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COMPOSITION AND SOME PROPERTIES OF SPRAY-DRIED RETENTATES OBTAINED BY THE ULTRAFILTRATION OF MILK

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Abstract

Retentates containing 20, 27, and 34% total solids, obtained on commercial scale by the ultrafiltration of milk, were spray-dried on laboratory scale using centrifugal atomization and single-stage drying with the inlet air temperature of 220°C and the outlet air temperature of 90°C.

The protein content in the powders was 31% to 35% compared to 24.8% protein in the control whole-milk powder. Lactose contents were markedly lower in the retentate powders (~10.6%) than in the milk powder (40.4%). Storage of the powders at 37°C resulted in a marked increase in the 5-hydroxymethylfural contents with doubling of this content in the retentate powders and tripling in the milk powder.

When viewed by scanning electron microscopy, the spray-dried retentate powder particles had smooth surfaces free from wrinkles usually seen in spray-dried milk powders. When the same products were exposed to atmospheres having 75%, 85%, or 100% relative humidity, the retentate powders exhibited less lactose recrystallization than the milk powder.

The melting temperature (T_m) (as determined by differential scanning calorimetry) of lactose present in the retentate powders was not affected by the reduced lactose content in the powders but the fusion enthalpy (ΔH_{fusion}) of lactose was reduced in the retentate powders compared to the control milk powder.

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Introduction

To facilitate the spray-drying of milk, a great part of water present in the milk is removed by evaporation whereby the total solids content of the milk is increased to 35-50% [5]. All the components of the milk, *i.e.*, casein, whey proteins, lactose, minerals, as well as fat in the case of whole milk, are retained in the evaporated milk. Consequently, less water has to be removed in the spray-drier from the milk thus concentrated than from milk that has not been preconcentrated. Retentates obtained by the ultrafiltration of milk represent another product which may easily be spray-dried. As the result of the ultrafiltration of milk, high-molecular substances such as proteins are retained in the retentate on one side of the ultrafiltration membrane used, and low-molecular substances such as lactose and mineral constituents pass into the filtrate, which is called permeate. In the retentates, the concentrations of the low-molecular substances are reduced and the relative concentration of the proteins is increased. The altered chemical composition may affect a number of functional properties of the spray-dried retentates compared to milk powders. For example, in regular milk powders, the presence of anhydrous lactose in a glassy form leads to their hygroscopicity [7, 22] which is particularly noticeable in spray-dried whey powders having a high lactose content [24]. Anhydrous lactose in spray-dried milk powders rapidly absorbs water when the powders are exposed to humid atmosphere and may crystallize in the α-monohydrate form. The development of lactose crystals on the surface of milk powder particles during storage indicates that the moisture content had exceeded the safe level. Associated with exposure to excessively high humidity is the development of lumpiness and caking which reduce the quality of the milk powders [26] during storage under such conditions. To better understand these phenomena, crystallization of lactose in milk powders has been studied by many authors [3, 13, 16, 18, 20, 22-26]. As the use of ultrafiltration in modern dairy technology is extended, it is important to find proper conditions for storage and transportation of the ultrafiltration retentate which would be economical and yet would ensure good quality of the product.

The two objectives of this study were (*a*) to characterize the composition and structure of spray-dried ultrafiltration milk retentates as a consequence of different degrees of concentration prior to drying, and (*b*) to evaluate the effect of differences in composition of the retentates on their functional behaviour under elevated relative humidity storage conditions, as compared to ordinary milk powder spray-dried under the same conditions as the retentates. Scanning electron microscopy (SEM) was used to examine fresh spray-dried retentates as well as the spray-dried retentates exposed to high relative humidity atmosphere.

Materials and Methods

Ultrafiltration and spray-drying of milk

Pooled cows' milk from the Somboled Dairy in Sombor, Yugoslavia, was used in all experiments. The milk was pasteurized in a high-temperature-short-time (HTST) plate pasteurizer at 77°C for 15 s and was standardized at 3.7% fat in a separator.

The milk was ultrafiltered under industrial conditions using the Ultrafiltration Module Type 35 fitted with GRPP61 membranes (DDS, Pasilac, Denmark). The ultrafiltration yielded retentates containing 20%, 27%, and 34% total solids.

The retentates were spray-dried under laboratory scale conditions using a Type LAB 1 APV spray-drier (APV Anhydro, Copenhagen, Denmark). Centrifugal atomization and single-stage drying were used under the following conditions: 220°C inlet air temperature, 90°C outlet air temperature, 5 kW electric air heater power.

Whole non-ultrafiltered milk was concentrated prior to drying by evaporation to 20.2% total solids (5.38% protein and 6.30% fat) and was spray-dried under the same conditions as the retentates to produce a control sample.

The milk and retentate powders were stored for 8 months either at 4° or at 37°C in sealed pouches made from PVC foil. The relative humidity of the storage atmosphere was not controlled.

Spray-dried buttermilk of commercial origin [10] was also examined for comparison.

Chemical analysis

The fresh retentates, containing approximately 20%, 27%, and 34% total solids, and the spray-dried retentates as well as the control spray-dried milk sample, all stored at 4°C or 37°C for 8 months, were analyzed according to AOAC [1] and IDF [8] analytical methods for total solids, total protein, lactose, mineral matters, lipids, pH, and solubility. In addition, the fresh and spray-dried retentates were analyzed for non-casein nitrogen (NCN), non-protein nitrogen (NPN), and proteose-peptone contents using the methods by Rowland [21], and for 5-hydroxymethylfural (5-HMF) according to Keeney and Bassette [12]. Data for casein, serum proteins, and true proteins were obtained by calculation.

Differential scanning calorimetry (DSC)

Thermal characteristics of the spray-dried retentate powders were examined by DSC using a DuPont 1090 Thermal Analyser equipped with a 910 DSC cell base. The samples (5-10 mg) were sealed in DuPont polymer-coated pans. A sealed empty pan was used as a reference. The pans were heated at a programmed rate of 10°C/min and were scanned in the range of 140-250°C. The melting temperature (T_m, °C) and enthalpy of fusion (ΔH_{fusion}, J/g) of lactose were computed from thermograms by the 1090 Thermal Analyser. Indium was used to calibrate the analyser for temperature and enthalpy calculations.

Scanning electron microscopy (SEM)

Each spray-dried powder was spread in a thin layer on the sticky surface of a dry-mount film disc attached to an SEM aluminum stub using a silver-based cement (Ladd Industries, Burlington, Vermont, USA). Additional spreading was done with a fine sable brush. The powders were sputter-coated in a Hummer II Technics sputter coater to form a gold layer approximately 20 nm thick and were examined in an ISI DS-130 scanning electron microscope operated at 20 kV. Micrographs were taken on 125 ASA 35-mm film [2, 11].

The effect of humid atmosphere on the crystallization of lactose in the powders was studied by exposing the powders (mounted on the sticky film discs or spread on microscope glass slides in layers less than 0.5 mm thick) to 75%, 85%, and 100% relative humidity in glass dishes (55 mm in diameter and 35 mm high) having ground lids. The experiments were carried out at 25° and 40°C for periods ranging from 2 to 72 h [24]. Atmosphere with 75% relative humidity developed in the presence of a saturated solution [17, 24] of NaCl, atmosphere with 85% humidity was provided by a saturated KCl solution, and 100% relative humidity was provided by saturation of the atmosphere over distilled water.

Results and Discussion

Chemical composition

Chemical composition of the retentates prior to spray-drying is listed in Table 1. The concentrations of the individual constituents increased in proportion to the intended differences in the total solids contents except total proteins and

Table 1. COMPOSITION OF RETENTATES OBTAINED BY THE ULTRAFILTRATION OF MILK

Component:	Approximate solids contents (%) in the retentates		
	34	27	20
Total solids	34.2	27.2	20.07
Mineral matter	1.26	0.94	0.78
Lipids	15.00	13.00	10.00
Lactose	3.65	3.84	4.02
Total proteins	21.21	8.87	6.57
Non-casein nitrogen	0.159	0.147	0.105
Non-protein nitrogen	0.014	0.020	0.017
Proteose-peptone	0.070	0.047	0.033
Casein	10.3	7.93	5.90
Whey proteins	0.96	0.51	0.35
True proteins	11.1	8.74	6.46
5-HMF* (umol/L)	11.5	16.7	10.2
pH	6.8	6.2	6.5

* 5-Hydroxymethylfural

Table 2. COMPOSITION, pH, AND SOLUBILITY OF SPRAY-DRIED RETENTATES AND SPRAY-DRIED MILK

	Approximate solids contents (%) in the retentates before drying						Milk	
	34		27		20			
Temperature of storage: Component:	37°C	4°C	37°C	4°C	37°C	4°C	37°C	4°C
Total solids	97.8	96.4	98.0	96.6	97.6	96.1	97.6	97.3
Mineral matter	3.05	3.25	3.29	3.61	3.01	3.74	5.35	5.47
Lipids	48.0	46.4	44.8	43.2	40.8	43.2	26.4	27.2
Lactose	10.7	10.5	14.2	13.7	20.1	19.6	41.1	39.8
Total proteins	35.1	35.2	33.7	33.5	31.1	31.1	24.8	24.8
Non-casein nitrogen	0.49	0.50	0.53	0.51	0.53	0.50	0.58	0.50
Non-protein nitrogen	0.09	0.09	0.07	0.07	0.09	0.07	0.11	0.11
Proteose-peptone	0.22	0.18	0.34	0.16	0.27	0.20	0.29	0.16
Casein	32.0	32.0	30.3	30.2	27.7	27.9	21.1	21.6
Whey proteins	1.14	1.50	0.78	1.84	1.07	1.50	1.14	1.50
True proteins	34.5	34.6	33.3	33.1	30.5	30.7	24.1	24.1
5-Hydroxymethylfural (µmol/L)	120.2	60.2	125.6	70.3	117.9	59.6	40.7	14.5
pH*	6.3	6.5	6.3	6.5	6.4	6.5	6.7	6.6
Solubility (%)	---	90.90	80.14	94.16	78.59	93.61	90.16	89.85

* Measured in the retentates before spray-drying.

5-HMF in the 34% total solids retentate. Data on the composition, pH, and solubility of the spray-dried retentates compared to those of spray-dried milk are presented in Table 2. There were no major differences in most micro and macro constituents among the spray-dried retentates. However, the initial total solid contents of the retentates before spray-drying and the resulting differences in the thermal treatment during spray-drying led to some variations in the physico-chemical characteristics of the powders. For example, there was a trend toward a higher protein content in the powders made from the retentates which were concentrated to higher total solids contents. The powders, made from the 20%, 27%, and 34% total solids retentates and subsequently stored at 4°C, contained 32.3%, 34.7%, and 36.5% total proteins per 100% total solids, respectively.

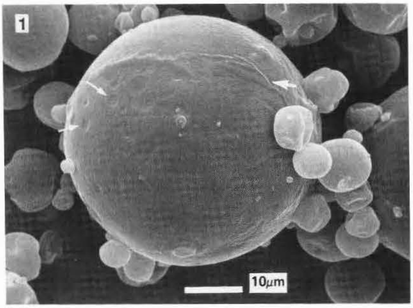
Table 2 also shows the composition of the control milk powder. As a result of ultrafiltration, ash (mineral matter) was lower in the dried retentates (3.42% in 100% total solids) than in the milk powder (5.55% in 100% total solids). The effect of ultrafiltration was also clearly evident from indices related to the lipid content (45.7% fat in the retentates compared to 27.5% fat in milk per 100% total solids basis) as well as the protein content (34.3% protein in the retentates compared with 25.5% protein in milk). However, whey proteins were approximately the same in the retentates (1.34%) as in the dried milk (1.35%) based on the same 100% total solids level.

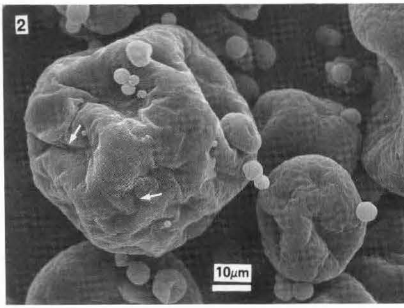
Lactose concentrations were sufficiently high in all retentates to initiate the Maillard reaction with proteins. The concentration of 5-HMF was used to monitor the rate of the early stages of this reaction before the brown pigments started to develop. The lowest 5-HMF concentrations (10.2-16.7 µmol/L) were found in fresh retentates (Table 1). There was little difference in spray-dried milk stored at 4°C (14.5 µmol/L) but an almost threefold increase (40.7 µmol/L) was found in milk powder stored at 37°C for 8 months. In spray-dried retentates, the 5-HMF concentrations were considerably higher than in spray-dried milk (Table 2). They varied between 59.6 and 70.3 µmol/L in spray-dried retentates stored at 4°C and were increased approximately twice to 117.9-125.6 µmol/L in retentate powders stored at 37°C.

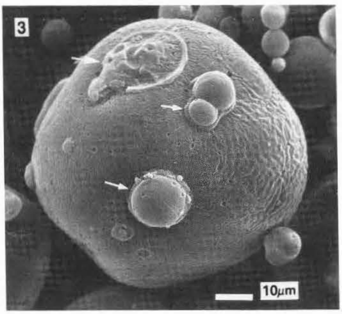
Solubilities of the retentate powders stored at 4°C fluctuated between 90.9% and 94.2% but were decreased to 78.6-80.1% in powders stored at 37°C indicating an adverse effect of an elevated storage temperature.

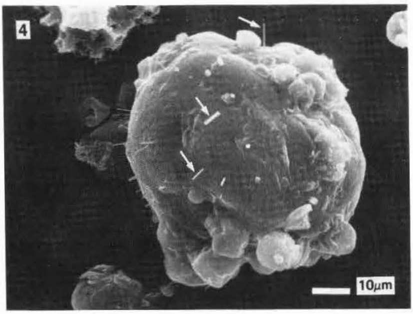
Structure of the retentate powders

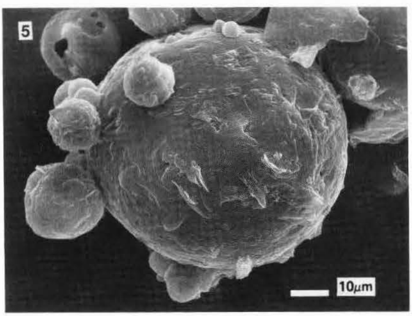
Macroscopically, all retentate powders had a moist-looking appearence. The small particle aggregates, however, separated easily on contact. Under a scanning electron microscope, the particles of fresh spray-dried retentates used in this study had relatively smooth surfaces irrespective of the extent of concentration by ultrafiltration prior to spray-drying. There were only a few major topographic features of note. Shallow "dimples" (Figs. 1, 11, and 12) were seen on most retentate particles. Simple "venation" (Fig. 1) was also frequently present. Smaller globules, either individual or in clusters, were occasionally seen to be fused to larger particles. Only a small part of the globular retentate particles had deeply wrinkled surfaces. In this respect, the retentate particles differed from skim milk and whole milk powders (Fig. 2) [4, 6, 22, 25, 26] which were characterized by both deep and shallow wrinkles on most particles. The retentate particles also differed from spray-dried buttermilk of commercial origin, the particles of which featured characteristic crater-like rims surrounding small globules attached to the larger particles (Fig. 3) [10], and from spray-dried whey powders which had deep narrow wrinkles [24]. The differences in topography of the various particle surfaces and their











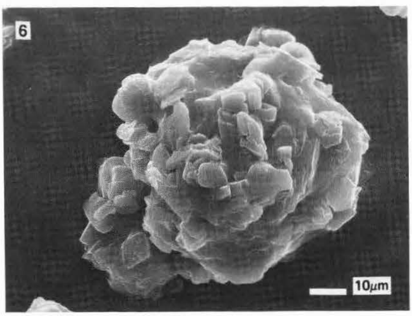
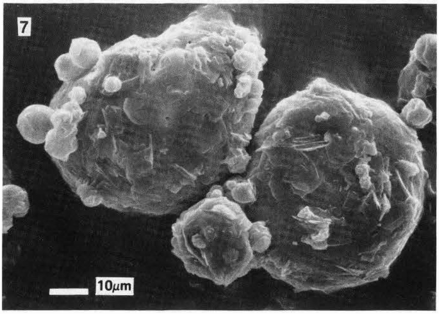


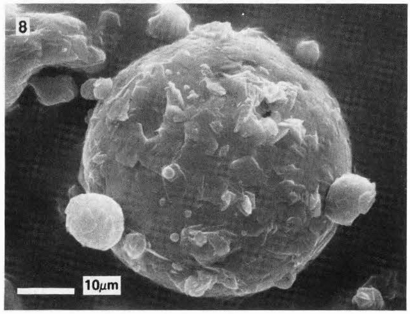
Fig. 1. Fresh spray-dried milk retentate powder particles have smooth surfaces with shallow dimples (small arrows) and occasional simple "venation" (large arrow).

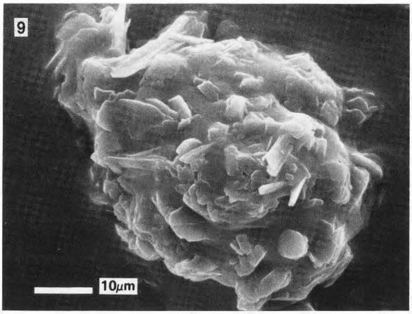
Fig. 2. Fresh spray-dried whole-milk powder particles have wrinkled (arrows) surfaces.

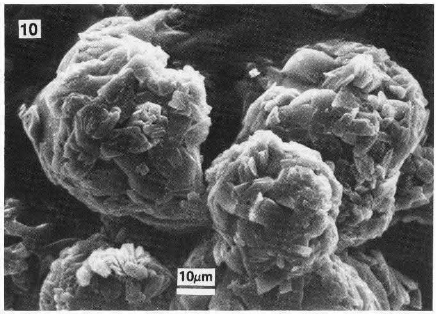
Fig. 3. Commercial spray-dried buttermilk particles have crater-like (large arrow) surface topography with smaller globules attached and surrounded with rims (small arrows).

Figs. 4 to 6. Whole-milk powder exposed for 24 h to an atmosphere having 75% (Fig. 4), 85% (Fig. 5), and 100% (Fig. 6) relative humidity at 25°C. Arrows in Fig. 4 point to needle-like crystals.







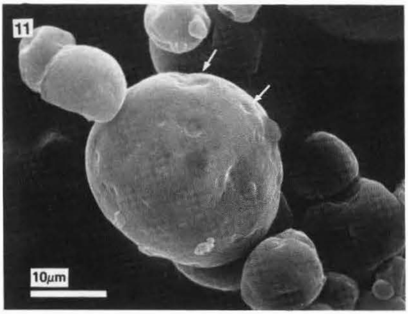


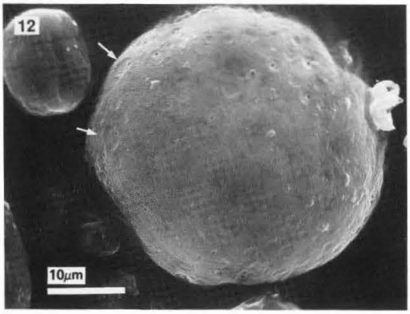
Figs. 7 to 9. Whole-milk powder exposed for 3 d to an atmosphere having 75% (Fig. 7), 85% (Fig. 8), and 100% (Fig. 9) relative humidity at 40°C.
Fig. 10. Spray-dried buttermilk exposed for 2 h to an atmosphere having 100% relative humidity at 25°C. The buttermilk particles were completely covered with recrystallized lactose.

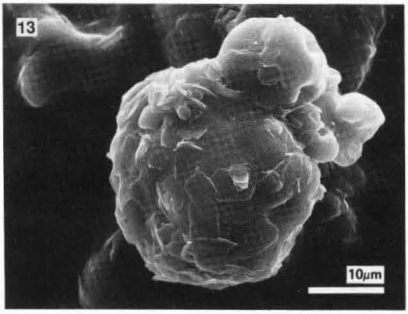
association with the technology of spray drying were discussed earlier by Carić and Kaláb [6]. Particle surfaces free of crystals were seen under a scanning electron microscope in all freshly spray-dried milk and retentate powders. Lactose present in the powder particles was apparently in the amorphous (glassy) form which resulted from the rapid dehydration of milk and retentate droplets during spray drying [26].

Exposure of milk powders to a humid atmosphere led to the absorption of water by the amorphous α- and β-lactose forms and their conversion into crystalline α-monohydrate. The crystallization rate increased with the increases in lactose concentration in the powder and the relative humidity of the atmosphere. Saltmarch and Labuza [24] studied lactose crystallization in hygroscopic spray-dried sweet whey which contained 66% lactose. Lactose crystallization was already noticeable after a week at 53% relative humidity at 25°C. Milk powders which were used as a control in our studies, started developing α-monohydrate lactose crystals after exposure to 75% humidity at 25°C for 24 h (Fig. 4). The development was slightly more advanced at 85% humidity (Fig. 5). At 100% relative humidity, however, the milk powder particles were almost completely covered with lactose crystals (Fig. 6). By extending the exposure of the milk powder to 75%, 85%, and 100% humidity to 3 days, the incidence of the lactose α-monohydrate crystals on the particle surface was increased and was even higher in powders exposed to the humid atmospheres at 40°C for 3 days (Figs. 7 to 9). Commercial spray-dried buttermilk made from sweet cream [10] was more susceptible to lactose crystallization than the milk powders and the buttermilk particles were almost completely covered with α-monohydrate crystals following an exposure to 100% humidity at 25°C for only 2 h (Fig. 10).

In contrast to the milk and buttermilk powders, the retentate powders exhibited less lactose crystallization when exposed to humid atmosphere. In powders obtained from retentates which







Figs. 11 and 12. Lactose did not crystallize on the surfaces of milk retentate powders which were exposed for 3 d to an atmosphere having 75% (Fig. 11) or 85% (Fig. 12) relative humidity at 40°C. Although the "venation" was not noticeable in these micrographs, the dimples (arrows) were observed on most retentate particles.

Fig. 13. Lactose crystals developed on milk retentate particles exposed for 3 days to an atmosphere having 100% relative humidity at 40°C.

contained 34% total solids prior to spray-drying, no lactose crystals developed following exposure of the powders to 75% and 85% humidities at 25°C or even at 40°C for 3 days (Figs. 11 and 12). In retentate powders exposed to 100% humidity for 3 days, plate crystals developed on particle surfaces (Fig. 13). At 40°C, the double adhesive tape, to which the powder particles were attached during their exposure to humidity, softened considerably and the smaller powder particles sank into the sticky layer.

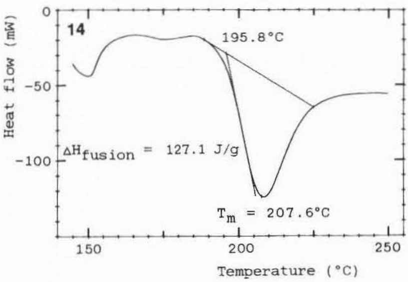
Compared to powder particles which remained separated from each other during their exposure to humidity because they were mounted on an adhesive tape, powders in the form of compact layers spread on microscope glass slides which had been exposed to the humid atmosphere, fused into aggregates in a process similar to the manufacture of instant milk powders or the process which takes place during lumping and caking of milk powders stored in an atmosphere having excessively high humidity.

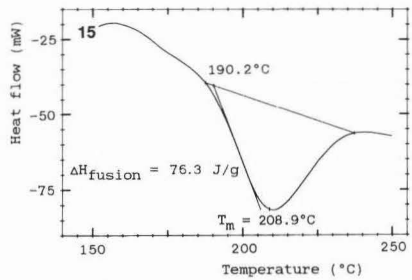
Differential scanning calorimetry

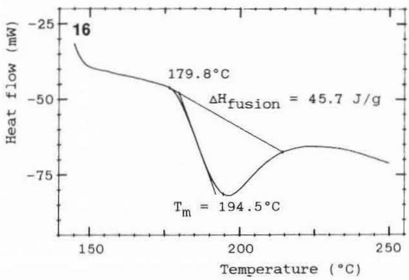
In spray-dried milk powders, lactose is present in both microcrystalline (α- and β-forms) and amorphous states. The amorphous state develops when lactose dissolved in milk is dried rapidly [15]. Amorphous (glassy) lactose is slowly transformed into crystalline lactose on exposure to moisture. Characterization and determination of crystalline lactose in milk powders by differential scanning calorimetry (DSC) was suggested by several authors [9, 16, 19, 20].

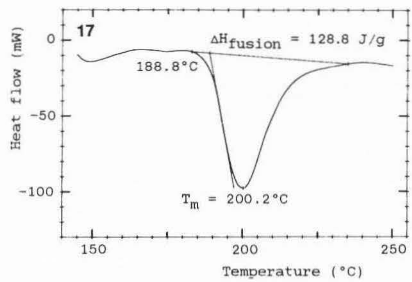
When subjected to DSC, all milk and retentate powders under study produced thermograms, each showing one major endothermic peak. The melting temperatures (T_m) ranged from 194° to 208°C. In addition, two minor endothermic peaks occurred at approximately 150°C and 175°C (Figs. 14-16). The T_m values observed markedly differed from the melting temperatures of anhydrous lactose published in the literature [15, 19]. The melting temperature T_m of the anhydrous α-form was reported to be ~215°C and the melting temperature T_m of the β-form was reported to be ~235°C [15, 19]. Since crystallization water in the lactose hydrate evaporates at temperatures below 150°C [15, 19], the melting points observed are those of the anhydrous forms [19]. The T_m values obtained in this study are lower than those listed above and correspond more closely to the T_m values of the complexes of α- and β-lactose reported in the literature [15]. Although α- and β-lactose differ in their T_m values and the difference has been used to determine the levels of these lactose forms in whey powders [20], two separate melting points, one for the α- and the other for the β-form were not observed with the retentate powders. It is not possible, therefore, to estimate the α/β ratio from the T_m data.

The fusion enthalpy (ΔH_{fusion}) of lactose present in the milk and retentate powders was









Figs. 14 to 16. Fusion thermograms of a milk powder (Fig. 14) and milk retentate powders (Fig. 15: 20% total solids before drying, and Fig. 16: 34% total solids before drying).

Fig. 17. Fusion thermogram of milk powder exposed to 100% relative humidity at 40°C for 3 days.

Table 3.

LACTOSE FUSION CHARACTERISTICS (ΔHfusion) IN MILK AND ULTRAFILTRATION RETENTATE POWDERS

Powder:	Tm(°C)	ΔHfusion (J/g)
Milk	206.6 ± 0.5	125.0 ± 10.8
Retentate (20% TS*)	208.1 ± 5.6	73.5 ± 14.2
Retentate (27% TS*)	204.7 ± 2.0	61.2 ± 8.9
Retentate (34% TS*)	194.4 ± 2.9	49.5 ± 11.3

* Total solid levels before spray-drying.

related to the total solids content of the retentates prior to spray-drying (Table 3). However, as these total solids contents affected the concentration of lactose in the retentates, it was concluded that the ΔH_{fusion} values reflected the lactose concentration.

Exposure of the milk and retentate powders for 3 days at 40°C to atmosphere having 100% relative humidity did not affect the fusion thermograms (Fig. 17), except that the T_m values were slightly lower than with the freshly spray-dried powders.

Conclusions

Higher concentration rates used during the ultrafiltration of milk resulted in increased protein, fat, and ash contents in the retentates and lower lactose contents. These shifts in chemical composition of the retentates were reflected by the composition of the resulting spray-dried powders. The lower lactose content in the retentate powders caused the powders to exhibit less crystallization and recrystallization of lactose on exposure to humid atmosphere. The low lactose content was also apparent when the retentate powders were subjected to differential scanning calorimetry: the fusion enthalpy values (ΔH_{fusion}) expressed in J/g were smaller with retentate powders than with whole-milk powders. Storage of the powders at an elevated temperature of 37°C intensified the Maillard reaction (noticeable from the 5-HMF values) in the retentate powders and had a deleterious effect on their solubility as compared to storage at 4°C.

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References

1. AOAC. (1984). Official Methods of Analysis. 14th ed., S Williams (ed.), Association of Official Analytical Chemists, Inc., Arlington, VA, USA. Dry Matter Code: 16.032, Ash Code: 16.035, Milk Fat Code: 16.064.
2. Bond EF, Kaláb M. (1988). An external oscilloscope improves photography with the ISI DS-130 scanning electron microscope. EMSA Bull. 18(1), 90-91.
3. Buma TJ. (1970). Determination of crystalline lactose in spray-dried milk products. Neth. Milk Dairy J. 24(2), 129-132.
4. Buma TJ, Henstra S. (1971). Particle structure of spray-dried products as observed by a scanning electron microscope. Neth. Milk Dairy J. 25, 75-80.
5. Carić M. (1985). Dairy Technology. 1. Concentrated and Dried Products. Naučna knjiga, Beograd, 285 pp. (In Serbian).
6. Carić M, Kaláb M. (1987). Effects of drying techniques on milk powders quality and microstructure. A review. Food Microstruc. 6, 171-180.
7. Hall W, Hedrick TI. (1966). Drying Milk and Milk Products. The AVI Publ. Co., Inc., Westport, Connecticut, USA, 152-155.
8. International Dairy Federation Document No. 28. (1974). Int. Dairy Fed., Bruxelles, Belgium, 2 pp.
9. Itoh T, Satoh M, Adachi S. (1977). Differential thermal analysis of α-lactose hydrate. J. Dairy Sci. 60, 1230-1235.
10. Kaláb M. (1980). Possibilities of an electron-microscopic detection of buttermilk made from sweet cream in adulterated skim milk. Scanning Electron Microsc. 1980;III:645-652.
11. Kaláb M. (1981). Electron microscopy of milk products. A review of techniques. Scanning Electron Microsc. 1981;III:453-472.
12. Keeney M, Bassette R. (1959). Detection of intermediate compounds in the early stages of browning reaction in milk products. J. Dairy Sci. 42(6), 945-960.
13. King N. (1965). The physical structure of dried milk. Dairy Sci. Abstr. 27, 91-104.
14. Milić B, Carić M, Vujičić B. (1988). Nonenzymatic browing reactions in food products. Naučna knjiga, Beograd, Yugoslavia, 169 pp. (In Serbian).
15. Morrissey PA. (1985). Lactose: Chemical and physicochemical properties. In: Developments in Dairy Chemistry - 3. Lactose and Minor Constituents. PF Fox (ed.), Elsevier Applied Science Publ., London and New York, 1-34.
16. Raemy A, Hurrell RF, Löliger J. (1983). Thermal behaviour of milk powders studied by differential thermal analysis and heat flow calorimetry. Thermochim. Acta 65(1), 81-92.
17. Rockland LB. (1960). Saturated salt solutions for static control of relative humidity between 5° and 40°C. Anal. Chem. 32, 1375-1376.
18. Roetmann K. (1979). Crystalline lactose and the structure of spray dried milk products as observed by scanning electron microscopy. Neth. Milk Dairy J. 33, 1-11.
19. Ross KD. (1978). Effects of methanol on physical properties of α- and β-lactose. J. Dairy Sci. 61, 152-158.
20. Ross KD. (1978). Rapid determination of α-lactose in whey powders by differential scanning calorimetry. J. Dairy Sci. 61, 255-259.
21. Rowland JS. (1938). The determination of the nitrogen distribution in milk. J. Dairy Res. 9, 42-47.
22. Saito Z. (1985). Particle structure in spray-dried whole milk and in instant skim milk powder as related to lactose crystallization. Food Microstruc. 4(2), 333-340.
23. Saito Z. (1988). Lactose crystallization in commercial whey powders and in spray-dried lactose. Food Microstruc. 7(1), 75-81.
24. Saltmarch M, Labuza TP. (1980). SEM investigation of the effect of lactose crystallization on the storage properties of spray-dried whey. Scanning Electron Microsc. 1980;III: 659-665.
25. Warburton S, Pixton SW. (1978). The moisture relations of spray dried skimmed milk. J. Stored Prod. Res. 14, 143-158.
26. Warburton S, Pixton SW. (1978). The significance of moisture in dried milk. Dairy Ind. Int. 43(4), 23, 26-27.

Discussion with Reviewers

N. Singer: The evidence of an apparent increase in Maillard reaction somehow induced by the ultrafiltration process needs to be emphasized.

M. Saltmarch: Could the 5-hydroxymethylfural (5-HMF) levels noted for the 34% retentate correspond to the level on non-protein nitrogen (NPN) in the retentate, *i.e.*, lower NPN, lower rate of 5-HMF development?

Authors: We doubt that the 5-HMF levels in the retentates would be affected by the NPN concentrations. Casein participates most actively in Maillard reactions. β-Lactoglobulin also reacts to some extent [14]. Primary reactive groups in proteins are non-ionized amino groups of branched diamino acids or terminal α-amino groups of proteins. About 90% of all free amino groups in milk proteins are ε-amino groups of lysine.

No significant differences were found in the 5-MHF levels in various retentates. However, the 5-HMF contents in retentate powders stored at 4°C and 37°C were approximately 4 and 3 times, respectively, as high as in milk powders stored at the two corresponding temperatures.

M. Saltmarch: What could have contributed to the lesser degree of lactose recrystallization in the retentates than in the whole milk powder?

Authors: A markedly lower lactose content in the retentate powders is the most probable reason.

P. Jelen: What does the term "moist-looking appearance" of the retentate powders mean? The powders were presumably dry.
Authors: Yes, they were dry, yet they looked and behaved as if they were moist, *i.e.*, the particles stuck together when taken out of the pouch and handled.

P. Jelen: The comment on the double adhesive tape seems odd - why bother mentioning it?
Authors: A double adhesive tape is convenient in order to mount powders for SEM examination. However, the powders are seldom exposed to a high temperature (40°C) for several days under high relative humidity (100%) conditions prior to SEM. Our observation may be important to someone who intends to study particles smaller than spray-dried retentates at high temperature and high relative humidity. For that purpose, it would be advisable to replace the tape with another material.

N. Singer: Fig. 3 raises the following questions: How do rims form around minute globular particles which are seen attached to larger particles of spray-dried buttermilk? Could some light be shed on this structure by performing cross sections? Would we see a "root" or a shallow cup-like interface?
Authors: In the spray-drier, minute buttermilk droplets dry and solidify more rapidly than larger particles. It is probable that the minute solid droplets collide with the still-liquid but already highly viscous larger particles. As a result of the impact, the minute solidified droplets form craters, in which they become embedded. The mass pushed aside by these colliding solid droplets surrounds them in the form of the rims seen. If this is true, we would see shallow cup-like interfaces such as the one marked with an arrow in Fig. 3, that was left on the surface of the larger particle when a smaller droplet broke off, rather than "roots". It is interesting to note, however, that the rims were observed only with spray-dried buttermilk but not with other milk powders.

Shallow dimples were seen in spray-dried milk retentates. It is probable that in this product, small solidified droplets collided in the spray-drier with the larger particles at a stage when the larger particles were no longer liquid but were still soft. The small solid droplets left their imprints ("dimples") on the surface but, unlike in spray-dried buttermilk, did not become attached to it.

P. Jelen: If there was any recrystallization at the 3-day storage, why were the T_m values the same?
Authors: The T_m values have been tabulated by Morrissey for pure lactose and may not exactly apply to spray-dried milk and retentate powders, where proteins and other constituents are present at high concentrations.