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Combined pressure–temperature effects on the chemical marker (4-hydroxy-5-methyl- 3(2H)-furanone) formation in whey protein gels

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ABSTRACT

Chemical markers, such as furanone, are intrinsically formed in foods at elevated process temperatures, and have been successfully used as indirect indicators of heating patterns in advanced thermal processes such as aseptic processing, microwave sterilization and ohmic heating. However, very limited information is available on suitability of these chemical markers during combined pressure–heat treatment. The present study was conducted on the formation and stability of chemical marker M-2 (4-hydroxy-5-methyl-3(2H) furanone, a by-product of Maillard reaction) as a function of pressure, temperature and pH. Whey protein gels (containing 1g ribose/100g gel mix) at pH 6.1 and 8.3 were subjected to pressure assisted thermal processing (PATP; 350 and 700 MPa, 105 °C), high pressure processing (HPP; 350 and 700 MPa, 30 °C) and thermal processing (TP; 0.1 MPa, 105 °C) for different holding times. Unprocessed gel was used as control. The marker yield was quantified using HPLC. The initial concentrations of M-2 in the gels were 9.17 and 6.1 mg/100 g at pH 6.1 and 8.3, respectively. As expected, heat treatment at 105 °C, 0.1 MPa increased M-2 concentration. The marker yield increased with increase in holding time, following a first order kinetics and decreased with increasing pH. Pressure treatments from 350 to 700 MPa at 30 °C reduced the chemical marker formation for both pH values investigated. Marker formation during combined pressure-temperature (105 °C, 350 and 700 MPa) was influenced by both heat (which favored the marker formation) and pressure (which hindered marker formation). The net final concentration of the marker formed during PATP was higher than HPP, but lower than thermal treatments. This study suggests that 4-hydroxy, 5-methyl, 3(2H) furanone may not be a suitable marker for evaluating pressure–heat uniformity during PATP.

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1. Introduction

Pressure-assisted thermal processing (PATP) offers new opportunities to the food industry for processing high quality low-acid, shelf-stable foods. Although shelf-stable, low-acid foods processed by this technology are not current commercially available, the technology can be used for processing heat-sensitive products such as mashed potatoes, dinner kits, meats and sauces, soups, egg products, coffee, and tea (Balasubramaniam & Farkas, 2008; Juliano et al., 2006). During a typical PATP process, the food is subjected to a combination of elevated pressures (500–900 MPa) and moderate heat (90–121 °C) for a short time (≤15 min). One of the unique advantages of PATP is its ability to provide a rapid increase in the temperature of treated food samples. Rapid compression heating and subsequent expansion cooling on decompression help to reduce the severity of thermal effects encountered with conventional processing techniques (Rajan, Ahn, Balasubramaniam, & Yousef, 2006).

The sample temperature increase when exposed to high pressure, also known as heat of compression, is well documented in the literature (Delgado, Baars, Kowalczyk, Benning, & Kitsubun, 2007; Patazca, Koutchma, & Balasubramaniam, 2007; Rasanayagam et al., 2003; Torres, Sanz, Otero, Perez-Lamela, & Saldana, 2009). This increase in temperature is influenced by food composition, product initial temperature and target pressure. As a result, temperature gradient may exist within the pressure vessel, possibly due to the differences in the thermal properties such as specific heat capacity, thermal conductivity and physicochemical properties such as composition, density, etc. (Ramaswamy, Balasubramaniam, & Sastry, 2005. pp. 1–6). Previous attempts to study the temperature distribution profile within the high pressure chamber involve use of

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thermo-fluid dynamic based mathematical models (Carroll, Chen, & Fletcher, 2003; Chen, Zhu, Ramaswamy, Marcotte, & Le Bail, 2007; Hartmann & Delgado, 2005; Hartmann et al., 2004) and enzyme/protein based time-temperature-pressure indicators (Gogou, Katapodis, & Taoukis, 2010; Grauwet, Plancken, Vervoort, Hendrickx, & Van Loey, 2010; Rauh, Baars, & Delgado, 2009; Van der Plancken, Grauwet, Oey, Van Loey, & Hendrickx, 2008). Most enzyme based time-temperature-pressure indicators have been studied at high pressure processing (HPP) conditions utilizing modest process temperatures (<70 °C).

Development of biochemical indicators to monitor thermal process non-uniformities within a pressure chamber during PATP could help the industry to ensure product safety and optimize the process. Kim and Taub (1993) suggested that certain chemical compounds, such as Maillard reaction products, formed in the food during thermal processing could be used as indicators of heating patterns. Three biochemical markers have been commonly identified in foods, viz. 2,3-dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one (referred to as M-1), 4-hydroxy-5-methyl-3(2H)-furanone (M-2) and 5-hydroxymethylfurfural (M-3) (Kim & Taub, 1993). These markers are the degradation products of Maillard reaction between carbonyl group of a reducing sugar and amine group of a suitable reactive amino acid (Lau et al., 2003; Wang, Lau, Tang, & Mao et al. 2004). Number of earlier studies (Kim et al., 1996; Ramaswamy, Awuah, Kim, & Choi, 1996) utilized these markers for investigating temperature distribution during ohmic and aseptic processing. The relatively fast reaction rates for the formation of marker M-2 in protein rich substrates at temperature beyond 100 °C make this marker particularly useful in studying heat distribution during short-time sterilization processes (Lau et al., 2003; Pandit, Tang, Liu, & Mikhaylenko, 2007; Pandit, Tang, Mikhaylenko, & Liu, 2006). Also, M-2 marker yield can be positively correlated with thermal lethality and, thus, can be effectively used to locate colds spots in packaged foods during microwave sterilization processes (Pandit, Tang, Liu, & Pitts, 2007).

The objective of this study was to evaluate the feasibility of using the chemical markers to investigate temperature induced process non-uniformities during combined pressure–heat treatment.

2. Materials and methods

2.1. Materials

Whey protein isolate (WPI), 93.2 g/100g (Bipro) (wet basis), and whey protein concentrate (WPC), 78.4 g/100g (wet basis), were purchased from Davisco foods international, Eden Prairie, MN, USA. WPC had 8.41g lactose/100g WPC (wet basis). D-ribose (≥99 g/100g) and 4-Hydroxy-2,5-dimethyl-3(2H)-furanone (purum ≥99 g/100 g) (M-2 chemical marker standard) were purchased from Sigma–Aldrich, St. Louis, MO, USA. Non-iodized food grade salt (Morton International, Chicago, IL, USA) was purchased from a local grocery store. Sodium acetate (anhydrous) and potassium bicarbonate (99.5–101.5 g/100g USP) were purchased from Fisher scientific, Pittsburgh, PA, USA.

2.2. Buffer solutions

10g/100 ml acetate buffer (pH 7.0) and 5 g/100 ml bicarbonate buffer (pH 10.0) were prepared by dissolving respective amounts of sodium acetate and potassium bicarbonate in water.

2.3. Preparation of whey protein gels

Whey protein gels were prepared by modifying the formulation suggested by Lau et al. (2003). The formulation was modified (by optimizing the concentrations of whey protein concentrate, isolate and water) to minimize syneresis of whey protein gels under high pressure and thus prevent the migration of M-2 marker. 200 g batches of whey protein gel consisted of 24 g whey protein concentrate/100g gel mix, 11g whey protein isolate/100 g gel mix, 1 g D-ribose/100 g gel mix, 0.8 g salt/100 g gel mix and 63.2 g de-ionized water/100 g gel mix. Lactose from WPC amounted to ~2 g/100 g gel mix. The total amount of protein contributed by WPC and WPI was ~29 g/100 g gel mix. Briefly, respective quantities of D-ribose and salt were dissolved in water and mixed with weighed amounts of WPC and WPI in a lab blender (Oster 10 speed blender, Boca Raton, FL, USA) for 1 min to obtain a paste like consistency. The natural pH of the paste was 6.1. Appropriate amounts of sodium acetate and potassium bicarbonate buffer solutions were added to prepare paste with a pH of 8.3. The samples were stored overnight under refrigerated conditions to ensure complete protein hydration. 200g hydrated paste was poured in rectangular Nalgene bottle and the bottle were covered with aluminum foils to prevent evaporation of water during gel formation. Gel was formed by placing the Nalgene bottles containing the hydrated paste in a water bath (Isotemp 128, Fisher Scientific, Pittsburgh, PA, USA) maintained at 80 °C for 40 min. The whey protein gel was immediately cooled in an ice–water mixture and refrigerated at 4 °C till further processing and analysis. Earlier studies have shown that heating at 80 °C for 40 min causes negligible browning in whey protein gels (Lau et al., 2003), the gels containing D-ribose show prominent browning at temperatures only above 100 °C (Pandit, Tang, Liu, & Mikhaylenko, 2007). The gels contained 9.17 mgM-2 marker/100 g whey protein gel.

2.4. Processing the whey protein gels

Uniform 7 cm × 2 cm × 0.1 cm sections were cut from the whey protein gel blocks and immediately vacuum packaged (Spiromac vacuum sealer, model 450 T, Québec, Canada) in polypropylene pouches (76.2 μm) Deli, NS1D30-155215, Thomson equipment and supply (Cincinnati, OH, USA). Vacuum packaging did not have any observable effect on the physical characteristics of the gel. The packaged samples were subjected various pressure–heat combinations as outlined below.

2.5. High-pressure kinetic tester

A high-pressure kinetic tester (pressure test unit PT-1, Avure Technology Inc., Kent, WA, USA) was used to process the gel samples. A 54-ml stainless steel (SS-316) pressure chamber was immersed in a temperature-controlled bath to maintain the desired process conditions (30 °C for HPP and 105 °C for PATP). Propylene glycol (57-55-6, Avatar Corporation, University Park, IL, USA) was used as the pressure transmitting medium as well as heating medium in the temperature-controlled bath. The desired pressure was generated at the rate of 18.42 MPa/s using an intensifier (M-340 A, Flow International, Kent, WA, USA) connected to a hydraulic pump (model PO45/45-OGPM-120, Interface Devices, Milford, CT, USA). The depressurization time was approximately 2 s. The pressure holding times provided in Table 1 do not include pressurization or depressurization times. More details about the equipment are described elsewhere (Rajan et al., 2006).

2.6. High pressure processing

Whey protein gel samples (~3.5 g each) vacuum sealed in pouches were compressed to 350 or 700 MPa and held for 0, 5, 10 and 20 min at 30 °C in the high pressure PT-1 kinetic tester. Before HPP treatment, the samples were preconditioned in ice–water mixture for 10 min and placed inside a 10-ml polypropylene

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