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Formation and degradation kinetics of organic acids during heating and drying of concentrated tomato juice

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A B S T R A C T

Tomato products are often thermally processed or concentrated to obtain their desired shelf life and to facilitate transport. However, processing negatively affects the quality of tomato products. This study focused on the influence of processing on the presence of important tomato taste markers, i.e. citric acid, malic acid, ascorbic acid and pyroglutamic acid (PCA). Isothermal heat treatment of tomato juice was experimentally assessed at varying moisture content (0.18–0.95 kg/kg total), temperature (60–100 °C) and time (0–18 h) combinations. Increasing ascorbic acid degradation (up to 70%) and PCA formation (up to 0.032 mmol/g FT) were measured, while citric acid and malic acid were unaffected. A first order reaction kinetics described the degradation and formation of ascorbic acid ($R^2 = 0.76$) and PCA ($R^2 = 0.98$), where the coupled effect of both moisture content and temperature on the reaction rates was modelled with an Arrhenius-type equation. Higher temperature enhanced both reaction rates with factors 4.2 and 5.1 for ascorbic acid and PCA, respectively (from 60 to 100 °C at 95 w/w%), while at lower moisture content the rate of the ascorbic acid degradation decreased with factor 3.5 and the rate of the PCA formation increased with factor 3.5 (both from 95 down to 5 w/w% at 90 °C). Finally, by implementation of the kinetic models in a process model it was estimated that 25% of ascorbic acid degrades during cocurrent drying while after countercurrent drying only 21% degrades. Similarly, during cocurrent drying 0.021 mmol/g FT PCA is formed, which is more than during countercurrent drying (0.008 mmol/g FT). This approach yields interesting insight on the effect of processing on presence of ascorbic acid and PCA and thus offers opportunities for process optimization.

1. Introduction

The main purpose of thermal processing and drying in the food industry is preservation. During thermal treatment, microbial and enzymatic activities are reduced, while drying aims at reduction of the water activity preventing microbial growth and occurrence of undesired chemical reactions during storage. In addition, dried products have reduced volume and are easier to handle during storage and transportation. However, during processing various physical and chemical reactions may occur that negatively affect the product quality including for example decline of the nutritional properties, aroma loss, as well as changes in taste and colour (Qiu et al., 2015). The impact of processing on product quality can be minimized by optimization of the process conditions, for example by a short time - high temperature heat treatment. Minimally processed foods are perceived more fresh by consumers while having extended shelf-life (Krebbers et al., 2003).

The focus in this study is the thermal processing and drying of (concentrated) tomato juice. Tomato (*Lycopersicum esculentum*) is amongst the most popular fruits globally (Akanbi, Adeyemi, & Ojo, 2006). Tomato is considered a useful source of fibres, proteins, minerals, vitamins, lycopene, and antioxidants and thus fits in a healthy diet (Gahler, Otto, & Böhm, 2003; Shi & Maguer, 2000). Tomatoes are consumed fresh and incorporated in processed foods, such as juice, puree, sauce, canned varieties and dried products (Toor & Savage, 2005). Annually, over 40 million tons of tomatoes are processed world-wide into a large variety of foods (Valerio, Lovelli, Perniola, Di Tommaso, & Ziska, 2013).

As discussed above it is desired that the processing of tomato should have minimum effect on the perceived freshness and nutritional properties of the final product. Numerous studies reported the impact of processing on tomato quality specifically in terms of nutritional quality decline and colour retention. Only a few

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studies focused on retention of non-volatile taste characteristics, such as sour taste. The sour taste of tomato is an important organoleptic quality attribute connected to the perceived freshness and is related to the presence of specific organic acids (Anthon, LeStrange, & Barrett, 2011; Petro-Turza, 1986; Thakur, Singh, & Nelson, 1996). Organic acids comprise over 0.15 kg/kg dry weight of tomatoes. The most abundantly present organic acids in tomatoes are citric, malic, and ascorbic acid (Marconi, Floridi, & Montanari, 2007; Petro-Turza, 1986). Specifically, ascorbic acid, also known as vitamin C, is well known for its sensitivity towards heat and presence of oxygen and thus degrades during processing and storage (Dewanto, Wu, Adom, & Liu, 2002; Jacob, Periago, Böhm, & Berruezo, 2008).

During thermal processing some organic acids are formed as well, which results in an overall increase of the total amount of organic acid. An important organic acid with large influence on the taste of tomato products is 5-oxopyrrolidine-2-carboxylic acid, or pyroglutamic acid (PCA). PCA is the degradation product of glutamine or glutamic acid (Chelius et al., 2006; Marconi et al., 2007; Schoenemann & Lopez, 1973). The formation route of PCA in tomato juice can be catalysed both enzymatically and non-enzymatically. The enzymatic reaction is facilitated by γ-glutamylcysteine synthetase (γ-GCS) and Glutamate-5-Kinase (G5K), with optimum reaction conditions of 35 °C at pH 7.9 and 83 °C at pH 6.0, respectively (Grill, Löffler, Winnacker, & Zenk, 1989; Krishna & Leisinger, 1979; Kumar & Bachhawat, 2012; Pérez-Arellano, Carmona-Álvarez, Martínez, Rodríguez-Díaz, & Cervera, 2010). The non-enzymatic reaction is catalysed by weak acids and is enhanced at elevated temperatures (Fig. 1) (Beck et al., 2001; Mena, Baab, Zielke, Huang, & Zielke, 2005). Formation of PCA contributes to the perceived loss of freshness and gives the product a bitter and undesirable sour taste, and leads to the off-flavour of processed tomato (Petro-Turza, 1986; Thakur et al., 1996). Quantitative understanding of the changing levels of citric acid, malic acid, ascorbic acid and PCA in tomato products could provide better control to retain taste during processing.

In the present study, we investigated the kinetic modelling of ascorbic acid degradation and PCA formation. The developed models can be applied to optimize heating and drying processes of tomato juice. In most previous studies the degradation of ascorbic acid and the formation of PCA were studied as a function of the temperature only (Arii, Kobayashi, Kai, & Kokuba, 1999; Tritsch & Moore, 1962; Uddin, Hawlader, & Zhou, 2001). Major challenge here is to extend the kinetic modelling to describe the combined effect of temperature and moisture content. The combined effect on the degradation of ascorbic acid were studied when storing the kiwifruits and air drying the fruit rosehip (Erenturk, Gulaboglu, & Gultekin, 2005; Uddin et al., 2001), but no studies on tomato processing were carried out. In terms of the PCA formation, no kinetic models considering the combined effect of temperature and moisture content have been proposed.

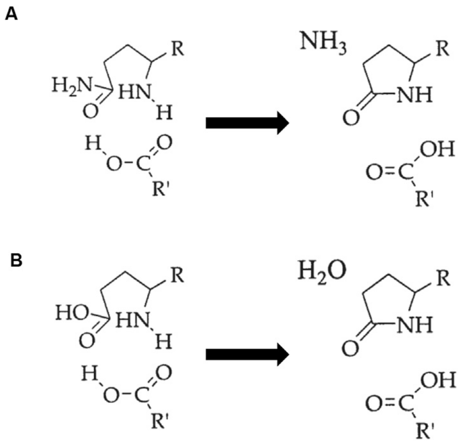

Fig. 1. Schematic conversion of (A) glutamine and (B) glutamic into pyroglutamic acid (PCA) catalysed by a weak acid (Beck et al., 2001).

Therefore, the objective of this study is twofold: (1) to experimentally assess the levels of citric acid, malic acid, ascorbic acid and PCA of tomato juice after thermal processing and drying; (2) to develop kinetic models that can predict ascorbic acid degradation and PCA formation considering the effect on both temperature and moisture content.

2. Mathematical models

2.1. Kinetic modelling

First order kinetics are applied to describe the ascorbic acid degradation (Uddin et al., 2001):

$$-dC/dt = kC \tag{1}$$

in which C is the concentration of the ascorbic acid, t is time and k is the reaction rate constant ($time^{-1}$).

Integration of Eq. (1) yields:

$$C_{AA,t}/C_{AA,0} = \exp(-k_{AA}t) \tag{2}$$

where $C_{AA,t}$ is the concentration of ascorbic acid after a specific time and $C_{AA,0}$ is the initial concentration of the ascorbic acid.

Glutamine and glutamic acid are converted into PCA during thermal processing of tomato as depicted in Fig. 1 (Chelius et al., 2006; Kumar & Bachhawat, 2012; Schoenemann & Lopez, 1973; Tritsch & Moore, 1962). This conversion reaction is also assumed to follow a first order reaction kinetics and the total concentration of glutamine and glutamic acid can then be described as follows as function of time (Arii et al., 1999):

$$C_{Glu,t} = C_{Glu,0} \times \exp(-k_{PCA} \times t) \tag{3}$$

Because PCA is the product of the conversion it can be described as:

$$C_{PCA,t} = C_{Glu,0} - C_{Glu,t} \tag{4}$$

Substitution of Eq. (4) into Eq. (3) yields the following expression:

$$C_{PCA,t} = C_{Glu,0} \times (1 - \exp(-k_{PCA} \times t)) \tag{5}$$

where $C_{PCA,t}$ and $C_{Glu,0}$ are the concentrations of PCA and the total initial concentration of glutamic acid and glutamine in tomato, respectively.

The temperature dependency of both reactions can be described with the following modified Arrhenius equation:

$$k = k_{ref} \times \exp\left[-E_a/R \times \left(1/T - 1\Big/T_{ref}\right)\right] \tag{6}$$

Where T is temperature, T_{ref} is a reference temperature, k_{ref} is the reaction rate constant at T_{ref}, E_a is the activation energy, and R is the ideal gas constant.

The dependency on moisture content is incorporated in this modelling approach by making the reaction rate coefficients (k_{ref} and E_a) moisture content dependent (Luyben, Liou, & Bruin, 1982). Perdana, Fox, Schutyser, and Boom (2012) investigated and