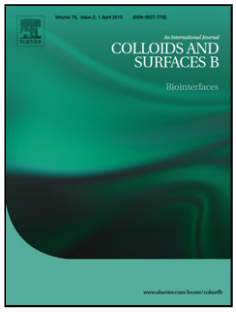

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The Impact of Atomization on the Surface Composition of Spray-dried Milk Droplets

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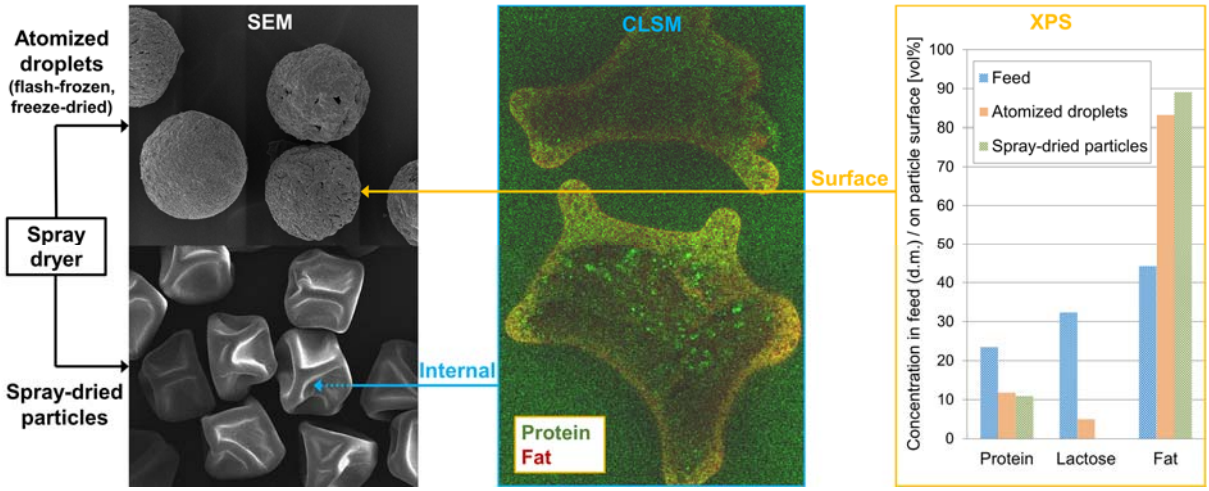
Graphical abstract



Highlights

- The effect of atomization on the surface composition of spray-dried milk particles
- Droplet atomization is responsible for fat surface film
- Feed jet preferably disintegrates along oil-water interface of fat globules
- During drying stage fat film remains on surface and protein accumulates underneath

Abstract

The dominant presence of fat at the surface of spray-dried milk powders has been widely reported in the literature and described as resulting in unfavourable powder properties. The mechanism(s) causing this phenomenon are yet to be clearly identified. A systematic investigation of the component distribution in atomized droplets and spray-dried particles consisting of model milk systems with different fat contents demonstrated that atomization strongly influences the final surface composition. Cryogenic flash-freezing of uniform droplets from a microfluidic jet nozzle directly after atomization helped to distinguish the influence of the atomization stage from the drying stage. It was confirmed that the overrepresentation of fat on the surface is independent of the atomization technique, including a pressure-swirl single-fluid spray nozzle and a pilot-scale rotary disk spray dryer commonly used in industry. It is proposed that during the atomization stage a disintegration mechanism along the oil-water interface of the fat globules causes the surface predominance of fat. X-ray photoelectron spectroscopic measurements detected the outermost fat layer and some adjacent protein present on both atomized droplets and spray-dried particles. Confocal laser scanning microscopy gave a qualitative insight into the protein and fat distribution throughout the cross-sections, and confirmed the presence of a fat film along the particle surface. The film remained on the surface in the subsequent drying stage, while protein accumulated underneath, driven by diffusion. The results demonstrated that atomization induces component segregation and fat-rich surfaces in spray-dried milk powders, and thus these cannot be prevented by adjusting the spray drying conditions.

Key words: Milk powder; Spray Drying; Flash-Freezing; Surface fat; Atomization; Oil-water interface

Introduction

Many studies on the spray drying of milk or similar emulsions have reported an unwanted fat coverage on the powder surface, concomitant with detrimental effects on the

product characteristics, such as deteriorated storage stability (Granelli et al., 1996, Hardas et al., 2000, Keogh et al., 2001), reduced solubility (Fäldt and Bergenståhl, 1996b, Millqvist-Fureby et al., 2001) and reduced flowability (Kim et al., 2005, Nijdam and Langrish, 2006). To explain the segregation process of lipid, protein and lactose in the course of spray drying of milk droplets, various concepts have been proposed on the basis of different physical properties of these main components. The material segregation process is often perceived to take place simultaneously to the drying process after atomization. Fäldt and Bergenståhl (1996a) suggested a movement of milk protein to the air-water interface as a consequence of surface activity, an explanation that has been adopted in other studies (Gaiani et al., 2006, Adhikari et al., 2009). Meerdink and van't Riet proposed that material segregation takes place in a drying milk droplet due to differences in the component diffusivities (Meerdink, 1994, Meerdink and van't Riet, 1995), which has been mentioned in subsequent studies (Kim et al., 2003, Fu et al., 2011a, Chew et al., 2014, Nikolova et al., 2015). In addition, the crust composition of a drying droplet might be influenced by the solubility of the dissolved solutes (Charlesworth and Marshall, 1960), the concept of which was later applied on dairy systems (Kim et al., 2009, Wang and Langrish, 2009). It was argued that, once part of the solidified crust, the precipitated material does not diffusion anymore and thus a lower solubility could lead to a higher concentration near the surface. When the fat is in molten state during the drying process because of the exposure to high temperatures, a convection to the surface through a network of pores and cracks, driven by capillary forces or overpressure of internal vacuoles, is also a potential reason (Nijdam and Langrish, 2005). Different combinations of these hypotheses are often presented as an explanation for fat surface accumulation in spray-dried milk powders, and accordingly the discussion has been restricted to the drying stage in most reports.

However, a small number of studies have discussed the possibility that an atomization induced mechanism might already impact the material distribution ahead of the actual drying process, although the conclusions were based on the final product surface while the atomization process itself was not investigated. Fyfe et al. (2011) compared the surface composition of commercial milk particles (skim milk, whole milk, milk protein concentrate) with the products of a pilot-scale and a laboratory-scale spray dryer. Protein dominate the surfaces of the skim milk and milk protein concentrate powders due to their low bulk fat content, but nevertheless in all powders fat was overrepresented at the surface in relation to the bulk content. A noticeably lower protein surface content in commercial skim milk powder and a substantially higher fat overrepresentation in commercial whole milk powder were found. There was no difference in surface composition between pilot and lab scale production of whole milk powder, and only a minor deviation for skim milk powder. Xu et al. (2013) found that the surface fat content increased with smaller emulsion droplet sizes in powders

comprising different protein isolates, maltodextrin and sunflower oil from a bench-top spray dryer. This was explained by a mechanism of liquid fat leakage and consequent spreading of a thin fat film at the particle surface caused by rupture of the fat globule membranes, which become less stable with larger sizes (Vignolles et al., 2009). Since Xu et al. (2013) only analysed the powder properties, their study could not determine whether the supposed rupture occurs due to differential stress on the membranes as they shrink at constant fat globule volume during drying or due to high shear rates imposed on the globules during atomization. Kim et al. (2009) reported a fat coverage of more than 90 % and 18 %, respectively, on the surface of commercial whole milk and skim milk powders. Significant fat surface overrepresentation was also observed for particles that were dried at very high temperatures and consequently under rapid solidification and material immobilization. Thus, it was concluded that the fat coverage must have occurred, at least in part, during atomization. A film disintegration during droplet formation along the oil-water interface of lipid globules was proposed as a possible mechanism. In addition, it was hypothesized that the surface becomes further enriched in fat during the subsequent drying process because of the relatively low diffusivity of fat globules. It is difficult to draw a reliable conclusion about the impact of atomization from the final product powder characteristics only. For this reason, Wu et al. (2014) attempted to analyse droplet surface compositions directly after atomization with a microfluidic jet nozzle by flash-freezing the droplets in liquid nitrogen (LN_2). Comparison with corresponding spray-dried powders indicated that the atomization step predominantly determines the final surface composition. The study, however, was limited to skim milk and to only one atomization technique that is not used in commercial milk powder manufacturing.

The aim of the present study was to extend the approach by Wu et al. (2014) to conduct a systematic investigation of the impact of atomization on the surface composition of spray-dried milk powders. A microfluidic multi-jet spray dryer was used for the production of monodisperse particles to understand the influences of initial droplet size and emulsion fat content. The results were compared with those from different atomization techniques more common in an industrial setting. Spray-dried particles and flash-frozen droplets were analysed in terms of surface composition by X-ray photoelectron spectroscopy (XPS), internal material distribution by confocal laser scanning microscopy (CLSM), and size and morphology by light microscopy and scanning electron microscopy (SEM), respectively.

Material and Methods

Feed Preparation

Two model milk emulsions with different fat contents were used. The first was a mixture of dissolved lactose, calcium caseinate and whey protein with a very low fat content of 0.3 % w/w in dry matter (d.m.) to form a low-fat model powder (LFMP) emulsion. The other one was a fat filled milk powder (FFMP) emulsion that featured a composition typical for both bovine whole milk and commercially sold FFMP. The solid content of the FFMP emulsion amounted to 20 % w/w, and it contained 40.8 % w/w lactose, 31.1 % w/w fat and 27.0 % w/w protein in d.m. The LFMP emulsion resembled the composition of the FFMP emulsion excluding the fat, and thus had a solid concentration of 14 % w/w. For preparation of the FFMP emulsion, commercial skim milk powder (Coles Supermarkets Australia Pty Ltd, Australia) was reconstituted together with sustainably sourced refined *Elaeis guineensis* palm oil fat (Auroma, Australia). For the LFMP emulsion, a mixture of α-lactose monohydrate (Sigma-Aldrich Co., USA), calcium caseinate isolate (Nutrients Direct Pty Ltd, Australia) and whey protein isolate (Nexius Pty Ltd, Australia) with a caseinate/whey ratio of 4:1 was used instead of commercial skim milk powder in order to reduce the fat content as far as possible. Both model systems were prepared with deionised water at 45 °C for 1 h, and then were prehomogenized in a high-speed colloid mill (WiseMix Homogenizer HG-15D, Daihan Scientific, South Korea) at 1000 rpm, followed by homogenization in a high pressure homogeniser (EmulsiFlex-C5, Avestin, Canada) with three passes at 1,000 bar and two subsequent passes at 500 bar. After homogenization the droplet size distribution was analysed by dynamic light scattering (Zetasizer Nano ZS, Malvern Instruments Ltd, UK) to consistently ensure lipid droplet diameters below 1 µm. Dynamic viscosities were measured at 25 °C with a cone and plate rheometer (Haake Mars, Thermo Fisher Scientific, USA).

Fresh commercial whole milk, which contained 31.1 % w/w fat in d.m. and a solid concentration of 12.5 % w/w, was purchased locally (Pauls Full Cream Milk, Parmalat Australia Pty Ltd, Australia) for comparison with the FFMP emulsion. To investigate the surface composition of skim milk powder spray-dried under conditions comparable with industrial milk powder production, samples were also taken from a pilot milk processing site (CSIRO Food and Nutrition, Werribee, Australia). Prior to spray drying, raw milk (Tatura Milk Industries Ltd, Australia) was skimmed in a rotary cream separator and high temperature, short time pasteurized to obtain 0.86 % w/w fat in d.m. and a solid content of 9.2 % w/w.

Atomization and Spray Drying with a Microfluidic Multi-Jet Spray Dryer

A microfluidic multi-jet spray dryer (MFMJSD), fabricated by Nantong Dong-Concept New Material Technology Co Ltd, P.R. China, was used to facilitate monodisperse droplet generation with uniform drying history. Depending on the amount of powder required, one to three microfluidic jet nozzles could be operated simultaneously. The design was similar to the nozzle used in the work of Wu et al. (2014), which has been described in detail elsewhere (Wu et al., 2011). In brief, each nozzle consisted of a glass tube with an orifice of 50, 100 or 150 µm in diameter. A piezoelectric ceramic jacket surrounded the nozzle tip, as illustrated in Figure 1 a, and was electrically connected to a wave generator (DG1000, Rigol Technologies Inc., United States). It imposed a sinusoidal pulse of adjustable frequency on the feed emulsion stream passing through the glass tube and broke it up into individual droplets. The optimum pulse frequency setting was 10 kHz for all feed emulsions, which was found by photographing the jet disintegration with a D7000 digital LSR camera, equipped with an AF Micro-Nikkor 60mm f/2.8D micro-lens and a SB-300 high speed flash light (Nikon Corp., Japan). A typical image of the droplet generation is given in Figure 1 b. With increasing orifice diameter the feed pressure had to be reduced from 110 to 33 and 17 kPa, respectively, to allow for uniform droplet generation. The nozzles could either be operated detached from the MFMJSD instrument for cryogenic flash-freezing of the generated droplets, or positioned onto the drying tower for spray drying. Experiments were conducted with fresh whole milk, FFMP and LFMP emulsions.

A schematic diagram of the MFMJSD is presented in Figure 1 c. Three individual tubes transferred the feed from 1.5 l steel reservoirs to each nozzle by pneumatic pressure. The nozzles were placed in water-cooled holders, and air streams coming from holes in the nozzle holders dispersed the droplet jets. The droplets then passed through a double-walled stainless steel drying chamber with embedded ceramic fibre insulation of 3.2 m in height and 0.6 m in diameter. The concurrent drying air flow was generated by means of a ring blower (W2PB-410-H06, XDS, P.R. China) and heated with a 3300 W electrical heating element, before being evenly dispensed into the tower through two perforated metal sheets. The temperature of the entering air was controlled with a thermocouple, and four thermocouples were inserted into the drying chamber to monitor the temperature gradient along the tower. The data was read out *via* a Picolog USB TC-08 data logger (Pico Technology, United Kingdom) and recorded with a desktop computer. Spray drying was performed at drying air temperatures of 190 °C at the tower top (‘T1’ in Figure 1 c), 87 °C at the tower bottom (‘T4’), and 132 °C and 102 °C in between (‘T2’ and ‘T3’, respectively).

Spray Drying with Rotary Pilot-Scale Spray Dryer and Atomization with Pressure-Swirl Nozzle

The freshly prepared skim milk was spray-dried at CSIRO with a pilot-scale spray dryer (Niro, GEA Group AG, Germany), which was equipped with a rotary disc atomizer and had a water evaporation capacity of 15-18 l/h. The feed was preheated to 75 °C, the inlet air temperature was 185 °C and the outlet air temperature was 80 °C. The instrument did not contain an integrated bed, and samples were collected for 1 min at 30 °C.

Furthermore, FFMP and LFMP droplets were flash-frozen subsequent to atomization in pressure-swirl single-fluid spray nozzles (MT Brass Series, AmFog Nozzle Technologies Inc, USA). Two nozzles with different orifices of 0.2 or 0.3 mm in diameter were tested at feed pressures of 450 and 600 kPa.

Cryogenic Flash-Freezing and Subsequent Freeze-Drying

To investigate the droplets directly after atomization, a modified methodology from Rogers et al. (2008) was applied. Droplets were collected in liquid nitrogen at a distance of 10 cm (if not stated otherwise) from the nozzle, which was operated outside of the spray dryer. The droplet jet required 0.03 ± 0.01 s to travel this distance, as calculated based on the mass flow rate measured by jet collection on a balance and on the approximate jet diameter read out from scaled camera images. The flash-frozen droplets were subsequently kept frozen by storage in dry ice and freeze-dried in a FreeZone 2.5 l benchtop freeze dry system (Labconco Corp., USA) at -80 °C and 0.1 mbar for 48 h.

Confocal Laser Scanning Microscopy

Selected FFMP samples were prepared for CLSM investigation by dual labelling with fluorescent dyes prior to mixing and further processing based on a procedure reported by Taneja et al. (2013). The aqueous solution of already dissolved protein and the molten fat were stained with 0.01 % w/w hydrophilic Fast Green FCF and 0.02 % w/w hydrophobic Nile Red (Sigma Aldrich Co., USA), respectively. After mixing and processing to powder as described above, the labelled powder samples were prepared on a microscope slide with DPX mounting medium (Sigma Aldrich Co., USA) and investigated by CLSM with a Nikon A1$^+$ confocal microscope system (Nikon Corp., Japan). The Fast Green FCF and the Nile Red stains were sequentially excited with a 487 nm argon laser light and a 637 nm helium-neon laser light, respectively. Images were taken with a 60x/1.4 oil immersion objective at a resolution of 512x512 pixels.

Spectroscopic Surface Composition Analysis

Powder surface compositions were determined by XPS using an AXIS Ultra DLD spectrometer (Kratos Analytical Inc., UK) with a monochromated Al K_α source, a hemispherical analyser operating in the fixed analyser transmission mode and the standard aperture (analysis area: 0.3 mm × 0.7 mm). The total pressure in the main vacuum chamber during analysis was typically 10-8 mbar. Samples were filled into shallow wells of custom-built sample holders. One lot of each sample was prepared and 2 different locations were analysed on each sample at a nominal photoelectron emission angle of 0º with respect to the surface normal. Since the actual emission angle is ill-defined in the case of particles (ranging from 0º to 90º), the sampling depth may have ranged from 0 nm to approximately 10 nm. All elements present were identified from survey spectra. The relative atomic concentrations of the detected elements were calculated using integral peak intensities and the sensitivity factors supplied by the manufacturer. The concentrations in lactose, protein and fat can be assumed to be linear combinations of the atomic surface composition (Fäldt et al., 1993). The surface concentration in each component, expressed in percentage by volume, was hence estimated by linearization based on representative structural formulas for milk protein, lactose and fat as described elsewhere (Chew et al., 2014).

Particle Morphology and Size Distribution Measurement

A field-emission scanning electron microscope (FEI Nova NanoSEM 450 FE-SEM, FEI Corp., USA) operated with a 5 kV electron beam was employed to study the morphology of spray and freeze-dried powder. Additionally, to study the inner particle structure based on a modified procedure of Rosenberg et al. (1985), powders were suspended in a resin and then cut with a Reichert Ultracut S ultramicrotome (Leica Microsystems, Austria) equipped with a Cryotrim 45 knife (DiATOME, USA). A cold-setting resin (Epofix, Electron Microscopy Sciences, USA), which was cured at room temperature overnight, was used to avoid heat damage to the particles. Both the microtomed and the free powder samples were coated with a 4 nm thick Iridium layer to prevent electrical charging.

Information about particle size distributions was acquired by images taken of the powder samples with a light microscope (B1-211A, Motic, P.R. China) through a 4x objective. By means of ImageJ 1.48 (National Institutes of Health, USA) the projected surface areas were measured of 50 particles for each sample obtained with the microfluidic nozzles and of more than 100 particles for every other sample. The equivalent diameters were calculated from the projected surface areas.

Results and Discussion

Morphology and Size of Particles Atomized and Spray-Dried in the Microfluidic Multi-Jet Spray Dryer

To better understand the surface formation mechanism during spray drying, the MFMJSD instrument was used to produce monodisperse particles of identical drying histories (Rogers et al., 2010, Fu et al., 2011b). Each spray-dried and freeze-dried powder produced with the microfluidic jet nozzles featured a very narrow size distribution with small standard deviations (refer to Figure A.1 in the appendix). Exemplary SEM images are shown in Figure 2. The uniformity allowed direct correlations of the impact of different emulsion compositions and orifice sizes on the particle surface composition, which are difficult to derive from powders produced by conventional spray drying techniques with their wider size and morphology distributions (Masters, 1991). Furthermore, since the atomized droplets were ultra-rapidly flash-frozen at -196 °C and the succeeding freeze-drying occurred at a very low drying rate, migration of the solid components and structural changes subsequent to the collection in liquid nitrogen were prevented (Ishwarya et al., 2014). The spray-dried particles had a non-porous crust and were inwardly buckled in shape. This can be explained by an initial inflation due to air expansion in particles of nearly dry condition which is then followed by deflation and shrivelling in colder dryer regions (Kim et al., 2009) or by compressive stress on the particle crust attributable to capillary forces and rapid moisture removal (Tsapis et al., 2005, Rogers et al., 2010). Figure 2 c displays a typical cross-sectional image of a spray-dried particle that had been embedded and microtomed, containing some hollow areas and internal porosities. The freeze-dried particles were spherical, since they were flash-frozen as freshly generated droplets, and were traversed by porous structures as a result of water sublimation during freeze-drying (Figure 2 d).

As can be seen in appendix A (Figure A.1), for the microfluidic jet nozzles of 50, 100 and 150 µm in orifice diameter, there was an almost linear relationship between size of the orifice and the resulting LFMP droplets; a three times bigger orifice diameter lead to a 2.8-fold increase in droplet size. For the same microfluidic jet nozzle size of 100 µm, the LFMP droplets were appreciably larger than the FFMP droplets (diameter of 135.8 and 115.6 µm, respectively). The feed pressure and piezoelectric pulse frequency were identical, and thus the size difference most likely originated from a change in disintegration behaviour of the emulsions as a result of their different viscosities or fat contents. Due to its additional fat content, the viscosity of the FFMP emulsion (2.9 mPa·s at a shear rate of 200 s^{-1}) was greater than the one of the LFMP emulsion (2.4 mPa·s). Typically, a higher viscosity results in a delayed disintegration of the jet during atomization, as the Reynolds number is reduced and the jet stability is increased. Thus, an increased viscosity is to be expected to favor the

formation of larger droplets (Lefebvre, 1989). Here, however, a converse trend was observed. It was consequently concluded that the presence of more fat reduced the intrinsic stability of the FFMP emulsion jet upon atomization. The emulsion might have been less stable against disintegration along the oil-water interfaces formed by the lipid globules. With a higher number of fat globules, the emulsions became virtually 'perforated' by these areas of lower cohesion, where the emulsion could disintegrate into droplets more easily. Such a perforation mechanism was also discussed in a study by Dombrowski and Fraser (1954), in which fan-shaped flat sheets consisting of either pure water or a soluble oil-water emulsion were generated with a single-hole fan-spray nozzle and the film disintegration was observed by a rapid light flash photographic technique. In the presence of oil the films broke significantly closer to the nozzle. Zakarian and King (1982) investigated similarly shaped flat sheets of an aqueous sucrose solution with a dispersed phase of peanut oil, and found that the point of disintegration was particularly sensitive to the fat content in a range of 0 to 0.1 % w/w fat. Though the atomization technique and emulsion types were different to the present study, it seems likely that a comparable perforation mechanism was induced in the FFMP emulsion (lipid level of 6.2 % w/w), and also, at a less pronounced extent, in the LFMP emulsion (lipid level of 0.04 % w/w).

Impact of Microfluidic Jet Atomization on Particle Surface Composition and Influence of Feed Composition

The FFMP emulsion proved to be a suitable model system for fresh whole milk in terms of surface formation behaviour during spray drying, as shown in Figure 3 a,b for the MFMJSD instrument equipped with a 100 µm nozzle. According to their similar dry matter feed compositions, the droplet and particle surface compositions of the FFMP emulsion and fresh whole milk were in good agreement as analysed by XPS. Most notably it was found that the atomized droplets' surfaces were already covered almost completely by fat. The surface fat contents of the atomized droplets was approximately double that of the dry matter feed fat content, occupying between approximately 83 % and 92 % of the surface. Protein was underrepresented on the droplet surface with occupying only half as much volume as may be expected based on the feed compositions. The results agree with the decline in droplet size with increasing fat content, and further support the hypothesis that the presence of fat globules caused a perforation of the emulsion that resulted in an easier jet disintegration along the oil-water interfaces during atomization. As the jet preferably broke up along the fat globules, the fat globules were immediately at the surface as soon as individual droplets had been formed.

The component segregation observed in the flash-frozen particles was a direct result from the atomization step, and was not formed in the time after leaving the nozzle and

before entering the liquid nitrogen. No substantial difference in surface composition was observed for a considerably longer travelling time when the distance between nozzle and liquid nitrogen was increased to 60 cm (Figure 3 a). Moreover, water evaporation from the droplets, which could have induced a component segregation caused by different diffusivities, was negligible as the temperature between the nozzle and the collection tank was 15 °C. In addition, the droplet residence time of less than 0.05 s between nozzle and liquid nitrogen prevented any appreciable component diffusion to or from the surface driven by, for instance, surface activity or concentration gradients formed during atomization. The diffusion time scales over a diffusion length of 10 µm were estimated to be of more than 20 and 70 seconds, respectively, for fat globules and protein at 15 °C (refer to Table B. 1 in appendix B).

Whereas the atomization stage considerably influenced the particle surface composition, no significant impact of the subsequent drying process on the chemical surface composition was observed for high fat contents (changes smaller than 6 % v/v for every component as shown in Figure 3 a,b). There was only a minor increase in fat on the FFMP particles. Lactose comprised very small proportions on the surfaces of both the atomized droplets and the spray-dried powders. This demonstrated that the atomization step primarily determined the final surface composition of whole milk powder obtained with a MFMJSD, being responsible for a high fat overrepresentation, and thus strongly influenced the functional product properties. The observation of a pronounced fat accumulation on the droplet surface during atomization in microfluidic jet nozzles was consistent with the study on the atomization of skim milk conducted by Wu et al. (2014), where a feed of 33 % w/w solid content containing 35 % protein and 0.7 % fat in d.m. resulted in 40 % protein and 29 % fat on the surface of the atomized droplets. However, Wu et al. (2014) observed a significant change in surface composition during the following drying step with an increase in protein to 52 % and in fat to 38 %. This was in contrast to the here investigated whole milk and FFMP emulsions. In the drying whole milk and FFMP droplets, the dense surface fat layer presumably concealed any underlying component segregation. This was confirmed by spectroscopic analysis of the surface of atomized and spray-dried particles consisting of the LFMP feed (Figure 3 c). Again, an over-stoichiometric amount of surface fat in relation to the dry matter feed concentration was formed during atomization. Yet, due to the low feed fat content, this time the fat did not dominate the surface region analysed by XPS with a surface proportion of approximately 13 %. This allowed the observation of a slight overrepresentation of protein that already emerged during atomization. In course of the following drying stage, a pronounced rise in protein surface coverage from approximately 51 % to 74 % was found.

Development of Material Distribution and Impact of Orifice Size in Microfluidic Multi-Jet Spray Drying

To understand the mechanism that governed the protein migration to the surface during the drying stage of the microfluidic spray drying process, the influence of the droplet drying time was studied by using nozzles with a smaller and a larger orifice size (Figure 4). The protein surface content rose only slightly from 57 % after atomization to 65 % after spray drying for a 50 µm orifice. For a 150 µm orifice, the increase in protein was about double as high from 57 to 77 %. The initial droplet diameters generated with the 50 µm and 150 µm nozzle were 81.5 and 199.5 µm, respectively. The larger the droplets, the longer was the drying time as the drying air temperature profile was kept constant. The drying time dependency of the extent of protein enrichment near the surface suggested that diffusion controlled the protein migration to the surface. At elevated droplet temperature, 100 °C for instance, such a segregation mechanism seems to be possible, given that the diffusion time scales of the fat globules, casein micelles, calcium caseinate molecules and lactose lied within the droplets' residence time inside the spray dryer (refer to Table B. 1 in appendix B). Firstly, the protein diffusion to the surface is believed to be mainly driven by the surface activity of milk protein. At a diffusion-controlled rate the proteins travelled to the droplet surface, where they were adsorbed at the air-water interface (Graham and Phillips, 1979). Secondly, the surface accumulation of protein might have been enhanced by a slower diffusivity than the one of lactose. As water evaporates from the surface, the radial water gradient from the particle centre to the surface was accompanied by component concentration gradients in opposite direction, causing the components to diffuse towards the centre. There was a distinct difference in diffusivities (Table B. 1), and hence the surface might have become enriched in the larger, slower diffusing species. As the diffusivity of lactose is one to two magnitudes greater than the one of protein, at the surface the protein concentration would increase with a simultaneous reduction of lactose. The fat globule diffusivity is approximately three orders of magnitude lower than the one of lactose, but there was no significant increase in fat surface content from atomized droplet to spray-dried product. According to a simple mass balance, this indicates that the surface region with 10-15 % v/v fat and a depth of 10 nm (i.e. the penetration depth of the XPS measurements) already comprised approximately the entire fat contained in a LFMP droplet.

The XPS results were compared with the confocal laser scanning microscopy results, which allowed a qualitative insight into the internal component distribution. FFMP particles with labelled protein and lipid were investigated after atomization and after completed spray drying, and typical result images are presented in Figure 5. Illustrating the CLSM response intensities of labelled protein and fat in form of individual graphs as obtained from sequential excitation at 487 and 637 nm enabled a discussion of the individual protein and fat

distributions. The pixel brightness represented a qualitative measure of the local concentration in each component. In the atomized droplets, a thin layer of fat was formed all around the surface and also underneath this layer the fat content was higher than in the droplet centre, whereas the protein was homogeneously distributed throughout the whole droplets (Figure 5 a,c). This agrees with the XPS observation of an atomization induced fat coverage on the droplet surfaces. The surface fat layer comprised small amounts of protein, which might have been entrapped inside the fat as it had been part of the membranes that surround the fat globules in the homogenized feed emulsions. Thus, the XPS analysis detected less than 100 % surface fat. Due to the spray drying stage, the fat gradient was further increased with almost all the fat being eventually accumulated near the surface (Figure 5 d), which can be ascribed to the hydrophobicity and low diffusivity of the fat globules. The CLSM images indicated that the initial fat layer thickness already exceeded the penetration depth of the XPS analysis. Therefore, the surface fat content as measured by XPS did not increase appreciably from atomized droplets to spray-dried particles. Also a clear gradient in protein from high concentration close to the surface to very low levels in the particle centre was developed during the drying stage (Figure 5 b), concordant with the XPS measurements. Due to its high diffusivity, lactose dominated in regions far away from the surface inside the spray-dried particles (dark areas). The strong underrepresentation of lactose in surface-near regions, as observed by XPS and CLSM for both model emulsions, presumably had a detrimental impact on the powder's rehydration behavior, since lactose promotes the solubility in high-protein powders (Anema et al., 2006, Baldwin and Truong, 2007). In contrast, the surface fat film reduces the solubility rate of the particles as the wettability is lowered. Recent studies have shown that also a dominant amount of native casein, as present in milk protein concentrate and phosphocaseinate powders, negatively affects the rehydration behavior of aggregated powders in aqueous medium (Gaiani et al., 2007, Mimouni et al., 2010). These powders have been described to feature decelerated water penetration (Schuck et al., 2007) and poor dispersibility (Havea, 2006, Crowley et al., 2016) due to a network of interconnected casein micelles.

While the development of radial concentration gradients in both fat and protein can be seen in the split channel images, these images did not reveal which component is in fact dominating at the surface. For this purpose, the response channels of a spray-dried FFMP particle were merged together with protein and fat being depicted in green and red, respectively (Figure 5 e). Additionally, **Error! Reference source not found.** provides an animation of the cross-section stack in 1 µm depth steps from the top to about the middle of the particles (supplementary information available in online version only). It can be seen that fat dominated at the outermost particle surface, as a thin film of fat had been formed around the particles. This corresponds well with the XPS analysis. The existence of a fat film rather

than individual lipid islands on the atomized droplets indicated that the fat globules were ruptured during the atomization process, which caused a homogeneous spreading of fat over the particles. Maximal protein concentrations did not typically occur at the very surface, but immediately underneath that fat film. For the high fat FFMP and fresh whole milk emulsions, the XPS measurements only captured the fat surface layer and thus no increase in protein throughout the drying stage was detected. Because there was only a very thin fat layer (smaller than the XPS penetration depth of 10 nm) in case of the LFMP feed, the adjacent increase in protein was captured by the XPS measurements.

Impact of Conventional Atomization Techniques on Surface Composition

The microfluidic jet nozzles did not represent a droplet generation technique that is typical for commercial milk powder manufacturing. The jet was disintegrated by normal stress imposed *via* sinusoidal pulsation in the microfluidic jet nozzle type, as opposed to industrial-scale spray drying where primarily shear stress causes a dispersion of emulsion films. Employing a spray dryer with a rotary disk atomizer, it was confirmed that a very high surface overrepresentation of fat is also formed under spray drying conditions comparable to industrial milk powder production (Figure 6). As the spray dryer did not include any integrated fluidised beds or other powder post-processing steps, the particle surface formation can be attributed to the actual spray drying process, and thus most likely occurred during the atomization stage.

To study a third atomization technique, FFMP and LFMP droplets were generated with a pressure-swirl single-fluid spray nozzle and afterwards flash-frozen and freeze-dried for XPS analysis (Figure 7). The particle surface compositions were similar to the ones obtained from microfluidic jet atomization. The FFMP particle surface consisted of approximately 9 % protein and 92 % fat, and the LFMP particle surface was composed of approximately 63 % protein and 20 % fat. It can thus be concluded that atomization induced component segregation and fat surface coverage take place over a range of different atomization techniques.

In contrast to the droplets and particles obtained from microfluidic jet atomization, the skim milk powder produced with the pilot-scale rotary spray dryer had a wide size distribution of 26.3 ± 13.5 µm in diameter, and the FFMP and LFMP droplets that were atomized with the pressure-swirl nozzle also had a wide size distribution of 24.3 ± 12.2 µm in diameter (results not shown here). The investigated emulsion fat contents and orifice sizes did not have an impact on the mean droplet size generated with the pressure-swirl nozzle. Accordingly, the mean droplet drying time was similar and the droplet surface composition was independent from these two parameters, as depicted by the standard deviations in Figure 7. This agrees with the results of Fyfe et al. (2011), where the difference in surface

composition between milk powders spray-dried in pilot and lab scale was found to be less than approximately 7 % and 2 % in any of the three main components for skim milk powder and whole milk powder, respectively, despite some differences in nozzle configuration and atomization pressure. Their observation of a discrepancy in comparison with commercial milk powder might be due to the post-processing steps following spray drying in industrial settings, such as fluidised beds, or the application of additives.

For the range of atomization techniques investigated, atomization induced fat accumulation on spray-dried model milk powders with different fat contents occurred whatever atomization technique was used. Though protein enriched towards the surface region during the drying stage, a fat film always remained at the outmost surface. Therefore, an efficient lipid encapsulation in a shell consisting of protein by adjusting the spray drying conditions seems not to be achievable. Future work is hence needed to investigate whether the perforation mechanism during atomization can be prevented by a specific feed pre-treatment. Furthermore, a numerical multi-component simulation of drying milk droplets can help predicting the final chemical powder surface composition. In such models, the considerable influence of atomization on the material distribution prior to the actual drying step must be taken into account in the form of initial concentration conditions.

Conclusions

In the present study, a systematic investigation of the impact of atomization on the surface composition of spray-dried model milk powder was conducted on monodisperse particles using a microfluidic multi-jet spray dryer. It was additionally demonstrated that the observed processes also occur in atomization techniques typically used on industrial scale. Cryogenic flash-freezing of the droplets allowed the impact of the atomization stage to be distinguished from the drying stage. For the range of emulsions and spray drying techniques investigated, the findings indicate that the component segregation and surface predominance of fat in spray-dried milk powder should not be attributed to the drying stage, but were already formed during atomization. For emulsion fat contents of 0.5 and 44.2 % v/v in d.m., surface fat coverages of 9-13 and 83-92 % v/v, respectively, were detected on the atomized droplets. Because the droplet surfaces were immediately covered by fat after atomization and the droplet size became smaller with higher fat content, it was concluded that a perforation along the oil-water interfaces formed by the fat globules made the emulsions less stable against disintegration with increasing lipid content. However, further studies on the complex relation between the fat content in the presence of milk protein, the emulsion viscosity and the jet stability against disintegration upon atomization need to be conducted. In the following drying stage, the fat film remained on the surface and additional

fat enriched near the surface due to its hydrophobicity and low diffusivity. Also protein migrated from the droplet centre towards the surface, but accumulated underneath the fat layer and did not penetrate it. Because the protein migration was more distinct for larger droplet sizes and at accordingly longer drying times, it was presumably driven by the protein's surface activity and differences in the component's diffusivities. Beyond milk systems, the presented approach could be applied on other emulsions to investigate whether atomization also induces wanted or unwanted component segregation in other food or pharmaceutical spray drying applications.

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Appendix A: Droplet Diameters and Shrinkage in MFMJSD

In Figure A.1, the mean particle diameters of powders produced in the MFMJSD with microfluidic jet nozzles of different orifice size and for high and low-fat content are presented together with the corresponding initial droplet diameters immediately after atomization. Both the spray-dried particles and the initial droplets had each small standard deviations in size. For the freeze-dried particles, the equivalent diameter calculated from the projection surface areas in the light microscope images reflected their actual volume due to their spherical shape. Because of the buckled shape of the spray-dried particles, however, their calculated equivalent diameter overestimated the actual particle volume to some degree. A relative comparison between the sizes and shrinkage ratios of the different powders was still possible, nevertheless. The size and shape of the atomized particles could be assumed to be unaffected by the freeze-drying step, which gives an accurate knowledge of the initial droplet size. This was useful for discussing the shrinkage behaviour and the influence of drying time and rate on the resulting particle surface composition (Pısecký, 1997, Kim et al.,

2009). In previous studies, the initial droplet size could only be roughly deduced from the final particle size under assumption of a certain shrinkage model (Van Mil et al., 1987). For comparison, the hypothetical product diameters for perfect shrinkage behaviour are included in Figure A.1, which shows that shrinkage was less pronounced for smaller droplets. The measured equivalent diameters of the spray-dried low-fat particles were 28, 48 and 56 % bigger than the corresponding values in case of perfect shrinkage for a 150, 100 and 50 µm orifice, respectively, and 48 % bigger for FFMP and a 100 µm orifice. Because the temperature profile of the drying air was kept identical for all spray drying runs, the smaller droplets reached a dried condition earlier and thus the air enclosed in the particles presumably experienced higher temperatures for the remaining time that the particles spent in the dryer, leading to greater inflation of the internal structures.

Appendix B: Diffusivities of Fat Globules, Protein and Lactose

The diffusion time scales over a diffusion length of 10 µm were estimated by means of binary diffusion coefficients obtained from Stokes-Einstein's equation (Einstein, 1905):

$$D_i = \frac{k_B T}{6\,\pi\,\mu\,R_i}$$

$$\tau_i = \frac{x^2}{D_i}$$

where D_i is the binary diffusion coefficient of component i, k_B the Boltzmann's constant, R_i the component radius, T the temperature, µ the dynamic viscosity of water, τ_i the diffusion time and x the diffusion length.

The resulting approximation of the components' diffusivities and diffusion time scales are presented in Table B. 1. The values were calculated for 15 °C (temperature in the space between nozzle and liquid nitrogen in the atomization studies) and for 100 °C (estimate for mean particle temperature in spray dryer). The values only give a qualitative impression of the difference in diffusion speed between the three main milk components. The absolute values should be treated with caution considering the limitations of Stoke-Einstein's equation, such as an assumption of infinite dilution.

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Figure captions

Figure 1: The Microfluidic Multi-Jet Spray Dryer (MFMJSD): (a) Schematic of a microfluidic jet nozzle; (b) typical photograph of monodisperse FFMP droplets (20 % w/w solids) generated with a microfluidic jet nozzle; and (c) schematic of the MFMJSD instrument.

Figure 2: SEM images of FFMP particles obtained from three MFMJSD nozzles (100 µm): (a), (b) spray-dried particles; (c) cross-section of such a particle after embedding in resin and microtomic slicing through its middle; and (d) particle that had been flash-frozen after atomization and then freeze-dried.

Figure 3: XPS particle surface composition for a MFMJSD with a 100 µm orifice nozzle under variation of the feed emulsions: (a) fresh whole milk, (b) FFMP, and (c) LFMP*: Surface composition of particles that were spray-dried and of droplets that were flash-frozen directly after atomization and subsequently freeze-dried, in comparison to the dry matter feed compositions.*

Figure 4: XPS surface composition of LFMP under variation of the MFMJSD nozzle orifice diameter, (a) 50 µm and (b) 150 µm: Surface composition of particles that were spray-dried and of droplets that were flash-frozen directly after atomization and subsequently freeze-dried, in comparison to the dry matter feed composition.

Figure 5: CLSM images of protein and fat distribution in FFMP particles: Particles were (a,c) flash-frozen directly after atomization and subsequently freeze-dried (cross-section through middle of particles); and (b,d,e) spray-dried (two cross-sections through three-dimensional image stacks as indicated by the dotted lines). (a)-(d) Split channels: the greater the pixel brightness, the higher the local concentration in Nile Red (fat dye) and Fast Green FCF (protein dye), respectively. (e) Merged channels: Nile Red (fat dye) depicted in red and Fast Green FCF (protein dye) in green.

Figure 6: XPS particle surface composition of skim milk powder from a pilot-scale single-stage spray dryer with rotary disk atomizer, in comparison to the dry matter feed composition.

Figure 7: XPS surface composition of droplets atomized with a pressure-swirl single-fluid spray nozzle in comparison with the dry matter feed compositions: (a) LFMP emulsion; and (b) FFMP emulsion. The standard deviations for different spray drying conditions with a feed

pressure of 450 or 600 kPa and a nozzle orifice diameter of 0.2 or 0.3 mm are shown. The droplets were flash-frozen directly after atomization and subsequently freeze-dried prior to analysis.

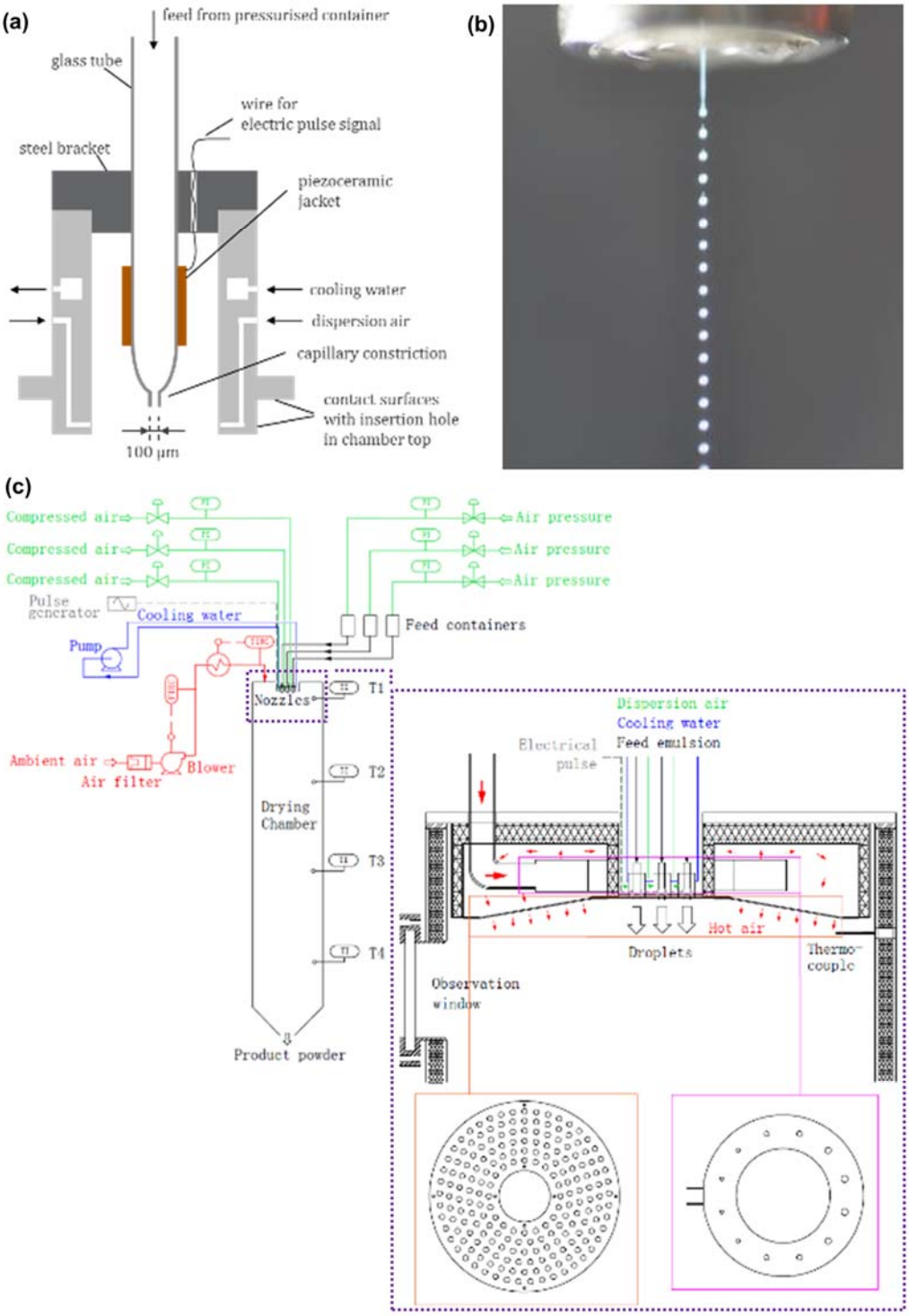

Fig 1

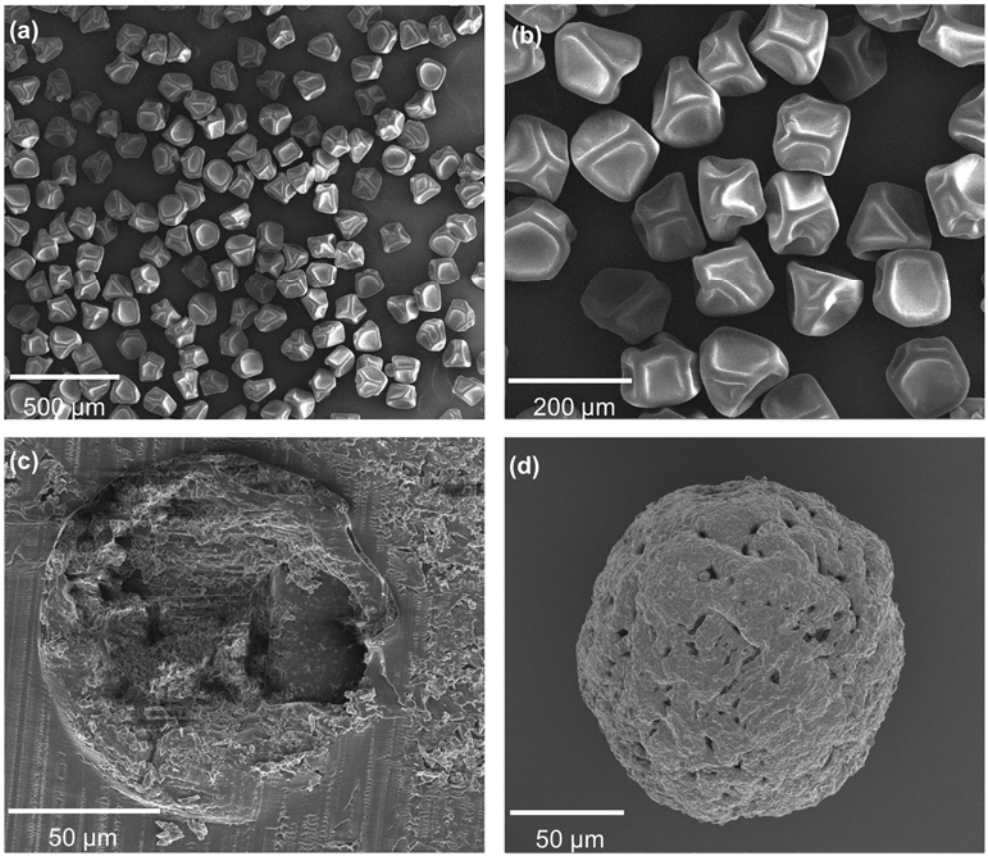

Fig 2

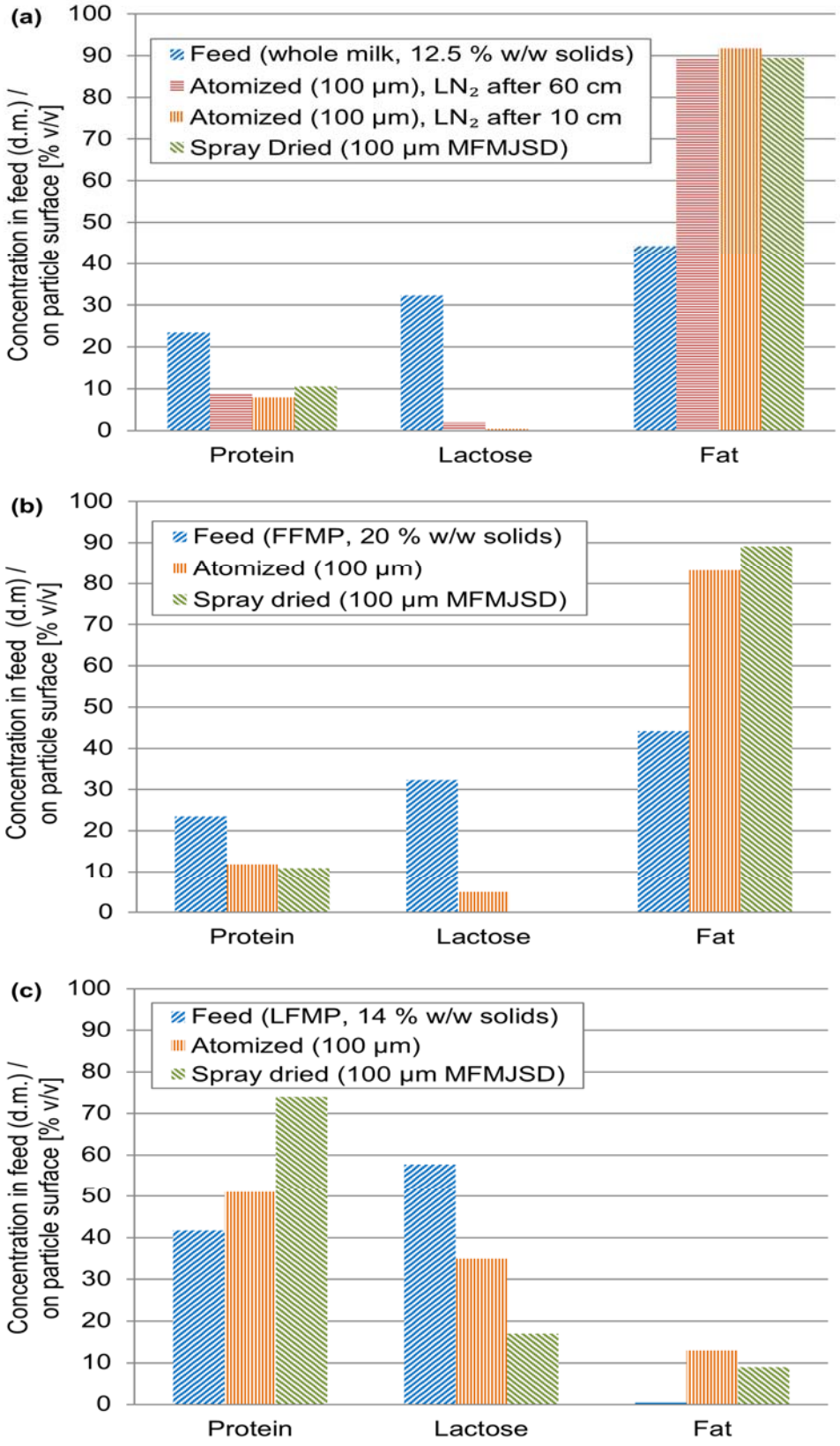

Fig 3

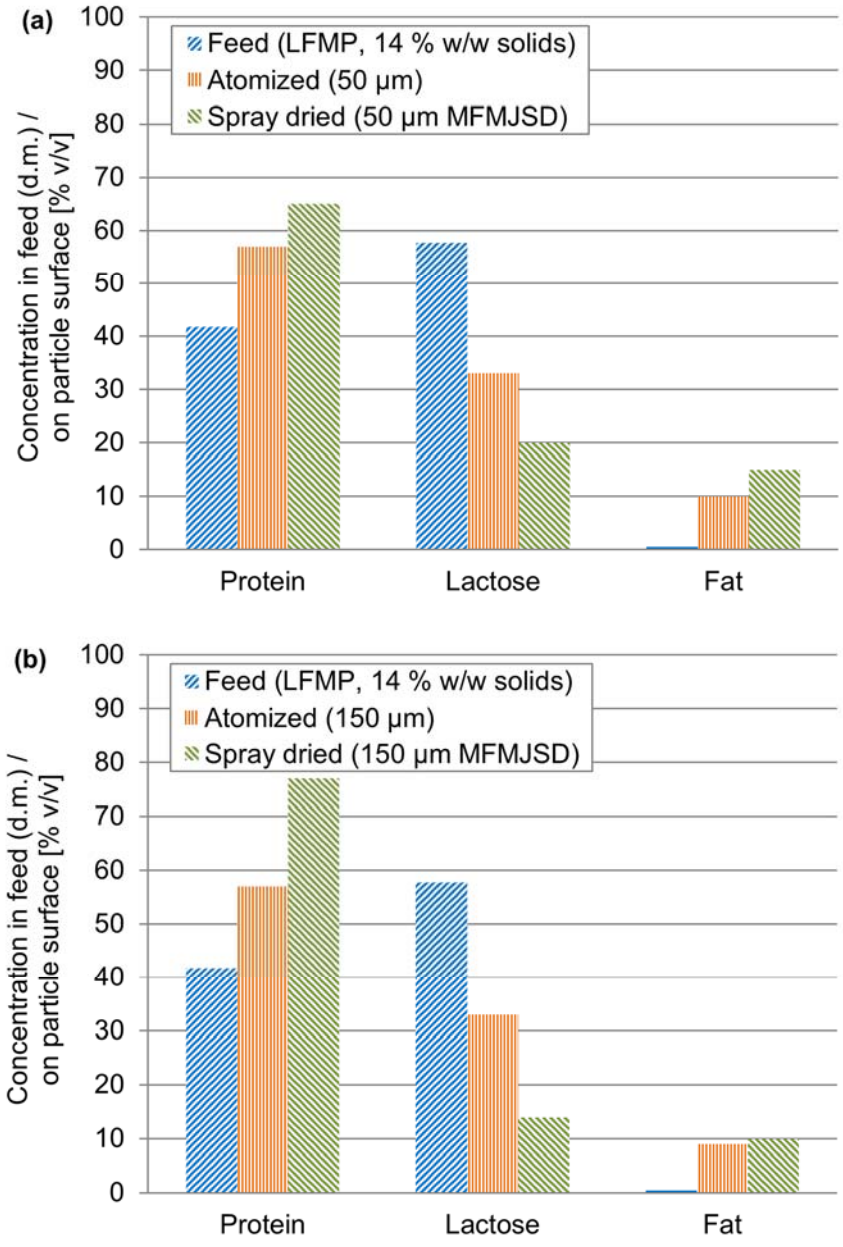

Fig 4

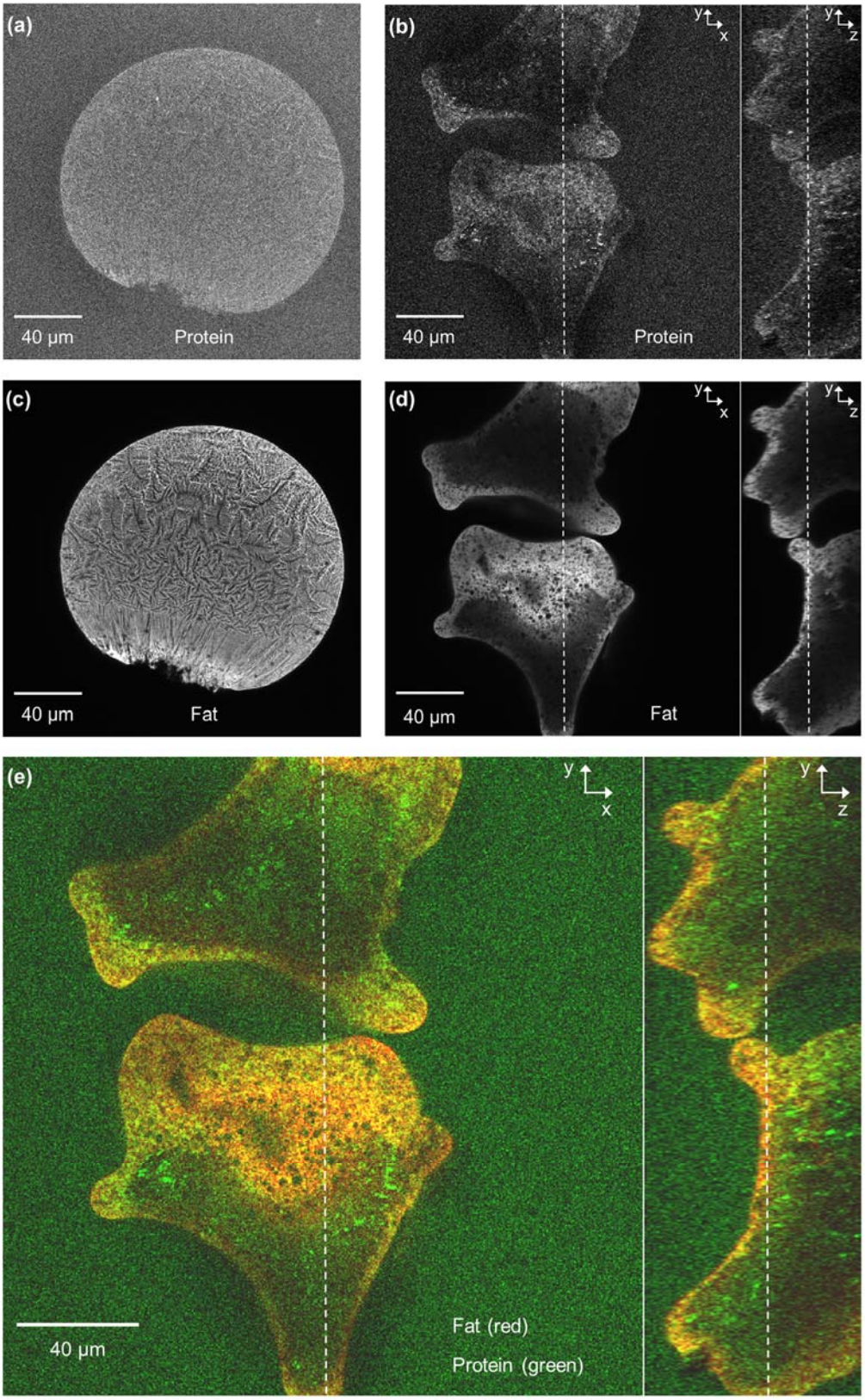

Fig 5

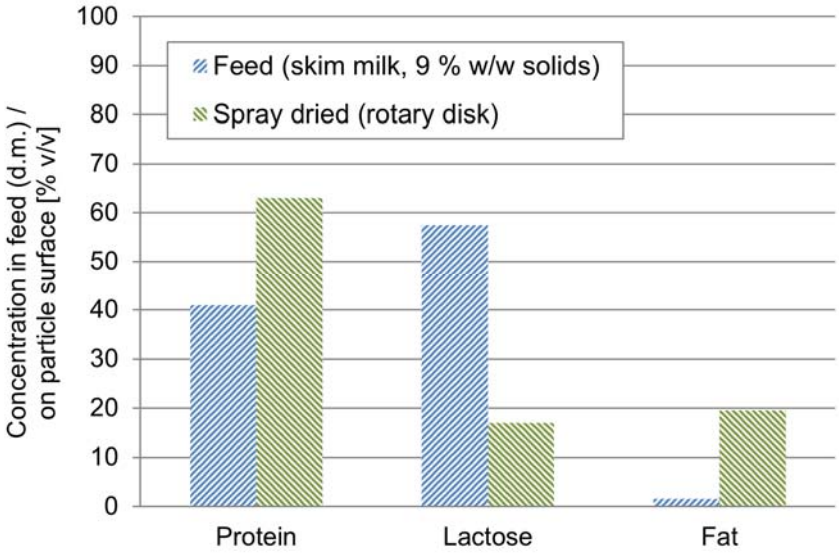

Fig 6

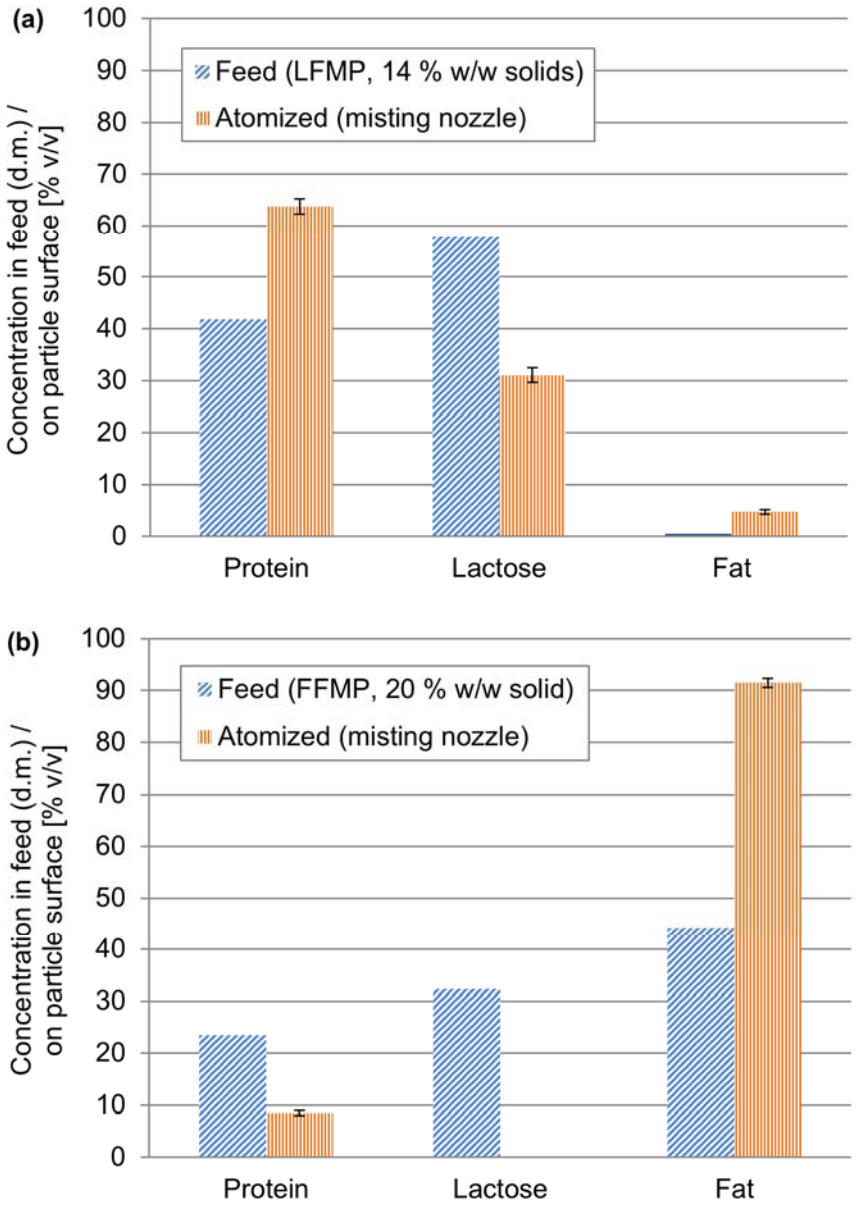

Fig 7

Appendices:

Figure A.1: Mean diameter and standard deviation of atomized droplets and the corresponding spray-dried particles from the MFMJSD: The microfluidic jet nozzles had orifice diameters of 50, 100 and 150 µm. The atomized droplets were flash-frozen directly after atomization and then freeze-dried. For comparison, the theoretical diameters of dried particles under the assumption of perfect shrinkage are given for each atomized droplet diameter (red lines).

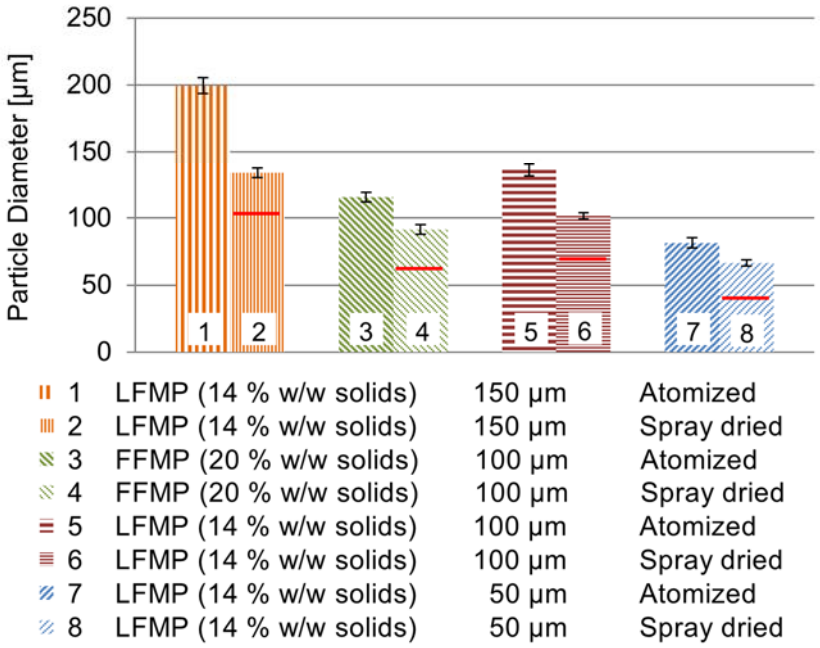

Table B. 1: Estimation of binary diffusion coefficients and diffusion time scales for 10 µm diffusion length in water at infinite dilution: Values are based on the approximate radius of casein micelles, calcium caseinate and fat globules as measured by dynamic light scattering and the mean radius of lactose in milk according to (Bylund, 2003).

	Mean radius [nm]	Diffusivity [m^2/s]		Diffusion time scale [s]	
		at 15 °C	at 100 °C	at 15 °C	at 100 °C
Fat globules	300	$7.0 \cdot 10^{-13}$	$4.6 \cdot 10^{-12}$	71	11
Protein micelle/caseinate	75	$2.1 \cdot 10^{-12}$	$2.7 \cdot 10^{-11}$	18	3
Lactose	0.5	$4.2 \cdot 10^{-10}$	$2.7 \cdot 10^{-9}$	0.1	0.02