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Effects of skim milk pre-acidification and retentate pH-restoration on spray-drying performance, physico-chemical and functional properties of milk protein concentrates

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ABSTRACT

This study investigates the effects of pre-acidification (pH 6.7–5.4) of skim milk, followed by pH-restoration of the retentates, on spray-drying performance, physico-chemical properties and functionality of the resulting milk protein concentrate (MPC). Powder recovery decreased with decreasing pH of pre-acidification but improved with pH-restoration. Colloidal calcium was gradually solubilized with decreasing pH of pre-acidification but was slightly recovered by pH-restoration. Dissociation of micellar caseins increased with decreasing pH of pre-acidification of skim milk and was further increased by pH-restoration. Casein micelles maintained their overall structures at pre-acidification pH of 6.7–6.0, and partially disintegrated into loosely entangled aggregates at pH 5.7–5.4; while after pH-restoration, micelles generally maintained their overall structures at pre-acidification pH of 6.0, and completely disintegrated at pH 5.7–5.4. Solubility and emulsifying properties of MPC improved with decreasing pH of pre-acidification and with pH-restoration. Heat stability of MPC declined with decreasing pH of pre-acidification but improved with pH-restoration.

1. Introduction

Milk protein concentrate (MPC) is a multi-functional dairy protein ingredient that is manufactured from pasteurized skim milk using ultrafiltration, diafiltration and spray-drying, and contains both caseins and whey proteins in the same ratio (4:1) as skim milk. It is available in protein contents ranging from 40% to 90% on a dry weight basis (Uluko, Liu, Lv, & Zhang, 2016). The majority of caseins are still in a state that strongly resembles the original casein micelles in skim milk (Eshpari, Tong, & Corredig, 2014). In recent years, MPC has been increasingly employed for milk extension instead of skim milk powder (SMP), given that the higher lactose content of SMP may result in a sandiness mouthfeel in condensed milk, an undesirably high acidity in yogurt, and a high residual lactose content in cheese leading to unacceptable browning when cheese is utilized as a pizza topping (Mistry, 2002).

A major deterrent for some applications of MPC, especially one containing more than 70% protein, has been its poor functionalities such as solubility, and heat stability and interfacial properties of the reconstituted solution, when compared to sodium caseinate (Bansal, Truong, & Bhandari, 2017; Ji et al., 2016; Uluko et al., 2016). For example, poor solubility of MPC may lead to nugget formation in cheeses, texture hardening in nutritional bars, and flocculate deposition in mixed drinks (Marella, Salunke, Biswas, Kommineni, & Metzger, 2015). The functionality of MPC is essentially related to the structure of the casein micelles it contains, and the structural integrity of micelles is primarily maintained by colloidal calcium phosphate (CCP) (Luo, Vasiljevic, & Ramchandran, 2016). Therefore, manipulating the state of CCP through processing conditions appears to be a promising strategy to tailor the functionality of MPC.

Acidification of skim milk prior to membrane filtration is a potential approach to induce structural modifications of casein micelles in the

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resulting MPC due to the solubilization of CCP (Liu, Li et al., 2017). Currently, except for few studies, there is limited information regarding systematic investigations of the effects of skim milk pre-acidification on the fundamental properties of casein micelles and the functionalities of the corresponding MPC. Marella et al. (2015) reported that acidification of skim milk to pH 5.8 by injecting CO_2 during membrane filtration significantly increased the solubility of MPC80. Eshpari et al. (2014) reported that pre-acidification of skim milk to pH 6.0 slightly increased the solubility of MPC80. Eshpari, Jimenez-Flores, Tong, and Corredig (2017) reported that pre-acidification of skim milk to pH 6.0 substantially decreased the heat stability of MPC65 and MPC80, while pH-restoration of reconstituted MPC65 and MPC80 through dialysis against skim milk significantly improved their heat stability. Luo, Ramchandran, and Vasiljevic (2015) also reported that pre-acidification of skim milk to pH 6.3–5.5 had a negative effect on the solubility and heat stability of MPC55, while pH-restoration of reconstituted MPC55 using NaOH improved its solubility and heat stability. These results suggest that pH-restoration of reconstituted MPC prepared from pre-acidified skim milk had a positive effect on some of its functionalities. However, whether pH-restoration of the retentate prepared from pre-acidified skim milk before spray-drying has a positive effect on the functionalities of MPC is still unknow. If so, the end-users of the resulting MPC will not need to perform a pH adjustment on the reconstituted MPC in order to improve its functionalities. Thus, the effects of pH-restoration of retentate prepared from pre-acidified skim milk on the spray-drying performance and the fundamental aspects of casein micelles, especially their overall and internal structures, in MPC need investigating.

In this paper, the effects of partial acidification of skim milk prior to membrane filtration, combined with pH-restoration of the retentates prior to spray-drying, on the spray-drying performance as well as the physico-chemical and functional properties of the resulting MPC are investigated. Skim milk was pre-acidified between pH 6.7 and 5.4 using glucono-δ-lactone (GDL) to achieve homogeneous acidification without casein aggregation. The subsequent membrane filtration process involved ultrafiltration and 3 stages of diafiltration each with a volume concentration factor (VCF) of 3 except for the last stage where a VCF of 6 was used, leading to the production of MPC85 (Chen et al., 2013).

2. Materials and methods

2.1. Materials

Pasteurized skim milk was purchased from Bright Dairy & Food Co., Ltd. (Shanghai, China) and sodium azide (0.02%, w/v) was added to prevent microbial growth. GDL and low gelling temperature agarose were obtained from Sigma-Aldrich Co. (St. Louis, MO, USA). All other chemicals used were of analytical grade.

2.2. Preparation of MPC

Predetermined amounts of GDL of 0, 15.0, 23.7, and 33.8 mM were added to skim milk under continuous stirring to obtain decreasing pH values of 6.7 (natural value), 6.0, 5.7 and 5.4, respectively. The subsequent membrane filtration was performed using a SPPM-24S-1 pilot plant unit (Suntar Membrane Technology Co., Ltd., Xiamen, China) equipped with a PW2540F-50P spiral-wound polyethersulfone membrane (10 kDa molecular weight cut-off; GE Water & Process Technologies, Trevose, PA, USA). Ultrafiltration was performed at 25–30 °C until a VCF of 3 was obtained as indicated by the measured volume of the permeate. The retentate was mixed with 2 volumes of distilled water and then diafiltered until a VCF of 3 was obtained. The diafiltration stage was repeated 2 more times with the final stage being further performed until a VCF of 6 was obtained. Each of the resulting retentate contained about 22% solids and was divided into 2 equal portions. For each pre-acidified milk, one portion of the final retentate was kept until further processing, and the other portion was mixed with the required amounts of 2 M NaOH to restore the pH to that of the retentate obtained from skim milk at pH 6.7. Then, both portions were spray-dried using a B-290 spray dryer (BUCHI Labortechnik AG, Flawil, Switzerland) with feed temperature maintained at 25 °C and with inlet and outlet temperatures maintained at 135 and 75 °C. The MPC powders accumulated in the powder collection chamber at the bottom of the cyclone were collected, and powder recovery was calculated as the solid content of the powder, expressed as a percentage of the solid content of the feed. Non-treated skim milk at pH 6.7 was also spray-dried as described above to obtain SMP. The moisture content and water activity of all powders were about 4.8% and 0.25, respectively.

2.3. Reconstitution of MPC

MPC and SMP powder samples were reconstituted in ultrapure water (Heal Force Water Purification System; Canrex Analytic Instrument Co., Ltd., Shanghai, China) to a final protein content of 3.2% (w/v). To ensure complete solubilization of powders, all dispersions were first stirred at 50 °C for 1 h using a magnetic stirrer (IKA Werke GmbH & Co. KG, Staufen, Germany) and then held at 4 °C for 24 h.

2.4. Physico-chemical property analyses

2.4.1. Fractionation for analyses

Reconstituted samples were ultracentrifuged at 100,000 × *g* for 1 h at 25 °C using an Optima L-100XP ultracentrifuge (Beckman Coulter, Inc., Indianapolis, IN, USA), and a portion of the resulting supernatants were ultrafiltered at 2000 × *g* for 1.5 h at 25 °C using Vivaspin 6 concentrators (10 kDa molecular weight cut-off; Sartorius Stedim Biotech GmbH, Goettingen, Germany).

2.4.2. Determination of calcium

Reconstituted samples and their ultrafiltrates (Section 2.4.1) were hydrolysed with nitric-perchloric acid (4:1, v/v) using a MARS Microwave Digestion System (CEM Corp., Matthews, NC, USA), and the calcium fractions in the corresponding hydrolysates were determined as the total and soluble calcium, respectively, using a Varian SpectrAA 220 atomic absorption spectrometer (Varian Medical System, Inc., Palo Alto, CA, USA). The colloidal calcium was calculated as the difference between the total and soluble calcium.

2.4.3. Determination of protein

The protein content of the ultracentrifuged supernatants (Section 2.4.1) were determined according to the method of Bradford (1976) using MPC (86.2% protein on a dry weight basis; Fonterra Co-operative Group Ltd., Auckland, New Zealand) as a standard and the corresponding protein profiles were determined by reversed-phase high-performance liquid chromatography using a Waters e2695 Separations Module (Waters Corp., Milford, MA, USA) equipped with a 2489 UV/Visible detector and a XBridge BEH C18 column (250 mm × 4.6 mm I.D.) according to the method of Liu, Li et al. (2017).

2.4.4. Dynamic light scattering (DLS)

To measure the particle size of casein micelles, DLS was performed at 25 °C using a Zetasizer Nano ZS (Malvern Instruments Ltd., Worcestershire, UK) according to the method of Silva et al. (2013) with slight modifications. Reconstituted samples were diluted 1:50 (v/v) using the corresponding ultrafiltrates (Section 2.4.1) with a refractive index of 1.33 measured using a 2WAJ refractometer (CSOIF Co., Ltd., Shanghai, China) and with a viscosity of 0.894 mPa·s. A refractive index of 1.57 for protein particles was used (Liu, Yu et al., 2017). The analysis used a general purpose model for spherical particles, and the intensity weighted z-average diameter was derived using the Cumulant analysis of the correlation function.