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Component Segregation During Spray Drying of Milk Powder

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Introduction

Bulk Composition of Whole Milk

Whole milk, skim milk, and infant formula emulsions are regularly spray dried to powder form at large industrial scale for preservation with increased stability against oxidative rancidity, reduced bulk volume for economy of transportation, and easier processing as ingredient in food products (Vega and Roos, 2006; Schuck, 2002). While the exact composition of bovine whole milk can vary considerably, on average it has a solid content of 12%–13% w/w and, as presented in Table 1, the major components are lactose with an approximate content of 40% w/w in dry matter, fat with 32% w/w, and protein with 28% w/w (neglecting minerals and vitamins). The milk fat is dispersed inside the aqueous continuous phase in form of spherical fat globules of 0.1–10 μm in diameter (Michalski et al., 2002). The globules are stabilized by a surrounding layer of fat globule membranes, which are composed of a complex combination of phospholipids, lipoproteins, other proteins, organic acids, bound water, traces of metals, and enzymes (Singh and Gallier, 2016). About 80% of the total protein content in bovine milk is made of caseins. These phosphoproteins are held together in form of submicron-sized micelles by hydrophobic interaction and calcium ions (Müller-Buschbaum et al., 2007). In studies that investigate milk model emulsions, native casein is often replaced by sodium caseinate as emulsifier. It is produced

Table 1   Composition of bovine whole milk (Bylund, 2003)

Species	Concentration (% w/w)
Water	87.5
Lactose	4.8
Fat	3.9
Protein, total	3.4
Casein	2.71
α_{s1}-casein	1.04
α_{s2}-casein	0.27
β-casein	1.05
κ-casein	0.34
Whey protein	0.65
α-lactalbumin	0.13
β-lactoglobulin	0.33
Miscellaneous	0.19
Fat globule membrane proteins	0.04
Minerals, vitamins	0.8

from precipitated casein by the addition of sodium hydroxide and is soluble in water without developing a micelle structure (Jost, 2002). The remaining protein fraction in milk consists of whey proteins, which are primarily comprised of α-lactalbumin and β-lactoglobulin. Whey protein is also known as milk serum protein due to its greater water solubility than that of casein.

Powder Surface Composition After Spray Drying

The main components at the surface of spray-dried milk powder usually differ substantially in proportion from the bulk composition of the original milk emulsion because of an overrepresentation of fat at the surface. The surface layer of fat is unwanted, as the chemical surface composition strongly influences the functional powder properties, with surface fat leading to several detrimental effects on the product characteristics (Vignolles et al., 2007). This includes enhanced lipid oxidation during storage and thus faster expiration (Granelli et al., 1996; Hardas et al., 2000; Keogh et al., 2001), reduced reconstitution behavior (Fäldt and Bergenståhl, 1996b; Millqvist-Fureby et al., 2001), and greater stickiness (Kim et al., 2005a; Nijdam and Langrish, 2006). This can cause a deteriorated product quality for the end user, as well as lower production efficiencies due to significant product losses and the requirement of additional processing steps, such as coating with lecithin. Furthermore, an enrichment of protein at the surface of particles from low-fat milk emulsions is sometimes observed. Although being less of a concern for skim and whole milk, in powders that contain particularly high proportions of native casein, the rehydration behavior can also be detrimentally affected by too much surface protein as a result of a network formation between the casein micelles (Schuck et al., 2007; Havea, 2006; Mimouni et al., 2010). It is therefore of great interest to identify the segregation mechanism that induces the surface fat formation or other component segregation processes during spray drying of milk powders. A better understanding will help to find technical solutions to establish more desirable surface compositions. Moreover, knowledge about the chemical surface formation in drying milk droplets is relevant for modeling purposes of industrial applications to predict the functional product properties and to optimize spray dryer designs.

An analysis of the whole manufacturing process of milk powder has indicated that spray drying is the determining step, whereas the following fluidized bed and handling stages have a negligible influence on the surface composition (Kim et al., 2009b). As such, the studies on the surface formation of milk particles reported in literature have mostly focused on the spray drying process itself. It has been attempted to explain the component segregation by mechanisms occurring during the drying stage between droplet generation and completion of the spray drying process (segregation induced by diffusivity, surface activity, and crust formation), or prior to this during disintegration of the feed emulsion into individual droplets (segregation induced by atomization). It is still under debate which of those mechanisms is in fact the predominating driving force, with the respective studies providing either one specific segregation concept as explanation (Table 2) or a combination of two or more (Table 3).

Chemical Surface Composition of Milk Particles

Presence of Surface Fat and Effect of Spray Drying Conditions

In general, Tables 2 and 3 show that there is a wide agreement in the observation of a dominant presence of surface fat on convectively dried milk powder, which could not be prevented by variation of the drying parameters or spray dryer type. For milk (model) emulsions with fat contents similar to whole milk, the particles were found to be covered by an almost consistent fat layer that occupied more than 90% of the outmost surface area (Kim et al., 2003; Murrieta-Pazos et al., 2012; Foerster et al., 2016a,b). This corresponds to a fat surface overrepresentation of approximately three times in relation to the feed bulk composition. Skim milk (model) emulsions and milk protein concentrates were observed to also translate into a fat accumulation on the powder surface with 3.5%–45.9% surface fat for fat contents of 0.6%–1.5% in the bulk (Kim et al., 2009a; Nikolova et al., 2014; Kelly et al., 2015; Murrieta-Pazos et al., 2012; Fyfe et al., 2011). This corresponds to a surface overrepresentation of 6–30 times in comparison with the bulk composition. Nevertheless, in contrast to whole milk particles, it has been shown that the surface of skim milk and milk protein concentrate powders is not dominated by fat because of the low overall fat proportion. The remaining surface area of low-fat milk powders was found to primarily consist of protein (42.0%–62.7% on the very surface for 35.0%–38.5% in the bulk), indicating a slight surface enrichment in protein during drying. Independent from the overall fat content, a distinct lack in lactose has been consistently reported for all milk powders that were subject of the studies listed in Tables 2 and 3, with lactose being sometimes almost completely absent from the outmost surface region (Gaiani et al., 2006; Nijdam and Langrish, 2006).

To some degree, within the above described range of surface compositions, the exact amount of fat and protein at the particle surface has been reported to be influenced by the drying conditions. Fyfe et al. (2011) studied commercial skim and whole milk powders as well as powders obtained from laboratory- and pilot-scale spray drying. Comparison of the powders showed that there was a difference in surface composition depending on the spray dryer type, albeit always featuring a distinct fat overrepresentation and, for skim milk powders, a moderate protein overrepresentation. Commercial milk powders consisted of more fat and less protein at the surface than the powders produced with laboratory and pilot spry dryers. It remained unclear if this can be ascribed to a larger particle size and higher feed solid content of the industrial drying processes or to the differences in atomization techniques applied. Some studies have indicated that the final particle surface composition will conform more with the bulk composition if the drying rate is increased, for instance by means of a higher drying temperature or a smaller droplet size as influenced by the atomization pressure (Nikolova et al., 2015a; Gaiani et al., 2010; Kelly et al., 2002).

Table 2　Summary of studies on component segregation in droplets consisting of milk protein and fat: organized by concepts provided as explanation—part 1: only one concept per study

Concept	System	Surface composition (XPS)	Analysis	Author
Diffusivity	Aqueous solution of sucrose/caseinate in agar gel matrix	20% protein overrepresentation	XPS	Meerdink and Van't Riet (1995)
Diffusivity	Industrial spray dried skim and whole milk	Overrepresentation of fat (whole milk: 98% on surface/29% total, skim milk: 18% on surface/1% total), also enrichment of protein near the surface	XPS, free fat extraction	Kim et al. (2003)
Diffusivity	Single droplet drying of whole and skim milk	Hydrophobic surface due to surface fat	Dissolution behavior	Fu et al. (2011)
Diffusivity	Spray drying of skim milk in pilot scale	Overrepresentation of fat (5.8%–7.4% on surface/0.9% total) and protein (43.0%–49.8% on surface/36.9% total), slight increase in component segregation with longer drying times	XPS	Nikolova et al. (2015a, 2014)
Surface activity	Spray drying of lactose/soybean oil/whey protein or sodium caseinate	Overrepresentation of fat for whey protein, better fat encapsulation with sodium caseinate (whey protein: 45% on surface, caseinate: 3% on surface/30% total)	XPS	Fäldt and Bergenståhl (1996a, 1995)
Surface activity	Spray drying of sucrose/whey protein or sodium caseinate	Overrepresentation of protein (up to 50%–58%/0.5%–1% total)	XPS	Adhikari et al. (2009)
Surface activity	Spray drying of phosphor-caseinate/lactose/milk fat	Overrepresentation of fat (14.5%–18.7% on surface/0.4% total)	XPS	Gaiani et al. (2006)
Surface activity/ hydrophobicity	Spray drying of milk protein concentrate with various protein contents	Overrepresentation of fat (3.5%–10.2% on surface/0.6%–1.4% total) and protein (62.7%–97.2% on surface/35.4%–85.8% total)	XPS	Kelly et al. (2015)
Crust formation	Industrial spray dried skim and whole milk	Overrepresentation of fat (whole milk: 93.3% first 5 nm, 58.6% first μm/28.4% total, skim milk: 45.9% first 5 nm, 22.8% first μm/1.5% total) and slight overrepresentation in protein for skim milk (45.1% first 5 nm, 34.4% first μm/38.5% total)	XPS, EDX, free fat extraction	Murrieta-Pazos et al. (2012)

EDX, energy dispersive X-ray analysis; XPS, X-ray photoelectron spectroscopic analysis

Furthermore, the properties of the feed emulsion can affect the surface composition. A higher droplet viscosity and earlier crust formation due to an increased feed solid content have been reported to reduce the extent of component segregation during drying of skim milk (Wu et al., 2014; Kim et al., 2009b). The fat encapsulation efficiency was improved by a stronger reduction in fat globule size during homogenization in studies conducted by Kim et al. (2009b) and Millqvist-Fureby (2003), whereas the surface composition data sets provided by Xu et al. (2013) and Keogh and O'kennedy (1999) did not demonstrate such a statistically significant relationship for the range of droplet sizes investigated. Gaiani et al. (2010) and Fäldt and Bergenståhl (1996a) observed an influence of the kind of milk protein employed as emulsifier. The use of casein, particularly in the presence of lactose, resulted in less surface fat than the use of whey protein, presumably due to casein's greater surface activity and resistance to denaturation under heat (Vega and Roos, 2006).

Analysis Techniques of Component Distribution

X-ray photoelectron spectroscopic (XPS) analysis, also referred to as electron spectroscopy for chemical analysis in this context, is the prevailing method to quantify the chemical surface composition of milk particles. In this sensitive surface analysis technique, the powder samples are irradiated with an X-ray beam of a well-defined energy level under high vacuum, and electrons are emitted if their binding energy is surpassed by the photon energy. Detection of the number of emitted electrons and their respective kinetic energy, which is characteristic for each chemical element, yields the sample composition and the chemical state of the elements. Fäldt et al. (1993) suggested a transformation of the obtained elemental particle surface concentrations, i.e., the relative amounts in carbon, nitrogen, and oxygen, into the surface percentages that are covered by lactose, protein, and fat by means of a matrix linearization based on each component's representative structural formula. This approach has been widely adapted in literature, and the

Table 3   Summary of studies on component segregation in droplets consisting of milk protein and fat: organized by concepts provided as explanation—part 2: combinations of concepts

Concept	System	Surface composition (XPS)	Analysis	Author
Diffusivity, surface activity	Spray drying of lactose and fat with casein or whey protein	Overrepresentation of fat for all powders and of protein for many powders, less fat enrichment for casein instead of whey protein and for higher temperatures	XPS	Gaiani et al. (2010)
Diffusivity, surface activity	Spray drying of lactose/rapeseed oil/whey protein	Overrepresentation of fat (55%–65% on surface/30% total)	XPS, free fat extraction	Millqvist-Fureby et al. (2001)
Surface activity, crust formation	Spray drying of whole and skim milk	Overrepresentation of fat (significant) and protein (less distinct)	XPS	Nijdam and Langrish (2005, 2006)
Surface activity, crust formation	Spray drying of walnut oil and skim milk (with Tween 80 or maltodextrin)	Overrepresentation of fat (85.6%–92.5% on surface/50% total)	XPS, free fat extraction	Shamaei et al. (2016)
Diffusivity, surface activity, crust formation	Single droplet and spray drying of milk model emulsions at various fat contents and of milk protein concentrate	Overrepresentation of fat (milk emulsion with e.g., 76%–87% fat on surface/29%–42% total, milk protein concentrate: 17%–27% on surface/1.5% total)	XPS	Chew et al. (2015, 2014)
Surface activity, crust formation, atomization	Spray drying of whole and skim milk (lab and pilot scale), compared with commercial powders	Overrepresentation of fat in form of thin patches on all powders (e.g., commercially dried skim milk: on surface 16.5%/0.7% total, pilot scale: similar, laboratory scale: less surface fat)	XPS, CLSM	Fyfe et al. (2011)
Diffusivity, surface activity, crust formation, atomization	Spray drying of whey protein/sunflower oil/maltodextrin	Overrepresentation of fat (17.7%–34.1% on surface/10% total) and protein (19.8%–42.7% on surface/10% total)	XPS	Xu et al. (2013)
Diffusivity, surface activity, crust formation, atomization	Industrially spray-dried powders of skim and whole milk	Overrepresentation of fat (whole milk: >90% on surface/26% total, skim milk >18% on surface/1% total), slight protein overrepresentation for skim milk (42% on surface/35% total)	XPS	Kim et al. (2009a,b)
Diffusivity, surface activity, atomization	Spray drying of skim milk	High fat overrepresentation and lower protein overrepresentation, surface fat content already high directly after atomization	XPS, flash-freezing of atomized droplets	Wu et al. (2014)
Diffusivity, surface activity, atomization	Spray and single droplet drying of low-fat and regular-fat model milk	High fat overrepresentation and lower protein overrepresentation, surface fat content already high directly after atomization	XPS, CLSM, flash freezing of atomized droplets	Foerster et al. (2016a,b),

CLSM, confocal laser scanning microscopy; *XPS*, X-ray photoelectron spectroscopic analysis

surface compositions presented in Tables 2 and 3 were determined in this manner. Nikolova et al. (2015b) discussed the possibility of a distortion of the XPS analysis toward higher carbon contents as a result of organic pollution inside the vacuum chamber and therefore proposed a modified approach where the linearization matrix is derived from experimental measurements of XPS spectra for lactose, protein, and lipid standard samples. Either way, it is generally accepted that component compositions derived from XPS atomic spectra should be considered as semiquantitative estimations only. In addition, it needs to be noted that XPS analysis accounts only for the first few nanometers of the sample surface (about 0–10 nm), with the exact sampling depth being difficult

to quantify because of the surface curvature of the milk particles. As such, it only describes the outmost surface layer of the analyzed powders, which does not allow a conclusion about the overall amount of free surface fat, especially for high-fat milk powders.

The total amount of free surface fat, often expressed by the encapsulation efficiency of a powder sample, is frequently quantified by surface fat extraction. In this method, the mass of extracted fat is determined by measuring the sample weight before and after extraction with a nonpolar, organic solvent, such as hexane or petroleum ether. In terms of powder concentration, duration of the extraction process and intensity of the contact between powder and solvent during mixing, no standard procedure has been established yet and the techniques reported in literature vary considerably among each other, as summarized by Vega and Roos (2006). The amount of extracted fat further depends on the particle size and porosity (Twomey et al., 2000; Vignolles et al., 2007). A significant amount of extractable fat is believed to not originate from the particle surfaces, but from inner free fat that is extracted from the inside of the particles through pores and cracks, in particular at relatively intense mixing and long exposure times to the solvent (Buma, 1971; Buchheim, 1982). For this reason, the results from fat extraction of milk powder samples might most often represent the amount of free fat instead of the amount of free surface fat (Kim et al., 2005b). As a consequence, free (surface) fat extraction might provide a more suitable technique than XPS to quantify the total amount of surface fat, but is typically limited to a qualitative comparison among samples analyzed with the same extraction technique, rather than giving robust absolute values.

Other, less-frequently employed analysis methods include confocal laser scanning microscopy (CLSM) for the protein and fat distribution inside the whole particle (Taneja et al., 2013), transmission electron microscopy (TEM) for protein–lipid or protein–protein interactions (Mckenna et al., 1999), and energy dispersive X-ray (EDX) analysis of the atomic surface composition at a sampling depth of about 1 μm (Murrieta-Pazos et al., 2012). As these analysis techniques describe the particle composition at different distances from the extreme surface, often various combinations are employed to obtain a comprehensive insight into the component distribution, such as XPS measurements together with free fat extraction and CLSM investigation (Vignolles et al., 2009) or XPS and EDX analysis (Murrieta-Pazos et al., 2012).

Potential Segregation Mechanisms

Diffusivity

As illustrated in **Fig. 1B**, Meerdink and van't Riet suggested that the component segregation could occur due to differences in the components' diffusivities (Meerdink, 1994; Meerdink and Van't Riet, 1995), a concept that has been adopted in a series of subsequent studies (Kim et al., 2003; Fu et al., 2011; Chew et al., 2014; Nikolova et al., 2015a). As water evaporates from the droplet surface, radial gradients in the component concentrations are formed and cause the components to diffuse toward the inside of the droplet. Because the diffusivity of a species increases with decreasing hydrodynamic radius, the outer droplet region might become depleted in the smaller, faster diffusing components, such as lactose. As a first approximation of the binary diffusion coefficient of a species in liquid medium, there is an inverse proportionality between the hydrodynamic radius of the species and its diffusivity according to the Stokes–Einstein equation (Cussler, 2009). In homogenized, bovine whole milk, the radius is in the range of 100–10,000 nm for lipid globules (Leman et al., 1989; Michalski et al., 2002), 50–300 nm for casein micelles
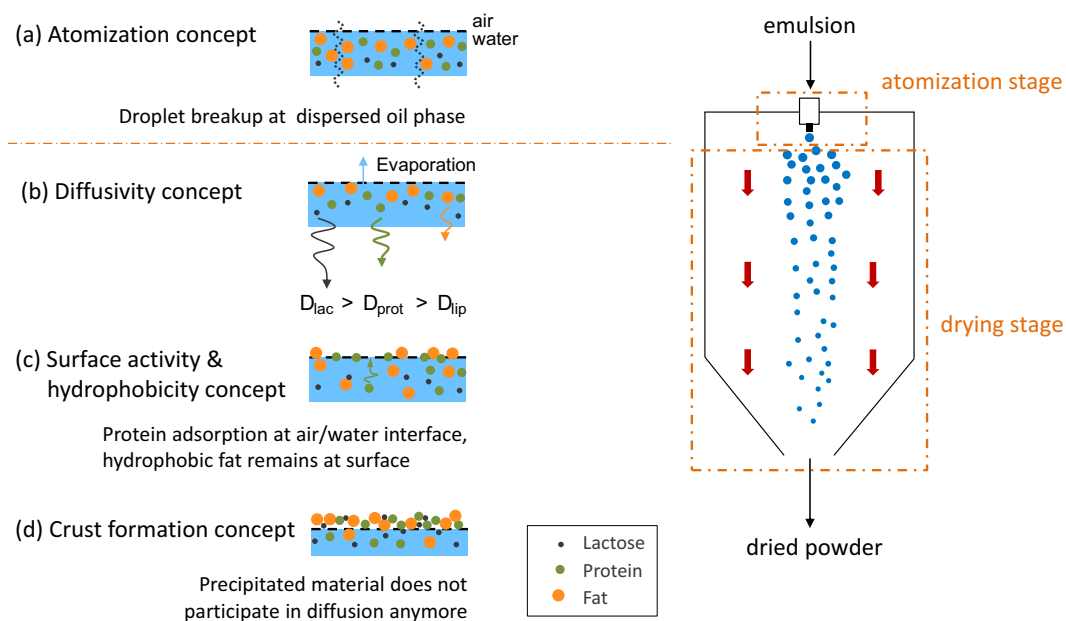
Figure 1 Explanations proposed in literature for the component segregation in drying milk droplets: Schematics of (A) atomization concept, (B) diffusivity concept, (C) protein surface activity and fat hydrophobicity concept, (D) crust formation concept.

(Dewan et al., 1974; Müller-Buschbaum et al., 2007), and 0.1–1 nm for lactose (Bylund, 2003). Thus, the diffusivity of lactose is two to five orders of magnitude greater than the diffusivity of the fat globules. The longer the drying process takes (for instance the lower the drying temperature or the higher the initial water content), the stronger might the diffusivity effect influence the component segregation (Kentish et al., 2005; Nikolova et al., 2015a; Vehring et al., 2007).

Protein Surface Activity and Fat Hydrophobicity

Furthermore, the surface composition of milk powder might be influenced by the components' interaction with the air–water interface (Fig. 1C). Milk protein's surface activity has mostly been used as explanation of the protein surface overrepresentation observed in several studies. Milk proteins and particularly casein, due to its relatively flexible molecule structure, feature a high degree of surface activity as a result of an amphiphilic nature (Leman et al., 1989). Thus, their adsorption at the air–water interface has been widely reported, with the movement to the interface being primarily controlled by diffusion, although other factors such as convection as a result of temperature and pressure gradients can also have an influence (Graham and Phillips, 1979; Landström et al., 1999). Fäldt and Bergenståhl observed a migration of milk protein to the surface of drying emulsion droplets consisting of soybean oil, lactose, and either whey protein or sodium caseinate (Fäldt and Bergenståhl, 1996a, 1995) and explained this by the protein's surface activity. This concept has been adopted in other studies (Gaiani et al., 2006; Adhikari et al., 2009). Additionally, as the adsorbed protein is bound to the air–water interface, this impacts the gradient in protein concentration inside the droplet and counteracts any concentration driven diffusion processes away from the surface (compare to section Diffusivity). Similarly, the hydrophobic nature of milk fat might attenuate diffusion away from the droplet surface toward the inside of the droplet for fat globules that have already accumulated at the air/water interface (Fu et al., 2011). Furthermore, it has even been suggested that the hydrophobicity causes fat globules to migrate from the droplet center toward the surface (Kelly et al., 2015).

Crust Formation Concept

It has additionally been proposed that the final particle surface composition might be subject to the crust formation and the solubility of the dissolved protein and lactose solutes (Fig. 1D), as first discussed by Charlesworth and Marshall (1960) and later adopted by others on dairy droplets (Kim et al., 2009b; Wang and Langrish, 2009). These reports argued that the precipitated solutes, once part of the solidified crust, do not participate in the diffusion process anymore. Assuming a decreasing water concentration from the droplet center to the surface due to evaporation, saturation concentrations, and consequent precipitation are first reached near the droplet surface. A lower solubility of one component could thus lead to an enrichment near the surface in comparison with the other components.

Furthermore, it has been suggested that on advanced solidification of the dying droplet the fat phase might move through the crust's network of cracks and pores as driven by overpressure imposed by internal vacuoles and capillary forces (Nijdam and Langrish, 2005). As a result of mechanical stress during drying or atomization, the fat globule membranes might become ruptured to some extent and the lipid phase could hence spread freely inside the drying particle and on its surface at the elevated temperatures of the spray drying process, thus forming a consistent fat surface film (Xu et al., 2013).

Atomization Concept

As Tables 2 and 3 illustrate, the component segregation in drying milk droplets has primarily been presumed to take place during the drying stage of the spray drying process, with different combinations of the three concepts described above being most often presented as potential driving forces.

However, a smaller number of reports have considered the possibility that an atomization-induced segregation mechanism might take place prior to the drying stage (Fig. 1A). In a study by Fyfe et al. (2011), a pilot-scale spray dryer resulted in a considerably greater fat overrepresentation on skim milk particles' surfaces in comparison with the same powders produced with a laboratory-scale spray dryer, despite both instruments employing the same atomizer type and drying air temperature profile. It was speculated whether this observation can be ascribed to an influence of the different pressure and shear levels during atomization on the disintegration process of the feed emulsion film. Xu et al. (2013) investigated powders that were produced with a bench-top spray dryer from emulsions consisting of sunflower oil, maltodextrin, and whey protein. An increasing fat content on the particle surface with larger fat globule size of the emulsions after homogenization was found. This was explained by 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 globule sizes. The rupture was supposed to take place either during atomization as a result of shearing or during the drying stage as a result of differential stress on the membranes as they shrink at constant fat globule volume. Kim et al. (2009b) reported respective surface fat contents of more than 90% and 18% on whole milk and skim milk particles that had been dried at a drying air inlet temperature of 205 °C. Because of the intense heat exposure and the consequent fast solidification and immobilization of the components during the drying stage, it was concluded that the surface fat must have already been formed, at least in part, during the preceding atomization stage.

As it is difficult to draw reliable conclusions about the impact of the atomization step from the powder characteristics after completed spray drying, Wu et al. (2014) and Foerster et al. (2016a) compared the surface composition of atomized droplets immediately after atomization, as obtained by cryogenic flash freezing, with the one of the corresponding spray-dried particles. Their work

showed that the surface fat on the skim and whole milk particles was caused by the atomization stage for the range of emulsions and spray dryers investigated. After atomization the milk droplets featured surface fat contents of 9%–13% and 83%–92% v/v fat for feed emulsions of 0.5% and 44.2% v/v fat (dry matter basis), respectively, and the surface fat contents remained relatively unchanged throughout the following drying stage (Foerster et al., 2016a). Foerster et al. (2016a), along the argumentation of Kim et al. (2009b), proposed that the atomization-induced fat accumulation on freshly generated milk droplets might originate from the impact of the dispersed fat phase on the disintegration behavior of the emulsion feed. A perforation mechanism was provided as explanation where the milk emulsions preferably disintegrate along the fat globules, causing the fat globules to cover the surface as soon as individual droplets have been formed. This hypothesis was based on earlier photographic investigations of the break-up behavior of emulsions as a function of oil content (Dombrowski and Fraser, 1954; Zakarlan and King, 1982).

Relevant Mathematical Modeling Approaches

Mathematical simulation of the component distribution in drying milk droplets promises further insight into the segregation mechanism and a useful tool for the theoretical prediction of powder properties at certain drying conditions. A number of modeling approaches on the convective drying of droplets are available in literature, such as models that incorporate the concept of the characteristic drying curve (Keey, 1991; Langrish and Kockel, 2001; Harvie et al., 2002; Tran et al., 2016) or the lumped reaction engineering approach (Chen and Putranto, 2013; Lin and Chen, 2005). The former approach divides the drying process into a perfect shrinkage stage (shrinkage proportional to volume reduction as governed by a constant evaporation rate) and a second stage defined by a falling evaporation rate, whereas the latter approach utilizes empirical correlations between the overall droplet moisture content and the water vapor pressure at the surface as well as the droplet diameter. Although in their simplest form these approaches only incorporate a global mass balance without computation of concentration gradients, some basic models allowing spatiotemporal resolution of one or more species concentrations emerged from these in the 1970s and 1980s and were further refined in recent times. The majority of models discussed in the following section was developed for description of food material droplets during spray drying and was validated against the drying kinetics obtained from single droplet drying experiments. Their accuracy is usually limited by the difficulty of finding reliable formulations for the influence of the forming crust on the droplet shrinkage rate, on the effective diffusivities of water and the components due to a rising viscosity and mass transport resistance of the solidified material, and on the partial vapor pressure at the surface and thus on the evaporation rate (Kentish et al., 2005).

Approaches With a Spatiotemporal Water Mass Balance

The earliest spatiotemporal approaches modeled water concentration profiles in drying skim milk droplets (Cheong et al., 1986; Ferrari et al., 1989; Sano and Keey, 1982; Wijlhuizen et al., 1979). An evaporation term was set as outer boundary condition and Fick's second law of diffusion was incorporated along the droplet radius for the water mass balance. The challenge to describe the effective diffusivity and evaporation rate more accurately was addressed in ensuing models. A work by Seydel et al. (2004) described the formation of hollow salt particles by simulating the radius-dependent change in particle density, which was unique in its attempt to account for component precipitation by means of a population balance that was solved independently from the mass and energy balances. Handscomb et al. (2009) formulated a model that aimed to predict shrinkage and shell thickening rates by balancing capillary contraction forces with the structural strength. The complexity of the crust properties and their effect on evaporation and shrinkage was further highlighted in a study by Vehring et al. (2007) on the drying of a protein-in-water droplet. Using the Peclet number, the model predicted the drying time until commencement of precipitation to stop the simulation at that point, because from then on a sufficient accuracy in simulating the declining evaporation rate was considered to be not feasible. Particularly, the effective diffusion coefficient of moisture through a solidified porous crust medium is difficult to predict with reasonable precision from theoretical equations (Perré, 2014).

Approaches With Spatiotemporal Binary Mass Balances

Adhikari and coworkers have been pioneering the simulation of binary component migration in drying droplets to work toward the prediction of the surface composition (compare to Table 4), presenting a model on fruit juice samples (Adhikari et al., 2003, 2004, 2007). Lumping together the juice components into one averaged component, a pseudo-binary system was formulated. The model was based on a discretization of the spatial coordinate, which was divided into equally long increments. Each of the increments represented a spherical disk with homogeneous composition under radial symmetry assumption. Diffusive fluxes were calculated from the differences in concentration and length between the centers of adjacent disks according Fick's first law of diffusion. The increasing evaporation resistance was incorporated via estimation of the moisture-dependent water activity in the surface disk and perfect shrinkage was assumed. The differential equations were solved with the method of lines (Iserles, 2009). After the simulated drying kinetics had been compared with suspended single droplet drying experiments for validation, the model was applied on spray drying conditions to predict the particle stickiness from the glass transition temperature.

Gopireddy and Gutheil (2013) utilized a description of the diffusion resistance imposed by the solid surface layer and water activity correlations to account for the retardation caused by solidification. Solving a set of differential diffusion and energy equations with a finite difference approach, in this way the concentration profiles of mannitol or polymer solutions during the early stages of single droplet drying were simulated.

Table 4   Modeling approaches that can be applied for prediction of the surface composition of binary or multicomponent droplets during drying: overview of included segregation mechanisms, consideration of the influence of solidification and experimental validation

Components	Incorporated segregation concepts					Influence of crust formation on			Validation	Author
	Diffusivity	Surface activity	Hydrophobicity	Precipitation	Atomization	Diffusivity	Evaporation	Shrinkage		
Lumped fruit juice solids	n/a	n/a	n/a	no	no	no	yes	no	Drying rate and temperature during SDD	Adhikari et al. (2007)
Mannitol	n/a	n/a	n/a	yes[a]	no	yes[a]	yes[a]	yes[a]	Drying rate and temperature of pure water during SDD	Gopireddy and Gutheil (2013)
Lactose, caseinate	yes	yes	n/a	yes	no	no	yes	no	Surface composition after SD and drying rate during SDD	Wang et al. (2013)
Sucrose, caseinate	yes	yes	n/a	yes	no	yes	yes	no	Experiments used to fit simulation parameters	Meerdink and Van't Riet (1995)
Sucrose, whey protein	yes	yes	n/a	no	no	no	no	no	–	Porowska et al. (2015)
Lactose, milk protein, fat	yes	no	no	no	no	yes	no	no	Surface composition after SD	Chen et al. (2011)
Lactose, milk protein, fat	yes	yes	no	no	yes	yes	yes	yes	Surface composition during SDD	Putranto et al. (2017)

SD, spray drying; *SDD*, single droplet drying.
[a] only early drying stages.

Approaches With Spatiotemporal Multicomponent Mass Balances

To date, only a few models can be found in literature that allow theoretical prediction of the concentration profiles of more than one component (see Table 4). A computation of the component distribution requires a spatiotemporal resolution of the mass balances, either as a set of simple ordinary differential equations by spatial discretization or as a set of partial differential equations. A global energy balance is typically sufficient under the assumption of a uniform temperature profile. This has been validated by dimensionless analysis (Biot numbers well below unity) for spray drying applications and even for significantly larger droplets in single droplet drying configurations (Chen and Peng, 2005; Patel et al., 2005). Furthermore, radial symmetry is generally assumed.

A spatiotemporal multicomponent model by Wang and coworkers was applied to resemble the spray drying process of an aqueous lactose/caseinate solution by variation of the Reynolds number and drying air temperature over time (Wang and Langrish, 2009; Wang et al., 2013). Spatial discretization of the droplet radius comparable to the above described work by Adhikari and coworkers, under the assumption of perfect shrinkage, allowed a simple incorporation of precipitation by comparison between the saturation concentration of each component and the calculated concentration in each disk at each time step. Also the protein surface activity was incorporated into the mass balance of the surface disk. Therefore, the model stands out in respect to its applicability on the component segregation during convective drying of milk droplets. The component diffusivities were expressed as temperature-dependent functions, but lacked an influence of the water concentration. The water evaporation rate was governed by an additional term in the water mass balance of the surface disk as a function of local water activity, which was estimated from the components' individual moisture-dependent water activity correlations. As available isotherms describing how the presence of solids affect the water activity have been either generated from liquid phase or fully formed solids, however, using either one to describe the entire drying process may not provide a precise description of the evaporation rate. The model was validated via comparison of the simulated surface composition with particles obtained from spray drying experiments. A surface overrepresentation of protein, which was decreasing with higher drying temperature, was predicted. From a sensitivity study it was concluded that the difference in component diffusivities and the protein surface activity were the major driving forces for component segregation, while the components' solubility imposed a subordinate influence.

Three other models were less comprehensive, but nevertheless interesting in their unique approach. Meerdink and Van't Riet (1995) described the component segregation during drying of small sucrose/sodium caseinate solution slabs. The model contained Maxwell–Stefan partial differential equations with concentration-dependent diffusion coefficients. Since measuring and approximation tools for Maxwell–Stefan multicomponent diffusion coefficients in concentrated aqueous solutions are lacking, the parameters of the diffusivity equations had to be fitted so that the simulated concentration profiles agreed with the experimental results. In the modeling work by Porowska et al. (2015) on drying whey protein/sucrose droplets, the phenomena taking place during crust formation were largely disregarded. The focus was laid on the surface activity of the whey protein, and it was supposed that the adsorption process would halt upon commencing shell formation. The protein surface activity was described with the aid of experimental determination of the dynamic surface tension as a function of protein bulk content and time. Also noteworthy, despite not being a spatially resolved model, Chen and coworkers presented an analytical continuum approach to simulate the solid formation in the outermost layer of a drying water droplet with dissolved lactose, fat and milk protein (Chen et al., 2011, 2013; Xiao and Chen, 2014). Under the assumption that the concentration only changes in a thin surface region, an explicit equation for the surface composition was obtained. Protein surface activity was not covered by this model. The Stokes–Einstein equation was introduced in an extended form to account for the concentration dependency of the effective component diffusivities.

Putranto et al. (2017) utilized the same modified Stokes–Einstein equation for a model on drying low-fat milk droplets. It accounted for the protein's surface activity as a boundary condition. Spatiotemporal balances for energy, momentum and mass of water, lactose, protein, and fat formed a set of partial differential equations that was solved with the method of lines. A realistic description of the influence of solidification on the water diffusivity, evaporation rate, and particle shrinkage was aspired by incorporation of semiempirical drying and shrinkage kinetics, which were obtained from suspended single droplet drying experiments and expressed via the reaction engineering approach. As such, the model required some experimental work to obviate the need for a perfect shrinkage assumption and for approximations of the effective water diffusivity. A new single droplet drying technique was employed for result validation, which allowed tracking of the changes in chemical surface composition over time. The experimentally and theoretically obtained surface concentrations agreed reasonably well, but better agreement might have been impeded as solute precipitation and the influence of the fat's hydrophobic nature on the component distribution had not been implemented. From the experimental study also the initial surface composition of the droplets was known, which was used as initial condition for the component mass balances of the simulation. The study highlighted the influence of the atomization stage on the component distribution in drying milk droplets. Accordingly, it was concluded that the use of experimentally observed initial surface compositions after droplet generation are critical for an accurate simulation of the component distribution in spray-dried milk particles.

Concluding Remarks

The surface composition of milk powder imposes a critical influence on its functional properties. It is widely accepted that a strong overrepresentation of fat, in comparison with the bulk composition, emerges on the surface during spray drying at both industrial- and laboratory scale with detrimental impact on the powder quality. However, the surface formation process is far from being thoroughly understood. Four different processes might potentially affect the component segregation in drying milk droplets; the components' diffusivities, the components' interaction with the air/water interface (protein's surface activity and the lipid phase's hydrophobicity), the crust formation/precipitation process, and the atomization process. As the degree of influence of each of these

mechanisms is still under debate, further experimental work is required to test and validate the different concepts. While the subordinate enrichment of protein is most often perceived to take place during drying due to its lower diffusivity than lactose and primarily due to its surface activity, the atomization stage seems to have a critical impact on the formation of surface fat. Some promising modeling approaches have been published in recent times that are, in principle, capable of simulating the component distribution of drying milk droplets. These should be further developed to account for all of the four potential segregation mechanisms for a better understanding of the surface formation and a more accurate prediction of the powder properties.

Acknowledgment

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