 100 $^{\circ}$C) are higher than 40-50 $^{\circ}$C (T_g of fructose and glucose +20 $^{\circ}$C) of the amorphous honey powder.

Both process based (e.g. the mechanical scraping of the drying chamber wall; introduction of cold air at the bottom and the use of low temperature/low humidity air) and material science based approaches (e.g. the adding of drying aids such as maltodextrin, gum arabic and starch into feed solution) have been proposed to minimize the sticky problem (Jayasundera et al., 2011 a, b, c). However, some drawbacks related to high cost and low product quality were also found in these 2 approaches (Jayasundera et al., 2011 a, b; Fang and Bhandari, 2012). Recently, an alternative and novel way to minimize the stickiness problem is to modify the surface properties of the droplets/particles with small amounts of proteins (Adhikari et al., 2009 a, b). The surface active property of proteins (i.e. preferential migration to the surface of droplets/particles) couple with their film–forming ability upon drying can overcome the stickiness of sugar solutions (Adhikari et al., 2009b). The effect of

addition of proteins on the spray drying efficiency have been reported for model sugar–rich foods (Adhikari et al., 2009 a, b; Jayasundera et al., 2010; Jayasundera et al., 2011 a, b, c; Fang, Wang, & Bhandari, 2013) and real sugar–rich food (Wang et al., 2011; Fang and Bhandari, 2012). However, based on the authors' knowledge, no data are available for spray drying of honey using protein alone or in combination with maltodextrin (MD) as drying aids. Therefore, the objectives of the present study were (1) to assess the effectiveness of different drying aids consisting of whey protein isolate (WPI) alone or in combination with MD (DE=10) at various ratios during spray drying of honey; (2) to reveal the mechanism of WPI on spray drying of honey by analysis of surface tension of feed solution, surface protein concentration and T_g of honey powders; and (3) to characterize the physicochemical properties of spray dried honey powder by analysis of the powder recovery, moisture content, water activity, bulk density, particle size, hygroscopicity and colour parameters.

2. Materials and methods

2.1. Materials

Capilano Natural Australian honey (Capilano Honey Ltd., Brisbane, Australia) was purchased from Coles, Toowong in Brisbane. The physical and chemical properties of honey were analysed and indicated as follows: pH 3.67±0.02, specific gravity 1.440±0.006, total soluble solid (TSS) 80.2±0.12^o Brix, viscosity 14333±329 cP, colour parameters of L^* 56.89±1.07, a^* –1.50±0.11, b^* 24.73±0.92, moisture content (MC) 16.49±0.21% and sugar content (by HPLC method) with fructose 47.037±1.122 g/100g, glucose 31.783±1.193 g/100g and sucrose 1.253±0.118 g/100g.

Whey protein isolate (WPI) with a protein content and MC of 92.56±1.20% and 6.21±0.09%, respectively was purchased from Muscle Brand Pty Ltd (Petersham, NSW, Australia). Maltodextrin (MD, DE=10) with MC of 6.07±0.51% was purchased from Penford Australia Ltd (Lane cove, NSW, Australia). The WPI and MD were used as received. Distilled water was used for preparation of aqueous dispersions to be spray dried.

2.2. Spray drying

The feed solutions were prepared by heating the solution at 45±5 $^{\circ}$C and gently agitating with a magnetic stirrer and maintained at this temperature throughout the spray drying process. From the preliminary experiment, the TSS content of all prepared feed solutions for spray drying was fixed at 10g/100g and 300 g of solution was spray dried for each run. The ratio of honey TSS to MD and WPI based on the dry mass is shown in Table 1. The experiments were carried out in a Büchi B–290 mini spray dryer (Büchi Labortechnik AG, Switzerland) at drying air inlet and outlet temperatures of 150±1°C and 85±1°C, respectively. The air flow rate was maintained at 36m^3/h with the aspirator rate of 100% and nozzle cleanness of 6 times/min. After each spray drying process, the honey powders were collected from the cyclone into a pre-weighed polystyrene (PS) collection bottle and immediately sealed and stored in a desiccator containing excess silica gel to prevent subsequent moisture uptake. The spray drying processes were all performed in triplicate.

2.3 Analytical methods

Feed solutions were analysed for viscosity and surface tension (ST). Spray dried

honey powders were analysed for powder recovery (R_P), moisture content (MC), water activity (a_w), bulk densdity (D_B), particle size, colour parameters, hygroscopicity (HYG), glass transition temperature (T_g) and Electron spectroscopy for chemical analysis (ESCA). All analytical measurements were carried out in triplicate and the results were expressed as means ± standard deviations.

2.3.1. Viscosity and Surface tension (ST)

Viscosity of solution gives information regarding the resistance offered by liquid/solution molecules to the motion and is a factor influencing stickiness. A Viscometer (DV–ΙΙ$^+$, Brookfield Engineering Laboratories. Ins., Stoughton, MA, USA) was used to determine the viscosity of the feed solutions.

Surface tension (ST) indicates how strongly the surface molecules of a liquid/solution are attracted by the adjacent molecules and the tendency of molecules to move preferentially to the air–droplet interface (Adhikari et al., 2007; Jayasundera et al., 2010). ST measurements of the feed solutions before spray drying were determined using a ST9000 surface tensionmeter (Nima Technology Ltd., Coventry, UK). The tensionmeter was calibrated with a standard weight of 100 mg and the surface tension of distilled water was determined as 71.83±0.92 mN/m. The STs of the sample solutions were recorded on a connected computer running the measuring software. The analysis was repeated 6 times for each sample.

2.3.2. Powder recovery (R_P)

The Powder recovery (R_P) was calculated as the ratio of the mass of solids collected after spray drying to the mass in the feed solution on a dry basis

(Jayasundera et al., 2010).

2.3.3. Moisture content (MC)

The Moisture content (MC) was determined gravimetrically by drying the powder samples in a vacuum oven (Thermoline Scientific, Australia) at 70 $^{\circ}$C and –0.090 MPa until constant weigh were obtained (AOAC, 2000).

2.3.4. Water activity (a_w)

An AquaLab 3TE Series water activity meter (Decagon Devices, Inc., Pullman, USA) was used to measure the a_w of the spray dried honey powder. The temperature was maintained at 24.5 ± 0.5 $^{\circ}$C during the measurement.

2.3.5. Bulk density (D_B)

The bulk density (g/mL) of the powders was determined by gently adding 2 g of honey powder into an empty 10 mL graduated cylinder and holding the cylinder on a vortex vibrator for 2min. The bulk density (D_B) was calculated by dividing the mass of the powder by the volume occupied in the cylinder (Goula and Adamopoulos, 2004).

2.3.6. Particles size

The particle size was measured using a Malvern Laser Diffraction Particle size analyser (Mastersizer 2000, Malvern Instruments, Malvern, UK). A small amount of powder sample was suspended in sunflower oil (refractive index 1.465) (O'Brien, 2009) under magnetic agitation. The powder samples in oil were subjected to sonication for better dispersion of the powders and the particle size distribution was monitored during each measurement until successive readings became constant. The

particle size was expressed as the mean volumetric size (De Brouckere mean diameter, $D_{[4,3]}$,), which represents the mean diameter of a sphere with the same volume and is commonly used to characterize a particle size.

2.3.7. Colour characteristics

The color characteristics parameters (*L*, *a* and *b*) of spray dried honey powders were measured quantitatively by a CR–400 Chroma meter (Konica Minolta Sensing Inc., Tokyo, Japan). The Chroma meter was calibrated with a white standard plate before actual colour measurement. In this system, *L* indicates lightness; +*a* value indicates redness and –*a* to greenness; +*b* values indicates yellow and –b to blueness.

2.3.8. Hygroscopicity (HYG)

Hygroscopicity (HYG) was determined by adapting the method proposed by Tonnon et al. (2008). Powder samples (approximately 1 g) were placed in plastic vials, accurately weighed and placed in desiccators at 25 $^{\circ}$C and equilibrated over saturated solution of NaCl with relative humidity (RH) of 75.3%. The samples were weighed periodically during 7 days equilibration process and the HYG was expressed as g of adsorbed moisture per 100g of dry solids (g /100 g).

2.3.9. Glass transition temperature (T_g)

The glass transition temperature (T_g) of the powders and liquid honey was measured with a Mettler–Toledo differential scanning calorimeter (mode DSC1, Mettler–Toledo, USA). The instrument was calibrated for heat flow and temperature using indium (melting point 156.6±0.3 $^{\circ}$C, ΔHm=28.45±0.6 J/g). The purge gas used was dry nitrogen (25 mL/min). The transfer of samples from the desiccators to the

DSC pan was done in a sealed 'dry box' containing excess silica gel to avoid unwanted moisture absorption by the sample (Shrestha et al., 2007). Samples of about 10 mg were enclosed in hermetically sealed aluminum pans just before analysis and then loaded onto the equipment at room temperature. An empty aluminum pan was used as reference.

For the powder samples, DSC scanning program are as follows: (1) cooling from 25 ℃ to –40 ℃ at 10/min; (2) isothermal at –40 ℃ for 5min; (3) heating from –40 ℃ to 90 ℃ at 10/min; (4) isothermal at 90 ℃ for 5min; (5) cooling from 90 ℃ to –40 ℃ at 10/min; (6) isothermal at –40 ℃ for 5min; and (7) heating from –40 ℃ to 160 ℃ (200 ℃ for single WPI and MD powders) at 10/min. A double scanning program of samples was used in this method to reduce the enthalpy relaxation of the amorphous samples which appears in the first scan, thereby enhancing the accuracy of T_g measurement on DSC thermogram (Telis and Sobral, 2001; Shrestha et al., 2007; Shi et al. 2012). For the liquid honey, annealing procedure is required to identify clear and accurate glass transition ranges, achieve maximum-freeze-concentration conditions and avoid exothermic crystallization peaks (Sablani et al., 2010) and DSC scanning program were as follows: (1) cooling from 25 ℃ to –120 ℃ at 10/min; (2) isothermal at –120 ℃ for 5min; (3) heating from –120 ℃ to –35 ℃ at 10/min; (4) isothermal at –35 ℃ for 30min; (5) cooling from –35 ℃ to –120 ℃ at 10/min; (6) isothermal at –120 ℃ for 5min; (7) heating from –120 ℃ to 100 ℃ at 10/min. All analyses were carried out in triplicate and each thermogram was analyzed for the onset, mid and end of transition temperature using STARe evaluation software (Mettler–Toledo). The

midpoint of the glass transition (T_{gm}) was considered as the characteristics temperature of the transition.

2.3.10. Electron spectroscopy for chemical analysis (ESCA)

The electron spectroscopy for chemical analysis (ESCA) measurements were carried out to determine the surface elemental composition of the spray dried honey powder with the addition of WPI and MD. This technique was aimed to measure the relative atomic concentration of carbon, nitrogen and oxygen in the surface layer of the samples (depth of less than 100 Å). Firstly, ESCA measurements for WPI, MD and freeze–dried pure honey were performed to determine the surface composition of these materials. Secondly, the surface elemental composition of all spray dried powders was determined. The samples were degassed under vacuum for 72 h before subjecting them to ESCA. The ESCA analysis was performed on a Kratos AXIS Ultra photoelectron spectrometer (Kratos Analytical Ltd, Manchester, UK) with a 150W monochromatic A1 X–ray source, and the procedure was reported elsewhere (Shrestha et al., 2007; Adhikari et al., 2009b). A matrix inversion method based on the ESCA data was employed to determine the protein coverage of the samples (Fäldt et al., 1993; Shrestha et al., 2007; Adhikari et al., 2009b).

2.4. Statistical analysis

The analysis of variance (ANOVA) were performed and the least significant difference at $p<0.05$ was calculated using the Duncan Multiple Range Test on Origin statistical software (Version 7.5, company information).

3. Results and discussion

3.1. Viscosity and Surface tension (ST) of feed solution

The viscosity of feed solutions containing different ratio of honey, MD and WPI varied from 6.00 to 8.00cP (data not presented), and no significant differences ($p>0.05$) were observed among them. The low concentration of feed solution (10%) might be the reason for very little variation of viscosity.

Fig. 1 displays the ST values of feed solutions with different ratio of honey, MD and WPI. The ST of honey solutions with the TSS ratio of Honey: MD: WPI of 40: 60: 0 and 60: 40: 0 were 52.04±0.55 and 51.84±0.39 mN/m, respectively. However, ST of feed solution with Honey: MD: WPI = 60: 40: 0 significantly ($p<0.05$) decreased from 51.84 to 49.18 and 48.50 mN/m when MD was replaced by 0.10% and 0.25% of WPI, respectively (data not presented). The ST further decreased to 47.70±0.48 mN/m as the WPI ratio increased to 0.5%. However, no significant differences ($p>0.05$) were found for the ST values when the WPI ratio kept on increasing to 1.0–40% (Fig. 1). Since sugars are not surface active, the addition of MD at any ratio showed no influence ($p>0.05$) on the surface tension of the feed solution. The is in agreement with the results of Fang and Bhandari (2012), who found that addition of MD at any ratio showed no influence on the ST of the bayberry juice. Proteins, on the contrary, are surface active ingredients, which preferentially migrate to the air/water interface, and lower the ST of the solutions (Adhikari et al., 2009b). The results also suggested that there might be a saturated state (for example 1.0–2.5%) of proteins on the air/liquid interface of honey solutions, so that the ST remained almost constant when the protein ratio was further going up. Similar results were reported by Fang and

Bhandari (2012) for the ST of the bayberry juice with the addition of proteins.

3.2. Powder recovery (R_P)

The spray dried honey powders were collected from the product collection vessel only, which were used for the calculation of R_P. Particles deposited on the dryer chamber and connection pieces (i.e. between the dryer chamber and cyclone) were discarded to avoid unnecessary calculation errors (Fang and Bhandari, 2012). The pure WPI and MD were also spray dried as controls, and their R_Ps were $72.0\pm2.1\%$ and $71.3\pm1.8\%$, respectively.

Preliminary experiments were carried out to determine the suitable TSS ratio of honey to MD and WPI alone as a carrier to accomplish a marginally successful spray drying according to the criteria of 50% R_P proposed by Bhandari et al. (1997). The spray drying of pure honey at a feed concentration of 10% was also carried out, but all the honey solids were sticky on the dryer wall and no powder was recovered in the collection vessel. When 60% of the honey TSS was replaced by MD, the R_P increased to $51.4\pm4.2\%$, which can be regarded as a successful spray drying. However, when at least 30% of the honey TSS was replaced by WPI, a successful spray drying can be obtained with the R_P of $62.2\pm3.5\%$. A similar result was also reported by Jayasundera et al. (2011b) who found that when 30% fructose was replaced by sodium caseinate (NaCas) the total (cyclone + sweep) fructose? recovery rose to $81.5\pm2.0\%$. However, different results were reported by Fang and Bhandari (2012) that a small amount of protein (1%) was efficient to spray dry the bayberry juice. The variation was assumed to the differences in sugar compositions in different spray drying materials.

Furthermore, preliminary experiments were also carried out when 30% of the honey TSS was replaced by different ratio of MD and WPI, namely, Honey: MD: WPI of 70:10:20, 70:20:10, 70:25:5, 70:25.5:2.5, 70:29:1 using the same spray drying conditions described in Section 2.2. The results showed that no powder was recovered for all the treatments except Honey: MD: WPI = 70: 10: 20, with the R_P of 57.3%.

The R_P significantly increased ($p<0.05$) to 75.78±2.36% when 40% of the honey TSS was replaced by WPI. When 40% of the honey TSS was replaced by different ratio of MD and WPI, the R_P varied from 57.35±4.71% to 75.78±2.36% (Table 1). When 40% of honey TSS was replaced by MD only (Honey: MD: WPI = 60: 40: 0), no powder was recovered in the collection vessel. However, When 0.1%, 0.25% and 0.5% of MD was replaced by WPI, the R_P increased to 7.60±2.34%, 47.60±3.25% and 57.35±4.71%, respectively. The R_P increased significantly ($p<0.05$) when 2.5% of MD was replaced by WPI comparing with that of 0.5%. However, when increasing the protein ratio to 2.5–30%, although the R_P further increased, but no significant differences ($p>0.05$) were observed (Table 1). The greatly enhanced powder recovery with addition of small amount of WPI could be related to the lower ST of protein added to honey solution. During spray drying, once the feed solution is atomized into the drying chamber as droplets, the adhesion property (stickiness) between the particles and the drying chamber wall is of vital importance. If the droplet surface was mainly occupied by low molecular sugars, a greater adhesive bond between the drying droplets and the wall surface will be formed, which results in a particle deposit on the wall (Bhandari and Howes, 2005). However, when proteins (WPI in present study) are

introduced into the feed solution, proteins preferentially migrate to the air–water interface of sugar solutions and form a protein–rich film. This film is converted into a glassy skin when it is encountered with hot and dry air. The resultant glassy skin is capable of overcoming the coalescence of droplets as well as sticky interactions of the particles at the drying chamber of the spray dryer (Adhikari et al., 2007). Therefore, the remarkable increase in recovery from a small addition of protein is attributed to the combination of surface-active properties of proteins (i.e. preferential migration to the droplet/air interface) along with their excellent skin-forming properties upon drying, allows for the stickiness of the honey-protein solutions to be overcome (Wang et al., 2011; Fang and Bhandari, 2012).

3.3. Moisture content (MC) and water activity (a_w)

The MC and a_w of the spray dried powders were measured immediately after sample collection. The MC ranged from 3.10±0.48% to 5.04±0.93% and a_w ranged from 0.173±0.002 to 0.264±0.048 (Table 1). These values fall within the commonly observed moisture and aw values in industrial spray drying (Masters, 1991).

Generally, MC of powders decreased with decreasing WPI concentration or increasing MD concentration in the feed solution. The honey powder produced with TSS ratio of Honey: MD: WPI of 60: 0: 40 exhibited a higher ($p<0.05$) MC than the powders produced with Honey: MD: WPI of 60:39:1, 60:39.5:0.5 and 40:60:0. However, no significant differences ($p>0.05$) were observed between the powders produced with Honey: MD: WPI ranged from 60:0:40 to 60:37.5:2.5 and from 60:10:30 to 60:39.5:0.5. Protein (including WPI) has a strong ability to bind water

(reference?). Moreover, MD, due to its high molecular weight, is less hygroscopic. Consequently, the hygroscopicity of the final powder is reduced, resulting in lower powder MC. Similar behavior were observed when spray dried pineapple juice (Abadio et al., 2004), sweet potato puree (Grabowski et al. 2006), and gac fruit aril (Kha et al., 2010) with the addition of MD.

Water activity measures the available free water in food that is responsible for biochemical reactions and is an important index to determine microbial stability of food. All the spray dried honey samples showed a_w below 0.30 (Table 1), which is benefit to the powder stability, because the low aw values represent less free water available for microorganism growing and biochemical reactions and therefore, longer shelf life (Fennema,1996). According to Table 1, the a_w of honey powder produced with Honey: MD: WPI = 40:60:0 showed a higher ($p<0.05$) a_w than the powders produced with other ratios. However, no significant differences ($p>0.05$) were found between the powders produced with Honey: MD: WPI of 70: 0: 30 and from 60: 0: 40 to 60: 39.5: 0.5.

3.4. Bulk density (D_B)

Knowledge of D_B is of fundamental importance to the studies of the properties of materials and industrial processes, relevant to the storage, processing, packaging and distribution conditions. The D_B is the mass of the solid particles including moisture, divided by the total volume occupied by the particles, surface moisture, and all the pores, closed or open to the surrounding atmosphere, and is generally used to characterize the final product obtained by milling or drying (Barbosa-Cánovas and

Juliano, 2005).

The D_B of the spray dried powders was significantly ($p<0.05$) affected by the compositions of feed solution. An increase in MD ratio in the feed concentration from 0 to 39.5% (TSS), namely a decrease in WPI ratio in the feed concentration from 40 to 0.5% (TSS) led to an increase in powder D_B from 0.318 to 0.513 g/mL (Table 1). The honey powders produced with TSS ratio of Honey: MD: WPI ranged from 60:3 9.5: 0.5 to 60: 37.5: 2.5 exhibited higher ($p<0.05$) D_B than the powders produced with Honey: MD: WPI of 70: 0: 30 and from 60:0:40 to 60:35:5. However, no significant differences ($p>0.05$) were observed between the powders produced with Honey: MD: WPI of 70: 0: 30 and from 60: 0: 40 to 60: 30: 10; 40: 60: 0, 60: 35: 5, 60: 30: 10 and 60: 20: 20; 40: 60: 0 and from 60: 37.5: 2.5 to 60: 39.5: 0.5, respectively. The D_B of powders is affected by chemical composition, particle size and moisture content as well as by processing and storage conditions (Beristain et al., 2001). D_B increased with increasing MD ratio in the feed concentration, which might be related to their high degree of agglomeration and structural collapse which could result in subsequent decrease in volume of the powder particles (Fuchs et al., 2006). Furthermore, higher D_B is associated with lower MC, as particles with higher MC can result in non-completely dry agglomerates, which are larger than the particles, leading to a lower D_B (Goula et al. 2004).

3.5. Particle size

Particle size is one of the most important physical parameters of powders. The flow out of storage bins, the blending of different components and compaction and

segregation of a mixture could be affected by the powder particle size. Moreover, the essential properties of food products, such as aroma, texture and appearance are all significantly influenced by powders' particle size (O'Hagan et al., 2005).

The volumetric mean diameter $D_{[4,3]}$ of the spray dried powders was significantly ($p<0.05$) affected by the compositions of feed solution. An increase in MD ratio in feed concentration from 0 to 39.5% (TSS), namely an decrease in WPI ratio in the feed concentration from 40 to 0.5% (TSS) led to gradual increase in powder particle size from 16.46±0.98 to 66.84±1.52 um (Table 1). This phenomenon may relevant to the higher viscosity of the feed solutions. The viscosity of the feed solution increased with increasing MD concentration and therefore gave rise to large droplets at a constant atomizer speed (Tonon et al., 2008).

The honey powders produced with TSS ratio of Honey: MD: WPI of 60:39.5:0.5 presented bigger ($p<0.05$) particle size than the powders produced with Honey: MD: WPI of 70: 0: 30, 40: 60: 0, and from 60: 0: 40 to 60: 39: 1. Significant differences ($p<0.05$) were also observed between the powders produced with Honey: MD: WPI of 60: 39: 1, 40: 60: 0, 70: 0: 30 and from 60: 0: 40 to 60: 37.5: 2.5. However, no significant differences ($p>0.05$) were observed between the powders produced with Honey: MD: WPI of 70: 0: 30 and from 60: 0: 40 to 60: 30: 10. The increased tendency of powder particle size with increasing MD ratio in the feed solution might be attributed to a beginning of the agglomeration process, where the formation of irreversible link bridges leads to the production of particles with greater size (Tonon et al., 2008). Similar results were observed by Bae and Lee (2008) in spray drying of

avocado oil using WPI and MD as wall materials and Tonon et al. (2008) in spray drying of açai powder.

3.6. Hygroscopicity (HYG)

Honey powder is expected to be hygroscopic due to its high sugar (mainly fructose and glucose) content. Fig. 2 shows the HYG of the spray dried honey powders produced with different carriers agents. HYGs of honey powders increased sharply from 10.82 to $14.15 g_{H2O}/100g$ sample after 18h equilibration process at 25^oC and 75.3% RH, which implies easier moisture adsorption of honey powders. HYGs of honey powders kept increasing and HYG values ranged from 20.13 to 25.29 $g_{H2O}/100g$ sample after 168h storage at $25 \, ^{\circ}C$ and 75.3% RH. Tonon et al. (2008) evaluated the hygroscopicity of spray dried açai powder at the same conditions of the present work, with HYG range of 12.48–15.79g absorbed water/100g powder, which is much lower than those of the honey powders obtained in this work. The difference might attribute to the different sugar composition of honey and açai powder.

The powder produced with TSS ratio of Honey: MD: WPI = 40: 60: 0 exhibited a lower ($p<0.05$) HYG value than the powders produced with other ratios. Generally, decreases in WPI concentration, namely increases in MD concentration gave rise to a higher HYG of the powders. However, no significant differences ($p>0.05$) were found among the samples. On the one hand, the phenomenon of moisture adsorption by a carbohydrate is attributed to the links between the hydrogen present in water molecules and the hydroxyl groups available in the amorphous regions of the substrate, as well as in the surface of crystalline regions (Tonon et al., 2011).

Incorporating MD can modify the balance of hydrophilic/hydrophobic sites of the powder particles and decrease the amount of absorbed water (Pérez-Alonso et al., 2006). MD (DE=10) is less hydrolyzed, showing less hydrophilic groups and thus, adsorbing less water. On the other hand, the lower the particles MC, the higher their HYG, i.e., the greater their capacity to adsorb ambient water, which is related to the greater water concentration gradient between the product and the surrounding air (Tonon et al., 2008; Goula et al., 2004). Therefore, the HYGs of honey powders produced with different carrier agents are in a reasonable range.

3.7. Colour characteristics

The colour parameters of the powders are shown in Table 2. L^*, a^* and b^* ranged from 65.11±0.66 to 70.29±3.72, from –0.17±0.10 to 0.08±0.07 and from 3.03±0.39 to 5.13±0.98, respectively. The honey powder produced with TSS ratio of Honey: MD: WPI = 40: 60: 0 displayed a higher ($p<0.05$) L^* value than the powders produced with Honey: MD: WPI of 60:39:1 and from 60: 20: 20 to 60: 35: 5. However, no significant differences were observed between the powders produced with Honey: MD: WPI of 70: 0: 30, 40: 60: 0 and from 60: 0: 40 to 60: 39.5: 0.5 ($p>0.05$). The honey powder produced with TSS ratio of Honey: MD: WPI = 60: 35: 5 displayed higher ($p<0.05$) a^* than the powders produced with Honey: MD: WPI of 70: 0: 30, 40: 60: 0, 60: 39: 1, 60: 39.5: 0.5 and from 60: 0: 40 to 60: 20: 20. However, no significant differences ($p>0.05$) were observed between the powders produced with Honey: MD: WPI equaled 60: 35: 5, 60: 30: 10 and 60: 37.5: 2.5; 40: 60: 0, 70: 0: 30, 60: 39: 1, 60: 39.5: 0.5, and from 60: 0: 40 to 60: 20: 20; 60: 20: 20, 60: 30: 10 and

from 60: 37.5: 2.5 to 60: 39.5: 0.5. The honey powder produced with TSS ratio of Honey: MD: WPI = 60: 35: 5 displayed the lowest ($p<0.05$) b^*. However, no significant differences ($p>0.05$) were observed between the powders produced with Honey: MD: WPI of 60: 35: 5, 60: 30: 10 and 40: 60: 0; 60: 10: 30, 60: 20: 20, 60: 30: 10 and 40: 60: 0; 60: 37.5: 2.5 and from 60: 0: 40 to 60: 20: 20; 70: 0: 30, 60: 39: 1; 60: 39.5: 0.5 and 60: 39: 1.

3.8. Electron spectroscopy for chemical analysis (ESCA)

The surface elemental composition of the spray dried honey powders was estimated by ESCA. The elemental composition of oxygen, carbon and nitrogen at the surface of the honey-MD-WPI powders is presented in Table 3. The elemental compositions of spray dried MD and WPI powders and freeze dried pure honey powder (owing to powder cannot be obtained by spray drying alone) are given as references. The results indicated that 50.62±1.76% and 52.90±2.38% of the surface of the honey-MD-WPI particles were covered by protein (WPI) although the feed concentration of WPI were only 0.1% and 0.25% on a dry solid basis, respectively. As can be seen from Section 3.2, these levels of surface coverage increased the R_P from 0 to 7.60±2.34% and 47.60±3.25%, respectively. Increasing the feed concentration of WPI to 0.5% caused 53.06±3.15% of protein surface coverage and this gave rise to R_P of 57.35±4.71%. Further increasing in WPI ratio in feed concentration (TSS) from 1.0 to 40% resulted in gradually increase in protein surface coverage, which ranged from 53.02±3.73% to 71.48±1.60% (Table 3).

The protein surface coverage of the spray dried honey powder produced with TSS

ratio of Honey: MD: WPI = 60: 10: 30 was higher ($p<0.05$) than those of the powders produced with Honey: MD: WPI of 40: 60: 0, 70: 0: 30, and from 60: 35: 5 to 60: 39.5: 0.5. However, no significant differences ($p>0.05$) were observed between the powders produced with Honey: MD: WPI of 60: 39: 1 and 60: 39.5: 0.5; 70: 0: 30 and from 60: 37.5: 2.5 to 60: 20: 20; 60: 10: 30, 60: 0: 40, 60: 20: 20 and 60: 30: 10. The present results are in agreement with the proposal suggested by Shrestha et al. (2007) that there might be a rapid diffusion of protein toward the surface and that gets saturated very quickly, so that further increase in protein content does not increase the surface protein level, which was consistent with the results of surface tension measurements (Section 3.1).

3.9. Glass transition temperature (T_g)

The T_g of spray dried powders is a very important indicator to evaluate if a droplet or particle is likely to stick to the spray dryer wall. Generally, a practical rule is that if the droplet/particle temperature is 20 $^\circ$C above its T_g, it will be sticky (Bhandari et al., 1997). The T_g of liquid pure honey was -40.64 ± 1.58 $^\circ$C, which falls within the commonly reported ranges for Australian honeys (Sopade et al., 2002), Indian honey (Ahmed et al., 2007), Italian honey (Venir et al., 2010) and Spain honeys (Gómez-Díaz et al., 2012). The T_g of spray dried MD and WPI alone were were 148.46$\pm$5.31 $^\circ$C and 132.12$\pm$6.84 $^\circ$C, respectively . The T_g values of MD and WPI obtained in the present work were a little lower than those reported by Fang and Bhandari (2012). Probably, the different DSC scanning program or different moisture content of the MD and WPI being used (i.e. plasticization effect of water on the

amorphous constituents of matrix) could have contributed to the difference. The T_g of freeze dried pure honey was also analysed and the value was $18.00\pm1.45\,^\circ C$, which implies unstable nature of pure honey powder at ambient temperature, say $25\,^\circ C$, at which pure honey powder will experience glass transition phenomenon and present in the rubbery state.

The T_g of the spray dried powders was significantly ($p<0.05$) affected by the compositions of feed solution. An increase in MD ratio in feed concentration from 0 to 39.5% (TSS), namely an decrease in WPI ratio in the feed concentration from 40 to 0.5% (TSS) led to gradual increase in powder T_g from $47.54\pm1.35\,^\circ C$ to $76.69\pm2.53\,^\circ C$ (Table 4). The honey powder produced with TSS ratio of Honey: MD: WPI = 40: 60: 0 exhibited a higher ($p<0.05$) T_g value than the powders produced with other ratios. Moreover, significant differences ($p<0.05$) were observed between the powders produced with Honey: MD: WPI of 60: 39.5: 0.5, 60: 37.5: 2.5, 60: 0: 40 and from 60: 35: 5 to 60:10: 30. However, no significant differences ($p>0.05$) were observed between the powders produced with Honey: MD: WPI of 60: 0: 40 and 60: 10: 30; 60: 39: 1, 60: 37.5: 2.5 and 60: 39.5: 0.5. The T_g of honey powders produced with Honey: MD: WPI of 70: 0: 30, 60: 0: 40 and 60: 10: 30 was $49.84\pm1.99\,^\circ C$, $47.54\pm1.35\,^\circ C$ and $49.96\pm1.67\,^\circ C$, respectively, and no significant differences ($p<0.05$) were obtained among them, suggesting that the dominating protein added honey powders have similar T_g values. Similar T_g value ($53.43\pm1.18\,^o C$) of spray dried model sugar-rich food (Fructose: NaCas = 70: 30) was reported by Jayasundera et al. (2011b). Haque and Roos (2006) and Shrestha et al. (2007) observed that the sugar–protein systems

are not compatible and that the measured T_g mainly reflects the T_g of the sugar in the system. The honey powder produced with Honey-WPI systems with such low T_gs should easily to be sticky during spray drying according to the practical rule proposed by Bhandari et al. (1997). However, the earlier results (ST and ESCA data) indicated that the surface of the protein added honey particle was mainly (exceed 60%) covered by WPI, and its T_g is $132.12\pm6.84\ ^\circ$C. Although the DSC method in this work is unable to determine the T_g of the surface component (T_g surface), it was reasonable to deduce that the T_g surface of the protein-honey powders is much higher than their corresponding bulk T_g values, which can keep the safe glassy state and resist the heat stress during the drying process. Therefore, the honey solution can have an efficient spray drying performance with more than 50% of powder recovery, even if a small amount of protein (for example 0.5%) was employed (Table 1). On the other hand, the T_g of dominating maltodextrin added honey powders was totally different to those of the protein added samples. The T_g values of honey powders increased with the increasing of MD concentration. MD has a high T_g value ($148.46\pm5.31\ ^\circ$C). Meanwhile, MD is not a surface active material in solutions. MD forms a compatible matrix at the molecular level with the honey solid materials to increase the overall T_g of the honey powders, and therefore, to overcome the stickiness problem during spray drying (Fang and Bhandari, 2012).

4. Conclusion

Conversion of liquid honey into powder form by spray drying is difficult because the problems of stickiness and high hygroscopicity of low molecular weight sugars

(fructose and glucose) in honey. The effectiveness of whey protein isolate (WPI) and maltodextrin (MD) alone or with combination on spray drying of honey were evaluated. No powder was recovered when pure honey was spray dried. Powders were successfully achieved (powder recovery>50%) by adding MD and WPI alone with Honey: MD of 40: 60 or Honey: WPI of 70: 30, respectively. The combination of WPI and MD as carrier agents worked effectively for spray drying of honey. Powder recovery increased from 0 to 57.35±4.71% for Honey: MD: WPI = 60: 40: 0 when MD was replaced by 0.5% WPI. The remarkable increase in recovery from a small amount addition of protein is attributed to the combination of surface active properties of proteins (i.e. preferential migration to the droplet/air interface) along with their excellent skin forming properties upon drying, allows for the stickiness of the honey-protein solutions to be overcome. The amount of protein required for successful spray drying of honey-protein solutions depends on the amount of proteins present not on the bulk concentration, but on the droplet surface. However, the mechanism of MD to decrease the stickiness is due to the increase in the overall T_g of the honey powders. Powders moisture content, water activity and colour parameters were negligibly influenced by different carriers. Bulk density and particle size were positively affected by MD concentration, which might be related to agglomeration process and structural collapse together with lower moisture content of particles. Powders with lower moisture content were more hygroscopic, which is related to the greater water concentration gradient between the product and surrounding air.

Acknowledgments

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Figure captions:

Fig.1 Effect of whey protein isolate (WPI) addition on the surface tension of honey solution.

Fig 2. Effect of maltodextrin (MD) and whey protein isolate (WPI) addition on the hygroscopicity

of honey powders.

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Fig 2. Effect of maltodextrin (MD) and whey protein isolate (WPI) addition on the hygroscopicity
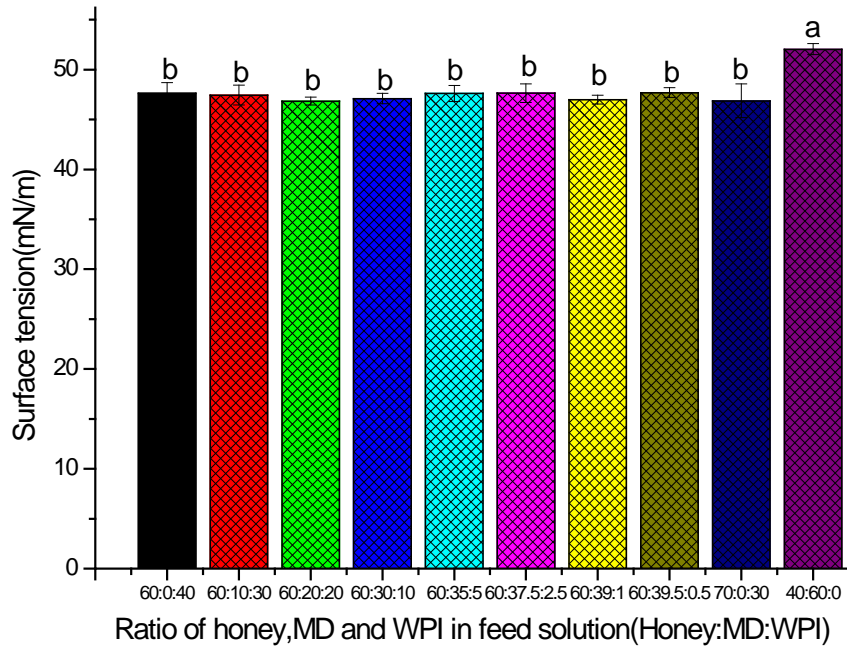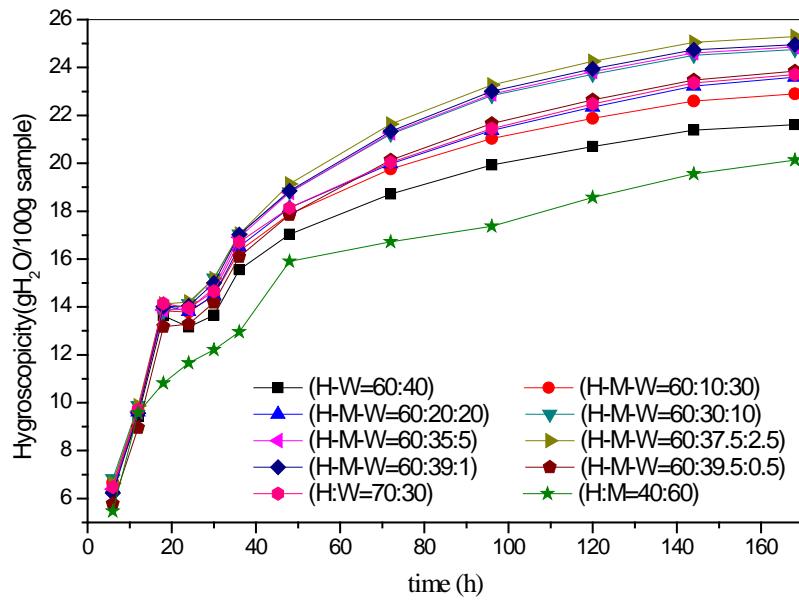
of honey powders.

Table captionss:

Table 1 Powder recovery, moisture content, water activity, bulk density and particle size of spray dried honey powder.

Table 2 Colour parameters of spray dried honey powder.

Table 3 Surface composition of reference samples and spray dried powders of honey-maltodextrin-whey protein isolate (WPI) powders.

Table 4 Glass transition temperature (initial point T_{gi}, mid point T_{gm} and end point T_{ge}) of spray dried honey powders.

Table 1

Powder recovery, moisture content, water activity, bulk density and particle size of spray dried honey powder [b].

Ratio of sample (d.b.)	R_P/%	MC/%	a_w	D_B (g/mL)	$D_{[4,3]}$ (um)
[a] H:M:W=60:0:40	[c] 75.78±2.36a	5.04±0.93[a]	0.200±0.020[b]	0.318±0.031[e]	16.67±0.62[fg]
H:M:W=60:10:30	72.73±2.43abc	4.46±0.41[ab]	0.181±0.002[b]	0.348±0.038[de]	16.46±0.98[g]
H:M:W=60:20:20	72.75±2.14abc	4.38±0.47[ab]	0.189±0.009[b]	0.378±0.059[cde]	17.43±0.72[fg]
H:M:W=60:30:10	72.15±0.86abc	3.88±0.24[ab]	0.180±0.022[b]	0.410±0.036[bcd]	18.80±1.90[f]
H:M:W=60:35:5	69.25±4.55bc	4.26±0.44[ab]	0.185±0.018[b]	0.434±0.044[bc]	22.75±0.93[e]
H:M:W=60:37.5:2.5	67.43±5.26cd	3.51±0.67[ab]	0.173±0.002[b]	0.506±0.039[a]	38.14±1.73[d]
H:M:W=60:39:1	62.23±4.55de	3.56±0.65[b]	0.175±0.005[b]	0.522±0.047[a]	45.85±1.86[b]
H:M:W=60:39.5:0.5	57.35±4.71ef	3.41±0.28[b]	0.174±0.012[b]	0.513±0.025[a]	66.84±1.52[a]
H:M:W=70:0:30	63.48±2.40d	4.48±0.93[ab]	0.179±0.015[b]	0.362±0.042[de]	17.11±0.77[fg]
H:M:W=40:60:0	52.75±3.29f	3.10±0.48[b]	0.264±0.048[a]	0.470±0.036[ab]	41.77±0.81[c]

[a] H, honey; M, maltodextrin; WPI, whey protein isolate.

[b] Values represent means±standard deviations (n=3).

[c] Different letters in the same column indicate that the samples are significantly different ($p<0.05$).

Table 2

Colour parameters of spray dried honey powder.

Ratio of sample (d.b.)	L^*	a^*	b^*
H:M:W=60:0:40*	68.57±2.20[ab]	-0.17±0.05[d]	4.20±0.51[bcd]
H:M:W=60:10:30	67.55±2.18[ab]	-0.10±0.04[cd]	3.69±0.25[de]
H:M:W=60:20:20	66.39±2.58[b]	-0.07±0.05[bcd]	3.66±0.31[de]
H:M:W=60:30:10	66.01±1.24[b]	0.03±0.07[ab]	3.08±0.17[ef]
H:M:W=60:35:5	65.11±0.66[b]	0.08±0.07[a]	3.03±0.39[f]
H:M:W=60:37.5:2.5	67.22±2.87[ab]	0.00±0.09[abc]	3.92±0.77[cd]
H:M:W=60:39:1	65.97±2.08[b]	-0.02±0.10[bcd]	4.63±0.23[ab]
H:M:W=60:39.5:0.5	67.07±0.14[ab]	-0.06±0.08[bcd]	5.13±0.98[a]
H:M:W=70:0:30	67.67±1.55[ab]	-0.17±0.10[d]	4.43±0.12[bc]
H:M:W=40:60:0	70.29±3.72[a]	-0.08±0.07[cd]	3.27±0.08[ef]

Honey as H, maltodextrin as M and WPI as W.

Values represent means±standard deviations (n=3).

Different letters indicate that the samples are considered significantly different at the 5% level ($p<0.05$).

Table 3

Surface composition of reference samples and spray dried powders of honey-maltodextrin-whey protein isolate (WPI) powders.

Ratio of sample (d.b.)	Oxygen(%)	Carbon(%)	Nitrogen(%)	Protein on surface(%)
Maltodextrin (MD)	39.11	60.52	0.37	
Whey protien isolate (WPI)	17.14	68.03	14.83	
Freeze dried pure honey	43.03	55.88	1.09	
H:M:W=60:0:40	24.34 ± 1.01^a	64.86 ± 1.74^a	10.80 ± 0.74^a	71.08 ± 3.02^{ab}
H:M:W=60:10:30	25.77 ± 0.17^a	63.09 ± 0.47^a	11.14 ± 0.32^a	71.48 ± 1.60^a
H:M:W=60:20:20	24.53 ± 0.87^a	64.91 ± 0.83^a	10.57 ± 0.25^a	69.61 ± 0.47^{abc}
H:M:W=60:30:10	24.93 ± 0.42^a	64.50 ± 0.57^a	10.47 ± 0.07^a	68.85 ± 0.60^{abcd}
H:M:W=60:35:5	25.84 ± 1.05^a	63.87 ± 1.24^a	10.34 ± 0.30^a	66.87 ± 0.04^{bcd}
H:M:W=60:37.5:2.5	26.99 ± 0.70^a	62.90 ± 1.08^a	10.11 ± 0.44^a	64.72 ± 1.89^d
H:M:W=60:39:1	27.17 ± 3.44^a	64.84 ± 4.35^a	7.98 ± 1.07^b	53.02 ± 3.73^e
H:M:W=60:39.5:0.5	26.64 ± 3.09^a	64.44 ± 4.18^a	7.93 ± 1.00^b	53.06 ± 3.15^e
H:M:W=70:0:30	23.96 ± 1.64^a	66.16 ± 2.04^a	9.88 ± 0.40^a	66.45 ± 0.53^{cd}
H:M:W=40:60:0	27.24 ± 6.70^a	69.42 ± 8.29^a	3.34 ± 1.58^c	27.83 ± 1.87^f

Honey as H, maltodextrin as M and WPI as W.

Values represent means±standard deviations (n=3).

Different letters indicate that the samples are considered significantly different at the 5% level ($p<0.05$).

Table 4

Glass transition temperature (initial point T_{gi}, mid point T_{gm} and end point T_{ge}) of spray dried honey powders.

Ratio of sample (d.b.)	Glass transiton temperatuere		
	T_{gi} (°C)	T_{gm} (°C)	T_{ge} (°C)
H:M:W=60:0:40	42.55±3.36[f]	47.54±1.35[g]	51.75±0.84[f]
H:M:W=60:10:30	43.82±1.59[ef]	49.96±1.67[g]	54.84±2.00[f]
H:M:W=60:20:20	47.70±0.87[e]	54.01±1.03[f]	59.10±1.12[e]
H:M:W=60:30:10	54.54±2.27[d]	61.97±1.53[e]	68.16±2.71[d]
H:M:W=60:35:5	59.54±0.88[c]	67.95±1.01[d]	75.17±1.05[c]
H:M:W=60:37.5:2.5	65.26±2.22[b]	71.29±2.09[c]	75.82±3.28[c]
H:M:W=60:39:1	67.89±5.01[b]	74.01±2.06[bc]	80.36±0.55[b]
H:M:W=60:39.5:0.5	69.35±2.30[b]	76.69±2.53[b]	82.96±1.59[ab]
H:M:W=70:0:30	44.45±2.31[ef]	49.84±1.99[g]	54.37±3.52[f]
H:M:W=40:60:0	75.54±2.77[a]	82.14±2.37[a]	86.42±3.09[a]
spray dried maltodextrin (MD)	142.23±5.75	148.46±5.31	151.30±5.22
Spray dried whey protein isolate (WPI)	134.12±6.61	132.12±6.84	133.72±6.89
Freeze dried pure honey	12.48±1.78	18.00±1.45	21.81±2.32
Liquid pure honey	-44.69±2.43	-40.64±1.58	-37.49±2.75

Honey as H, maltodextrin as M and WPI as W.

Values represent means±standard deviations (n=3).

Different letters indicate that the samples are considered significantly different at the 5% level ($p<0.05$).