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Kinetics of Strecker aldehyde formation during thermal and high pressure high temperature processing of carrot puree

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ABSTRACT

Strecker aldehydes have been negatively associated to flavor of heat sterilized plant-based foods. The present study demonstrated the importance of processing conditions (temperature, pressure and time) as a strong means for the control of Strecker aldehyde formation in vegetables purees. A kinetic study was set up (at isothermal and isothermal-isobaric conditions) to quantify the effects of single process parameters on the changes of 3-methylbutanal (3-MB) in carrot puree as a case study. The increase in 3-MB concentrations was best described by an empirical, logistic model. During the isothermal treatment at atmospheric pressure, the maximum reaction rate constant of 3-MB formation was increased as a function of processing temperature. However, the formation rate was clearly slower at high pressure (600 MPa) compared to the process at 0.1 MPa. Hence, the reduced formation of Strecker aldehydes under high pressure could open a new possibility for process control and optimization of the formation of these compounds.

Industrial relevance: High pressure high temperature (HPHT) processing is a relatively young technology and its effect on important quality-related chemical reactions is not as well understood as is the case for conventional thermal processing. The present work investigates the impact of processing conditions (e.g. pressure, temperature) on Strecker aldehydes formation, volatiles that have been negatively associated to flavor of heat sterilized plant-based foods. Based on the kinetic study, the formation rate of the Strecker aldehyde (3-methylbutanal) was clearly slower at high pressure (600 MPa) compared to the process at 0.1 MPa in carrot puree. Considering the fact that these compounds are often linked to off-flavor development, their reduced formation under high pressure could open a new possibility for process control and optimization.

1. Introduction

Since the year 2000, the use of high pressure high temperature (HPHT) processing for sterilization of foods has been the focus of intensive studies (although without industrial implementation so far) (Hoogland, de Heij, & Van Schepdael, 2001; Krebbers, Matser, Koets, Bartels, & Van den Berg, 2002; Matser, Krebbers, van den Berg, & Bartels, 2004; Wilson, Dabrowski, Stringer, Moezelaar, & Brocklehurst, 2008). HPHT is a relatively young technology and its effect on important quality related attributes is not as well understood as is the case for conventional thermal processing. Compared to conventional thermal processing, HPHT has an extra process variable, pressure, which can have a different effect on the rate constants of quality related chemical reactions. Depending on the thermodynamic properties (activation volume) of the constituting reactions, high pressure might have an overall slowing-down or accelerating effect on chemical reactions (Cheftel, 1995). In addition, HPHT processing takes advantage of compression heating and decompression cooling to achieve faster heating and cooling rates, which can result in shorter processing times as compared to conventional thermal processing (Barbosa-Canovas & Juliano, 2008; Wilson et al., 2008). For low-acid, conduction heating food products, the integrated effect of pressure, temperature and time can result in a better preservation of original quality attributes (Barbosa-Canovas & Rodriguez, 2005; Rastogi, Raghavarao, Balasubramaniam, Niranjan, & Knorr, 2007). Therefore, there is a need for comparative studies to identify the different effects of HPHT processing on quality aspects compared to conventional thermal processing (Oey, Van der Plancken, Van Loey, & Hendrickx, 2008b; Oey, Lille, Van Loey, & Hendrickx, 2008a; Van der Plancken et al., 2012). One of the key challenges is the development of an effective analytical and process engineering strategy to identify and study quality-related chemical reactions that are differently affected by this novel sterilization technique in comparison to thermal processing. From analytical point of view, food quality investigations

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have evolved from targeted single response studies toward a targeted multiresponse and untargeted multivariate fingerprinting approaches. In recent years, chemical fingerprinting emerged as an interesting approach to study food quality changes at the molecular level (Hall, 2011). In contrast to targeted approaches, in which focus is given to predetermined particular compounds of interest (which is a hypothesis-based approach), fingerprinting opens the possibility to uncover unexpected and unknown compound changes. As clearly outlined by Grauwet, Vervoort, Colle, Van Loey, and Hendrickx (2014) fingerprinting could be used as a hypothesis-free starting point to screen for key quality changes in particular food extracts. Once the discriminating compounds and reactions are identified, a kinetic study can be set-up to understand and quantify the effect of individual processing variables. From a process engineering point of view, either the integrated impact of the different set of processing variables or the effect of a single process variable, typically with a kinetic study, on quality changes can be investigated.

In our previous study, the potential of headspace fingerprinting as a fast screening tool for quality differences among thermal and HPHT sterilized carrot purees was demonstrated (Kebede et al., 2014). Aiming for a fair comparison, the processing conditions of both treatments were selected targeting at an equivalent microbial inactivation ($F_0 = 5$ min). Using the appropriate multivariate data analysis, chemical fingerprinting enabled the selection of markers, compounds of which the detected quantities are clearly different in the volatile food fraction of differently processed vegetables. In the carrot purees, Strecker aldehydes, such as 3-methylbutanal (3-MB), were detected in a significantly higher amount after microbial equivalent thermal sterilization compared to HPHT sterilization processes (Kebede et al., 2014). These volatiles are reaction products of the Strecker degradation. The reaction involves oxidative deamination and decarboxylation of α-amino acids (e.g. valine, isoleucine and leucine) in the presence of α-dicarbonyl compounds which are formed during Maillard reaction (Cremer & Eichner, 2000; Kerler, Winkel, Davidek, & Blank, 2010). The observed reduction by HPHT processing was interesting because the Strecker aldehydes are often linked to off-flavor development in processed plant-based foods (Yaylayan, 2003; Rizzi, 2008; Cremer & Eichner, 2000). Designing a process from an equivalent point of view (e.g. microbial impact, enzyme inactivation) is needed for an unbiased comparison between different processing technologies and allows insight only into the integrated effect of the different set of processing variables. However, since the effect of each processing variable is not investigated individually with this experimental set-up, it is not possible to link the observed differences in the formation of Strecker aldehydes to one of the process variables (e.g. pressure, temperature and time) in particular. In addition, given the fact that with the fingerprinting approach only relative differences could be determined, the absolute quantification was not a direct research output. Therefore, there is a need for a quantitative kinetic study.

In this work, a kinetic study was set-up for 3-MB to obtain quantitative insight into the separate effects of the process parameters pressure, temperature and time. This is an important research step toward process control and optimization of the formation of these reaction products. As a case study, an orange carrot puree was selected. To the best of our knowledge, even though the formation of Strecker aldehydes in foods and food-related model systems has been studied, the present work is the first in literature to report the kinetics of their formation during HPHT processing.

2. Materials and methods

2.1. Preparation of the carrot purees

A single batch of freshly harvested orange carrots (cv. *Nerac*) was purchased at a local market. The carrots were carefully washed, peeled and cut into standardized cylindrical pieces of approximately 1 cm thickness. The carrot pieces were packed into low-density polyethylene bags. To prevent enzymatic reactions during processing, storage and thawing, the packaged carrots were blanched at 95 °C for 8 min in a water bath (Haake W15 DC-10, Clausthal-Zellerfeld, Germany). The blanching conditions were validated using a qualitative and quantitative peroxidase test. After blanching, the plastic bags were immediately cooled in ice water for 10 min, frozen in liquid nitrogen and stored in a freezer at −40 °C until processing. Prior to processing, the samples were thawed overnight at 4 °C. In order to prepare the puree, deionized water was added to the blanched carrot (1/1 w/w), blended for 1 min using a Buchi mixer (B-400, BUCHI, Switzerland) and further homogenized by high pressure homogenization (at 1000 bar while temperature maintained <4 °C) (Panda 2K, Gea Niro Soavi, Mechelen, Belgium). The pH of the sample was 6.1.

2.2. Isothermal treatment

For the thermal treatments, stainless steel tubes (13 mm inner diameter, 16 mm outer diameter, 150 mm length) were completely filled with carrot puree (no headspace), tightly closed and immersed in an oil bath (Grant Instruments, UK) preset at the desired process temperature. Treatments were performed at three different temperatures, 118 (a similar processing temperature as our previous work, (Kebede et al., 2014)), 124 and 130 °C, for maximum holding times between 60 and 80 min at isothermal conditions. During the treatments, the temperature of the purees was monitored using an Ellab E-val temperature registration system (Ellab, Denmark) and thermocouples (type T, Thermo Electric Benelux, Belgium).

2.3. Isothermal-isobaric treatment

For the HPHT treatments, Teflon (polytetrafluoroethylene) sample holders (diameter 12 mm, length 85 mm) were selected. The tubes were completely filled with carrot puree (no headspace), closed with a movable stopper and vacuum-packed with double plastic bags. The treatments were performed in a laboratory-scale 6-vessel (diameter vessel 2 cm, volume 43 cm^3) high pressure equipment (Resato, Netherlands). This equipment was provided with computer-controlled pressure build-up and data logging software for pressure and temperature. Propylene glycol (PG fluid, Resato, Netherlands) was used as a pressure medium. The HPHT processes were performed at 600 MPa combined with a process temperature of 118 °C, for maximum holding times up to 180 min at isothermal-isobaric conditions. A higher temperature (i.e. 124 and 130 °C) could not be selected because the isothermal-isobaric conditions, desired for kinetic modeling, were difficult to maintain at these high temperatures. Using only compression heating, product temperatures cannot be raised to the desired process temperatures. Therefore, after loading the teflon sample holders into the pre-heated high pressure vessels, the samples were allowed to heat up to an experimentally determined initial temperature of 75 °C. When this temperature was reached, the pressure build-up started. For pressure increase, the equipment consists of a pressure prefill pump which builds up the pressure to 150 MPa with a single piston displacement after which a high pressure intensifier can further built up the pressure at a particular selected pressure build-up rate (10 MPa/s was used in this work). After reaching 600 MPa, the individual vessels were isolated, and an equilibration time of 1 min and 30 s was taken into account. At the selected holding times, the pressure was released from the vessels, which was accompanied by a fast temperature drop inside the product (decompression cooling).

2.4. Post treatment sample handling

Following both treatments, samples were immediately transferred to ice water to further cool the product. Afterwards, treated samples were emptied in a cooling room and transferred to a small volume (10 mL) polyethylene terephthalate tubes with a polyethylene cap.