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Acrylamide and 5-hydroxymethylfurfural formation during baking of biscuits: Part I: Effects of sugar type

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ABSTRACT

This study aimed to investigate the effects of sugar type on the reaction mechanism for formation of acrylamide and 5-hydroxymethylfurfural (HMF) during the baking of biscuits at 200 °C using multiresponse modelling. Four types of biscuits were prepared: (1) with sucrose, (2) with glucose and fructose, (3) with fructose only and (4) with glucose only. Experimental data showed that HMF concentration was highest in biscuits with glucose and fructose, whereas acrylamide concentration was highest in biscuits with glucose, also having the highest asparagine concentration. Proposed mechanistic models suggested that HMF is formed via caramelisation and that acrylamide formation follows the specific amino acid route, i.e., reducing sugars react with asparagine to form the Schiff base before decarboxylation, to generate acrylamide without the Amadori rearrangement product and sugar fragmentation. Study results contribute to understanding chemical reaction pathways in real food products.

1. Introduction

Sugar is one of the main ingredients in sweet bakery products. Under elevated baking temperatures, reducing sugars participate in caramelisation and in the Maillard reaction to generate the desired flavours and colours of food products. Along with the desired organoleptic properties of the bakery products, several compounds with possible mutagenic, carcinogenic and/or cytotoxic effects can be formed such as advanced glycation end products (AGEs), low-molecular mass browning products (<1 kDa), 5-hydroxymethylfufural (HMF) and acrylamide (Nursten, 2005). Acrylamide and HMF have received attention due to their common occurrence in heat treated bakery products such as bread and biscuits. According to a review by Capuano and Fogliano (2011), several studies demonstrated that acrylamide has neurotoxic effects in human and animals. It has been reported to be a reproductive toxicant, germ-cell mutagen and carcinogen to rodents (Shipp et al., 2006). Studies demonstrated that HMF may induce mutagenic and genotoxic effects in bacteria and human cells and promote colon and liver cancer in rats and mice (Glatt & Sommer, 2006; Monien, Engst, Barknowitz, Seidel, & Glatt, 2012). However, to date, there is no clear evidence concerning the carcinogenic and genotoxic effects of HMF in humans (Capuano & Fogliano, 2011).

At elevated temperatures, acrylamide is generated from the interaction between reducing sugars and asparagine (Mottram, Wedzicha, & Dodson, 2002; Stadler et al., 2002; Zyzak et al., 2003), and/or from reducing sugars and other amino acids that can produce acrylic acid, such as β-alanine, aspartic acid, carnosine, cysteine, and serine (Yaylayan, Locas, Wnorowski, & O'Brien, 2005). Given the presence of amino acids and reducing sugars in a food, the formation of acrylamide can follow either a generic amino acid route (Parker et al., 2012; Wedzicha, Mottram, Elmore, Koutsidis, & Dodson, 2005) or a specific amino acid route (only asparagine) (Parker et al., 2012; Stadler et al., 2002; Zyzak et al., 2003). A schematic overview of the pathway adapted from Parker et al. (2012) and Locas and Yaylayan (2008) is presented in Supplementary material (Fig. S1). The generic amino acid route involves a dicarbonyl intermediate. When a reducing sugar reacts with any amino group, a Schiff base is formed and re-arranges afterwards to give an Amadori product (in the case of an aldose) or a Heyns product (in the case of a ketose). These products dehydrate and fragment to form the highly reactive dicarbonyl compounds, deoxyosuloses and/or hydroxycarbonyl compounds. The dicarbonyl compounds then react with asparagine via Strecker degradation, leading to the generation of acrylamide. In the specific amino acid route, acrylamide is formed when reducing sugars react with asparagine to form the Schiff base that is thereafter decarboxylated to form

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acrylamide, without rearrangement of the Amadori products and fragmentation of sugar.

HMF can be formed from the caramelisation of sugars under thermal treatment and acidic catalysis. Sucrose can be decomposed to release a free glucose and a reactive intermediate, fructofuranosyl cation. This cation can quickly convert to HMF at temperatures above 250 °C and under dry pyrolytic conditions (Locas & Yaylayan, 2008). Studies have indicated that the formation of HMF from fructose has to undergo the generation of fructofuranosyl as a first step (Queneau, Jarosz, Lewandowski, & Fitremann, 2007; Román-Leshkov, Chheda, & Dumesic, 2006). Glucose and fructose can also generate HMF through the formation of a dicarbonyl intermediate, 3-deoxyglucosone (3-DG), from the Maillard reaction and caramelization (Degen, Hellwig, & Henle, 2012; Locas & Yaylayan, 2008). 3-DG is formed from fructose without the involvement of amino groups, whereas its formation from glucose needs an amino group (Kato, Hayase, Shin, Oimomi, & Baba, 1989).

The formation of acrylamide and HMF is dependent on the type and concentrations of sugars, amino acids, temperature, time, pH, water activity, leavening agents, antioxidants (such as extract of green tea (for acrylamide formation)), and $NaHSO_3$ and vitamin E content (Keramat, LeBail, Prost, & Jafari, 2011). Among these factors, sugars, amino acids, leavening agents, temperature and time are considered to be more important than the other factors mentioned. Ameur, Mathieu, Lalanne, Trystram, and Birlouez-Aragon (2007) found that during the baking of biscuits at temperatures below 250 °C, HMF accumulation in biscuits made from sucrose was less than in biscuits from fructose and glucose. Gökmen, Açar, Köksel, and Acar (2007) found that in baking biscuits at 205 °C, glucose had a more pronounced effect on the generation of acrylamide (by a factor of 2) and HMF than sucrose. The effect of reduced acrylamide formation using sucrose instead of reducing sugars (glucose and fructose) has been reported by others as well (Amrein, Schönbächler, Escher, & Amadò, 2004; Graf et al., 2006). However, these studies mainly reported on concentrations of the compounds, and their correlations, but did not provide any actual pathways leading to HMF and acrylamide formation in the studied products.

Several mechanistic models for the formation of acrylamide in model reaction systems, and a real food product (French fries), have been proposed using the multiresponse kinetic modelling approach (De Vleeschouwer, Plancken, Loey, & Hendrickx, 2008; De Vleeschouwer, Plancken, Van Loey, & Hendrickx, 2009; Knol, Linssen, & van Boekel, 2010; Parker et al., 2012; Wedzicha et al., 2005). Recently, a mechanistic model has also been proposed for the formation of both acrylamide and HMF in biscuits during baking (Van Der Fels-Klerx et al., 2014). However, the formation of the two compounds in this study was only modelled during the last 3 min of the baking process.

The aim of this study was to obtain more insights into the relative contribution of various types of sugars on the formation of acrylamide and HMF during the baking of biscuits, using multiresponse kinetic modelling. In this approach, all the measured concentration changes of reactants, intermediates and end-products are described quantitatively, so models can be tested rigorously and parametre estimation can be precise. Therefore, multiresponse kinetic modelling can help to unravel underlying reaction mechanisms.

2. Materials and methods

2.1. Chemicals

Solvents were obtained from Biosolve (Valkenswaard, the Netherlands). Standards for $^{2}D_3$-acrylamide, $^{15}N_2$-asparagine, hydroxymethylfurfural, fructose, glucose, sucrose, and acetonitrile were obtained from Sigma–Aldrich (St Louis, MO, USA). All chemicals used in this study were of analytical grade.

2.2. Composition and the baking of biscuits

Biscuits with different types of sugars were baked, and ingredients were provided by two suppliers. Wheat flour, refined palm oil, sucrose and glucose were provided by Kraft Europe. Leavening agents and fructose (food grade) were obtained from Sigma–Aldrich. The preparation and baking of the biscuits were carried out at the Dutch Bakery Center (NBC, Wageningen, The Netherlands). Biscuits were prepared using four different recipes, varying in types of sugar and their concentrations. Recipe 1 (R1) contained sucrose (35 g). Recipe 2 (R2) contained glucose (17.5 g) and fructose (17.5 g). Recipe 3 (R3) contained fructose (17.5 g). Recipe 4 (R4) contained glucose (17.5 g). The other ingredients were identical in all four recipes and included wheat flour (80 g), refined palm oil (32 g), tap water (17.6 g), $NaHCO_3$ (0.8 g) and NH_4HCO_3 (0.4 g). The biscuit recipe with sucrose (R1) was based on the AACC (American Association Cereal Chemists), and was also used by Van Der Fels-Klerx et al. (2014). The sugar concentrations in R2, R3 and R4 were selected based on results from a preliminary baking experiment.

Refined palm oil was mixed with the sugar and $NaHCO_3$ in a mixer in three subsequent steps of 1 min (total 3 min). After each mixing period, the mixture was peeled off from the mixer in order to mix well. After the third mixing step, NH_4HCO_3 dissolved in 17.6 g water was added and mixed in three subsequent steps of 20 s (total 1 min). After that, flour was added and mixed in three consecutive steps of 10 s (total 30 s). After each mixing step, the mixed dough was peeled off. Finally, the dough was allowed to rest for 30 min and then portioned as discs with a fixed diametre of 5 cm and a thickness of 3 mm. Biscuits were baked in separate but identical deck ovens, Columbus (Wachtel, Germany) at 200 °C for different durations. Biscuits from three recipes were baked simultaneously on a plate in one oven, with 6 biscuits per recipe (n = 18 biscuits). Biscuits of the three recipes were equally distributed over the plate such that from each recipe, two biscuits were in the middle and two were on each side of the plate. Every 2 min, at the so-called baking time point, one oven with 18 biscuits (3 recipes) was emptied. By using separate ovens it was ensured that the baking temperatures of biscuits collected at different baking intervals were not influenced by opening the oven. When the baking was finished, all biscuits were allowed to cool down for 30 min in a freezer at −20 °C. When frozen, they were packed in plastic bags and stored at −20 °C for one month prior to subsequent chemical analysis. Biscuits with glucose (R4) were prepared similarly but after one year. Biscuits from R4 were stored under the same conditions as the other biscuits. The wheat flour used for the preparation of biscuits R1, R2, and R3 had been stored at 4 °C before it was used for the preparation of biscuits R4.

Considerable variations in the measurements of compounds from the analytical duplicates in real foods are normally expected. Analytical results from the preliminary baking experiment showed marked variation. Having more data points from a replicated biscuit experiment cannot reduce this variation. Hence, a replicate baking experiment was not considered of added value to the current study and was therefore not performed.

2.3. Biscuit temperature determination

It was reported that acrylamide formation was concentrated in the surface of a crust-like model with a 10 mm thickness (Açar & Gökmen, 2009). The biscuit thickness of the current study was 3 mm. Therefore, the temperature gradient of the biscuit surface