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Influence of partial pressure of oxygen on ascorbic acid degradation at canning temperature

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ABSTRACT

Oxygen is known to be one of the major causes of oxidative degradations of nutrients. Ascorbic acid, a component of interest due to its health benefits, is reported to be highly oxygen sensitive. To understand better the influence of oxygen on ascorbic acid retention at canning temperature, thermal treatment was performed in model solution at pH = 3.5 with varying partial pressure of oxygen from 0 MPa (strict anaerobic conditions) to 0.1 MPa in the headspace gas, from 95 °C to 125 °C, starting from an initial concentration of 900 mg/L. Treatment of 320 min was not sufficient to completely degrade all ascorbic acid initially present in the medium under anaerobic conditions and with a partial pressure of oxygen in headspace at 0.03 MPa, but treatment of 120 min was sufficient to degrade all initial ascorbic acid when the partial pressure of oxygen in headspace was set at 0.1 MPa. Apparent reaction orders were calculated; they were of 1 under anaerobic conditions, and 0.5 or 0.75 depending on partial pressure of oxygen. Activation energy was calculated using the Arrhenius law under anaerobic conditions only (E_a = 67 kJ/mol). When oxygen is present, whichever its partial pressure in headspace, no acceleration of reaction was observed with increased temperature.

1. Introduction

Because of the increased demand for nutritive foods, there have been many attempts to maximise retention of nutrients during industrial process as well as during transport and storage (Sapei & Hwa, 2014). A thermal treatment must be efficient in order to destroy an appropriate number of targeted microorganisms to make the final product stable. Sterilization in hermetically closed vessels (canning) is actually the most relevant technique to ensure safe, shelf-stable hydrated food products.

During canning, nutritional quality can be lost by degradation of vitamins such as vitamin C, which is one of the main water-soluble vitamins and has a major role in collagen generation, prevents scurvy and may help prevent cold, anaemia, heart disease, obstructive pulmonary disease, asthma, fever, tuberculosis or infertility (EFSA, 2013). Due to its many benefits for human health and its high physico-chemical sensitivity, ascorbic acid is considered as good marker for food nutritional and sensorial quality. Ascorbic acid degradation is influenced by many factors, like oxygen (which can lead to oxidation) (Van Bree et al., 2012), temperature (ascorbic acid is described as very heat sensitive) (Bosch et al., 2013; Esteve, Frígola, Martorell, & Rodrigo, 1998; Hsu, Tsai, Fu, & Wu, 2012; Lin & Agalloco, 1979; Mesías-García, Guerra-Hernández, & García-Villanova, 2010; Sapei & Hwa, 2014), pH (ascorbic acid is more stable at low pHs) (Herbig & Renard, 2017), water activity (Berlinet, Brat, Brillouet, & Ducruet, 2006; Bosch et al., 2013; Golubitskii, Budko, Basova, Kostarnoi, & Ivanov, 2007; Mercali, Schwartz, Marczak, Tessaro, & Sastry, 2014; Sapei & Hwa, 2014) or presence of metallic ions, which can catalyse oxidation (Bosch et al., 2013; Lin & Agalloco, 1979; Soares & Hotchkiss, 1999).

Generally, it is assumed that ascorbic acid (AA) degradation can follow two pathways: one is the oxidoreductive pathway by the formation of dehydroascorbic acid (DHAA), and the other is the hydrolytic pathway, by direct cleavage of the lactone ring of ascorbic acid molecule (Yuan & Chen, 1998) (Fig. 1). This degradation can be described by the following kinetic equation:

$$\frac{d[AA]}{dt} = -k_H\cdot[AA] - k_{ox}\cdot[O_2]^{\alpha}\cdot[AA]^{\beta} \quad (1)$$

where $[AA]$ is the ascorbic acid concentration, $[O_2]$ the dissolved oxygen concentration, k_H the kinetic constant of the hydrolytic degradation pathway, k_{ox} the kinetic constant of the oxidoreductive degradation pathway, and α and β are respectively the partial reaction orders of oxygen and ascorbic acid for the oxidoreductive degradation pathway including both degradation pathways.

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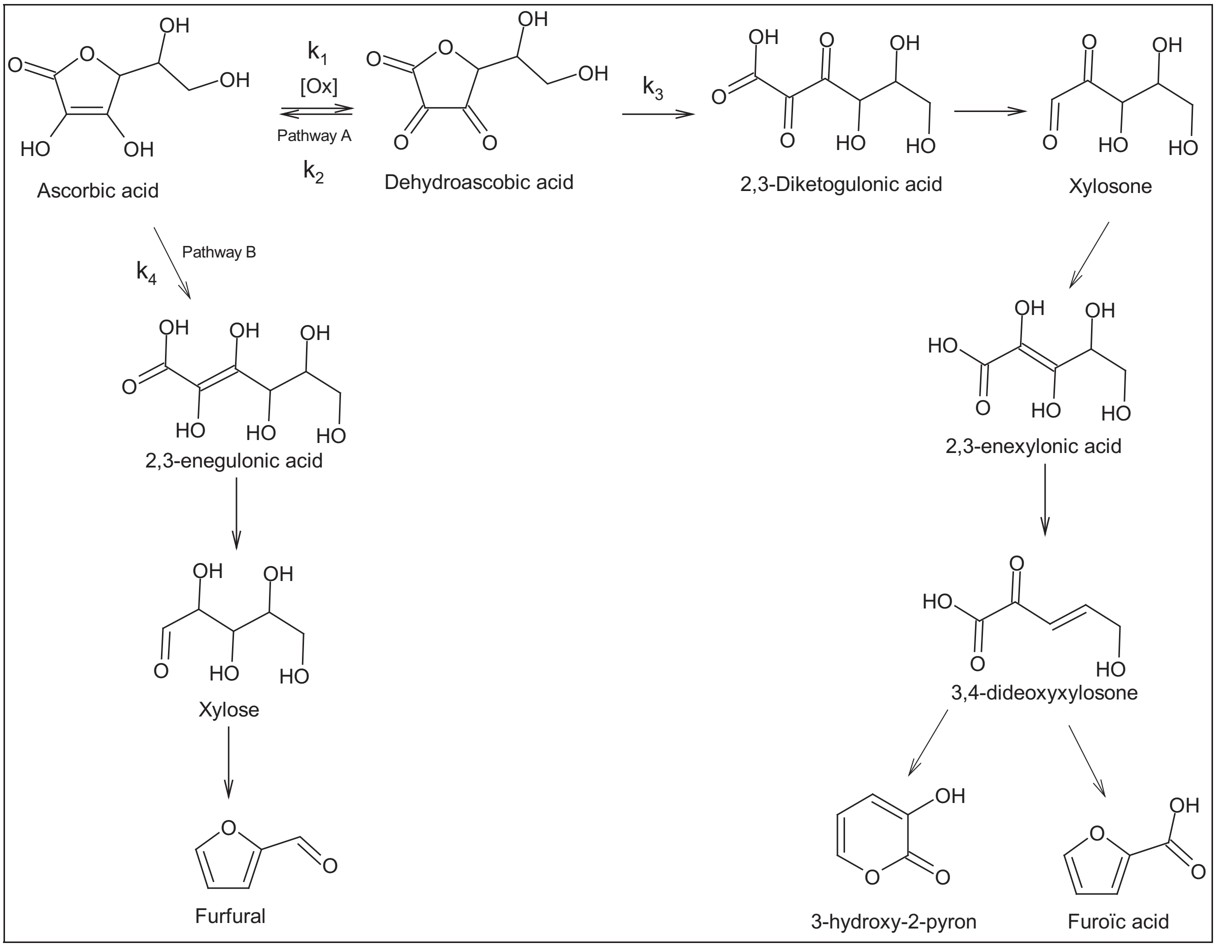

Fig. 1. Mechanisms for ascorbic acid degradation.
(Redrawn from Yuan & Chen, 1998).

Ascorbic acid degradation kinetics is poorly known at canning temperature, probably due to the difficulty to follow this type of degradation at high temperature. Esteve et al. (1998) have studied ascorbic acid degradation in asparagus (no indication of pH), Van den Broeck, Ludikhuyze, Weemaes, Van Loey, and Hendrickx (1998) in orange juice (pH = 3.5) and tomato juice (pH = 4.5) and Oey, Verlinde, Hendrickx, and Van Loey (2006) in model solution at pH = 7 (Blasco, Esteve, Frígola, & Rodrigo, 2004; Esteve et al., 1998; Oey et al., 2006; Van den Broeck et al., 1998). All these studies used nitrogen as headspace gas, but do not mention elimination of dissolved oxygen in the products. Furthermore, Van Bree et al. (2012) studying the influence of partial pressure of oxygen in headspace on ascorbic acid degradation, but at a storage temperature (22 °C), found that there was a linear relationship between partial pressure of oxygen in headspace and the first-order kinetic constant value. It is very difficult to insure anaerobic conditions at high temperature (> 100 °C) due to the difficulty to remove and quantify dissolved oxygen at these temperatures. Al Fata, Georgé, André, and Renard (2017) studied the influence of oxygen on ascorbic acid degradation at canning temperature by performing experiments under aerobic and anaerobic conditions (2016). Oxygen has more impact than temperature on ascorbic acid degradation at temperatures higher than 100 °C. Indeed, oxygen removal from both liquid and headspace seems to be the key factor to better preserve vitamins in these processes, but it remains difficult (Al Fata et al., 2017).

Van Bree et al. (2012) found a linear relationship between first-order kinetic constants of ascorbic acid degradation and the initial headspace oxygen concentration in fruit juice during storage, at 22 °C. Wilson, Beezer, and Mitchell (1995) and Miyawaki, Sugiyama, and Inoue (2016) found a relationship between kinetic constants and partial pressure of oxygen in closed reactors (Miyawaki et al., 2016; Wilson et al., 1995). Miyawaki et al. (2016) also found that the reaction order of ascorbic acid degradation was different when the experiment was performed in a closed (first order) or in an open (zeroth order) reactor, which they attributed to limiting oxygen supply in the first case. Under anaerobic conditions, it is assumed that only the hydrolytic pathway occurs. This degradation pathway is akin to sugar degradation and does not require oxygen (sugar hydrolysis). Al Fata et al. (2017) found that the degradation is much faster in presence of oxygen, indicating that the oxidative pathway remained the major degradation pathway even at temperatures above 100 °C (Al Fata et al., 2017). Removal of all the oxygen appeared to be the better solution to preserve ascorbic acid even at high temperature, but it can be difficult to perform this deareation and remove all the oxygen in a food matrix.

Another difficulty in understanding and modelling ascorbic acid degradation during canning is that data on oxygen solubility at temperatures around 100 °C and $p(O_2)$ close to 0.1 MPa (1 bar) is actually surprisingly scarce (Clever, Battino, Miyamoto, Yampolski, & Young, 2014; Geng & Duan, 2010). There is to our knowledge no experimental system to measure dissolved oxygen easily and rapidly in these operating conditions, as the fluorimetric probes still do not go higher than 80 °C (Cuvilier, Soto, Courtois, & Broyart, 2017; Herbig, Maingonat, & Renard, 2017). Oxygen solubility in water has been measured mostly at pressures under 0.1 MPa and up to 350 K, or by researchers in marine science and limnology, who therefore focussed on high pressures but low temperatures, or metallurgy with high temperatures and pressures.

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