Effects of type and concentration of proteins on the recovery of spray dried sucrose powder

Running title: Spray drying of sucrose with proteins

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Abstract: Dairy proteins (whey protein isolate, hydrolysed whey protein, calcium-caseinate, and hydrolysed caseinate) and plant proteins (soy protein isolate, pea protein isolate, and rice protein concentrate) were used to spray dry sucrose which is difficult to spray dry due to its stickiness property. Generally, dairy proteins were more effective than plant proteins as they resulted in higher powder recoveries. Rice protein concentrate was demonstrated to be the least effective candidate for spray drying of sucrose. The higher powder recoveries of some sucrose/protein systems were attributed to the higher surface active properties of the proteins, because they preferentially migrate to the surface of the droplets/particle and cover the powder particle surface with a thin-film of non-sticky protein.

Key words: proteins; sucrose; surface activity; spray drying; stickiness.

INTRODUCTION

Spray drying is a mature and practical commercial process for converting a liquid solution to a solid powder form, with the advantages of economical, flexible and continuous operation producing dried particles of good flowability [1]. This technology has been widely used for decades for encapsulation and drying of food ingredients such as milk, fruit juice, flavors, lipids, and carotenoids [2]. Because the heat stress to the material is relatively low, this technique can be applied to heat-sensitive foods and pharmaceuticals [3]. However, one limitation of spray drying for encapsulation is the limited availability of wall materials, because they must be soluble in water at an acceptable level [1]. The most commonly used wall materials include carbohydrates (e.g. starches, maltodextrins), gums (e.g. gum Arabic, mesquite gum), proteins (e.g. milk proteins, gelatine) and mixtures thereof Gharsallaoui et al. [4]. The use of proteins as wall materials in spray drying is considered to be very tedious and expensive because of their low water solubilities [1, 5]. For example, the solubility of a rice protein is less than 60% even in a 1 g/100g protein concentration solution in the pH range of 2-10 [6]. This limitation can be minimized if only small amount of proteins (for example, <1% wet basis) can effectively encapsulate target materials.

Another limitation of spray drying is that it is unsuitable for producing powders of sugar rich foods because they are sticky [4, 7]. The stickiness problem of sugars is mainly caused by their low glass transition temperatures (T_g) [8]. For example, the T_g of lactose, maltose, sucrose, glucose and fructose is 101 °C, 87 °C, 62 °C, 31 °C and 16 °C respectively, and the relative degree of stickiness increase accordingly [9, 10]. In practice, quantifiable sticky behaviour of a compound is observed at temperatures about 20 °C above its T_g. The spray drying outlet temperature for many food products

is generally between 60-100 °C [7], therefore, stickiness readily occurs if the material contains a high proportion of low molecular sugars. The hygroscopic nature of low molecular weight sugars also contributes to this problem [11]. The stickiness of the particles can cause inter-particle cohesion or material adhesion on the dryer surfaces, and result in particles sticking to the wall of the dryer. In addition, the product particles may clump together, adversely affecting the free-flowing property of the powder, thus decreasing the powder recovery and product yield [10].

Some available approaches to reducing stickiness have limitations in practice, such as high cost and low product quality [9]. For example, large amounts (often > 35%) of drying aids such as maltodextrins are required to convert sugar rich fruit juices into a powder form [12]. Addition of such large amounts of drying aids increases the cost and may alter the original flavour and taste of the product, risking consumer disapproval. An alternative and novel way to minimize the problem of stickiness is to modify the surface adhesive properties of the atomized droplets/particles with small amounts of proteins [13, 14]. The preferential migration of protein molecules at the water/air interface combined with their film forming property upon drying has been found useful for overcoming the surface stickiness of sugar/protein solutions [13]. Recently, the effects of using protein and maltodextrin in spray drying of sugar rich bayberry juice were compared, and the results indicated that a small amount of protein (1%) was sufficient (powder recovery > 50%) to spray dry the bayberry juice, while a large amount of maltodextrin (>30%) was needed for the same result [15]. It is suggested that the mechanism of improved spray drying of bayberry juice with added protein is mainly because the protein migrates preferentially to the surface of droplets/particles, reducing adhesive behaviour between particles and dryer wall [15].

To our knowledge, to date, only two types of proteins (whey protein isolate and

sodium caseinate) have been tested in spray drying of sucrose [13] and sugar rich bayberry juice [15]. Both showed amazing positive effects. It is reasonable to assume that other types of proteins may also be effective in spray drying of sugar rich foods, provided that they have good functional properties (e.g. surface activities). The objective of the project was to spray dry sucrose using 7 types of commercial available proteins, including dairy proteins and plant proteins, and evaluate their effectiveness in reducing stickiness. The surface activity, product recovery and powder characteristics were used to compare and evaluate the relationship between spray drying efficiency and the functionalities of these proteins.

MATERIALS AND METHODS

Materials

Seven types of protein (whey protein isolate, WPI; hydrolysed whey protein, HWP; calcium-caseinate, CCP; hydrolysed caseinate, HCP; soy protein isolate, SPI; pea protein isolate, PPI; rice protein concentrate, RPC) were purchased from Muscle Brand Pty Ltd (Petersham, NSW, Australia) and used as received. The measured moisture contents of the proteins ranged from 3.30 - 5.72%, and percent protein ranged from 84.55 - 90.05. The solutions were prepared with ultra-pure water produced by a Milli–Q Plus system (Millipore Corporate, MA, USA).

Spray Drying of Sucrose

Sucrose/protein solutions were prepared with the ratio of 99.75:0.25, 99.5:0.5, 99.0:1.0, 97.5:2.5, 95.0:5.0 and 90.0:10.0 respectively on a dry solid mass basis. The inherent protein and moisture contents (as indicated above) in protein samples were compensated for. Sucrose solutions were prepared first, and then proteins were dissolved by addition of pre-weighed samples in the sucrose solutions with the aid of magnetic stirring at 200rpm for about 30 minutes, until completely dissolved. If

necessary, solution temperature was increased (60~80 °C) to facilitate dissolution. The total solids content of all prepared solutions was fixed at 10g/100g and 100 g of feed solution was spray dried for each run. The nominal concentrations of the protein in the feed solutions varied between 0.025 –1.0% (w/w).

The solutions were fed into a Büchi B-290 mini spray dryer (Büchi Labortechnik AG, Switzerland) with the aspirator rate of 100% (35 m^3/h), atomisation air rotameter of 30 mm (439L/h) in co-current flow, and drying air inlet temperature of 150 °C. The pump rate was adjusted to maintain an outlet temperature of 80 °C. After the completion of the experiment, the samples were collected from the product collection vessel. The powders were immediately sealed to prevent subsequent moisture uptake and stored in desiccators in the presence of excess silica gel at room temperature. Each treatment run was conducted in triplicate.

Surface Tension of the Feed Solutions

The surface tension value can be used as an indicator of how strongly the surface molecules of a liquid/solution are attracted by the adjacent molecules. Generally, a lower surface tension value of the solution indicates a weaker attraction of surface molecules by the adjacent molecules, which is caused by a higher tendency of the solute migrating to the air/water interface [13]. A Nima ST9000 surface tension meter (Nima Technology Ltd, Coventry, UK) was used to determine the surface tension values of the prepared solutions before spray drying. The tension meter was calibrated with a standard weight of 100 mg and the surface tension of water was determined as 73.27 ± 1.42 mN/m. Sample solutions were filled in a test vessel and a platinum Wilhelmy plate was immersed into and raised out of the solutions slowly. The surface tension value was recorded on a computer running the measuring software. The analysis was repeated 5 times for each sample.

Product Recovery

The product recovery was defined as the ratio of the mass of powders obtained at the end of the spray drying period, to the mass of initial substances, including the sucrose and proteins, based on dry mass content.

$$\text{Product recovery } (\%) = \frac{\text{Spray dried powder (g)}}{\text{Sucrose (g)} + \text{proteins (g)}} \times 100$$

Moisture, Water activity (a_w) and Protein Determination

The moisture content of the powder was determined by vacuum drying (Thermoline Scientific, Australia) at 70 °C and 500 mbar for 24 h [16].

Water activity of the powders was determined using an AquaLab 3TE Series water activity meter (Decagon Devices, Pullman, WA, USA). The temperature was maintained at 24.5 ± 0.1 °C during the tests. All determinations were done in triplicate immediately after spray drying.

Precise protein content of the protein samples was determined by the AOAC [16] method using a LECO TruSpec CHN analyser (St. Joseph, MI, USA) with triplicate analysis.

Electron Spectroscopy for Chemical Analysis (ESCA)

ESCA measurements were carried out in order to determine the surface composition of each spray dried sucrose/protein powder sample. This technique measure the relative atomic concentration of carbon, nitrogen, and oxygen in the surface layer of the sample (depth of less than 100 Å). The analysis was performed on a Kratos AXIS Ultra photoelectron spectrometer (Kratos Analytical Ltd, Manchester, UK) with a 150W monochromatic A1 X-ray source, using a procedure reported elsewhere [13, 17]. Briefly, the samples were degassed for 24 h prior to ESCA measurements. Each analysis started with a one sweep survey scan from 0 to 1200 eV with a residence time of 100 ms, pass energy of 160 eV at steps of 1 eV. Data were

acquired through the spectrometer incorporating a 165 mm hemispherical electron energy analyzer. The incident radiation was Monochromatic A1 X-rays (1486.6 eV) at 225W (15 kV, 15 mA). The base pressure in the analyser chamber was maintained at 10^{-8} Torr during sample analyses [13]. Because there is no nitrogen in a sucrose molecule, the percentage of protein coverage on the surface layer of the spray dried sucrose/protein particles can be calculated by a matrix inversion method based on the ESCA data [13, 17-18].

Glass Transition Temperature (Tg)

The T_g of the powders was determined using a Mettler–Toledo differential scanning calorimeter (mode DSC1). 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. The purge gas was dry nitrogen. Indium (Mettler–Toledo standard) was used for temperature and heat flow calibrations. Samples of about 10 mg were scanned in hermetically sealed 40 µl DSC aluminium pans. An empty aluminium pan was used as a reference. The heating ramp rate was set to 10 °C/min and heat scanned from an equilibrium starting temperature of 0°C to 80 °C for spray dried sucrose/protein powders and from 0°C to 200°C for pure sucrose and proteins. The midpoint values for glass transition temperature of the samples were calculated using DSC STARe evaluation software. All analyses were done in triplicate.

Statistical Analysis

One-way analysis of variance (ANOVA) and Tukey's test (SPSS 20.0 statistics software, IBM, Somers, NY, USA) was used for the determination of differences between different protein concentrations within the same protein type. The results were expressed as mean ± standard error (SE) and considered significantly different

when $P < 0.05$.

RESULTS AND DISCUSSION

Surface Tension

It has been suggested that a lower surface tension value of a solution indicates a higher surface activity of the solute in water [13]. The surface tension values of pure water and sucrose solution were 73.27± 1.42 mN/m and 72.77± 1.35 mN/m respectively, which suggested that sucrose is not a surface active component and can not affect the surface tension of water in a statistical manner (Figure 1), thus the effect of sucrose on surface tension is ignored in the following discussion. However, an addition of WPI at a concentration of 0.025% can significantly lower the values both in water and sucrose solutions (Figure 1). The surface tension values decreased accordingly with the increase of protein concentrations, but not as significantly when the protein concentration was increased above 0.5% (Figure 1). While the surface tension values decreased sharply at low protein concentrations, they reached a limiting value at higher concentrations. This suggested that there might be a saturated state (about 0.5% protein in the present study) of the protein molecules on the surface of solutions, so that further increasing the protein concentration had no effect on the surface tension [19]. The ability of added proteins to lower the surface tension of solutions is attributed to their amphophilic properties, which cause them to diffuse to and adsorb onto the newly created water/air or water/oil interfaces as rapidly as they formed [20]. The adsorbed protein molecules partially unfold to expose a high proportion of their hydrophobic amino acid residues to the non-aqueous medium. The tendency of the protein molecules to partition between the aqueous and non-aqueous phases permits them to remain adsorbed on the interface, thus lowering interfacial tension [20]. In the present study, the property of proteins to preferentially migrate to

the air/water interface was referred to as surface activity, as has been proposed by previous researchers [13].

Although all the proteins tested can lower the surface tension values of sucrose solutions, and increasing the protein concentrations further decreased the surface tension values, indicating that they are surface active compounds, it is obvious that different proteins had different effects on surface tension (Figure 2). For example, at the same concentration level, WPI and RPC solutions had relatively higher surface tension values (implying lower surface activity) while CCP showed the lowest (implying higher surface activity). Another characteristic is that, except for WPI, the surface tension values of the plant protein solutions (SPI, PPI, RPC) were relatively higher than those of the dairy protein solutions (HWP, CCP, HCP), indicating that dairy proteins possessed higher surface activities. Among the dairy proteins, the surface tension value of the WPI solution was higher than those of caseinates (CCP and HCP), suggesting lower surface activity. Furthermore, the hydrolysed whey protein (HWP) solution showed a higher surface activity than the un-hydrolysed proteins (Figure 2), which might be caused by more lipophilic amino acids being released in the hydrolysed solutions [21]. However, the surface tension of hydrolysed caseinate (HCP) solutions was still higher than the un-hydrolysed counterpart (CCP), indicating that hydrolyzation has not increased the surface tension of CCP. This phenomenon may imply that increasing the degree of hydrolysis (DH) for this commercial HCP did not affect its surface activity, as only mild hydrolysis of whey protein (DH between 10 and 27%) can improve surface activity (emulsifying ability) [21]. Martínez, Sánche, Rodríguez Patino, & Pilosof also observed that low levels of hydrolysis (2-5%) can improve the surface activity of soy protein whereas a higher degree of hydrolysis has a negative effect [22]. In addition, the difference in surface

activity between whey protein and caseinate may result from their different protein constituency, as whey protein is mainly composed of β-lactoglobulin, α-lactalbumin, bovine serum albumin, and immunoglobulins, while caseinate is composed of κ-casein, α -casein, and β-casein [23]. The caseinates are prone to be adsorbed at water/air interfaces, whereas whey proteins are relatively less surface-active as a consequence of their close-packed globular structure [24].

With regard to the plant proteins, the principal proteins in soybeans are soluble glycinin and conglycinins [25], and pea proteins are composed of both soluble (50-60% globulin and 15-25% albumin) and insoluble proteins (15-30%) [26], whereas rice proteins contain mostly glutelin fraction (about 80%), which is a high molecular weight protein composed of subunits bound by disulfide linkages with limited solubility in water [27]. It has been suggested that the surface and emulsification properties of proteins are strongly correlated with their structure, and proteins with higher surface hydrophobicity always have higher emulsifying activity [28]. Although there is limited data about the surface activity (surface tension, surface hydrophobicity) of plant proteins, soy protein generally exhibits high emulsifying properties compared with other plant proteins [29], implying that it may have a high surface activity. This was confirmed in the present study by its lower surface tension values. It has also been reported that protein properties including interfacial and foaming properties are considerably influenced by the extraction source and method [30]. As information regarding the extraction methods for these commercial proteins is unavailable, we can only presume that the different surface activities of these proteins are related to their source and chemical nature.

Powder Recovery

Before spray drying of sucrose/protein solutions, individual sucrose and protein

solutions with the same feed concentration (10g/100g) were spray dried respectively as references. However, because the particles were deposited on the dryer chamber wall and formed a glass like film, no powder was recovered from the collection vessel after spray drying of sucrose alone. This result agrees with the previous observations that no powder was recovered from spray drying of sucrose in similar drying conditions [13]. For the protein only samples, the highest quantity of powder (around 85%) was recovered from hydrolysed proteins (HWP and HCP) Medium powder recovery (around 65%) was shown with WPI, CCP and SPI and with PPI (about 53%). RPC had the lowest recovery of about 44% (Table 1). The low recovery of RPC was because a large proportion of the aggregated dried particles had fallen to the bottom of the drying chamber and could not be transported to the collection vessel by the vacuum cyclone. The loss of powder during spray drying should have been a combination of some particles of the powder being deposited on the dryer chamber wall, some fine particles being pumped out through the dryer filter, and the losses of uncollected residues associated with manual operations [31].

Although no powder was recovered by spray drying of the sucrose solution, the powder recovery increased to about 50% when 0.25% of the sucrose was replaced by protein, with the exception of RPC (Table1). This indicated that the addition of small amounts of protein can enable successful spray drying of sucrose, with a greater than 50% powder recovery in the cyclone, which has been considered to be a criterion for successful drying of sticky material in laboratory driers [7]. Furthermore, increasing protein concentration increased powder recovery, although the response varied among proteins (Table1). Beyond 2.5% protein, further increasing the protein concentration did not improve the powder recovery significantly for most of the proteins. The exceptions were SPI, which showed improved powder recovery at 5% of added

protein, and CCP (10%). The powder recovery of sucrose/WPI in the present study was lower than that reported in the literature (around 80%) [13], probably because those authors collected particles both in the cyclone and by sweeping the dryer wall. In this experiment, only the particles in the collection vessel were recovered, and the particles deposited on the dyer wall were considered 'sticky' particles. Another reason might be that their protein sources were different to the present study and different proteins have different surface activities, which may result in different powder recovery [9, 32]. Furthermore, a laboratory Büchi B-290 mini spray dryer was used in the present study while Dr. Adhikari et al. [13] used a pilot scale spray dryer, which may also have contributed to the different powder recovery.

Another interesting finding was that the plant proteins (SPI, PPI, and RPC) generally resulted in lower powder recoveries than the dairy proteins (WPI, HWP, CCP, and HCP). Of the plant proteins, soy protein (SPI) had a relatively high powder recovery, comparable to that of HCP. For pea protein (PPI) powder recovery was around 50% independent of protein concentration. Rice protein (RPC) showed the lowest recovery (less than 40%), even at the highest additive level of 10% (Table1).

The results suggested that different proteins have different functional properties and these affect the spray drying powder recoveries. The lower spray drying sucrose powder recoveries shown by plant proteins might be a consequence of their different protein constituencies and therefore higher surface tension values (lower surface activities) as described above (Surface Tension). A correlation analysis was performed to evaluate the relationship between surface tension and powder recovery, which showed that except for PPI, the correlation coefficients (R) for all other proteins are above 0.8 (Table 2), indicating a strong relationship and implying that a protein with higher surface activity can provide a higher powder recovery. However,

the WPI dairy protein also had a relatively higher surface tension value compared with other proteins (Figure 2), but the powder recovery with this protein was relatively high (Table 1), suggesting the index of surface tension value may only be partly associated with the surface activity of proteins.

It is proposed that the proteins with high surface activity preferentially migrate to the water/air interface of atomised droplets during spray drying, and quickly form a film around the particle surface which avoids the stickiness/adhesive interaction between particles and dryer wall, consequently the dried particles are carried away by the drying air and collected as powder product [33]. A higher surface activity implies that more protein molecules might adsorb on the surface of the particles, favouring higher recoveries, because more particles can be collected. However, there may be a dynamically saturated state for protein molecules on the particle surface [19], whereby increasing the protein concentration above a certain level cannot further improve the powder recovery. In the present study, the sucrose powder recovery didn't increase significantly after the protein replacement exceeded 2.5% (Table 1). This trend correlated very well with the surface tension results as discussed above, although the critical concentration (0.5%) to influence the surface tension was lower.

Surface Protein Coverage of the Spray Dried Powders

The ESCA measurement was used to determine the relative atomic concentrations of carbon, nitrogen and oxygen on the surface layer of the sucrose/protein powders, and the percentage of surface protein coverage was calculated by a matrix inversion method based on the obtained data as described elsewhere [13, 17-18]. It can be seen from Table 3 that most of the spray dried powders have a surface protein coverage of higher than 45%, even when as low as 0.25% of sucrose was replaced by proteins (equivalent to 0.025% protein in the feed solution). The HCP showed the highest

surface protein coverage of 57% in the sucrose/protein systems, followed by WPI, SPI, CCP and HWP, all with a surface protein content of around 50%. A lower surface protein content of 45% was shown for PPI whereas the RPC had the lowest of 16% (Table 3). This agrees with the above results of the surface tension analysis, where plant proteins (especially rice protein) had relatively higher surface tension values, suggesting less preference for migrating to the particle surface than dairy proteins. Increasing the protein concentration also increased the surface protein coverage of the samples, and mostly achieved a likely saturated state at 2.5% of added protein, because further increasing the protein concentration had no significant effect. This confirms the finding of Adhikari et al. [13] and Shrestha et al. [17] that protein dominates the surface of the spray dried sugar/protein powder, even at low concentrations. It should be pointed out that, although WPI had a relatively higher surface tension value (Figure 2), implying less surface activity, the surface protein coverage was comparable with those of other dairy proteins (Table 3), indicating that it is still an effective surface active protein, enabling good powder recovery (Table1). The actual reason for this exception will need further investigation.

The correlation coefficients between powder recoveries and protein coverage are also given in Table 2, which shows that the *R* values for all proteins except PPI/sucrose powders are higher than 0.8, suggesting that the higher the surface protein coverage, the higher the powder recovery. Combining all the results and correlating surface tension, surface protein coverage and powder recovery, it is reasonable to propose that surface active proteins preferentially migrate to the surface of the solution and the composition of the powder surface reflects the composition of the air/water interface of the spray droplets prior to drying. Protein is accumulated at the air/water interface during, or prior to droplet formation at the immediate exit of the

atomizer and thus appears on the powder surface [34], which overcomes the stickiness/adhesive nature of sucrose and increases the powder recovery.

The results also revealed that, except for soy protein (SPI), plant proteins are not as effective in spray drying of sucrose. It seems that the surface tension and powder surface coverage of pea protein (PPI) did not influence the powder recovery, thus their correlation coefficients of *R* were unexpectedly low (Table 1, Table 2). One possible reason might be that the tested lowest concentration of 0.25% is already the saturated state for this protein/sucrose system, thus increasing the concentration did not reduce the surface tension and increase the powder recovery. Further studies are needed to identify the mechanism. The powder recoveries (<45%, Table 1) and surface protein coverage (<30%, Table 3) of spray dried sucrose powders with rice protein (RPC) are very low, even with the highest protein concentration (10%) added to the system, implying that it is not a good candidate for spray drying of sticky materials. This may also be a consequence of its protein (glutelin) nature, which has low water solubility and low surface activity, as discussed in the above sections.

Moisture Content, Water Activity (a_w), and Glass Transition Temperature (T_g)

The moisture content and a_w of powders were measured as soon as possible after collection, provided the powder temperature was equilibrated to room temperature. It can be seen from Table 4 that the highest moisture content and a_w of spray dried powder are 4.31% and 0.269, respectively. Although the values varied among different sucrose/protein ratios, all the a_w values are within the range of industrially spray dried powders (≈0.2) [14]. It has been proposed that one of the characteristics of spray-dried products is the low moisture content (less than 5%) [35]. The moisture content of all the powder samples are also well within this range (Table 4).

The glass transition temperature (T_g) of spray dried powders is a very important

indicator to assess stickiness because if the droplet/particle temperature is 20 °C above its T_g, it will generally be sticky [7]. The measured T_g and melting point of sucrose was 73.44 °C and 183.77°C, which is close to those in the literature of 65-70°C and 185°C, respectively [36]. The small difference is understandable because T_g varies with the amount of water in a compound [37]. The T_g of the spray dried pure proteins were within the range of 100°C-150°C (data not shown), whereas the T_g of spray dried sucrose/protein powders were in the range of 60-70°C (Table 4). It is clear that the T_g of the spray dried sucrose/protein powders are close to the measured T_g of sucrose 73.44°C and reported values of 65-70°C [36]. The relatively lower T_g could be the result of moisture absorption by the powders during handling [17]. This result agrees with previous studies that the sugar/protein systems are not compatible and the measured T_g mainly reflects the T_g of the sugar in the system [17]. In the case of the present study of sucrose/protein powders, the measured T_g might be the T_g of the sucrose, so varying the protein concentration didn't affect its value.

Because the main solid content in spray dried powders is sucrose, and the overall T_g values are 60-70°C, they will stick on the dryer wall if the drying temperature is around 80-90°C (20°C higher than T_g). The inlet and outlet temperatures of the spray dryer were set at 150 °C and 80°C respectively, and the contact temperature in the dryer may be higher than 80-90°C. Therefore, stickiness is likely to occur explaining why no powder was collected when spray drying of the sucrose only solution.

As has been discussed above, surface active proteins preferentially migrate to the air/water interface of atomised droplets/particles and their T_g are within the range of 100-150°C. The addition of proteins increases the particle surface coverage with high T_g proteins. Therefore, the sucrose/protein solution can have an efficient spray drying performance with more than 50% of powder recovery, even when a small amount of

protein was added (such as >0.25%). However, if the surface activity is relatively low (e.g. rice protein), protein coverage on the powder surface would be insufficient to overcome the stickiness of sucrose, and the powder recovery will be consequently reduced.

CONCLUSION

Four types of dairy proteins (WPI, HWP, CCP, HCP) and 3 types of plant proteins (SPI, PPI, RPC) were used for spray drying of the sticky material sucrose. Generally, dairy proteins were more effective than plant proteins in spray drying of sucrose as they can lower the surface tension values of the solutions before drying, resulting in higher powder recoveries with more protein coverage on the particle surface. The higher powder recovery was attributed to the surface active properties of the proteins because they are preferentially migrating to the surface of the droplets/particle, and form a glass state film upon drying, which can resist heat stress during the drying process. There seemed to be a saturated state of protein concentration (nominal concentration about 0.25%) in sucrose/protein solutions to improve their surface activity for spray drying, as higher protein concentrations did not increase the powder recovery significantly. The surface tension value can partly evaluate the surface activity of proteins while the surface protein coverage is a more accurate index. The results indicated that because of its protein structure and functionality, rice protein concentrate may not be a good candidate for spray drying of sugar rich sticky foods. It is suggested that other factors such as temperature and pH values of the solution on the surface activity of the proteins should be considered in future investigations. Furthermore, for deep understanding of the mechanism, more physical-chemical properties, including the protein solubility kinetics, particle morphology, and particle

size distribution would be helpful to explain the effect of protein surface activity on the spray drying efficiency of sticky foods.

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Figure captions:

Figure 1 Surface tension values of whey protein isolate (WPI) in pure water and in sucrose solutions (10g sucrose /100 g).

Figure 2 Effect of protein types and concentrations on the surface tension values of sucrose solutions (10g /100g). WPI, whey protein isolate; HWP, hydrolysed whey protein; CCP, calcium-caseinate; HCP, hydrolysed caseinate; SPI, soy protein isolate; PPI, pea protein isolate; RPC, rice protein concentrate.

Table 1 Powder recoveries of spray drying of sucrose/protein and protein only solutions [a]

proteins / Ratio	[b] WPI	HWP	CCP	HCP	SPI	PPI	RPC
99.75:0.25	[c]51.55±0.55a	50.48±0.65a	50.85±0.33a	57.71±0.77a	50.14±0.54a	48.47±0.72a	22.16±0.46a
99.5:0.5	57.12±0.43b	53.83±0.53b	53.61±0.46b	58.20±0.48ab	50.34±0.55a	48.71±0.77a	31.62±0.72b
99.0:1.0	57.96±1.02b	59.93±0.91c	54.03±0.44b	58.99±1.05ab	50.48±0.41a	49.34±0.81ab	31.76±0.95b
97.5:2.5	59.22±0.58bc	59.97±1.22c	57.62±1.01c	60.53±0.88b	54.41±0.65b	49.96±0.60ab	39.47±0.75c
95.0:5.0	60.95±0.87bc	60.33±0.81c	58.88±1.22c	60.66±0.90b	59.54±0.66bc	50.37±0.87b	40.31±0.77c
90.0:10.0	62.51±0.85c	60.61±1.33c	63.90±0.65d	61.03±0.89b	61.67±1.05c	51.87±1.12b	40.43±0.58c
Protein only	65.61±0.81d	85.82±1.11d	65.93±1.25d	65.66±1.57c	62.99±1.77c	53.77±1.04b	44.05±0.96d

[a] The feed concentrations of all samples were 10g/100g

[b] WPI, whey protein isolate; HWP, hydrolysed whey protein; CCP, calcium-caseinate; HCP, hydrolysed caseinate; SPI, soy protein isolate; PPI, pea protein isolate; RPC, rice protein concentrate.

[c] Same letters in the same column indicate no significant difference ($p>0.05$)

Table 2 Correlation coefficients (R) of the spray dried sucrose powder recoveries to the surface tension of feed solution and surface protein contents of sucrose/protein systems

Powder recovery	WPI	HWP	CCP	HCP	SPI	PPI	RPC
Surface tension	0.830	0.812	0.924	0.863	0.831	0.114	0.941
Surface protein	0.864	0.793	0.990	0.924	0.873	0.179	0.935

WPI, whey protein isolate; HWP, hydrolysed whey protein; CCP, calcium-caseinate; HCP, hydrolysed caseinate; SPI, soy protein isolate; PPI, pea protein isolate; RPC, rice protein concentrate.

Table 3 Distributions (%) of carbon, nitrogen and oxygen, and protein contents in the surface layer of the sucrose/protein powders

Samples	Oxygen	Carbon	Nitrogen	Protein on surface
[a]WPI	17.07±1.02	68.93±1.53	13.99±0.07	-
Sucrose	53.65±1.99	46.35±2.01	-	-
Sucrose: WPI (99.75: 0.25)	32.26±1.22	64.87±1.01	6.87±0.33	[b]52.42±0.87a
Sucrose: WPI (99.5:0.5)	30.41±2.12	61.86±1.97	7.73±0.45	54.42±1.56a
Sucrose: WPI (99.0:1.0)	30.57±1.03	62.03±1.55	7.40±0.12	53.90±2.26a
Sucrose: WPI (97.5:2.5)	28.61±1.44	63.81±2.87	7.58±0.46	60.67±1.75b
Sucrose: WPI (95.0:5.0)	28.74±2.05	63.23±3.48	8.03±0.33	60.17±3.76b
Sucrose: WPI (90.0:10.0)	28.28±1.55	63.35±1.03	8.36±0.66	61.73±2.88b
HWP	17.48±0.37	67.44±2.11	15.8±0.09	-
Sucrose: HWP (99.75: 0.25)	31.65±1.22	62.15±2.06	6.20±0.54	50.75±3.41a
Sucrose: HWP (99.5:0.5)	31.27±0.48	61.86±1.36	6.87±0.75	52.11±2.14a
Sucrose: HWP (99.0:1.0)	30.76±1.23	62.57±1.35	6.68±0.08	53.84±1.97ab
Sucrose: HWP (97.5:2.5)	30.47±1.65	61.98±2.33	7.55±0.16	54.91±3.08ab
Sucrose: HWP (95.0:5.0)	29.92±0.78	64.19±1.75	5.89±0.06	56.82±1.32ab
Sucrose: HWP (90.0:10.0)	29.00±1.56	62.60±1.65	8.40±0.37	60.01±2.05b
CCP	16.21±1.35	69.97±2.02	13.91±0.77	-
Sucrose: CCP (99.75: 0.25)	31.08±0.87	61.78±2.03	7.14±0.55	50.63±3.06a
Sucrose: CCP (99.5:0.5)	28.33±0.49	63.44±1.33	8.23±0.07	59.79±1.68b
Sucrose: CCP (99.0:1.0)	27.67±0.55	62.76±1.73	9.57±0.49	61.79±1.75b
Sucrose: CCP (97.5:2.5)	26.28±1.11	64.01±2.02	9.71±0.18	66.49±1.83bc
Sucrose: CCP (95.0:5.0)	25.16±1.55	64.75±2.04	10.1±0.31	70.24±2.06cd
Sucrose: CCP (90.0:10.0)	23.22±1.05	65.16±2.04	11.61±0.71	76.55±2.11d
HCP	19.80±0.57	69.77±1.88	10.43±0.33	-
Sucrose: HCP (99.75: 0.25)	31.14±1.35	62.40±2.07	6.46±0.51	57.01±2.11a
Sucrose: HCP (99.5:0.5)	29.96±1.73	62.58±3.12	7.45±0.08	61.17±3.85ab
Sucrose: HCP (99.0:1.0)	28.43±2.01	63.66±2.07	7.91±0.15	67.02±2.99bc
Sucrose: HCP (97.5:2.5)	26.62±1.56	63.88±3.33	9.49±0.58	73.37±4.11cd
Sucrose: HCP (95.0:5.0)	25.07±1.07	65.52±2.21	9.41±0.63	79.59±2.16d
Sucrose: HCP (90.0:10.0)	24.55±1.62	65.67±2.12	9.78±0.72	81.46±2.05d
SPI	17.93±1.43	67.53±2.37	14.54±0.29	-
Sucrose: SPI (99.75: 0.25)	31.54±1.45	60.89±2.18	7.56±0.46	52.08±2.53a
Sucrose: SPI(99.5:0.5)	31.19±0.76	61.95±2.17	6.86±0.23	53.28±2.61ab
Sucrose: SPI (99.0:1.0)	29.85±1.22	63.65±3.04	6.50±0.45	57.94±3.08abc
Sucrose: SPI (97.5:2.5)	29.14±0.85	63.00±2.54	7.87±0.59	60.50±2.81abc
Sucrose: SPI (95.0:5.0)	28.80±1.56	63.68±2.87	7.53±0.49	61.67±2.65bc
Sucrose: SPI (90.0:10.0)	28.50±1.38	63.54±2.54	7.96±0.65	62.73±2.35c
PPI	16.52±1.75	70.53±3.67	12.95±0.83	-
Sucrose: PPI (99.75: 0.25)	32.79±1.03	61.51±3.44	5.70±0.45	45.49±2.89a
Sucrose: PPI (99.5:0.5)	31.79±1.42	62.30±3.81	5.91±0.76	48.91±4.05ab
Sucrose: PPI (99.0:1.0)	29.97±1.45	63.01±2.65	7.02±0.54	54.92±3.22bc
Sucrose: PPI (97.5:2.5)	29.09±1.08	62.92±2.23	7.99±0.61	57.70±2.96c
Sucrose: PPI (95.0:5.0)	27.75±1.76	64.13±2.13	8.12±0.88	62.33±2.43c
Sucrose: PPI (90.0:10.0)	26.65±1.67	64.13±2.65	9.22±0.57	62.83±3.05c
RPC	18.10±1.65	76.39±3.05	5.51±0.67	-
Sucrose: RPC (99.75: 0.25)	41.23±1.33	57.81±1.55	0.96±0.62	16.14±2.08a
Sucrose: RPC (99.5:0.5)	40.70±1.49	58.25±2.71	1.05±0.48	20.04±1.97ab
Sucrose: RPC(99.0:1.0)	40.26±1.67	58.58±2.34	1.16±0.57	21.56±2.33abc
Sucrose: RPC (97.5:2.5)	39.61±1.55	58.85±2.75	1.54±0.54	23.54±2.08abc
Sucrose: RPC (95.0:5.0)	38.94±1.63	59.28±2.32	1.78±0.46	25.77±2.11bc
Sucrose: RPC (90.0:10.0)	37.80±1.57	60.17±3.03	2.03±0.65	29.77±3.02c

[a] WPI, whey protein isolate; HWP, hydrolysed whey protein; CCP, calcium-caseinate; HCP, hydrolysed caseinate; SPI, soy protein isolate; PPI, pea protein isolate; RPC, rice protein concentrate.

[b] Same letters in the same column within the same protein type indicate no significant difference ($p>0.05$)

Table 4 Moisture content, water activity (a_w), and glass transition temperature (T_g) of spray dried sucrose/protein powders [a]

Samples	Ratio	Moisture content (%)	a_w (24.6°C)	T_g (°C)
Sucrose: WPI	99.75:0.25	3.23±0.03bc	0.168±0.011a	65.34±1.32b
	99.5:0.5	3.53±0.22c	0.176±0.020a	61.33±2.03a
	99.0:1.0	2.98±0.10b	0.181±0.024a	66.41±0.76b
	97.5:2.5	2.93±0.02b	0.183±0.031a	68.65±2.15b
	95.0:5.0	2.93±0.09b	0.196±0.025b	69.70±0.74b
	90.0:10.0	2.28±0.13a	0.190±0.017b	69.86±0.57b
Sucrose: HWP	99.75:0.25	4.31±0.11c	0.269±0.021c	59.88±0.78a
	99.5:0.5	3.44±0.11b	0.237±0.032b	62.03±1.56ab
	99.0:1.0	3.02±0.66a	0.212±0.020b	65.34±1.88b
	97.5:2.5	3.41±0.07b	0.226±0.015b	63.05±2.07ab
	95.0:5.0	3.94±0.15c	0.206±0.023ab	60.25±1.33a
	90.0:10.0	3.71±0.05bc	0.175±0.014a	60.86±2.05a
Sucrose: CCP	99.75:0.25	2.33±0.04c	0.091±0.014a	61.35±2.35a
	99.5:0.5	2.07±0.24c	0.138±0.024b	60.48±1.66a
	99.0:1.0	1.95±0.08c	0.118±0.026ab	63.24±0.97a
	97.5:2.5	1.67±0.14b	0.103±0.021a	65.72±1.83b
	95.0:5.0	1.26±0.26a	0.129±0.033ab	66.15±0.97b
	90.0:10.0	1.66±0.02b	0.152±0.028b	65.65±2.39b
Sucrose: HCP	99.75:0.25	1.78±0.03a	0.142±0.012ab	68.54±0.75ab
	99.5:0.5	1.62±0.17a	0.136±0.019a	70.02±2.11b
	99.0:1.0	1.94±0.13ab	0.131±0.022a	67.38±1.35ab
	97.5:2.5	2.04±0.02b	0.164±0.037b	66.54±2.37ab
	95.0:5.0	2.12±0.01b	0.180±0.027b	66.18±1.76ab
	90.0:10.0	2.23±0.16b	0.179±0.023b	64.32±2.14a
Sucrose: SPI	99.75:0.25	2.41±0.09a	0.225±0.018b	64.88±0.86b
	99.5:0.5	2.78±0.11b	0.219±0.031b	63.47±1.08ab
	99.0:1.0	3.74±0.20b	0.190±0.019ab	61.85±1.37a
	97.5:2.5	3.77±0.28b	0.193±0.011ab	61.25±1.49a
	95.0:5.0	2.83±0.06b	0.173±0.035a	62.78±0.76ab
	90.0:10.0	2.36±0.14a	0.170±0.030a	65.14±2.05b
Sucrose: PPI	99.75:0.25	2.40±0.11a	0.256±0.017b	63.22±1.75ab
	99.5:0.5	2.12±0.03a	0.218±0.023a	64.08±2.04b
	99.0:1.0	3.83±0.12b	0.235±0.020ab	59.85±0.79a
	97.5:2.5	3.60±0.08b	0.218±0.021a	60.54±1.76a
	95.0:5.0	3.28±0.06b	0.207±0.021a	62.01±1.65ab
	90.0:10.0	3.47±0.09b	0.213±0.014a	61.89±2.06ab
Sucrose: RPC	99.75:0.25	3.07±0.14a	0.146±0.013b	60.58±1.44a
	99.5:0.5	3.69±0.04b	0.152±0.018b	59.45±1.63a
	99.0:1.0	3.63±0.10b	0.147±0.022b	60.18±0.79a
	97.5:2.5	3.01±1.11a	0.145±0.026b	60.97±1.32a
	95.0:5.0	3.39±0.06ab	0.138±0.022a	60.36±0.88a
	90.0:10.0	2.79±0.05a	0.136±0.014a	61.59±1.56a

[a] WPI, whey protein isolate; HWP, hydrolysed whey protein; CCP, calcium-caseinate; HCP, hydrolysed caseinate; SPI, soy protein isolate; PPI, pea protein isolate; RPC, rice protein concentrate.

Same letters in the same column within the same protein type indicate no significant difference ($p>0.05$)

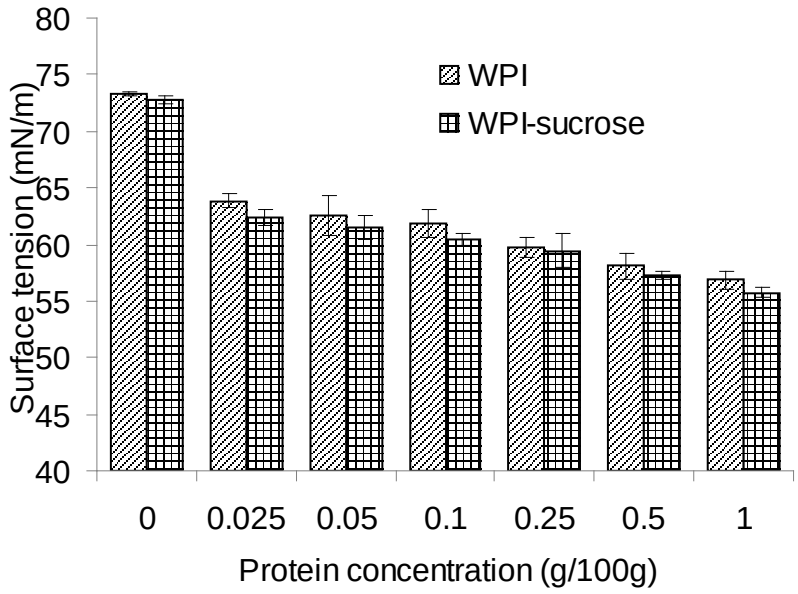
80
75
70
65
60
55
50
45
40
Surface tension (mN/m)
WPI
WPI-sucrose
0
0.025
0.05
0.1
0.25
0.5
1
Protein concentration (g/100g)

Figure 1

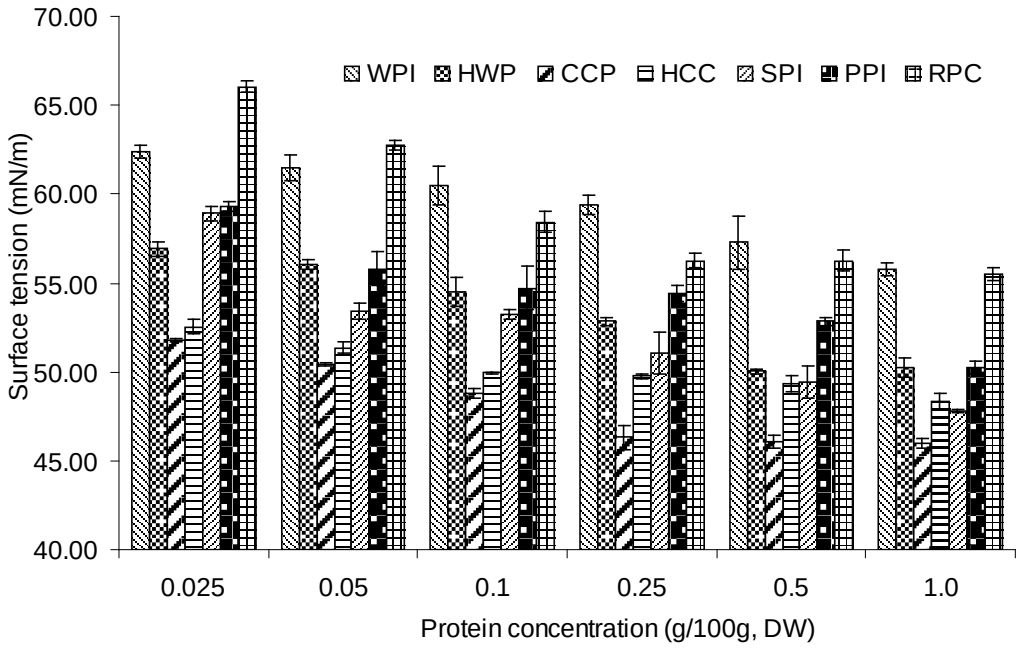
70.00
65.00
60.00
55.00
50.00
45.00
40.00
Surface tension (mN/m)
WPI
HWP
CCP
HCC
SPI
PPI
RPC
0.025
0.05
0.1
0.25
0.5
1.0
Protein concentration (g/100g, DW)

Figure 2