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Moderately acidic pH potentiates browning of sweet whey powder

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Abstract

Liquid whey may be subjected to various holding times and temperatures, potentially resulting in a moderate pH reduction. It is hypothesized that such a pH reduction may affect the browning of the resulting whey powders during storage. Spray-dried sweet whey powders (SWPs) with pH modified by exposure to vaporous acetic acid were subjected to storage at various temperatures in sealed containers. Colour, hydroxymethyl furfural (HMF) and lysine content were assayed at various time–temperature conditions. In general, browning was increased with higher temperature, longer storage times and lower pH. HMF levels were found to be higher in low pH samples confirming that the 3-deoxyosone pathway was involved. The lysine content was found to decrease with time; the lower pH sample had the lowest final lysine content. These results suggest that pH has a significant role in the browning of SWP by catalyzing the Maillard browning pathway involving the 3-deoxyosone intermediate.

Keywords: Sweet whey powder; Maillard browning; Colour

1. Introduction

High-quality sweet whey powder (SWP) is a free-flowing powder with a slight yellowish hue that can degrade into a brown colour during storage (Doob, Willmann, & Sharp, 1942; Labuza & Saltmarch, 1981). Colour measurement of 35 commercially available SWP samples showed a large variation in lightness (L^*: 76.36–81.64) and yellowness (b^*: 13.48–22.54) (Banavara, Anupama, & Rankin, 2003). It is well recognized that non-enzymatic browning (NEB) through the Maillard reaction is a major deteriorative mechanism active during the storage of SWP (Burin, Jouppilla, Roos, Kansikas, & Buera, 2000; Labuza & Saltmarch, 1981; Roos, Jouppila, & Zielasko, 1996). Various food processing and storage variables influence Maillard reaction rates. Such variables include the composition of raw materials, method of manufacture, time–temperature combination used during processing and storage, pH, water activity (a_w), presence of oxygen and oxidative metal ions, presence of NEB inhibitors such as sulphur dioxide, physical structure (porous or mechanically compressed) and the presence and physical state of sugars, e.g. glassy or crystalline (Ames, 1990; Burin et al., 2000). Many researchers have studied the effect of the above-mentioned factors on browning reactions. The various steps in the Maillard reaction are acid–base catalyzed, and thus pH becomes an important parameter (van Boekel, 2001). In the Maillard reaction, the acid catalyst increases the polarity of the oxo group; in basic pH catalysis, the nucleophilic character of the amino group increases (Szantay, 1971). The acid catalysis involves primarily the reaction of the sugar component. The amino group does not readily take part in acid-catalyzed reactions because of the loss of its free electron pair. The initial pH of the product and the buffering capacity of the system influence the rate and direction of the reaction (Ellis, 1959; Nursten, 1981). The type of amino group containing compounds, reducing sugars and pH of the medium affect the Maillard reaction rate (Kato, Yamamoto, & Fujimaki, 1969; Pomeranz, Johnson, & Shellenberger, 1963; Wolfrom, Kashimura, & Horton, 1974). The degradation of the Amadori

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compound, a key precursor in the browning reaction, is also influenced by pH. The degradation takes place through the 3-deoxyosone pathway via the 1,2-enolization route, favoured at low pH, while 1-deoxyosone pathway via the 2,3-enolization route is favoured at high pH (O'Brien, 1989). However, the effect of pH is not clearly understood and the reactions may take place by both the pathways, with the pH of the system influencing the ratio of products formed (Ames, 1990). Nursten (1986) has shown that several low molecular weight coloured products possess moieties derived from both the furfural and reductone routes.

Factors influencing the rate of Maillard reactions in aqueous model systems containing amino acids and reducing sugars have been studied at different pH values, temperatures and reactant concentrations (Ajandouz, Tchiakpe, Dalle Ore, Benajiba, & Puigserver, 2001; Ashoor & Zent, 1984; Baxter, 1995). In aqueous sugar–amino acid buffer model systems, alkaline pH increases the rate of browning (Ashoor & Zent, 1984; Kato et al., 1969; Wolfrom et al., 1974). Under the conditions used in the study (aqueous sugar–amino model systems, autoclaving at 121 °C for 10 min at pH < 6), no detectable browning was found, and the browning intensity increased with increasing pH to a maximum at a pH~10 (Ashoor & Zent, 1984).

Some researchers have suggested that acidic pH will inhibit Maillard browning in dried products. Nafisi and Markakis (1983) reported inhibition of the overall browning process by the addition of acidic amino acids. Baxter (1995) suggested that reducing the pH in powders along with controlled temperature storage is an effective method to reduce browning. Acidic pH in a dried product such as SWP may potentiate an alternate browning pathway, namely the furfural route (involving 3-deoxyosone). However, there are no detailed studies on the effect of pH in reduced water systems such as SWP.

In SWP processing, it is possible to reach moderately acidic pH due to handling and storage conditions of the liquid whey that allow continued fermentation. The objective of this study was to determine the effects of such pH reductions on the browning of SWP at different time–temperature storage conditions. Since low pH has been hypothesized to inhibit browning in reduced moisture systems or potentiate browning via the furfural pathway, it was of interest to study the effect of moderately acidic pH on the browning of SWP and track specific reactants to confirm the Maillard reaction pathways.

2. Materials and methods

2.1. Materials

Acetic acid glacial, Carrez reagent I (15% $K_4Fe(CN)_6$) w/v), Carrez reagent II (30% zinc acetate, w/v), sodium dodecyl sulphate (SDS), sodium tetraborate, ethyl acetate and chloroform (HPLC grade) were procured from Fisher Scientific (Fair Lawn, NJ, USA); 5-hydroxymethyl furfural (Aldrich, Milwaukee, WI, USA); *o*-phthalaldehyde (MP Biomedicals Inc., Eschwege, Germany), β-lactoglobulin (90%), 2-mercaptoethanol (Sigma-Aldrich Inc., St. Louis, MO, USA). Sweet whey powder was produced in-house from Swiss cheese whey as described.

2.2. Sweet whey powder manufacture

In-house SWP was produced from sweet whey (pH 6.3) recovered from Swiss cheese manufacture. Liquid whey of approximately 6.2° brix was concentrated to 44.5° brix in a single-effect vacuum evaporator (88.046 kPa vacuum, 65 °C) over approximately 4 h. The total initial volume of whey was 662.45 L. The concentrated whey was cooled and stored (~7 °C) in a jacketed vat with agitation to effect lactose crystallization for 18 h. The final total soluble solids were reduced to 30.5° brix as lactose crystals formed from solution. The crystallized whey was dried in a pilot-scale co-current spray drier (Invensys APV, Tonawanda, NY, USA) with a high-pressure nozzle atomizer. The spray drier parameters were as follows: inlet air temperature 229 °C, inlet product temperature 13 °C and outlet air temperature 80 °C. The nozzle pressure was maintained at 300 kPa.

2.3. Sample preparation

During the handling of liquid whey, it is possible to have SWP of varying pH as a function of the extent of fermentation. To model this phenomenon, SWP of low pH (4.2) and intermediate pH (4.9) were obtained by exposing the SWP (native pH~6.3) to acetic acid vapours for different periods in a desiccator. The pH of reconstituted SWP (2 g SWP + 10 mL distilled water) was measured using a pH meter (Accumet, Model 15, Fisher Scientific, Pittsburgh, PA).

Our studies indicated that samples in sealed vials showed faster browning rates than open vials. In our preliminary study, the browning of samples at low, intermediate and native pH was studied at 40, 60 and 80 °C. A temperature of 60 °C was intended to represent the conditions of handling wherein the SWP is spray dried, bagged and palletized immediately without adequate cooling. A temperature of 80 °C represented an accelerated storage condition for Maillard browning. Temperatures higher than 80 °C were not employed since this may also lead to caramellization.

In the present study, SWP (~25 g) at different pH values (4.2, 4.9 and 6.3) was placed in glass bottles, tightly sealed and subjected to storage at 80 °C for 0, 6, 12, 24, 48 and 72 h. The colour parameters (L^*, a^*, b^*