Innovative Food Science and Emerging Technologies 28 (2015) 22–30

Contents lists available at ScienceDirect

Innovative Food Science and Emerging Technologies

journal homepage: www.elsevier.com/locate/ifset

Kinetics of lactulose formation in milk treated with pressure-assisted thermal processing

Sergio I. Martínez-Monteagudo, Marleny D.A. Saldaña *

Department of Agricultural, Food and Nutritional Science, University of Alberta, Edmonton, AB, Canada

ARTICLE INFO

Article history:
Received 15 December 2011
Received in revised form 16 December 2014
Accepted 29 December 2014
Available online 8 January 2015

Keywords:
Activation energy
Activation volume
Lactose
Lactulose formation
Kinetic study
Weibull model
Pressure–temperature diagram

ABSTRACT

The combined effect of temperature and pressure on the kinetics of lactulose formation was investigated in the range of 100–120 °C and 100–600 MPa up to 15 min. The kinetics data were fitted using the Weibull model and the parameters were evaluated through joint confidence regions. The scale parameter (α) was affected by temperature and pressure, following Arrhenius-type and Eyring-type equations, respectively. The calculated kinetic parameters, $E_a = 182 \pm 8$ kJ mol^{-1} and $\Delta V^{\#} = -7.5 \pm 0.1$ cm^3 mol^{-1}, revealed that the combination of temperature and pressure accelerated the formation of lactulose, reaching a maximum concentration of 650 mg L^{-1} after 15 min of holding time at 120 °C and 600 MPa. Interestingly, lactulose contents obtained were lower after PATP treatments compared with values reported in the literature for equivalent UHT treatments. The formation of lactulose was also represented in pressure–temperature diagrams. This information can be used to determine the impact of pressure-assisted thermal processing in milk-based products.

Industrial relevance: The dairy industry uses the lactulose concentration as a heat damage indicator to distinguish between sterilized and pasteurized milk. Pressure-assisted thermal processing (PATP) is a relative new technology with potential applications in the dairy industry. This study provides new kinetic data on the formation of lactulose at PATP conditions. The information obtained in this study can be used to assess the impact of PATP on other shelf-stable dairy products, including functional beverages that contain milk.

1. Introduction

Milk is naturally rich in nutrients, such as proteins, carbohydrates, fats, minerals, and vitamins. Raw milk spoils within hours at room temperature. Therefore, milk is thermally processed to make it safe for human consumption and extend its shelf life (Claeys, Van Loey, & Hendrickx, 2002). Processes like High-Temperature-Short-Time pasteurization (HTST, 75 °C/15 s) provide a shelf life of 2 w at 6 °C. Combinations of higher temperatures and shorter holding times (130–150 °C/2–10 s) allow to achieve commercial sterilization, extending the shelf life up to 180 d at room temperature (Goff & Griffiths, 2006; Rysstad & Kolstad, 2006). However, various reactions occur during thermal sterilization that detriment the nutritional and sensory properties of milk. These changes in milk heated at sterilization conditions have been extensively reviewed by Burton (1983) and more recently by Chavan, Chavan, Khedkar, and Jana (2011). One of the main chemical changes is the isomerization of lactose to form lactulose, a compound not present in raw milk and therefore use as a heat damage indicator (Cattaneo, Masotti, & Pellegrino, 2008; Claeys, Smout, Van Loey, & Hendrickx, 2004; Marconi et al., 2004).

A new sterilization technology, known as pressure-assisted thermal processing (PATP), has been successfully used to achieve sterilization conditions without significantly changing the sensory and nutritional properties (Matser, Krebbers, van den Berg, & Bartels, 2004). This technology consists on applying high pressure (100–600 MPa) and high temperature (90–120 °C) to inactivate bacterial endospores. In 2009, the Food Drug Administration agency (FDA) approved the use of PATP to produce commercially sterile low-acid foods (Ratphitagsanti, Ahn, Balasubramaniam, & Yousef, 2009; Sizer, Balasubramaniam, & Ting, 2002). Sizer et al. (2002) provided a list of advantages of PATP, including the reduction of thermal damage due to the instant temperature increase and uniform pressure distribution.

The velocity of a chemical reaction can be markedly increased or decreased by pressure, according to whether its intermediate state for which the molar volume differs from that of its reacting components is less or more voluminous (Wentorf & DeVries, 2001). Further discussion on the effect of pressure on the kinetics of chemical reactions can be found elsewhere (Jenner, 2004; Van der Placken et al., 2012). The effects of pressure–temperature on a specific compound has been described as synergistic, additive or antagonistic, depending on the combinations of processing conditions (Gupta, Balasubramaniam, Schwartz, & Francis, 2010). In the case of lactose isomerization, Moreno, Villamiel,

* Corresponding author at: 3-18 A, Department of Agricultural, Food and Nutritional Science, Faculty of Agricultural, Life and Environmental Sciences, University of Alberta, Edmonton, AB T6G 2P5, Canada. Tel.: +1 780 492 8018; fax: +1 780 492 8914.
E-mail address: Marleny.Saldana@ales.ualberta.ca (M.D.A. Saldaña).

http://dx.doi.org/10.1016/j.ifset.2014.12.010
1466-8564/

and Olano (2003) evaluated the effect of 400 MPa and 60 °C after 3 h treatment of aqueous lactose solution (10%) in basic media (pH = 10). The authors found an inhibitory effect of pressure on the isomerization and degradation of lactose compared to samples treated at the same temperature and atmospheric pressure.

Weibull distribution function is an empirical model that allows fitting kinetic data regardless of the overall effect of pressure–temperature (synergistic, additive or antagonistic). Although the lactulose content is commonly used by the dairy industry to distinguish between sterilized and pasteurized milk, the kinetics of lactulose formation has not been studied at PATP conditions. The kinetics data of lactulose formation are relevant to evaluate the processing damage of milk during PATP treatment. Therefore, the main objective of this study was to develop a kinetic model for lactulose formation at PATP conditions of pressure (100–600 MPa), temperature (100–120 °C) and holding times up to 15 min. Other objectives were to analyze the kinetic data using mathematical models and to build pressure–temperature diagrams for lactulose formation at various PATP conditions.

2. Materials and methods

2.1. Raw milk and sample preparation

Raw whole milk was collected from the University of Alberta Dairy Unit (Edmonton, AB, Canada). The milk was centrifuged in a Beckman Coulter (Avanti® J-E, Fullerton, CA) at 10,000 g and 4 °C for 30 min to obtain full-cream and skim milk. The fat content in milk was standardized by adding 3% (w/v) of fat into the skim milk and mixed at 40 °C for 10 min using a homogenizer (Diax 900 Homogenizer, Rose Scientific Ltd., Edmonton, AB, Canada).

2.2. Pressure-assisted thermal processing

A multivessel system (Apparatus U111 Unipress, Warszawa, Poland) was used for evaluating the kinetics of lactulose formation in milk. The unit consists of four 8 mL high pressure vessels (Vessel 1-Vessel 4, Fig. 1). The vessels were heated with a circulator thermostat (Lauda Proline RP 855 Low Temperature, Lauda-Königshofen, Germany) using propylene glycol, which was the pressure transmission fluid. A type K thermocouple is equipped in each vessel to record the transmission fluid temperature (T1–T4).

Polypropylene tubes (Cryogenic vial, Fisher Scientific, Pittsburgh, PA) of ~3 mL were filled with raw milk and immersed in a propylene glycol bath at fixed preheating temperatures, ranging from 82 to 117 °C. The preheated temperatures were calculated considering that the milk temperature increases 3 °C per 100 MPa (Rasanavagam et al., 2003). After 2 min, the pre-heated samples were transferred to high pressure vessels already heated at 100, 110, 115 or 120 °C. Samples were pressurized to 100, 300, 400, or 600 MPa at a rate of ~10 MPa s^{-1}. Once the pressure and temperature were reached, the samples were held for 1, 3, 5, 7, 10 and 15 min. At the end of the holding time, the vessels were decompressed and the samples were removed immediately from the high pressure vessels and cooled down with ice to minimize any further lactulose formation. Samples treated with PATP were kept at −18 °C until further analysis. All experimental data were obtained in triplicates and all figures were made using Sigmaplot software V11 (SPSS Inc., Chicago, IL). This experimental protocol has been validated for kinetics studies as reported by Martínez-Monteagudo and Saldaña (2014).

2.3. Lactulose quantification

Lactose, lactulose and galactose contents were determined using high performance liquid chromatography (HPLC), according to the method 147B of the International Standard Federation (IDF, 1998).

2.4. Data analysis

The experimental data of lactose isomerization to form lactulose were analyzed using the Weibull model in the form of Eq. (1).

$$\frac{C_t - C_o}{C_f - C_o} = 1 - exp^{\left(-\left(\frac{t}{\alpha}\right)^{\beta}\right)}. \quad (1)$$

The term on the left side of Eq. (1) is known as the fractional conversion, defined as the amount of lactulose formed at a specific time/maximum amount of lactulose formed. C_t is the concentration of lactulose (mg L^{-1}) at a specific time; C_o is the initial concentration

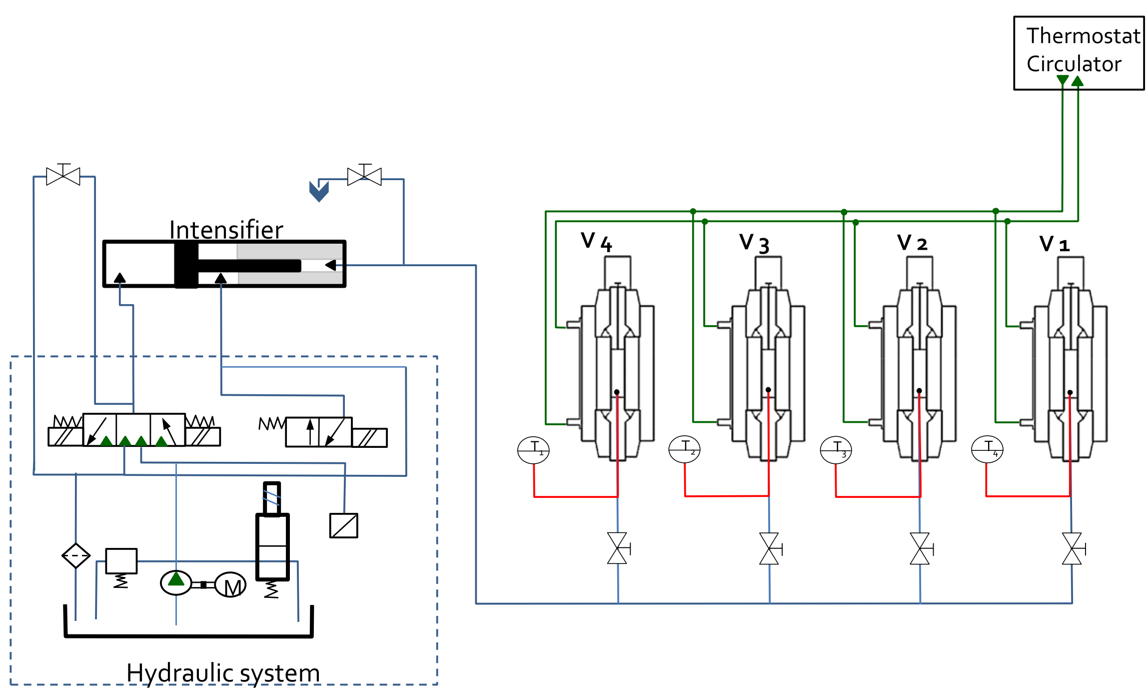

Fig. 1. Schematic representation of the multivessel system apparatus U111 Unipress. Valve (V_1–V_4), and temperature (T_1–T_4).