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Kinetic study of furan and furfural generation during baking of cake models

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ABSTRACT

This study describes the kinetics of furan and furfural generation in a cake model, for the first time. These process-induced compounds impact safety and sensory aspects of baked products. Understanding their generation with regards to process dynamics will serve food quality design. However, the complexity of real products makes this task challenging. This work provides a novel approach to understand and model chemical reactivity by implementing an inert cake model (starch, water and cellulose), specifically designed for mimicking a sponge cake structure. The addition of reaction precursors (glucose and leucine) to follow Maillard and caramelization reactions, resulted in browning and generated considerable levels of furanic compounds (up to 17.61 ng/g for furan and 38.99 μg/g for furfural, dry basis). Multiresponse data modeling resulted in a kinetic model which adequately describes experimental concentrations and makes it possible to estimate the degradation of precursors and the behavior of two hypothetic intermediates.

1. Introduction

Thermal processing of food is a dynamic process involving heat and mass transfer, thus leading to a number of physical and chemical changes. Baking is particularly interesting as high temperatures trigger reactions leading to the generation of numerous compounds. Many of them contribute to quality attributes such as color and flavor. Indeed, it has been shown that more than 540 volatile compounds can be formed during baking of cereal products (Cho & Peterson, 2010). Moreover, the generation of quality-related volatile compounds has been extensively studied in different bakery goods and the effect of processing conditions has also been investigated for some of them (Ait Ameur, Mathieu, Lalanne, Trystram, & Birlouez-Aragon, 2007; Fehaili, Courel, Rega, & Giampaoli, 2010; Petisca, Henriques, Pérez-Palacios, Pinho, & Ferreira, 2014; Pico, Bernal, & Gómez, 2015; Zoller, Sager, & Reinhard, 2007). Thermal reactivity, however, can lead not only to expected sensory characteristics, but also to the development of safety-related compounds. As a consequence, their mitigation is rapidly becoming a new challenge for food formulation and process engineering, since it has to be carried out without affecting the flavor profile of such products (Rannou, Laroque, Renault, Prost, & Sérot, 2016).

Among process-induced compounds, furanic compounds are of paramount interest. Furan has been classified as "possibly carcinogenic to humans" (Group 2B) by the International Agency for Research on Cancer (International Agency for Research Center on Cancer, 1995) and in recent years many studies found non-negligible furan levels in starchy and baked goods in a wide concentration range depending on the product (up to 200 ng/g) (Wegener & López-Sánchez, 2010; Zoller et al., 2007). This is mainly due to different formulation and processing conditions. On the other hand, furfural is known to be an odor-impacting compound in cereal products (Pico et al., 2015; Rega, Guerard, Delarue, Maire, & Giampaoli, 2009). In bakery products like cakes, breads and biscuits, furfural concentration also varies across a wide range of concentrations; however, it is usually found at higher levels than furan (Cepeda-Vázquez, Blumenthal, Camel, & Rega, 2017; Huault, Descharles, Rega, Bistac, & Giampaoli, 2016; Petisca et al., 2014).

The formation of these two compounds is closely linked as it can be due to mechanisms such as caramelization and Maillard reactions, occurring simultaneously during baking. Nevertheless, thermal degradation of certain amino acids (serine, alanine, aspartic acid, threonine, cysteine) and thermal oxidation of ascorbic acid and of polyunsaturated fatty acids can contribute to furan generation as well (Crews & Castle, 2007). Furfural is generated mainly by 1,2-enolisation pathway via 3-deoxyosone (Kroh, 1994; Nguyen, Fels-Klerx, Peters, & van Boekel, 2016; Rannou et al., 2016). On the other hand, Perez Locas and Yaylayan (2004) showed that furan

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is predominantly formed through the 2,3-enolisation pathway in a glucose and serine model. The degradation of hexoses, through direct enolization in the case of caramelization or enolization of Amadori compounds in the Maillard reaction, is the initial step. Reactivity studies may thus provide useful insight on such reaction pathways, in order to find meaningful optimization strategies towards furanic compounds occurrence.

Sponge cake is a good model to study the generation of these compounds as it contains all the precursors (sugars, proteins, amino acids, lipids) needed to trigger different pathways. It also has an alveolar structure that promotes uniform heat distribution throughout the product (Rega et al., 2009; Zhang et al., 2012). However, the complexity of the ingredients composition always makes it difficult to indicate the exact mechanism behind the generation and degradation of compounds in real products, due to the wide range of possible precursors and intermediates. This explains why the generation of reaction markers has been widely investigated in simpler liquid, semi-liquid and food models and mainly with respect to process and formula parameters (Ait Ameur et al., 2007; Blank, Devaud, Matthey-Doret, & Robert, 2003; Nie et al., 2013; Owczarek-Fendor et al., 2012; Mariotti-Celis, Zúñiga, Cortés, & Pedreschi, 2017). Nevertheless, findings in such simplified models cannot be directly extrapolated to understand the kinetics occurring in solid food, as they neglect the effect of the complex composition and structure of the food matrix. In fact, coupling reaction kinetics to reproducible thermal conditions is key to mapping the evolution of individual reactions during baking in a precise manner (Fehaili et al., 2010; Vleeschouwer, Plancken, Loey, & Hendrickx, 2009).

Hence, in order to fully comprehend the reaction schemes and their kinetics in solid food, there is a need for food models which can provide similar structures, in terms of reaction surfaces and transfers, as those of a real food. Bousquières, Bonazzi, and Michon (2017) recently developed a cake model having similar structural properties to those of a sponge cake but formulated with non-reactive ingredients.

To date, there are no studies focusing on the kinetics and modeling of furan generation during the processing of a solid food, due to the analytical challenges that furan analysis represents. Only recently Palmers et al. (2015) proposed a kinetic modeling of furan formation during storage of shelf-stable fruit juices, based on an empirical, logistic model. More recently, Kocadaglı and Gökmen (2016) described the formation and degradation of reaction markers in low moisture glucose/wheat flour systems by applying a multiresponse kinetic model for isomerization and degradation reactions of glucose. This approach seems promising to be further applied to furan generation studies in more structured food products.

The aim of this work is to perform a kinetic study of furan and furfural generation by means of a cake model containing glucose and leucine as precursors of caramelization and Maillard reactions. In this regard, the model's inertness towards producing any of the two compounds by itself was preliminarily assessed. An optimized analytical method for the simultaneous quantification of furan and furfural over a wide range of concentrations (Cepeda-Vázquez et al., 2017) was applied, in order to follow these furanic markers through the baking process under suitable conditions for kinetic modeling applications.

2. Material and methods

2.1. Reagents and ingredients

Furan-d4 (≥98%) and l-leucine (≥99%) were purchased from Sigma-Aldrich (St. Louis, MO). Furfural-d4 (≥99.7%) was obtained from CDN Isotopes (Pointe-Claire, Canada) and methanol (≥99.9%) was bought from Carlo Erba (Val de Reuil, France). Food grade hydroxypropylmethylcellulose (HPMC) and methylcellulose (MC) were purchased from Dow Chemical Company (Midland, MI), corn starch from Cargill (Wayzata, MN) and d-glucose monohydrate was kindly provided by Roquette Frères (France).

2.2. Cake model batter preparation

Reference cake models were produced according to an optimized method by Bousquières et al. (2017), using corn starch and a hydrocolloid mixture to obtain targeted rheological properties of the batter and thus reproduce the alveolar structure of a baked cake. HPMC and MC were mixed in adequate proportions (0.35% and 0.47%, respectively, see Table 1) and dispersed in hot distilled deionized water at 80 °C. The dispersion was refrigerated at 4 °C for 20 h for solvation and then battered for 10 min with a mixer (KitchenAid 5KSM150, Benton Harbor, MI) equipped with a vertical whisk at nominal speed 10. Starch was gradually added to the foam at speed 2 over 40 s, and the mixture was further blended for 2 min 20 s at the same speed. Two additional cake models were designed to study caramelization and Maillard reaction: model G containing glucose only, and model G + L containing both glucose and leucine (Table 1). In G and G + L formulas, glucose was added from the beginning to the HPMC and MC mixture and leucine was added with starch, for solubility and functional reasons. The amount of glucose was selected according to sugar content in a reference sponge cake, whereas leucine was chosen based on the content in free amino acids and total free amino groups measured in the same reference product (Bousquières et al., 2017; Fehaili et al., 2010) and considering that free amino acids are more reactive than proteins (Kearsley & Dziedzic, 1995).

2.3. Baking protocol

2.3.1. Baking conditions

For each cake model, seven aluminum molds (dimensions: 8 cm × 4.5 cm × 3.5 cm) were filled with 60 g of batter and baked at 170 °C at high ventilation speed (nominal conditions) in an oven specifically designed for uniform and reproducible baking and kinetic measurements (Fehaili et al., 2010). Whole cake models were sampled at different baking time intervals (4, 10, 25, 34, 60 and 90 min), stored immediately in air tight containers and kept at 20 °C. In order to evaluate the inertness of the reference cake model (R), one additional baking condition at 200 °C/34 min was tested.

2.3.2. Temperature and humidity measurements

For the nominal baking conditions, temperatures were measured at the bottom and at different points inside the model cake (4, 8, and 12 mm in height from the bottom) by means of an mold of similar dimensions, equipped with four thermocouples stretched and aligned in the center. Moreover, the temperature at the surface was measured by means of an Optris CT LT infrared

Table 1
Ingredient proportions in different model cakes.

Ingredients	Model R (g)	Model G (g)	Model G + L (g)
HPMC	0.35	0.47	0.47
MC	0.46	0.62	0.62
Leucine	–	–	5.00
Glucose	–	20.00	20.00
Corn starch	36.55	36.45	36.45
Water	62.64	62.46	62.46
Total Mix	100	120	125

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