Fat properties during homogenization, spray-drying, and storage affect the physical properties of dairy powders

M. L. Vignolles,*† C. Lopez,*† M. N. Madec,*† J. J. Ehrhardt,‡ S. Méjean,*† P. Schuck,*†¹ and R. Jeantet*†

*Institut National de la Recherche Agronomique (INRA), ÚMR1253, F-35000 Rénnes, France †Agrocampus Rennes, Unité Mixte de Recherche (UMR) 1253, F-35000 Rennes, France

Centre National de la Recherche Scientifique (CNRS), Nancy-Université, UMR 7564, Laboratoire de Chimie Physique et de Microbiologie pour l'Environnement, F-54600 Villers lès Nancy, France

ABSTRACT

Changes in fat properties were studied before, during, and after the drying process (including during storage) to determine the consequences on powder physical properties. Several methods were combined to characterize changes in fat structure and thermal properties as well as the physical properties of powders. Emulsion droplet size and droplet aggregation depended on the homogenizing pressures and were also affected by spray atomization. Aggregation was usually greater after spray atomization, resulting in greater viscosities. These processes did not have the same consequences on the stability of fat in the powders. The quantification of free fat is a pertinent indicator of fat instability in the powders. Confocal laser scanning microscopy permitted the characterization of the structure of fat in situ in the powders. Powders from unhomogenized emulsions showed greater free fat content. Surface fat was always overrepresented, regardless of the composition and process parameters. Differential scanning calorimetry melting experiments showed that fat was partially crystallized in situ in the powders stored at 20°C, and that it was unstable on a molecular scale. Thermal profiles were also related to the supramolecular structure of fat in the powder particle matrix. Powder physical properties depended on both composition and process conditions. The free fat content seemed to have a greater influence than surface fat on powder physical properties, except for wettability. This study clearly showed that an understanding of fat behavior is essential for controlling and improving the physical properties of fat-filled dairy powders and their overall quality.

Key words: free fat, structure, spray-drying, powder physical property

INTRODUCTION

Fat-filled spray-dried dairy powders have achieved great economic importance. These include whole milk powder, cream powder, whey derivatives, and milk ingredients enriched with various types of fat, either milk fat or vegetable oils. Fat contents usually range from 100 to 700 g/kg of DM. World production and international trade have increased greatly in recent years (International Dairy Federation, 2007). The major suppliers are New Zealand, the European Union, Argentina, Australia, and the United States (International Dairy Federation, 2007). In this context, it is of primary importance to increase the understanding of the parameters that affect the properties of fat-filled spray-dried dairy powders.

The drying process causes a range of structural and physicochemical modifications, which in turn influence the rehydration and handling properties of dairy powders and their shelf life (Westergaard, 1994). Furthermore, increasing the fat content leads to additional quality implications, such as poor rehydration and flow properties, and off-flavors attributed to the presence of free and surface fat. However, controlling the drying operation and the powder properties is still rather empirical in this case, and to date, few studies have focused on the whole issue (Vignolles et al., 2007).

The changes in fat properties must be determined before, during, and after the overall drying process to understand their subsequent consequences on powder physical properties and to improve the quality of fatfilled dairy powders. The objective of this study was to prepare well-controlled emulsions and to relate their characteristics to the properties of the powders. The originality of this work was that fat behavior was studied all along the drying process (i.e, from homogenization to storage) and a set of methods was combined, including specific methods for fats. Emulsions with coconut oil were characterized through their particle size, viscosity, and crystallization profile. Powders obtained from these emulsions were studied through 1) their fat properties, including particle size, free fat, surface fat as

Received May 23, 2008.

Accepted September 1, 2008.

¹Corresponding author: Pierre.Schuck@rennes.inra.fr

measured by x-ray photoelectron spectroscopy (**XPS**), thermal profiles, and in situ location by confocal laser scanning microscopy (**CLSM**), and 2) their physical properties.

MATERIALS AND METHODS

Materials

Hardened coconut oil (Ertilor C 32/34) was purchased from Fuji Oil Europe (Gent, Belgium). This vegetable oil is commonly used in fat-filled dairy powders. In its natural form, coconut oil includes 70% of short-chain fatty acids (C6:0 to C12:0), and only 6% of unsaturated fatty acids (Padley et al., 1986). High-heat skim milk powder from Epi Ingredients (Ancenis, France) was used to avoid proteolytic degradation during powder storage. Petroleum ether (40 to 60°C boiling point) of analytical grade, chloroform, and methanol of HPLC grade were obtained from Carlo Erba Reagents (Val de Reuil, France). Sodium dodecyl sulfate and EDTA were purchased from VWR-Prolabo (Fontenay-sous-Bois, France). Nile Red and PEG200 were obtained from Sigma-Aldrich (St. Louis, MO, and St. Quentin-Fallavier, France, respectively), and the antifading glycerol-PBS solution was from Citifluor Ltd. (London, UK).

Preparation of Emulsions. First, skim milk powder was dissolved in hot water ($60^{\circ}C$) and left under stirring conditions for 2 h in a 300-L tank. The optimal dissolution of the skim milk powder was assessed by laser light-scattering measurements (see method below); this powder had less than 3.50% (vol/vol) of insolubles. Melted hardened coconut oil $(60^{\circ}C)$ was then added at 100, 260, and 400 g/kg of fat in DM to the skim milk solutions, which were at 390, 340, and 300 g/kg of skim milk powder in water, respectively. Final DM was 400 g/kg in the 3 resulting mixes. The mixes were stirred gently for 15 min before processing and were maintained at 60°C throughout the experiment (approximately 180 min). In a first series of trials, the 3 mixes were homogenized at 16 MPa in the first stage and 4 MPa in the second stage by means of an APV Rannie LAB 12/51 H homogenizer (Assistance Techniques Spéciales, Moissy Cramavel, France). In a second series of trials, the 3 mixes were passed through the loosened heads of the homogenizer for each experiment. The flow rate was 100 L/h.

Spray-Drying of Emulsions and Storage of Powders. Emulsions were immediately dried in a pilot-scale multistage spray dryer (GEA-PE, St Quentin en Yvelines, France) at Bionov (Rennes, France). The evaporation rate was 70 to 100 kg/h. A high-pressure pump fed the emulsion to the drying chamber at a flow rate of 100 L/h. The spray-dryer operated concurrently and had a spray nozzle with an orifice of 0.73 mm in diameter. Inlet air humidity was controlled and adjusted by a dehumidifier (Munters, Sollentuna, Sweden) at 1 g/kg of water in dry air. Inlet and outlet gas temperatures were 190 and 90°C, respectively. Powders were granulated by recycling the fine particles from the cyclone (the so-called dusty) at the top of the drying chamber. They were collected in 25-kg paper bags at temperatures ranging from 20 to 30°C.

Powders were stored under a controlled temperature of 20° C, in sealed bags under low-vacuum conditions, and kept away from light. They were analyzed regularly for 12 mo. Hereafter, the terms low-fat, medium-fat, and high-fat refer to emulsions or powders with 100, 260, or 400 g/kg of fat in DM, respectively.

Methods

Fat Droplet and Powder Particle Sizes. Fat droplet and powder particle sizes were measured by laser light scattering with a MasterSizer 2000 instrument (Malvern Instruments, Malvern, UK) equipped with a 5-mW helium-neon laser ($\lambda = 633$ nm) and an electroluminescent diode ($\lambda = 466$ nm). A refractive index of 1.449 was used for coconut oil and 1.333 was used for the aqueous phase; the absorption value was 0.01. For measurements after homogenization and atomization through the spray nozzle, the emulsion samples were diluted (1:5) in distilled water or in a solution of SDS at 1% (wt/vol). Sodium dodecyl sulfate allowed the dissociation of bridged-flocculated droplets (i.e., the so-called clusters) by displacing proteins from the interface. Then, 1 mL of 35 mM EDTA at pH 7 was added directly to the diluted emulsion samples in the circulating cell (to both samples in distilled water and samples with SDS) to dissociate CN micelles. For the determination of fat droplet size in the powders, emulsions were obtained by rehydrating the powders at 100 g/kg in distilled water at 60° C, for 30 min before measurements, and under gentle stirring conditions to avoid secondary emulsification. The emulsion samples were 1) directly introduced in the circulating cell or 2) previously diluted (1:5) in SDS at 1% (wt/vol). One milliliter of 35 mM EDTA at pH 7 was then added to the emulsion samples (both native and with SDS). Each result was the mean of 2 independent samplings and 3 successive measurements each time. The results were recorded as volume distributions, volume-weighted average diameters,

$$d_{43} = \sum_{i} n_i d_i^4 / \sum_{i} n_i d_i^3$$
^[1]

(where n_i is the particle number of average diameter d_i), modes, and specific surface areas, which were calculated by the software. Powder particle size distribution was determined by using a dry powder feeder attachment, and the standard optical model presentation for particles dispersed in air was used. The results were recorded as surfaceweighted average diameters,

$$d_{32} = \sum_{i} n_i d_i^3 / \sum_{i} n_i d_i^2$$
^[2]

(where n_i is the particle number of average diameter d_i).

Viscosity Measurements. Rheological measurements were carried out with an AR1000 viscometer (TA Instruments France, Guyancourt, France) with an aluminum concentric cylinder (stator outer radius: 25 mm; rotor inner radius: 23.05 mm; cylinder immersed height: 30 mm; and bottom gap: 4 mm). Samples were equilibrated at the measurement temperature $(20^{\circ}C)$ for 3 min by using a Peltier temperature control system. Samples were then sheared at continuous shear rates from 1 to 300 s^{-1} for 4 min 20 s and from 300 to 1 s^{-1} for 4 min 20 s. Each step lasted 10 s and the result was the mean of the last 2 s for each step. Samples were either Newtonian, or shear-thinning. Apparent viscosities were calculated at high shear rates (300 s^{-1}) from the Herschel-Bulkley mathematical model taking the following form:

$$\tau = \tau_0 + \mathbf{a} \times \dot{\gamma}^n, \qquad [3]$$

where $\boldsymbol{\tau}$ is the shear stress (Pa), $\boldsymbol{\tau}_0$ is the yield stress (Pa), a is the viscosity at 1 s⁻¹ (Pa·s), $\dot{\boldsymbol{\gamma}}$ is the shear rate (s⁻¹), and n is the rate index. Only emulsions with 260 g/kg of fat in DM were analyzed in duplicate.

Thermal Properties. Thermal properties of emulsions and powders were investigated by differential scanning calorimetry (\mathbf{DSC}) with a TA Q-1000 calorimeter (TA Instruments France), using aluminum hermetic pans. Cell calibration was achieved with indium. The crystallization properties of fat in emulsions were recorded from 60 to -5° C at 2° C/min (sample size of 15 to 20 mg). The overall thermal profiles of fat in powders were recorded from 60 to -40° C and from -40 to 60° C at 2°C/min. Melting profiles of fat and the glass transition of lactose (\mathbf{T}_{g}) in powders that had been stored at 20°C for various times were successively recorded from 20 to 70°C at 2°C/min (sample size of 7 to 10 mg). Each sample was analyzed in duplicate. The instrument software, TA Instruments Universal Analysis 2000 4.1, was used to calculate thermal characteristics such as the initial temperature of fat crystallization (\mathbf{T}_{onset}) , the T_{g} , and enthalpies of phase transitions (ΔH).

Microstructure Observations. Emulsions were observed by phase-contrast light microscopy with an Olympus BX 51, TF instrument (Olympus France,

Rungis, France) by using a $100 \times$ oil immersion objective and an Olympus DP11 camera to record characteristic micrographs of each sample. In situ microstructural analysis of powder particles was performed by CLSM with a Nikon TE2000 Eclipse C1si (Nikon, Champignysur-Marne, France). Nile Red fluorescent dye was used to label fat. The powder of the fluorescent dye was dissolved in acetone (50 μ g in 1 mL). The preparation was added to a PEG200-Citifluor mix (1:1) onto a glass microscope coverslip. The solvent was able to evaporate. Powder particles were then added to the probe mixture and left for 30 min at 4°C to ensure a good diffusion of the fluorescent dye. Observations were performed with a $60 \times$ oil immersion objective and a helium-neon laser operating at an excitation wavelength of 543 nm (2) mW; intensity: 30%), which was close to the excitation maximum of Nile red. Each micrograph corresponded to the average of 5 pictures of the sample. Characteristic micrographs were selected among the 10 micrographs taken for each sample, including a complete z-depth observation of a powder particle.

Free Fat Extraction. The amount of free fat was evaluated by mixing 10 g of powder with 50 mL of petroleum ether. Extraction number varied between 2 and 3, until the solvent phase was limpid. A first evaporation of petroleum ether was performed at 40°C under vacuum with a rotary evaporator (Rotavapor, Büchi, Flawil, Switzerland). Fat extracted from the powder was removed into 12-mL glass flasks with a blend (chloroform:methanol, 2:1) according to the method of Folch et al. (1957), and a second evaporation under nitrogen was conducted with an N-Evap 111 instrument (Organomation Associates Inc., Berlin, MA). Samples were stored at -20° C and kept away from light. Each sample was analyzed in duplicate.

Elemental Surface Composition Determina*tion.* The elemental surface composition of the powders (analysis depth <10 nm) was measured by XPS with a Kratos Axis Ultra instrument (Kratos Analytical, Manchester, UK) to determine the percentage of powder particle surface covered by fat. The instrument was equipped with a monochromatic Al K α source and a delay-line detector, which allowed a high count rate. The instrument and the parameters used here for analysis and processing were described previously by Gaiani et al. (2006). The elemental composition in the sample was assumed to be a linear combination of the elemental composition of the pure components making up the samples. The relative atomic concentrations of carbon, oxygen, and nitrogen were quantified and used in a matrix formula related to the surface content of the different compounds making up the sample (i.e., protein, lactose, and fat), in agreement with the method presented by Fäldt et al. (1993):

$$I^{C} = \alpha P I^{CP} + \alpha' L I^{CL} + \alpha'' F I^{CF}, \qquad [4]$$

$$I^{O} = \alpha P I^{OP} + \alpha' L I^{OL} + \alpha'' F I^{OF}, \qquad [5]$$

$$I^{N} = \alpha P I^{NP} + \alpha' L I^{NL} + \alpha'' F I^{NF}, \qquad [6]$$

where I^C, I^O, and I^N were the molar fractions of carbon, oxygen, and nitrogen at the sample surface (values obtained from the areas of the carbon 1s, oxygen 1s, and nitrogen 1s XPS peaks); I^{CP} , I^{CL} , and I^{CF} were the molar fractions of carbon in protein, lactose, and fat; I^{OP} , I^{OL} , and I^{OF} were the molar fractions of oxygen in protein, lactose, and fat; and I^{NP}, I^{NL}, and I^{NF} were the molar fractions of nitrogen in protein, lactose, and fat. Experimental values obtained from the reference samples (micellar CN, whey proteins, hardened coconut oil, and α -monohydrated lactose) were used to carry out these calculations. The relative occupied surfaces were determined for protein, lactose, and fat [i.e., (αP) , $(\alpha' L)$, $(\alpha' F)$, respectively] by solving the matrix. In this model, the different powder components were assumed to be present at the surface in patches, which were thicker than the analysis depth of the XPS (2 to 10 nm). The relative coverage calculated here was expected to be close to the mass-based one because there are small differences between the relative atomic mass of carbon (12), oxygen (16), and nitrogen (14). For direct comparison with the bulk composition of powders, the relative coverage in this paper was assumed to be mass based.

The survey scan revealed the presence of carbon, oxygen, and nitrogen, and traces of calcium, phosphorus, chloride, potassium, and sulfur. The elemental concentrations of carbon, oxygen, and nitrogen amounted to at least 99% of all the elements registered; thus, the remaining elements were ignored in the analysis.

The high-resolution carbon 1s, oxygen 1s, and nitrogen 1s peaks were decomposed according to the model of Gerin et al. (1995) for biochemical compounds. Deconvolution of the carbon 1s peak led to 4 peaks attributed to the <u>C</u>-(C,H), C-(O,N), O-C-O, and O-C=O functions. The oxygen 1s peak was decomposed in 3 peaks corresponding to the <u>O</u>=C, C-<u>O</u>H, and H₂O functions. The nitrogen 1s peak was deconvoluted in the C-(<u>N</u>H, <u>N</u>H₂) and C-(<u>N</u>H₃⁺) functions.

Surface fat was calculated from the carbon, oxygen, and nitrogen percentages in the samples by using the surface elemental composition of the references (Table 1) and equations [4] to [6]. The experimental compositions of the references were in agreement with theoretical values (Fäldt et al., 1993; Kim et al., 2005b).

Two independent samplings and the subsequent measurements on the same powder allowed for the estima-

 Table 1. Relative elemental composition of the reference samples

 measured by x-ray photoelectron spectroscopy for extrapolation of the

 surface composition

	Relative	atomic conce	ntration, %
Reference sample	Carbon, %	Oxygen, %	Nitrogen, $\%$
Protein			
Native phosphocase in the second seco			
Experimental value	71.12	17.53	11.36
Theoretical value ¹	65.00	19.00	16.00
Error^2	9.42	7.74	29.00
Whey proteins			
Experimental value	70.64	15.95	13.41
Theoretical value ¹	65.00	19.00	16.00
Error^2	8.68	16.05	16.19
Fat (hardened coconut oil)			
Experimental value	89.38	10.62	
Theoretical value ¹	86.00	14.00	
Error^2	3.93	24.14	
α -Monohydrated lactose			
Experimental value	54.61	45.39	
Theoretical value ¹	52.17	47.83	
Error ²	4.67	5.09	

¹Theoretical values: lactose, sodium caseinate for protein from Fäldt et al. (1993) and Kim et al. (2005b), and coconut oil for fat from Fäldt and Bergenståhl (1993).

²Error (%) = [(experimental value – theoretical value)/theoretical value] \times 100.

tion of standard errors, which were 0.000% for carbon, 0.002% for oxygen, and 0.019% for nitrogen (df = 1). Given the small standard errors, powder samples were analyzed once.

Physical and Sensorial Properties of Powders. Wettability and dispersibility indexes were obtained according to the Niro Atomizer standards (Sørensen et al., 1978); the solubility index was obtained according to International Dairy Federation (1988) standards. Water activity $(\mathbf{a}_{\mathbf{W}})$ was assessed with a Novasina RTD 200/0 a_w meter (Novasina AG, Pfäfficon, Switzerland) at 25°C. Flowability, floodability, aerated density, and tapped density were measured with a PT-N powder characteristics tester (Hosokawa Micron, Evry, France). In the standards given by the powder tester, a high flowability is a good powder property: from 60 to 100 the index is normal to very good. Conversely, a high floodability is considered as a poor property: an index above 40 means that the powder tends to flush or flushes. Each sample was analyzed in duplicate. True density of the powder particles was determined by gas pycnometry with both helium and nitrogen on a Pycnomatic ATC instrument (Thermo Fisher Scientific, Courtabœuf, France). Each sample was analyzed in triplicate. Densities were calculated for the nonfat matter fraction to avoid any influence of the total fat content. Interstitial air and occluded air were determined from density measurements as follows (Westergaard, 1994):

			$d_{43},^1~\mu{ m m}$		Viscosity, ²	mPa·s
Fat content, g per kg of DM	Homogenization pressure, MPa	After homogenizing	After spraying	After drying	After homogenizing	After spraying
100	20	0.44	0.38	0.57	70	117
260	20	0.59	0.44	0.65	68 ± 1	78 ± 2
400	20	0.45	0.41	0.68	270	165
100	0	5.02	0.80	1.40	45	101
260	0	3.09	0.65	2.41	42 ± 14	168 ± 43
400	0	5.55	1.21	5.20	19	235

Table 2. Fat content and homogenizing conditions affecting fat droplet mean diameters (d_{43}) and viscosities in emulsions

¹Samples dispersed in SDS and EDTA. Data are means \pm sample standard errors. Sample standard errors were <0.001 for the modality 20 MPa and <0.2 for the modality 0 MPa (df = 5).

²Apparent viscosities at 300 s⁻¹. Data are means \pm sample standard errors when available (df = 1).

Interstitial air content = (1,000/aerated density)

$$-(1,000/\text{tapped density}) (\text{mm}^3/\text{g})$$
[7]

Occluded air content = (1,000/true density)

- interstitial air content (mm^3/g) [8]

To detect off-flavors, sensorial assessments on the rehydrated powders at 100 g/kg of powder in water were performed by 3 independent trained panels of 5 to 10 tasters each.

RESULTS AND DISCUSSION

Properties of Fat After Homogenizing and After Spray Atomization

Emulsion Droplet Size and Aggregation Depend on Both Homogenizing Pressures and Spray Atomization. After homogenizing the liquid preparations, tiny and coarse emulsions were obtained by applying a pressure of 20 and 0 MPa, respectively, as assessed by laser light-scattering measurements (Table 2). In the tiny emulsions, the size fraction from 2 to 40µm was easily removed after the addition of EDTA. SDS, or both (results not shown). In the coarse emulsions, SDS reduced the maximal size class in the range of 15 to 20 μ m instead of 40 to 50 μ m (Figure 1A). In both cases, clustering (i.e., aggregation) appeared between fat droplets. Walstra and Jenness (1984) previously attributed clustering to aggregation between the CN micelles adsorbed at the surface of fat droplets. Hence, both EDTA and SDS were used to approach the size of individualized fat droplets, for the direct comparison of the various emulsions. After the addition of EDTA and SDS in the various tiny emulsions, the mean diameter (d_{43}) ranged from 0.4 to 0.7 µm (Table 2) which corresponded to specific surface areas in the range of 17.2 to 21.5 m^2/g of fat. This was observed regardless of the initial fat content. The overall size

distribution was mainly monomodal (Figure 1B); the maximal fat droplet size was 2.0 μ m. In the various unhomogenized emulsions, the d_{43} ranged from 3.1 to 5.6 μ m and the specific surface area ranged from 3.5 to 5.6 m²/g of fat. Their overall size distributions were mainly bimodal with 2 modes: 0.18 and 5.5 μ m (Figure 1C); the maximal fat droplet size was 18 μ m.

After spray atomization of the emulsions through the spray nozzle, the clustering phenomenon was more pronounced for previously homogenized emulsions with 260 and 400 g/kg of fat in DM. It was also observed with previously unhomogenized emulsions with 100 g/ kg of fat in DM.

After the addition of EDTA and SDS, the smallest particles ($d_{43} < 0.5 \ \mu$ m) did not undergo a significant modification of their size after atomization through the spray nozzle (Table 2). They were slightly reduced and the surface area was thus increased to a small extent. Conversely, particles with mean diameters (d_{43}) above 3 μ m were further reduced from 4.5 to 6 times, with a subsequent increase in the surface area from 2.5 to 3.5 times. Indeed, fat droplets can be disrupted as they undergo a shear rate during the atomization step (Walstra and Jenness, 1984). Ye et al. (2007) also observed smaller fat droplets after spray-drying and found some very large fat droplets (up to 80 μ m) that they attributed to coalescence.

However, the proper influence of the spray nozzle on fat droplet size cannot be evaluated separately because the emulsions additionally passed through a highpressure pump that fed the spray nozzle and drying chamber. Shear rate attributable to flowing through pipes should also be considered because it may lead to fat droplet disruption (Walstra and Jenness, 1984).

Emulsion Viscosity Is Greater After Spray Atomization Than After Homogenizing. Spray atomization of the unhomogenized emulsion had the same increasing effect on viscosity as homogenizing, excluding the high atypical value of 270 mPa·s (Table 2). The increase in viscosity was mainly due to the



Figure 1. Size distributions are characteristic of the processing steps the product underwent. Examples of high-fat emulsions and the corresponding rehydrated powders. (A) Unhomogenized emulsion in its native state (solid line), with addition of EDTA (\bullet), and with SDS (×). Emulsions and rehydrated powders (B) with a 20-MPa homogenization and (C) without homogenization pressure. Symbols: after homogenizing (\diamond), after spray atomization (\Box), and after drying (\blacklozenge). The phase-contrast micrographs were taken in the rehydrated powders (scale bar: 10 µm).

decrease in fat droplet size, with subsequent increases in fat droplet numbers and interfacial area (Prentice, 1992). However, for similar fat droplet sizes, viscosities were significantly greater after spray atomization than after homogenizing, and could no longer be correlated with the d_{43} . These 2 processing steps would implicate different mechanisms of protein adsorption and subsequent aggregation between fat droplets, as mentioned above. Here, the greater viscosity was related to a slightly larger proportion of clusters above 10 μ m after spray atomization: 2.4 to 7.8% vs. 0.6 to 1.5% in homogenized emulsions, and 14.0 vs. 8.7% in the low-fat unhomogenized emulsion. Large clusters are known to increase viscosity (Prentice, 1992), which further accelerates fat droplet aggregation and coalescence (Walstra and Jenness, 1984). Hence, fat droplet stability would be affected in subsequent manufacturing stages.

It should be noted that the shear rates used for the viscosity measurements were much lower than the shear rates actually implied during the process. For instance, they were assumed to be 10 to 10^3 s^{-1} for mixing and stirring, and 10^3 to 10^4 s^{-1} for spray-drying (Macosko, 1994).

Crystallization Properties of Fat in the Emulsions Are Related to the Supramolecular Structure of the Fat. The crystallization profile of anhydrous coconut oil in bulk recorded by DSC on cooling showed the formation of 2 successive exothermic events (Figure 2). The first event was minor and corresponded to the crystallization of the first crystals of anhydrous coconut oil in bulk, with a initial crystallization temperature (T_{onset}) of 20.1 \pm 0.0°C (df = 2). The second event was a marked and narrow peak (temperature: 16.1 ± 0.1 °C; df = 2). The total enthalpy of crystallization of anhydrous coconut oil in bulk was 119.0 \pm 0.1 J/g of fat (df = 2). The crystallization profile of fat dispersed in emulsion droplets homogenized at 20 MPa showed a larger exothermic peak. The T_{onset} was moved toward the lower temperatures (i.e., 11.9 ± 0.0 ; df = 1) compared with anhydrous coconut oil in bulk. The crystallization profile of fat dispersed in unhomogenized emulsion droplets showed a first exothermic peak that was marked and narrow ($T_{onset} = 12.8 \pm 0.0^{\circ}C$; df = 1). The second exothermic peak was large and barely noticeable. The discrepancy toward the lower temperatures was observed, regardless of the fat droplet size and fat content. A nucleus in each droplet, instead of one in the bulk fat, is needed to initiate crystallization, for instance in milk fat (Walstra and Jenness, 1984). This assessment has 2 consequences. First, the discrepancy in the T_{onset} can be attributed to the organization of fat as small droplets within the emulsions, which was confirmed by laser light-scattering measurements and light microscopy. The crystallization kinetics of fat was then



Figure 2. Thermal profiles of the emulsions reflecting fat organization. Example of crystallization profiles of fat in the high-fat emulsions and in anhydrous coconut oil in bulk. a.u. = arbitrary units.

faster in unhomogenized emulsions: unless the T_{onset} was equivalent, the slope of the first peak was greater than in homogenized emulsions and was more similar to the slope of the anhydrous coconut oil in bulk. In unhomogenized emulsions, the crystallization profile of fat showed 2 exothermic events that may correspond to the bimodal distribution of fat droplet size. The trends in fat crystallization described after homogenizing were also observed after spray atomization of the emulsions (results not shown).

Properties of Fat After Drying

Emulsion Droplet Size in Powders Is Significantly Increased After Drying. Fat droplet size was significantly affected during drying, regardless of the composition, homogenization pressure, and drying conditions (P < 0.01; Table 2). Powders obtained from tiny emulsions showed a bimodal size distribution with little polydispersity after their rehydration (Figure 1B). The main size classes were 0.08 to 2.5 µm and 2.5 to 10 µm.

Powders obtained from coarse emulsions had a greater increase in their d_{43} , which resulted in a highly polydisperse size distribution with 3 main size classes after their rehydration: 0.1 to 0.3 µm, 0.3 to 2.5 µm, and 2.5 to 45 µm (Figure 1C). The d_{43} after spray atomization was then similar or even greater than the d_{43} after homogenizing, except for the low-fat powder.

The fat droplet size after drying was strongly correlated with the fat droplet size after homogenizing: R^2 was 0.96, excluding data from the unhomogenized low-fat emulsion. However, it was not correlated with the fat droplet size after spray atomization: similar size distribution patterns after spray atomization led to 2 size distribution patterns after drying, depending on the homogenizing conditions. Rosenberg and Young (1993) reported that the size of fat droplets did not vary from the original emulsion to the powder, in contrast with our results. However, the authors dried very tiny emulsions dedicated to microencapsulation. In addition, Ye et al. (2007) stated that the size distribution of fat droplets in powders was independent of fat droplet size after homogenizing, regardless of the experiment; however, they studied tiny emulsions.

In situ qualitative CLSM observations were consistent with the droplet size measurements performed by laser light scattering. Powders from homogenized emulsions showed a homogeneous distribution of very small fat droplets within the powder particles (Figure 3A). Conversely, powders from unhomogenized emulsions revealed the presence of very large fat droplets (Figure 3B). Actually, these large droplets were measured by laser light scattering; hence, they would not be an artifact attributable to powder rehydration before measurements.

These results indicate that spray atomization did not have the same stabilization effect as homogenizing, as already stated with the emulsion viscosity measurements. Both processing steps led to a reduction in fat droplet size, which involved an increase in the specific surface area. Adsorption of surface-active ele-



Figures 3. Confocal laser scanning micrographs of high-fat powders after a 6-mo storage period (A) with a 20-MPa homogenization, and (B) without homogenization pressure. Fat appears in the gray level. The solid arrow indicates free fat and the open arrow indicates coalesced fat. V stands for vacuole. Scale bar: 20 μm.

ments (here, milk proteins) is necessary to reconstitute the interface between lipids and the aqueous phase (Walstra and Jenness, 1984). Our hypotheses were that 1) milk proteins or protein conformation involved during homogenizing and spray atomization were not the same, 2) kinetics during spray atomization were too fast for protein adsorption, 3) the maximal shear rate was different at the inner wall of the homogenization heads and the spray nozzle orifice for equivalent pressure and because of different gap sizes, or 4) there was a combined effect of 2 or 3 of these hypotheses. The emulsion retention time was much greater in the homogenizer compared with the instantaneous drying of the droplet after spray atomization (i.e., less than 10^{-3} s; Masters, 2002), whereas the adsorption time of CN micelles was assumed to be generally less than 10 μ s (Walstra and Jenness, 1984). Size distributions did not change significantly during the 12-mo storage period, except for the high-fat powder from an unhomogenized emulsion, for which the d_{43} increased from 5.2 \pm 0.2 μ m to $6.8 \pm 0.02 \ \mu m \ (df = 5)$.

Free Fat Is a Pertinent Indicator of Fat Instability in the Powders. Free fat in powders is not entirely protected by surface-active elements or by a matrix of proteins and amorphous lactose, as stated by Vignolles et al. (2007). Size measurements were applied to rehydrated powders both before and after free fat extraction with petroleum ether. These indicated a significant decrease in the d_{43} after the extraction (P < 0.01). The polynomial coefficient of determination (\mathbb{R}^2) was 0.75 between the free fat content and the proportion of fat droplets with diameters greater than 2 µm. Free fat was thus related to larger fat droplets in addition to nonglobular fat.

In a previous study (results not shown), no influence of the free fat extraction method was found on powder particle integrity, but it had an influence on powder particle aggregates. When the free fat content was great enough (i.e., above 7 g per 100 g of total fat), the number of individualized powder particles increased after the extraction with petroleum ether because the interstitial free fat was removed.

Results showed that the greater the initial fat content, the greater the free fat content in the powders (Figure 4), in agreement with previous studies (Buma, 1971; Young et al., 1993). The polynomial coefficient of determination (\mathbb{R}^2) was 0.99 between the free fat content and the total fat content.

For the same initial fat load, free fat was greater in powders from unhomogenized emulsions. This was consistent with laser light-scattering measurements and in situ CLSM observations (Figure 3A and 3B): the presence of very large fat droplets (i.e., unstable fat droplets) could lead to the formation of free fat. Indeed, the free fat content has already been correlated with greater fat droplet diameters (Fink and Kessler, 1985),



66

Figure 4. Homogenization conditions (i.e., fat droplet size) and total fat content were the parameters having the most influence on the free fat content. ^{a-d}Different letters above the bar plots indicate significant differences at P < 0.01.

and small fat droplets (less than 1 μ m) are known to favor emulsion stability and enhance fat retention (Hogan et al., 2001). However, the presence of free fat was confirmed just after drying, regardless of the fat droplet size.

No correlation was found between the free fat content and the moisture content, in contrast to the studies by De Vilder et al. (1979) and Kelly et al. (2002). The free fat content was increased only in high-fat powders from unhomogenized emulsions, which is consistent with their high content in unstable large fat droplets. The presence of free fat was observed both at the surface and within the powder particles (Figure 3B), in agreement with previous studies (Westergaard, 1994; Kim et al., 2005a,b).

Thermal Profiles Measured in Situ in Powders Are Related to Fat Supramolecular Structure and Lactose State. On heating the powders that had been stored at 20°C for various times, the recording of at least 1 endotherm by DSC, corresponding to the melting of fat (mainly constituted by triacylglycerols), demonstrated the presence of crystallized fat in all the powders (Figure 5). A second endotherm was also recorded at higher melting points during storage (solid arrow, Figure 5). The temperature determined at the maximum of the first endothermic peak decreased significantly during the 12-mo storage period. The peak temperature was 27.6 \pm 0.2°C at time 0, 24.2 \pm 0.1°C after 6 mo, and 22.8 \pm 0.0°C after 12 mo (df = 1). The same trend was observed for the temperature determined at the maximum of the second endothermic peak: it decreased significantly from $38.9 \pm 0.2^{\circ}$ C at time 0, to $33.1 \pm 0.1^{\circ}$ C after 6 mo, and to $28.1 \pm 0.1^{\circ}$ C after 12 mo (df = 1; solid arrow, Figure 5). The final melting temperature of fat (T_{offset}) decreased slightly

from 42.6 ± 0.2 °C at time 0, to 41.8 ± 0.1 °C after 6 mo, and to $41.1 \pm 0.0^{\circ}$ C after 12 mo (df = 1). The enthalpy of the first endotherm decreased significantly during the 12-mo storage period: it was 36.7 ± 2.4 J/g of fat at time 0, 20.1 \pm 0.2 J/g of fat after 6 mo, and 8.1 \pm 0.1 J/g of fat after 12 mo (df = 1). Conversely, the enthalpy of the second endotherm significantly increased: it was 5.2 ± 0.6 J/g of fat at time 0, 12.6 ± 1.1 J/g of fat after 6 mo, and 35.5 ± 0.1 J/g of fat after 12 mo (df = 1). These changes in the thermal profiles of the powders correspond to the structural reorganization of fat at a molecular level. The increase in enthalpy associated with the second endotherm was attributed to the formation of more compact polymorphic forms corresponding to more stable fat crystal structures, as was observed previously for milk fat (Lopez et al., 2007). Identification of the various polymorphic forms of fat crystals that have been formed in the powders requires the use of techniques such as x-ray diffraction. These changes in the DSC melting curves showed that the fat phase dispersed in the powder particle matrix was unstable on a molecular scale. This was due to the polymorphism of triacylglycerols (i.e., their ability to adopt several organizations and evolve from the most unstable to more stable states; Lopez et al., 2007). Further studies are required to relate the changes in fat structure observed on a molecular level by using DSC and the formation of free fat characterized on a microscopic scale.

The DSC curves recorded on heating of the powders and the anhydrous coconut oil allowed the solid fat content (SFC) in the powders to be determined at 21°C over a 12-mo storage period, according to the method developed by Lopez et al. (2006). The partial enthalpy of the melting of powders ($\Delta H_{partial}$) was combined with the total enthalpy of melting of anhydrous coconut oil ($\Delta H_{total} = 118.9 \pm 0.7$ J/g of fat; df = 1), and the SFC was calculated as follows:

Solid fat content at 21°C (%) = $(\Delta H_{partial} \text{ coconut})$ oil in powder/ ΔH_{total} anhydrous coconut oil) × 100.

A first group of powders had an SFC in the range of 75 to $95 \pm 3.2\%$ (df = 1); this corresponds to the low free-fat powders, with a free fat content between 1 and 13% of the total fat. A second group had an SFC in the range of 63 to $73 \pm 1.5\%$ (df = 1); this corresponds to the high-fat powder from an unhomogenized emulsion, with a free fat content between 55 and 64% of the total. The hypothesis that a greater SFC may lead to a greater free fat content was not validated. Fat crystals were supposed to disrupt the fat droplets and then contribute to the formation of free fat in the



Figure 5. Melting profiles of the powders reflecting the structure of fat crystals and the lactose state: melting profiles of fat and glass transition of lactose within the high-fat unhomogenized powder during storage. The solid arrow indicates the second melting peak of fat and the open arrow indicates the signal of the glass transition of lactose. T_g stands for the glass transition temperature of lactose. a.u. = arbitrary units.

powders. Differential scanning calorimetry allowed the determination of SFC in the powders, but did not give information on the size and location of fat crystals within small fat droplets (powders from homogenized emulsion) or in free fat inclusions (powders from unhomogenized emulsions). According to the larger size of free fat inclusions, fat crystals may grow more easily in the high-fat powder from an unhomogenized emulsion. Fat crystals could create prominent angles within fat droplets and could even lead to their disruption (Walstra and Jenness, 1984), all the more if they can move partially within the fat globules or in their surroundings, as in the case of free fat. Fat crystals may then act as a destabilizing factor when the powder is subjected to a physical stress (e.g., handling).

The T_g in powders was also determined from the DSC curves recorded on heating (Figure 5). The T_g always remained far above the storage temperature of 20°C, mainly in the range of 45 to 60°C. This means that lactose did not crystallize and that it could not be responsible for fat droplet damage and the subsequent coalescence or release of fat, as mentioned in the literature (Labrousse et al., 1992; Fäldt and Bergenståhl, 1996). The decrease of T_g could be attributed to a water uptake because the a_W increased over storage (Table 3).

Figure 6 shows the DSC profiles of the powders. Crystallization profiles of fat in the powders were similar to

those obtained for the emulsions. This also shows that fat in the high-fat powder crystallized at a lower temperature after removing the free fat. Indeed, only small fat droplets remained within the powder particles, as mentioned above. However specific, the overall thermal profiles of fat in the powders were not sensitive enough to show and indirectly quantify free fat. Indeed, melting profiles were identical before and after free fat extraction in all powders (Figure 6). In fact, 1) the melting range of hardened coconut oil was too tight to show any difference, or 2) free fat would not have a different composition than the hardened coconut oil used for the manufacture of the powders. The latter hypothesis contradicts previous statements; however, the authors used milk fat, and the process of powder manufacture was not specified (Kim et al., 2005a).

Surface Fat Is Overrepresented, Regardless of the Composition and Process Parameters. Surface fat was detected just after drying and increased with the initial fat content ($\mathbb{R}^2 = 0.78$). It reached a maximum of 86% in the high-fat powder from an unhomogenized emulsion (Table 3). There was an overrepresentation of fat at the particle surface, regardless of the initial fat content in the powder, which was consistent with previous studies (Fäldt et al., 1993; Kim et al., 2005b; Gaiani et al., 2006). This overrepresentation concerned both total and free fat in low-fat powders. In high-fat powders, the powder particle aggregates were modified after the removal of free fat with petroleum ether. As mentioned above, there were more individualized powder particles, so we could not draw conclusions about the overrepresentation of free fat at the surface of the high-fat powder particles.

Surface fat increased during storage of most of the powders, although fat migration was not expected in an amorphous matrix. Indeed, the storage temperature was always below the T_g , as measured by DSC. Conversely, surface fat tended to decrease in the medium-fat and high-fat powders from unhomogenized emulsions. This was previously attributed to 1) a decrease in the free fat content (Celestino et al., 1997), which was not observed here, and 2) the formation of VFA at the outermost surface because of lipolysis and the oxidation of surface fat.

The presence of surface fat was confirmed by in situ CLSM observations (Figure 3B). It was present both as fat droplets and as free fat. Nonetheless, to date, low-resolution CLSM has not allowed for the semiquantitative determination of fat at the extreme surface and the correlation with XPS measurements.

Powder Physical Properties

Powder physical properties are presented in Table 3. Powders with high levels of total fat and surface fat (as measured by XPS) had poor wettability properties. This corroborates studies mentioning the importance of surface fat to predict powder wettability (Fäldt and Bergenståhl, 1996; Kim et al., 2005a). Nevertheless, wettability was not improved here after the removal of free fat in high-fat powders. This would implicate elements other than surface fat, such as surface amorphous lactose, powder particle size, and porosity.

The size of emulsion droplets (which can be modulated by using homogenizing conditions) as well as total fat, free fat, and surface fat contents affected the flowability and floodability properties of the powders (Table 3). Small fat droplets dispersed in low free-fat powders improved both the flowability and the floodability. However, all powders showed indexes in a narrow range of values. Kim et al. (2005b) reported that free surface fat would be responsible for poorer flowability in the powders. Both the structure of fat and, more particularly, the free fat content and its thermal properties (solid fat content at a given temperature) may affect the flowability of the powders. The partial melting of fat, which may occur when recycling the fine particles, could be responsible for the formation of liquid bridges between particles (interstitial fat), and subsequent cooling could enhance the cohesion through crystallized fat, which strengthened the bridges (Fitzpatrick et al., 2007).

at content, /kg of DM	Homogenization, MPa	Free fat, g per 100 g of total fat	Surface fat, %	Wettability, s	Dispersibility, $\%$	Solubility, % vol/vol	aw	Flowability	Floodability	$d_{32},$ $\mu \mathrm{m}$	Interstitial air, mm^3/g	$Occluded$ air, mm^3/g
00	20	1	46(67)	30	>99	>99	$0.16\ (0.24)$	68	50	153	449(444)	367(352)
60	20	2	67(84)	30(55)	>99	>99	$0.14 \ (0.24)$	65(70)	47(51)	174	580(385)	233(418)
00	20	7	84(93)	>120	80	>99	$0.11 \ (0.25)$	67(70)	52	183	594 (549)	279 (306)
00	0	2	55(89)	30	>99	>99	0.15 (0.24)	63(65)	50	168	626(531)	175(246)
60	0	11	78 (67)	30(110)	>99	>99	0.17 (0.25)	63(65)	50(56)	179	749(679)	$64\ (132)$
00	0	55(64)	86 (78)	>120	>99	>99	0.11(0.23)	72(67)	55(46)	230	589(504)	273(347)

Results in parentheses indicate values after a 12-mo storage period if different

conditions affecting the physical properties of the powders

fat, and homogenizing

and surface

Total, free,

с.

Table



Figure 6. Thermal profiles of the powders reflecting the fat supramolecular structure: crystallization and melting profiles of fat within the high-fat unhomogenized powder before (solid line) and after (dashed line) free fat extraction. a.u. = arbitrary units.

Powder porosity changed with the fat supramolecular structure, mainly the formation of free fat. Over the 12-mo storage period, the interstitial air content tended to decrease, whereas the occluded air content tended to increase. Baechler et al. (2005) previously observed the presence of empty cavities that were formerly occupied by globular fat after a fat release induced by a heat treatment on whole milk powders. Here, the free fat content increased only in the high-fat unhomogenized powder, but it is likely that pycnometry is more sensitive to changes in fat organization (including fat release) than is solvent extraction of free fat.

The sensorial characterization of the powders showed that the high-fat powder, which had been manufactured from an unhomogenized emulsion, exhibited more offflavors during sensorial assessments. This default could be related to its high free-fat content: a good dispersion of fat droplets within the solid matrix is known to avoid the propagation of oxidation to the overall powder (Turchiuli et al., 2005).

CONCLUSIONS

An understanding of fat behavior after homogenizing and spray-drying and during storage is essential for controlling the physical properties of fat-filled dairy powders. The spray atomization of unhomogenized emulsions decreased the fat droplet size but did not strengthen the fat droplet supramolecular structure; only small fat droplets obtained after homogenizing preserved their size through the subsequent drying step and during storage. However, drying always increased the fat droplet size, regardless of the conditions; even in homogenized emulsions, a small proportion of fat droplets underwent coalescence. Free and surface fat were detected in all powders and mainly depended on the total fat content and the homogenizing conditions. It is worth noting than surface fat was always overrepresented, regardless of the composition and process parameters. Free fat was also related to the presence of fat crystals that could damage their integrity. Powder physical properties depended on the composition and process conditions. They were already specific just after the drying process, even though they tended to become poorer during storage. The free fat content seemed to have a greater influence on powder physical properties than did surface fat, except for wettability.

ACKNOWLEDGMENTS

The authors are indebted to Bretagne Biotechnologies Alimentaires (BBA, Rennes, France) for stimulating discussions and financial support. Marie-Hélène Famelart, Valérie Briard-Bion, and Florence Rousseau (UMR 1253 STLO, INRA–Agrocampus, Rennes, France) are acknowledged for technical support and valuable discussions on viscosity measurements, fat extraction, and particle size measurements, respectively. The authors also thank Anne Dolivet for technical support on the analysis of emulsions and powders. Jacques Lambert (UMR 7564 LCPME, CNRS–Nancy-Université, Nancy, France) is acknowledged for technical support and valuable discussions on surface analysis.

REFERENCES

- Baechler, R., M.-F. Clerc, S. Ulrich, and S. Benet. 2005. Physical changes in heat-treated whole milk powder. Lait 85:305–314.
- Buma, T. J. 1971. Free fat in spray-dried whole milk. 10. A final report with a physical model for free-fat in spray-dried milk. Neth. Milk Dairy J. 25:159–174.
- Celestino, E. L., M. Iyer, and H. Roginski. 1997. The effects of refrigerated storage of raw milk on the quality of whole milk powder stored for different periods. Int. Dairy J. 7:119–127.
- De Vilder, J., R. Martens, and M. Naudts. 1979. The influence of the dry matter content, the homogenization and the heating of concentrate on physical characteristics of whole milk powder. Milchwissenschaft 34:78–84.
- Fäldt, P., and B. Bergenståhl. 1993. Encapsulation of fat in spraydried food emulsions. Int. Dairy Fed. (Special Issue 9303).
- Fäldt, P., and B. Bergenståhl. 1996. Spray-dried whey protein/lactose/ soybean oil emulsions. 2. Redispersability, wettability and particle structure. Food Hydrocoll. 10:431–439.
- Fäldt, P., B. Bergenståhl, and G. Carlsson. 1993. The surface coverage of fat on food powders analyzed by ESCA (electron spectroscopy for chemical analysis). Food Struct. 12:225–234.
- Fink, A., and H. G. Kessler. 1985. The effect of heating on the storage stability of unhomogenized cream (30%). Milchwissenschaft 40:326–328.
- Fitzpatrick, J. J., K. Barry, P. S. M. Cerqueira, T. Iqbal, J. O'Neill, and Y. H. Roos. 2007. Effect of composition and storage conditions on the flowability of dairy powders. Int. Dairy J. 17:383–392.
- Folch, J., M. Lees, and G. H. Sloane-Stanley. 1957. A simple method for the isolation and purification of total lipids from animal tissues. J. Biol. Chem. 226:497–509.
- Gaiani, C., J. J. Ehrhardt, J. Scher, J. Hardy, S. Desobry, and S. Banon. 2006. Surface composition of dairy powders observed by X-ray photoelectron spectroscopy and effects on their rehydration properties. Colloids Surf. B Biointerfaces 49:71–78.
- Gerin, P. A., P. B. Dengis, and P. G. Rouxhet. 1995. Performance of XPS Analysis of Model Biochemical-Compounds. J. Chim. Phys. 92:1043–1065.
- Hogan, S. A., B. F. McNamee, E. D. O'Riordan, and M. O'Sullivan. 2001. Emulsification and microencapsulation properties of sodium caseinate/carbohydrate blends. Int. Dairy J. 11:137–144.
- International Dairy Federation. 1988. IDF Standard 129A. Dried milk and dried milk products. Determination of insolubility index. Int. Dairy Fed., Brussels, Belgium.
- International Dairy Federation. 2007. The World Dairy Situation 2007—Bulletin of the International Dairy Federation 423/2007. Int. Dairy Fed., Brussels, Belgium.

- Kelly, J., P. M. Kelly, and D. Harrington. 2002. Influence of processing variables on the physicochemical properties of spray dried fatbased milk powders. Lait 82:401–412.
- Kim, E. H. J., X. D. Chen, and D. Pearce. 2005a. Melting characteristics of fat present on the surface of industrial spray-dried dairy powders. Colloids Surf. B Biointerfaces 42:1–8.
- Kim, E. H. J., X. D. Chen, and D. Pearce. 2005b. Effect of surface composition on the flowability of industrial spray-dried dairy powders. Colloids Surf. B Biointerfaces 46:182–187.
- Labrousse, S., Y. H. Roos, and M. Karel. 1992. Collapse and crystallization in amorphous matrices with encapsulated compounds. Sci. Alim. 12:757–769.
- Lopez, C., C. Bourgaux, P. Lesieur, and M. Ollivon. 2007. Coupling of time-resolved synchrotron X-ray diffraction and DSC to elucidate the crystallisation properties and polymorphism of triglycerides in milk fat globules. Lait 87:459–480.
- Lopez, C., V. Briard-Bion, B. Camier, and J. Y. Gassi. 2006. Milk fat thermal properties and solid fat content in Emmental cheese: A differential scanning calorimetry study. J. Dairy Sci. 89:2894– 2910.
- Macosko, C. W. 1994. Rheology: Principles, Measurements and Applications. Wiley-VCH, New York, NY.
- Masters, K. 2002. Spray-air contact, particle formation and drying. Pages 180–215 in Spray Drying in Practice. SprayDryConsult International ApS, Charlottenlund, Denmark.
- Padley, F. B., F. D. Gunstone, and J. L. Harwood. 1986. Occurrence and characteristics of oils and fats. Major vegetable fats. Pages 55–112 in The Lipid Handbook. F. D. Gunstone, J. L. Harwood, and F. B. Padley, ed. Chapman and Hall Ltd., New York, NY.
- Prentice, J. H. 1992. Dairy Rheology: A Concise Guide. Vol. 1. VCH Publishers Inc., New York, NY.
- Rosenberg, M., and S. L. Young. 1993. Whey proteins as microencapsulating agents. Microencapsulation of anhydrous milkfat—Structure evaluation. Food Struct. 12:31–41.
- Sørensen, I. H., J. Krag, J. Pisecký, and V. Westergaard. 1978. Méthodes d'analyses des produits laitiers déshydratés. 4th ed. Niro A/S, Soeborg, Denmark.
- Turchiuli, C., M. Fuchs, M. Bohin, M. E. Cuvelier, C. Ordonnaud, M. N. Peyrat-Maillard, and E. Dumoulin. 2005. Oil encapsulation by spray drying and fluidised bed agglomeration. Innovative Food Sci. Emerg. Technol. 6:29–35.
- Vignolles, M.-L., R. Jeantet, C. Lopez, and P. Schuck. 2007. Free fat, surface fat and dairy powders: Interactions between process and product. A review. Lait 87:183–236.
- Walstra, P., and R. Jenness. 1984. Milk fat globules. Pages 254–300 in Dairy Chemistry and Physics. P. Walstra and R. Jenness, ed. John Wiley and Sons, New York, NY.
- Westergaard, V. 1994. Milk Powder Technology—Evaporation and Spray Drying. Niro A/S, Copenhagen, Denmark.
- Ye, A., S. G. Anema, and H. Singh. 2007. Behaviour of homogenized fat globules during the spray drying of whole milk. Int. Dairy J. 17:374–382.
- Young, S. L., X. Sarda, and M. Rosenberg. 1993. Microencapsulating properties of whey proteins. 1. Microencapsulation of anhydrous milk fat. J. Dairy Sci. 76:2868–2877.