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Original Research Paper

The influence of the chemical surface composition on the drying process of milk droplets

Martin Foerster [a], Thomas Gengenbach [b], Meng Wai Woo [a], Cordelia Selomulya [a,*]

[a] Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia
[b] CSIRO Manufacturing, Bayview Avenue, Clayton, Victoria 3168, Australia

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ABSTRACT

The functional properties of multi-component particles are strongly affected by their chemical surface composition, for instance in pharmaceutical and food applications. The powders are often produced from emulsions and solutions by convective drying, such as spray drying. A detailed understanding of the drying and shrinkage kinetics of the material is hereby crucial to optimise process design and product characteristics. In this study, a modified analysis technique was implemented into filament single droplet drying to observe the changes in component distribution of two milk model emulsions with drying time as well as the impact thereof on the water evaporation resistance and shrinkage behaviour. The drying droplets were cryogenically flash-frozen at discrete drying times and, subsequent to freeze-drying, investigated in terms of their chemical surface composition and internal fat and protein distribution. The droplets of a high-fat milk model emulsion were covered by a continuous fat film throughout the whole drying process, whereas the droplets of a low-fat model emulsion featured a surface overrepresentation of protein in comparison to the bulk concentration. The protein further enriched near the surface with increasing drying time. In the high-fat system, the lipid surface film reduced the extent of particle shrinkage and impeded the drying process.

1. Introduction

A high content of fat on the surface of spray-dried milk particles, which greatly exceeds the bulk fat content, is typically encountered independent of the atomization process. This surface dominance of fat causes detrimental effects on the powder particles' oxidative stability [24,25,27], affinity to caking [28,36] and dispersibility as well as wettability during reconstitution in water [16,35]. As a result, post-processing steps, such as coating with lecithin, are often used in industry for further processing and to prolong storage. Various potential mechanisms have been proposed to describe the component segregation mechanism between lipid, protein and lactose that leads to this fat accumulation at the surface during convective drying of milk droplets. Previously, it has often been attributed to the components' different physical properties that come into effect during the actual drying process subsequent to film disintegration. These include surface activity [15,22,1], diffusivity [33,30,20,37] and solubility [5,29,49]. Yet, it was recently shown that it was, in fact, the atomization process that induces the fat surface coverage [18]. Immediately after atomization, the surfaces of milk model droplets were found to have fat contents of 9–13 and 83–92% v/v, respectively, for 0.5 and 44.2% v/v of fat on dry matter basis (d.m.) in the feed emulsions. In the subsequent drying stage, the layer of fat remained on the surface, while protein accumulated underneath the fat layer as drying proceeded. The comparison between atomized droplets and fully spray-dried particles was made possible by flash-freezing the atomized droplets. However, no information could be obtained on the droplet surface composition at intermediate drying times inside the drying tower. Moreover, the impact of the forming crust and of the corresponding surface composition on the drying and shrinkage kinetics of the droplets would be of great interest for optimization of industrial dryer design and operation.

In contrast to spray drying experiments, single droplet drying facilitates a direct monitoring of the convective drying of a solution or emulsion droplet at any point of the drying process [48,45]. The filament single droplet drying technique, where an individual droplet is suspended at a thin filament and dried in a conditioned air

* Corresponding author. Fax: +61 399055686.
E-mail addresses: martin.foerster@monash.edu (M. Foerster), thomas.gengenbach@csiro.au (T. Gengenbach), meng.woo@monash.edu (M.W. Woo), cordelia.selomulya@monash.edu (C. Selomulya).

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stream, has often been applied for this purpose, for instance the drying of aqueous droplets containing fruit pulp, milk and lactose [8,7,32]. Parameters such as relative air velocity, drying air humidity and temperature can be adjusted to observe the resulting changes in droplet mass, diameter and temperature in situ. Chen and Xie [9] introduced a semi-empirical model, the Reaction Engineering Approach (REA), to process this experimental data for description of the 'apparent activation energy of evaporation' as a measurement of the evaporation resistance of the emerging crust as a function of the droplet moisture content. Evaporation is hereby treated as an activation process that has to overcome a certain energy barrier. The single droplet drying technique does not allow for the complex droplet-droplet and droplet-air interactions encountered within spray dryers and the droplet size is significantly larger than in spray drying. It offers, however, a practical way of replicating the actual drying process of an individual droplet to determine the characteristic convective drying behaviour of a certain material system. This information can then be fed into computational fluid dynamics (CFD) simulations to predict the changes in moisture content and droplet size for the given material system in a spray dryer environment. In this way, the evaporation and shrinkage kinetics, even for complex solidification processes, are described with high accuracy [50,39,51]. Mezhericher et al. [34] proposed an incorporation of REA into a numerical model of the mass and temperature change in drying skim milk droplets for a more realistic account of the water diffusion resistance caused by crust formation. Chew et al. [12] undertook an investigation of the surface composition of fully dried milk protein concentrate particles subsequent to completion of the single droplet drying. The dried particles were analysed regarding to their chemical surface concentration via X-ray photoelectron spectroscopy (XPS), and it was found that smaller droplet sizes as well as higher temperatures resulted in a decreasing fat content on the particle surface, although there was always a significant overrepresentation of fat on the surface. Fu et al. [20] conducted a wetting and dissolution study of fresh whole and skim milk particles obtained from single droplet drying to qualitatively classify the surface as hydrophobic or hydrophilic. After certain drying times, the drying air flow was stopped and a solvent droplet (ethanol or water) was attached to the (semi-)dried droplet. Based on the wetting behaviour observed with a camera, conclusions about the nature of the developed surfaces were drawn. Interpretation, however, was limited to a relative comparison between whole and skim milk, and the wettability until about 35 s from drying commencement could not be studied because of too high moisture contents.

In order to gain a better understanding of the material segregation process that occurs in a convective drying of milk droplets, the final surface concentration alone or ambiguous dissolution test videos are insufficient. To date, single droplet drying has not yet been applied for quantitative analysis of the surface composition at intermediate drying stages and directly after droplet generation. The aim of the present study was to widen the hitherto employed extent of single droplet drying analyses to also monitor, for the first time, the changes in surface composition and internal component distribution over drying time and over the corresponding droplet moisture content. Single droplet drying of low and high fat milk model emulsions was interrupted at discrete drying times by cryogenic flash freezing, and, following freeze-drying, the particles were analysed in terms of surface composition by XPS and internal component distribution by confocal laser scanning microscopy (CLSM). The data were compared with drying and shrinkage kinetics obtained from conventional single droplet drying experiments for a better understanding of surface formation and its impact on the convective drying behaviour of milk droplets. A requirement for these results to be representative for the surface composition and drying characteristics in a spray dryer was that the initial droplet states were comparable. It was hence to be validated that the component distribution in the droplets generated for single droplet drying matched the one of droplets atomized during conventional spray drying.

2. Material and methods

2.1. Emulsion preparation

Two model milk emulsions of different fat contents were investigated, as summarized in Table 1. A fat filled model emulsion (FFME) featured a composition typical for both bovine whole milk and commercially sold fat filled milk powder. It contained 40.8% w/w lactose, 31.1% w/w fat and 27.0% w/w protein in d.m. A low fat model emulsion (LFME) resembled the composition of the FFME in terms of protein-lactose ratio and solid content, whereas the fat content was significantly reduced to 0.3% w/w. The emulsions were prepared by dissolving 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 in water. For the FFME emulsion, sustainably sourced refined *Elaeis guineensis* palm oil fat (Auroma Pty Ltd, Australia) was added. Both emulsions were mixed with deionised water at 45 °C for 1 h, prior to pre-homogenization in a high-speed colloidal mill (WiseMix Homogenizer HG-15D, Daihan Scientific, South Korea) at 1000 rpm. This was followed by three passes at 1000 bar and two subsequent passes at 500 bar through a high pressure homogeniser (EmulsiFlex-C5, Avestin, Canada). The fat globule size distributions of each emulsion were measured by dynamic light scattering (Zetasizer Nano ZS, Malvern Instruments Ltd, UK) to ensure consistency (volume weighted mean diameter had to be $D[4,3] = 1.0\ \mu m \pm 0.05\ \mu m$).

2.2. Changes in component distribution over drying time via cryogenic flash-freezing

Information about changes in the internal and surface distribution of lactose, protein and fat with proceeding drying time was acquired from single droplet drying experiments conducted inside a suspension rig with well-defined drying environment. Compressed air flowed through a dehumidifying column (KF-DDF-125, Knight Pneumatics, Australia) and was electrically heated before entering the drying chamber from the bottom and leaving it through its top. The conditioned air stream had a temperature of 70 °C, a velocity of 0.75 m/s and a humidity of 0.0001 kg/kg. Individual FFME and LFME droplets of 3 μl (±0.05 μl standard deviation) were generated by means of a 5 μl micro-volume syringe (5FX, SGE Analytical Science, Australia) and were then suspended at the tip of a thin, vertically mounted glass filament. The tip of the filament consisted of a knob which had a hydrophilic coating

Table 1
Volumetric composition of the solid contents in the LFME and FFME model emulsions.

	Abbreviation	Solid concentration [% w/w]	Fat content in d.m. [% v/v]	Protein content in d.m. [% v/v]	Lactose content in d.m. [% v/v]
Low fat model emulsion	LFME	20.0	0.5	41.8	57.7
Fat filled model emulsion	FFME	20.0	44.2	23.5	32.4