Food Research International 49 (2012) 439–445

Contents lists available at SciVerse ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Effects of sugars in batter formula and baking conditions on 5-hydroxymethylfurfural and furfural formation in sponge cake models

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ARTICLE INFO

Article history:
Received 20 March 2012
Accepted 10 July 2012

Keywords:
5-Hydroxymethylfurfural
Furfural
Cake
Baking
Formation
Kinetics

ABSTRACT

5-Hydroxymethylfurfural (HMF) and furfural (F) could be formed in sugar-rich foods during baking. The effects of batter formula and baking conditions on the formation of HMF and F and the kinetics of HMF formation during baking were studied in 15 sponge cake models. A fixed amount of sucrose (40%) was included as minimum in sponge cake models to improve the batter consistency and texture of sponge cakes. The results showed that increase of the sugar and citric acid amount in the batter formula increased HMF and F formation during baking at 205 °C for 11 min. With increasing of the baking temperature and time, the concentrations of HMF and F were also increased in the sponge cake models, and the maximum concentrations of HMF and F attained were 4100 ± 11 mg kg^{-1} and 59 ± 1 mg kg^{-1}, respectively. Formation of HMF in the sponge cake models (Models 11–15) followed a first-order kinetics. By applying the Arrhenius equation, the activation energy (E_a) of sponge cake models was found to a span range between 15.4 kJ mol^{-1} and 25.8 kJ mol^{-1}. The results showed that sugar type, pH and baking temperature and time strongly affected HMF and F formation in sponge cake models.

1. Introduction

Bakery products, such as biscuit, cookie and cakes, constitute one of the most consumed foods in the world. Among them, cakes are particularly popular and associated in the consumer's mind with a delicious product. The major ingredients used in the preparation of sponge cakes are wheat flour, egg and sugar. Sugar not only imparts sweetness, but contributes to the fresh flavor quality of cakes during thermal processing and acts as a tenderizer by retarding and restricting gluten formation (Heenan, Dufour, Hamid, Harvey, & Delahunty, 2010). The cake batters in which the sucrose is replaced with different sugars result in cakes with different cake structure and cake volume (Ikawa, 1998).

Sponge cake batter is conventionally baked at high temperature (about 200 °C). Baking is a complex process in which chemical and physical changes take place simultaneously. During baking, the Maillard reaction and caramelization are responsible for the formation of desirable taste and color of baked products and furans, such as 5-hydroxymethylfurfural (HMF) and furfural (F) (Kroh, 1994). After hydrolysis of sucrose at high temperature, the sugar decomposes into furans by two possible pathways: caramelization and Maillard reaction (Ameur, Trystram, & Birlouez-Aragon, 2006). In caramelization, the reducing carbohydrates directly suffer 1,2-enolisation, dehydration and cyclization reactions (Kroh, 1994). In the Maillard reaction, the Amadori product is subjected to enolization and subsequent dehydration of the sugar moiety and the release of an intact amino acid (Hodge, 1953). The Maillard reaction is favored in foods with a high protein and carbohydrate content, intermediate moisture content, temperatures above 50 °C and a pH of 4–7, but the caramelization reaction needs more drastic conditions namely higher temperatures (>120 °C), pH and low water activity (Gökmen, Açar, Serpen, & Morales, 2008; Kroh, 1994). The formation of HMF and F is influenced by the concentrations and type of sugar and is favored by lower pH and low water activity (Ameur et al., 2006; Gökmen, Açar, Köksel, & Acar, 2007). In acidic medium, HMF and F are formed respectively by the decomposition of hexoses and pentoses during heating, after a slow enolization and a fast β-elimination of three water molecules (Belitz, Grosch, & Schieberle, 2009; Kroh, 1994; Pereira, Albuquerque, Ferreira, Cacho, & Marques, 2011). HMF and F have been evaluated as indicators of the quality of thermal processing in foods including fruit juices, biscuits, breakfast cereals and baby foods (Delgado-Andrade, Rufián-Henares, & Morales, 2009; Gökmen & Acar, 1999; Gökmen & Şenyuva, 2006; Rufián-Henares, Delgado-Andrade, & Morales, 2006). Along with the Maillard reaction and caramelization, the formation of HMF and F are particularly interesting because of their accumulation during the baking process.

HMF is not present in fresh, untreated foods, but it rapidly accumulates in sugar-rich foods during heating at high temperature (Ameur et al., 2006). The accumulation of HMF is considered undesirable in

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doi:10.1016/j.foodres.2012.07.012

thermally processed foods, and its presence in food is focused on some potential toxicological concern (Abraham et al., 2011). The toxicological relevance of HMF still remains unclear, and the subject of in vitro studies on genotoxicity and mutagenicity is still a matter of debate (Cuzzoni, Stoppini, Gazzani, & Mazza, 1988; Janzowski, Glaab, Samimi, Schlatter, & Eisenbrand, 2000; Surh & Tannenbaum, 1994). From a safety perspective and for food quality assurance, HMF legal limits were already issued for some foodstuffs, namely for concentrated rectified grape must: EC Regulation No. 1493/99 sets up a limit of 25 ppm (Abraham et al., 2011; Falcone, Tagliazucchi, Verzelloni, & Giudici, 2010).

The kinetic formation of HMF during heating has been studied in rice wine (Chen, Huang, Liu, Peng, & Huang, 2010), unifloral honey (Fallico, Zappalà, Arena, & Verzera, 2004) and cookie model system (Ameur, Mathieu, Lalanne, Trystram, & Birlouez-Aragon, 2007; Ameur et al., 2006), showing the influences of baking temperature, time and type of sugar. Ameur et al. (2007) reported that the accumulation of HMF followed a first-order kinetics, highly depending on the baking temperature and type of sugar, and sucrose-cookie produced less HMF than glucose-cookie or fructose-cookie at below 250 °C. However, less information is available for the effects of the type and concentration of sugars, pH and moisture content on the formation of HMF and F in sponge cakes.

The aim of this work was to investigate the effects of batter formula with different pH and concentrations of sugars (sucrose, glucose, fructose, lactose and maltose) and the baking process (temperature and time) on HMF and F formations in sponge cake model systems. Kinetic models for HMF formation in sponge cake models under the heating treatment were also determined. The changes of moisture content and pH of sponge cake models were studied to discuss their effect on HMF and F formation during baking.

2. Materials and methods

2.1. Materials

High purity (>99%) HMF (5-hydroxymethylfurfural) standard was purchased from Sigma-Aldrich (St. Louis, MO, USA). Wheat flour (8.5% protein; 12.7% moisture content; 0.5% ash; 0.2% soluble reducing sugar) was supplied by Damofang (Beijing Damofang Flour Co., Ltd, China). Fresh egg was purchased from local supermarkets. The sucrose, glucose, fructose, lactose, maltose, zinc sulfate and $K_4Fe(CN)_6$ (all AnalaR grade) were purchased from Beijing Chemical Works (China). Methanol (HPLC grade) was purchased from Fisher Scientific (Fair Lawn, New Jersey, USA). The ultra-pure water (18.25 mΩ) was prepared in a Millipore apparatus (Simplicity, Canada).

Carrez I solution was prepared by dissolving 15 g of potassium hexacyanoferrate in 100 mL of water, and Carrez II solution by dissolving 30 g of zinc sulfate in 100 mL of water (García-Villanova, Guerra-Hernández, Martínez-Gómez, & Montilla, 1993).

2.2. Preparation of sponge cakes

The sponge cake models were prepared according to a recipe described by Gómez, Ruiz, and Oliete (2011), and Matsakidou, Blekas, and Paraskevopoulou (2010), with some modifications, in order to study the effects of type and amount of sugar (Models 1–5), the effect of amount of citric acid (Models 6–10) and baking conditions (Models 11–15) on HMF and F formation. Sponge cakes were prepared by wheat flour, whole egg, sugar and citric acid, and the composition of models is represented in Table 1.

The ingredients were thoroughly mixed into a cake batter according to these models, and then baked in an oven (BEC-OVST 03, Baker's Kingdom Shanghai Co., Ltd., China). Whole egg and sugar were mixed with a whip at 90 rpm for 5 min with a kitchen mixer (HK-TU, Baker's Kingdom Shanghai Co., Ltd., China), and then at 150 rpm for 7 min until it became foamy and formed stiff peaks. Then flour was added and gently folded into the whipped batter in small increments using a plastic kitchen spatula. A portion of the batter (10.0 ± 1.0 g) was placed into an aluminum foil baking cup with a diameter of 3 cm and a height of 1 cm and then baked. Two cakes were produced from each cake model system.

Batters of Models 1–10 were baked at 205 °C for 11 min (Gökmen et al., 2007). Batters from Models 11–15 were baked at different temperatures and times (8, 10, 12, 15 and 20 min at 220 °C and 210 °C; 10, 12, 15, 20 and 25 min at 200 °C; 10, 12, 15, 20, 25 and 30 min at 190 °C; 10, 12, 15, 20, 25, 30 and 35 min at 180 °C).

Table 1
The composition of models used to prepare sponge cakes.

Model	Ingredients (%)[a]							
	Wheat flour	Egg	Sucrose	Glucose	Fructose	Lactose	Maltose	Citric acid
1	100	100	0–120[b]	0	0	0	0	0
2	100	100	40	0–80[c]	0	0	0	0
3	100	100	40	0	0–80[c]	0	0	0
4	100	100	40	0	0	0–80[c]	0	0
5	100	100	40	0	0	0	0–80[c]	0
6	100	100	120	0	0	0	0	0–6.0[d]
7	100	100	40	80	0	0	0	0–6.0[d]
8	100	100	40	0	80	0	0	0–6.0[d]
9	100	100	40	0	0	80	0	0–6.0[d]
10	100	100	40	0	0	0	8.0	0–6.0[d]
11	100	100	120	0	0	0	0	0
12	100	100	40	80	0	0	0	0
13	100	100	40	0	80	0	0	0
14	100	100	40	0	0	80	0	0
15	100	100	40	0	0	0	80	0

The initial moisture content of cake batter is 22.5 ± 0.4%.
With adding citric acid 0, 2.0, 4.0, or 6.0%, the pH of cake batter is 7.5 ± 0.3, 4.3 ± 0.5, 3.7 ± 0.5 and 3.4 ± 0.2, respectively.
[a] Baker's percentages.
[b] 0, 40, 60, 80, 100, or 120%.
[c] 0, 20, 40, 60, or 80%.
[d] 0, 2.0, 4.0, or 6.0%.

2.3. Measurement of pH

A ground sample (0.4 g) of cake was mixed with 20 mL of water and vortexed for 3 min. The mixture was held at ambient temperature for 1 h to separate solid and liquid phases. The pH of the supernatant was measured using a Thermo Orion 868 pH meter (Thermo Fisher Scientific, Inc., Pittsburgh, PA).

2.4. Measurement of moisture

The moisture content of the cakes was measured using an electronic moisture analyzer (Sartorius Moisture Analyzer 150, Germany). The mean of two measurements was reported.

2.5. HMF and F measurements

HMF and F were measured using the method of Gökmen and Şenyuva (2006) and Gökmen et al. (2008) with some modifications. Sponge cake samples were ground and stored at −18 °C prior to analysis. A fraction sponge cake sample (1 g) was weighed into a 20 mL centrifuge tube with a cap. A total of 250 μL of Carrez I and 250 μL of Carrez II solutions were added, and the volume was completed to 10 mL with deionized water. The centrifuge tube was then shaken vigorously for 3 min, and centrifuged for 10 min at 10,000 × g, at 4 °C. The solution was filtered through a 0.45 μm disk filter, and stored at −18 °C until analysis. All the experiments were carried out in duplicate.

A Shimadzu model HPLC system (Shimadzu Corp., Kyoto, Japan) was employed for the HMF and F analysis. The chromatography