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Modeling the retention kinetics of conjugated linoleic acid during high-pressure sterilization of milk

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ABSTRACT

The retention kinetics of conjugated linoleic acid (CLA) in enriched milk treated by high-pressure sterilization conditions was studied at pressures of 100–600 MPa and temperatures of 90–120 °C. The experimental data were well described by the Weibull model. Pressure and temperature influenced the scale parameter, according to the Eyring and Arrhenius models. The remaining CLA content decreased with an increase of temperature and more CLA was retained with an increase of pressure. At 120 °C and 600 MPa, the ratio of oxygen consumed per CLA converted suggested that isomerization of CLA was the predominant reaction mechanism instead of oxidation. The retention of CLA in high-pressure sterilized milk was graphically illustrated through pressure–temperature diagrams. The processing conditions at which commercial sterilization can be achieved (120 °C and 600 MPa with 3 min of holding time) retained more than 80% of CLA.

1. Introduction

Conjugated linoleic acid (CLA) is a bioactive lipid found naturally in milk fat. The term CLA refers to a mixture of octadecenoic acids with two double bonds in a conjugated form (Villegas, Zhao, & Curtis, 2010). In each double bond, the configuration can be *cis*-/*trans*-, *cis*-/*cis*- or *trans*-/*trans*-. The predominant isomer is the cis-9/trans-11, which represents more than 80% of the total CLA (Fritsche et al., 1999). Studies from human and animal intervention revealed that CLA from ruminant possess health-promoting properties and more importantly *trans* fatty acids from ruminants are considered novel functional ingredients (Wang, Jacome-Sosa, & Spencer, 2012).

Dairy products can be viewed as delivery systems for bioactive lipids and efforts have been made to increase the concentration of CLA by manipulating the feeding regime of dairy cattle. A safflower oil supplemented diet was used for increasing the concentration of CLA in milk by 10-fold (Bell, Griinari, & Kennelly, 2006). However, changing the milk fat composition might affect the susceptibility towards oxidation during thermal processing. Indeed, Herzallah, Humeid, and Al-Ismai (2005) reported losses of 15% of CLA in conventional milk treated at 140 °C for 4 s. Similarly, an investigation showed 10% CLA reduction during thermal treatments in CLA-fortified milk (2% of CLA from the total fat) (Campbell, Drake, & Larick, 2003). The oxidation of CLA and other unsaturated fatty acids reduces the final quality of CLA-enriched product (Hillbrick & Augustin, 2002; Luna, De la Fuente, Salvador, & Marquez-Ruiz, 2007).

An alternative technology that reduces the thermal damage by applying hydrostatic pressure is known as high-pressure sterilization (HPS) or pressure-assisted thermal sterilization (PATS). This technology has become a viable possibility in cases where the traditional thermal treatments induce degradation of valuable compounds. The fundamentals and applications of HPS are reviewed elsewhere (Bermudez-Aguirre & Barbosa-Canovas, 2011; Juliano et al., 2012; Mujica-Paz, Valdez-Fragoso, Samson, Welti-Chanes, & Torres, 2011). Martínez-Monteagudo, Saldaña, Torres, and Kennelly (2012) reported that the combined effect of high pressure and temperature enhanced the retention of CLA in milk. However, the retention kinetics of CLA has not been reported. Predicting the retention of CLA through mathematical equations derived from kinetics studies is crucial to enable technology development for process design. Kinetic models have been used for stability of vitamins at HPS (Verbeyst, Oey, Van der Plancken, Hendrickx, & Van Loey, 2010; Verbeyst, Van Crombruggen, Van der Plancken, Hendrickx, & Van Loey, 2011). The Weibull model and its variations enable to fit experimental data regardless of the reaction order. This model has been used for modeling chemical reactions in various food systems (Corradini & Peleg, 2004; Manso, Oliveira, Oliveira, & Frias, 2001). Therefore, the objective of this study is to determine the retention kinetics of CLA during high-pressure sterilization of enriched milk and to model this CLA retention with the Weibull distribution model.

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2. Materials and methods

2.1. Milk rich in CLA

Milk rich in CLA was obtained from the Dairy Research and Technology Centre of University of Alberta (Edmonton, AB, Canada) after following the protocol developed by Bell et al. (2006) with minor modifications and described in detail by Martínez-Monteagudo, Saldaña, and Kennelly (2012). The raw CLA-enriched milk was divided into 200 mL portions and stored at −20 °C. Then, the raw CLA-enriched milk was warmed to 40 °C and the cream was separated by centrifugation (Beckman Coulter apparatus, Avanti® J-E, Fullerton, CA, USA) at 17,500 ×*g* for 45 min. A portion of the cream was added into skim milk to yield 2.7% (w/v) of fat and homogenized using a two stage APV-2000 homogenizer (Concord, ON, Canada). After homogenization, the milk was cooled immediately to 8 °C and stored for further use.

2.2. High-pressure sterilization (HPS) treatments

Aliquots of 2.7 mL of standardized and homogenized raw CLA-enriched milk were transferred to polypropylene tubes (Cryogenic vial, Fisher Scientific, Canada). Then, the tubes were capped and preheated in a thermostatic oil bath (~2 min) at different temperatures ranging from 72 to 117 °C, considering the adiabatic heat of 3 °C per 100 MPa (Rasanayagam et al., 2003). After preheating, the tubes were transferred to a high pressure multivessel system (Apparatus U111 Unipress, Warszawa, Poland). The high pressure unit was heated using a thermostat (Lauda Proline RP 855 Low Temperature, Lauda-Königshofen, Germany). The high pressure unit consists mainly of an intensifier and four high pressure vessels (Vessel 1–Vessel 4), working in parallel, and each one with an internal volume of 8 mL. The vessels were heated with a thermostating circulator bath (Lauda Proline RP 855 Low Temperature, Lauda-Königshofen, Germany) using propylene glycol, which was also the pressure transmission fluid. Each vessel is equipped with a type K thermocouple located at the bottom of the vessel, which allows recording of the transmission fluid temperature (T1–T4) in each vessel. Samples were compressed (~11 MPa s^{-1}) and held for 0, 5, 10, 15, 30, and 60 min. The holding time of 0 min was considered when isobaric and isothermal conditions were achieved. At the end of the holding time, samples were removed and cooled immediately with ice water. The experimental protocol for kinetic studies using this high pressure unit was previously validated by Hofstetter, Gebhardt, Ho, Gänzle, and McMullen (2013) and Martínez-Monteagudo, Saldaña, Torres, et al. (2012). All experimental points were conducted in triplicates.

2.3. CLA determination

A GC Varian 3400 (Palo Alto, CA, USA) was used to determine the CLA content. The GC was coupled with a splitless injection port and a flame-ionization detector. The samples were run on a SP-2560 column (100 m length × 0.25 mm; fused-silica capillary column, Supelco Inc., Belfonte, PA, USA). All samples were run following the chromatographic conditions reported by Cruz-Hernandez et al. (2004). Fatty acid methyl esters were obtained using base-catalyzed methylation, as previously reported by Martínez-Monteagudo, Saldaña, & Kennelly (2012). Methyl heptadecanoate (1 mL of 1 mg mL^{-1}) was used as an internal standard (Fluka #51633 purity 99.5%, Sigma-Aldrich, Saint Louis, MO, USA). All the GC data were processed with Galaxi software (version V1.19, Varian Inc., Walnut Creek, CA, USA) and the obtained peaks were identified with a milk fat reference standard (463-Nu Check Prep Inc., Elysian, MN, USA). The CLA content measured by GC represents the total CLA.

2.4. Modeling the CLA retention in milk treated by HPS

The retention of CLA in milk treated by HPS was analyzed using the Weibull model given in Eq. (1). This model allows fitting kinetic data regardless of the reaction order (van Boekel, 2002).

$$\frac{CLA_o - CLA_t}{CLA_o - CLA_f} = exp^{\left(-\left(\frac{t}{\alpha}\right)^{\beta}\right)} \tag{1}$$

where CLA_o, CLA_t, and CLA_f are the concentrations of CLA (mg g^{-1} fat) initially, at a given time (t) and at the end, respectively; α is the scale parameter, which reciprocally represents the reaction rate constant (k); and β is the shape parameter. In cases where $\beta = 1$, the reaction is considered to follow a first-order model. The left side of Eq. (1) represents the CLA fraction, which indicates the retained amount of CLA at a given time divided by the minimum CLA retained at the experimental conditions.

The influences of pressure and temperature on the scale parameter were expressed by the Eyring-type and Arrhenius-type models, Eqs. (2) and (3), respectively:

$$\frac{1}{\alpha} = \frac{1}{\alpha_P} \cdot exp^{\left(-\frac{\Delta V^{\neq}}{RT}\cdot\left(P - P_{ref}\right)\right)} \tag{2}$$

$$\frac{1}{\alpha} = \frac{1}{\alpha_T} \cdot exp^{\left(\frac{-E_a}{R}\cdot\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)} \tag{3}$$

where P is pressure (MPa); T is temperature (K); α_P and α_T (min) are scale parameters at a reference pressure (P_{ref}) and a reference temperature (T_{ref}), respectively; $\Delta V^{\neq}$ is the activation volume (cm^3 mol^{-1}); E_a is the activation energy (kJ mol^{-1}) and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). The average values of the experimental pressures and temperatures were used as the P_{ref} and T_{ref}, respectively.

Once the influences of pressure and temperature were determined, Eqs. (2) and (3) were individually incorporated into the Weibull model, yielding global kinetic equations (Eqs. (4) and (5)). These equations describe the retention of CLA as a function of holding time and pressure at a constant temperature (Eq. (4)) and the retention of CLA as a function of holding time and temperature at a constant pressure (Eq. (5)).

$$\frac{CLA_o - CLA_t}{CLA_o - CLA_f} = exp\left[-\left(\frac{t}{\alpha_P} exp^{\left(\frac{-\Delta V^{\neq}}{RT}\left(P - P_{ref}\right)\right)}\right)^{\beta_{avg}}\right]_T \tag{4}$$

$$\frac{CLA_o - CLA_t}{CLA_o - CLA_f} = exp\left[-\left(\frac{t}{\alpha_T} exp^{\left(\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)}\right)^{\beta_{avg}}\right]_P \tag{5}$$

where β_{avg} is the average of the β values at the range of conditions studied. The relation between the kinetic parameters was evaluated using joint confidence region plots (Claeys, Ludikhuyze, & Hendrickx, 2001).

At each experimental point, the k values calculated using Eqs. (4) and (5) were designated as observable rate constants (k_{obs}). Then, the k_{pred} was obtained by the Arrhenius–Eyring model (Eq. (6)) and the empirical model (Eq. (7)).

$$k = k_{ref} \cdot exp^{\left(\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right)} \cdot exp^{\left(\frac{-\Delta V^{\neq}}{RT}\left(P - P_{ref}\right)\right)} \tag{6}$$