Particle morphology and powder properties during spray drying of maltodextrin and whey protein mixtures

E.M. Both, R.M. Boom, M.A.I. Schutyser *

Laboratory of Food Process Engineering, Wageningen University and Research, Postal address: P.O. Box 17, 6700, AA, Wageningen, the Netherlands

A R T I C L E   I N F O

Article history:
Received 22 July 2019
Received in revised form 6 December 2019
Accepted 3 January 2020
Available online 07 January 2020

Keywords:
Droplet size
Morphology
Single droplet drying
Density
Pilot scale

A B S T R A C T

Application behavior of spray dried powders such as reconstitution behavior and flowability is indirectly influenced by powder particle morphology. We here investigated the influence of the drying conditions and composition for whey protein (WP), maltodextrin (MD) and their mixtures on particle morphology during pilot-scale spray drying. Even though all powders showed a variety of morphologies, MD powders contained more wrinkled particles and had high bulk density, whereas pure WP powders contained more hollow particles. Mixture powders (75:25 WP:MD) show more hollow particles with increasing inlet temperature, with a lower bulk density. The observed morphologies for different formulations corresponded roughly to previous observations during sessile single droplet drying, but the results indicate that the morphology is also influenced by the faster pilot-scale drying, which was not evident in the slower single droplet drying.

© 2020 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

The quality of a spray dried powder is determined by, among others, the reconstitution behavior and flowability. These properties are influenced by the morphology of the powder particles. The importance of size and shape on the flow of a powder was for example demonstrated for lactose [1], and for suspensions of glass spheres, calcium carbonate crystals, and plate-shaped talc [2]. The effects of the powder particle surface area, bulk density and porosity on the reconstitution behaviour were shown for maltodextrin powders [3]. The effect of drying conditions on morphology and subsequent powder properties is however still not fully understood and is of interest to optimise powder properties towards desired specifications.

The morphology development can be observed using single droplet drying, simulating the conditions during spray drying [4]. However, the translation of these results to actual spray dried droplets is not trivial. During single droplet drying one usually studies drying of droplets with a diameter of ~1 mm, while in spray drying the droplet diameter is between 10 and 100 μm. This difference in droplet diameter has large effect on the drying time, which scales quadratically with the droplet diameter. The large difference in drying rates may be expected to impact the morphology development, because powder particles are kinetically stabilized systems, with components migrating during drying, the matrix becoming more rigid, and pores being created upon skin formation. Next to the effect of the droplet size as such, during spray drying there is a wide droplet size distribution and different droplets experience different drying trajectories. These aspects contribute to variation in drying times and probably the morphology.

We here discuss pilot-scale spray drying of mixed maltodextrin and whey protein model formulations, and compare the results to single-droplet drying. With single droplet drying we observed that more concentrated solutions of whey protein (WP) formed particles featuring a single large vacuole, while solutions with more maltodextrin (MD) yielded wrinkled particles [5]. The ratio of MD and WP affected the transition temperature at which either a more hollow or a wrinkled morphology was observed. Typical transition temperatures were ~70 °C for 50% WP and 50% MD systems, with lower temperatures yielding hollow particles and higher temperatures wrinkled particles. For 75% WP and 25% MD systems a higher transition temperature (~90 °C) was found. We hypothesize that the differences in morphology upon different spray drying conditions are more likely for mixtures of MD and WP that have a transition temperature close to the temperature of the droplet during spray drying. It is expected that the droplet temperature will rise from the wet bulb temperature to the outlet air temperature during spray drying [6]. These temperatures are usually between 70 and 90 °C, which motivates the selection of 50:50 and 75:25 ratios (WP:MD) in this study.

Therefore, pilot-scale spray drying trials were carried out with MD, WP and selected WP–MD mixtures, with the objective to assess whether the observed morphologies during large scale spray drying are in line with the results from previous single droplet drying [5,7,8].
2. Materials and methods

2.1. Materials

Feed solutions were prepared by dissolving maltodextrin DE12 (Roquette, France), whey protein isolate (Volac, UK), and mixtures of those with a ratio of 75:25 and 50:50 (WP:MD) on mass basis, in tap water at a dry matter content of 30% (w/w). It should be noted that the WP isolate used in the current pilot-scale spray study had to be sourced from a different supplier than the WP used in our previous single droplet drying study [5]. The WP used here contained some insoluble components, probably denatured protein, of which preliminary single droplet drying experiments showed irregularities on the surface of the particles. These insoluble components can be removed by centrifugation before drying, after which smooth particles are again formed (data not shown). This centrifugation was not done before spray drying, and therefore these insoluble components will have influenced the morphologies observed in the pilot-scale drying.

2.2. Spray drying

A single stage pilot-scale spray dryer (DW1000 Spray dry works, Netherlands) was used, having a maximum evaporation capacity of 80 kg/h. The drying chamber was 2.4 m in diameter with a total height of 6 m, and was equipped with a single high pressure nozzle (SKY 17 66Y, Spraying Systems Co., USA). The spray dryer was operated in co-current mode at an air flow of 1000–1500 kg/m². The drying conditions were varied by choosing different inlet air temperatures, 140 °C, 150 °C or 190 °C, and relative humidities of the outlet air (RHout), 8% or 15%. The RHout was changed by varying the nozzle pressure, which in turn influenced the morphologies observed [11]. The quantitative morphology results were related to the particle size. Small particles (between 5 and 20 μm) were more often hollow, while larger particles (between 20 and 100 μm) were more often wrinkled. This may be explained by the initial higher heat and mass transfer coefficient for smaller droplets as described in the Ranz-Marshall equation [9], which results in faster evaporation [10], in turn leading to more rapid skin formation and thus to the formation of hollow particles [11].

The effect of the composition on the morphology was studied by drying all formulations at Tin = 190 °C and RHout = 8%. Within single batches different morphologies were observed (Fig. 2a–d), but the overall trend is clear: MD and 50:50 (WP:MD) powder contained more wrinkled particles, while WP more hollow and fragmented. The 75:25 (WP:MD) powder had both wrinkled and hollow particles. Further particle analysis was carried out using a Malvern Morphologi 4 particle characterization device. Three particle morphology groups could be differentiated: hollow particles, wrinkled particles and other particles. The first two groups were expected on the basis of the results obtained earlier with single droplet drying experiments, while the last group represented a mixture of fragmented or agglomerated particles without a distinctive morphology. The quantitative analysis confirms that the MD and 50:50 (WP:MD) powder contained more wrinkled particles, while WP more hollow and fragmented. The 75:25 (WP:MD) powder had both wrinkled and hollow particles. Further analysis was carried out using a Malvern Morphologi 4 particle characterization device.
temperatures lead to less wrinkled particles, with ~6% wrinkled particles at Tin 190 °C, 15% at Tin 150 °C, and ~20% wrinkled particles at Tin 140 °C (small particles, RH out 15%), and more hollow particles (Fig. 3f). The number of particles that could not be classified as hollow or wrinkled (i.e. ‘other’ particles) was also larger, especially at lower inlet air temperatures. This might be related to increased particle stickiness and subsequent agglomeration, or to particle fragmentation.

Higher outlet air humidity with at the same time a lower outlet air temperature did not have a pronounced effect on the morphology. We expect that outlet air conditions have only minor effect on the morphology, since skin formation and thus the onset of morphology formation happens in the very initial period of the drying process, while at the outlet, the outlet air and the surface of the particles will be close to equilibrium. At the latter conditions the morphology of the particles is fixed. Although not affected by the outlet air temperature, the two particle size categories show different morphologies, with small particles more often hollow. As discussed, this is probably caused by the faster initial drying kinetics as discussed before.

3.2. Relation between morphology and powder properties

The macroscopic powder properties, such as the bulk density and the size distribution are directly related to the particle morphology distributions and thus to the slurry composition and the drying conditions (Fig. 4).

First, the relation between the particle morphology and the powder bulk density was studied for mixed systems with compositional ratio 75:25 (WP:MD) (Fig. 4a). A clear relation can be observed: powders that contain more hollow particles, also have a lower bulk density. This may be explained by the larger porosity of the hollow particles, while at the same time the number mean diameter (D_{1,0}) remains constant. We use here the number mean particle size, since the percentage of hollow particles is also number-based. The volume mean particle size (D_{3,4}) was observed to increase with a smaller percentage of hollow particles. This difference between the number and volume-based diameter indicates a wider particle size distribution for powders with less hollow particles and thus more wrinkled particles. We expect that this is because of more agglomeration and the presence of a few large agglomerates when drying at lower inlet air temperature (especially 140 °C). The formation of these agglomerates may be due to the particles being dried at a slower rate, allowing stickiness for a longer time.

The MD powder had a much higher bulk density (~450 g/L) compared to formulations containing WP (Fig. 4c), while the particle size was comparable to other formulations dried at the same drying conditions (Fig. 4d). The differences between the other formulations were smaller, but present nonetheless. WP and 50:50 (WP:MD) powder had similar bulk densities (350–400 g/L), while the powder with a ratio of 75:25 (WP:MD) had a slightly lower bulk density (340–370 g/L at similar drying conditions). Similarly as for 75:25 (MD:WP) powder (Fig. 4a), the ratio 50:50 (WP:MD) shows that the bulk density can be increased by decreasing the inlet temperature. Although the
analysis was not done for these samples, it is expected that this corresponds to an increase in percentage of wrinkled and decrease in percentage of hollow particles. The two mixed formulations dried here show that the bulk density can indeed be influenced by adapting the inlet temperature.

An important process parameter is the nozzle pressure, which determines the feed rate and with that the outlet conditions of the spray tower. Moreover, it influences the droplet size of the spray, which in its turn influences the drying kinetics and final particle size. A higher nozzle pressure generates smaller droplets, which directly affects the morphology development as well. However, no clear trend can be seen on the final particle size (Fig. 4b). The large average particle size of the 75:25 (WP:MD) powder produced at 20 bar is probably caused by agglomeration due to stickiness of the drying droplets, caused by the low drying temperature (140 °C). Only the powders produced at the highest nozzle pressure (~70 bar) gave a slightly smaller particle size. Except for the latter observation, the nozzle pressure has thus only a small effect on the powder characteristics.

![SEM images of spray dried powders](image)

**Fig. 3.** Effect of drying conditions on 75:25 (WP:MD) spray dried powders on morphology, with SEM images: a) 190 °C inlet temperature/15% outlet relative humidity, b) 150 °C/15%, c) 140 °C/15%, d) 190 °C/8%, e) 150 °C/10%, and f) the results of the powder particle analysis with % wrinkled (orange), % hollow (blue) and % other (green) divided in two size groups: between 5 and 20 μm and between 20 and 100 μm. The error bars represent the absolute error. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
3.3. Relation to observations during single droplet drying

In this section we compare our pilot-scale spray drying results to our previous results from single droplet drying with similar compositions [5]. In our previous study, droplets of \( r_{\text{initial}} = 500 \mu m \) were dried with air (40–90 °C, 0% RH) with an airspeed of 0.3 m/s, while recording the drying at 0.5 fps. These conditions were set to mimic the conditions in a spray dryer as close as possible: the airspeed was in the same order of magnitude as the speed difference between the falling droplet and the air, and the bulk air temperature (80–90 °C) was comparable to typical spray dryer outlet temperatures. However, there are also differences between the drying conditions: in single droplet drying, the initial droplet size was larger and the drying times longer. The effects hereof on the results are discussed below.

Similar powder particle morphology types (i.e. hollow, wrinkled and mixed morphologies) were observed using both techniques. Specifically, during single droplet drying hollow particles were observed for \( 75:25 \) (WP:MD) over a wide temperature range, whereas for \( 50:50 \) (WP:MD) wrinkled particles were observed and only hollow particles for lower temperatures [5]. This corresponds to the observations in the pilot trial. Here, the 50:50 mixture contained much more wrinkled and less hollow particles compared to the \( 75:25 \) mixture. Spray-dried powders contain particles with different sizes, drying histories and thus will always yield distributed properties, from a distribution in particle morphology. Still, on average the morphologies obtained via spray drying correlated in a similarly way to the composition as during single droplet drying.

There was one clear difference between single droplet and spray drying, and that was in the influence of the droplet size on the final morphology. In pilot-scale experiments, larger particles were more wrinkled, while smaller particles were more hollow (Figs. 2e and 3f), whereas in single droplet drying this was the other way around [7]. Most likely, this difference originates from different phenomena in both drying processes. During single droplet drying, the drying time for the larger droplets of ~1 mm diameter is in the order of 2–3 min depending on the drying temperature. Such long drying times allow for phase separation in WP-MD formulations, promoting the formation of hollow particles [5]. Lower drying rates due to increasing droplet size or lower temperature during single droplet drying lead to more extensive phase separation within the droplet and thus more hollow particles. During pilot-scale spray drying, however, drying times are very short, and phase separation is unlikely to occur. We can also see more hollow, smaller particles for pure MD and WP systems in which no phase separation can possibly occur (Fig. 2e). The formation of more hollow particles for smaller droplets may be explained as discussed before by faster drying due to faster heat and mass transfer, relative to the demixing times. These observations suggest that the very fast drying in spray dryers influences the morphology as well, next to the effects of matrix composition.

4. Conclusions

Pilot-scale spray drying experiments showed that overall the particle morphologies observed for different formulations can be deduced from single droplet drying experiments, even though the fast drying rates during real spray drying inhibit demixing, which can occur during single-droplet drying, resulting in differences. By operating the spray dryer at very low inlet temperatures and/or low outlet humidity, we can increase the number of hollow particles from 32% to 59% for a \( 75:25 \) (WP:MD) powder, simultaneously reducing the number of wrinkled particles from 34% to 19%. While conditions like the lower inlet air temperature influence the capacity of the tower, the particle morphology can be steered and improved by changing operating conditions. Moreover, a spray dried particle’s drying trajectory is different for each particle, and different in all types and sizes of spray.
dryers. Therefore, extrapolating these results to different types of spray dryers is not evident. However, given the similarities between single droplet-scale and pilot-scale, we do believe it is possible to also steer the powder properties on industrial scale.

Ultimately, it is desired to tailor powder properties for fast reconstitution and high flowability. In industrial spray drying processes usually such powders are prepared by further agglomeration. In the current pilot-scale spray drying set-up the powder purposefully was not agglomerated, which allowed studying the influence of matrix and drying conditions on the primary particle properties. Future studies could continue by making agglomerated powders for the model systems studied [12,13].

Declaration of Competing Interest

None.

Acknowledgements

This work is an Institute for Sustainable Process Technology (ISPT) Project. Partners in this project were FrieslandCampina, Danone and Corbion. Jasper Vollenbroek, Koen van Dijke and David Hollestelle are thanked for their help with the pilot trials. Sandra Remijn and Nicole Bos are thanked for performing the Morphologi 4 measurements.

References

[1] X. Fu, D. Huck, L. Makein, B. Armstrong, U. Willen, T. Freeman, Effect of particle shape and size on flow properties of lactose powders, Particuology. 10 (2012) 203–208, https://doi.org/10.1016/j.partic.2011.11.003.

[2] M. Bunimiller, J. Carson, J. Presscott, A preliminary investigation concerning the effect of particle shape on powder’s flow properties, World Congress on Particle Technology, Sydney, Australia 2002, p. 4.

[3] C.Y. Takeiti, T.G. Kieckbusch, F.P. Collares-Queiroz, Morphological and physicochemical characterization of commercial maltodextrins with different degrees of dextrose-equivalent, Int. J. Food Prop. 13 (2010) 411–425, https://doi.org/10.1080/10942910802181024.

[4] M.A.I. Schutyser, E.M. Both, I. Siemens, E.M. Vaessen, L. Zhang, Gaining insight on spray drying behavior of foods via single droplet drying analyses, Dry. Technol. 0 (2018) 1–10, https://doi.org/10.1080/07373937.2018.1482908.

[5] E.M. Both, A.M. Karlina, R.M. Boom, M.A.I. Schutyser, Morphology development during sessile single droplet drying of mixed maltodextrin and whey protein solutions, Food Hydrocoll. 75 (2018) 202–210, https://doi.org/10.1016/j.foodhyd.2017.06.022.

[6] J. Pendana, A.A. Zubia, O. Kutabuya, M. Schutyser, M. Fox, Spray drying of Lactobacillus plantarum WCFS1 guided by predictive modeling, Dry. Technol. 33 (2015) 1789–1797, https://doi.org/10.1080/07373937.2015.1026975.

[7] E.M. Both, I. Siemens, R.M. Boom, M.A.I. Schutyser, The role of viscosity in morphology development during single droplet drying, Food Hydrocoll. 94 (2019) 510–518, https://doi.org/10.1016/j.foodhyd.2019.03.023.

[8] E.M. Both, M. Nuzzo, A. Millqvist-Fureby, R.M. Boom, M.A.I. Schutyser, Morphology development during single droplet drying of mixed component formulations and milk, Food Res. Int. 109 (2018) 448–454, https://doi.org/10.1016/j.foodres.2018.04.043.

[9] W.E. Ranz, W.R. Marshall, Evaporation from drops - part 1, Chem. Eng. Prog. 48 (1952) 141–148, https://doi.org/10.1002/crep.5600480320.

[10] T.T.H. Tran, J.G. Avila-Acevedo, E. Tsotsas, Enhanced methods for experimental investigation of single droplet drying kinetics and application to lactose/water, Dry. Technol. 34 (2016) 1185–1195, https://doi.org/10.1080/07373937.2015.1100202.

[11] J. Vicente, J. Pinto, J. Menezes, F. Gaspar, Fundamental analysis of particle formation in spray drying, Powder Technol. 247 (2013) 1–7, https://doi.org/10.1016/j.powtec.2013.06.038.

[12] C. Turchiuli, Z. Eloualia, N. El Mansouri, E. Dumoulin, Fluidised bed agglomeration: agglomerates shape and end-use properties, Powder Technol. 157 (2005) 168–175, https://doi.org/10.1016/j.powtec.2005.05.024.

[13] J. Ji, K. Cronin, J. Fitzpatrick, M. Fenelon, S. Miao, Effects of fluid bed agglomeration on the structure modification and reconstitution behaviour of milk protein isolate powders, J. Food Eng. 167 (2015) 175–182, https://doi.org/10.1016/j.jfoodeng.2015.01.012.