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ABSTRACT

This work highlights the importance of considering reactivity into the quality-driven design of heat-treated foods, which should cover the mitigation of process-induced contaminants and the improvement of the sensory properties of the foodstuff. The joint effects of formulation and baking conditions on reactivity and several quality aspects (i.e. volatile generation, physical properties, sensory and consumer tests), followed by product optimization (i.e. consumer liking and furan mitigation) were studied. While key markers are affected by all factors and their interactions, the effect of sugar and whole egg are the clearest. Furan would be predominantly generated from glucose via caramelization and/or Maillard reaction, whereas the formation of Strecker aldehydes and lipid oxidation products would be favoured by precursors in whole egg. Formulations with a low glucose content, baked at low temperatures/short times lead to optimal products. Egg-based ingredient content may be set according to preference or by applying different optimization approaches.

KEYWORDS

formulation, process conditions, heat-treated food, furfural, browning reactions, sensory evaluation, multivariate analysis, optimization

1. Introduction

Among common foodstuffs, thermally-treated products, such as baked goods, are widely consumed by population and are particularly important both from food safety and quality standpoints. During heat processing, food components and minor constituents may undergo different chemical pathways such as non-enzymatic browning and lipid oxidation, leading to a wide number of compounds. Some may impact aroma or colour, while others may be of health concern. Furan, in particular, has been widely addressed among process-induced toxicants in recent years, and is a current public health concern due to its possible carcinogenicity (European Food Safety Authority (EFSA), 2017; International Agency for Research on Cancer, 1995; Joint FAO/WHO Expert Committee on Food Additives, 2011). Its occurrence has been documented in a large number of foods including bakery products (Crews & Castle, 2007; Wegener & López-Sánchez, 2010; Zoller, Sager, & Reinhard, 2007). Even though strategies have been reported for its mitigation (Anese, Manzocco, Calligaris, & Nicoli, 2013; Rannou, Laroque, Renault, Prost, & Sérot, 2016), it remains a challenge since this compound can be produced from different precursors via several reaction pathways (i.e. caramelization, Maillard reaction, lipid oxidation, thermal amino acid degradation) (Crews & Castle, 2007; Perez Locas & Yaylayan, 2004; Srivastava et al., 2018; Stadler, 2012).

Sensory properties of baked goods (e.g. biscuits, cookies, bread) have been studied together with one or more additional aspects of quality (e.g. physical, chemical, nutritional) (Adebiyi, Obadina, Adebo, & Kayitesi, 2017; Gupta, Bawa, & Abu-Ghannam, 2011; Martins et al., 2015; Mudgil, Barak, & Khatkar, 2016; Poinot et al., 2008), but few research works consider them along with food safety. Indeed, only a handful of studies have been performed on furan mitigation along with sensory evaluation, namely in pasta (Manzocco et al., 2014), meat sauces and biscuits (Anese, Bot, & Suman, 2014). Moreover, to the best of our knowledge, only one piece of work has been done on furan mitigation and consumer testing, specifically in tomato juice (Bahçeci, Akıllıoğlu, & Gökmen, 2015). Needless to say, although quality driven design of bakery products has been carried out in several works (Demirekler, Sumnu, & Sahin, 2004; Hadiyanto, Esveld, Boom, van Straten, & van Boxtel, 2008; Purlis, 2014), these have mainly focused on colour and texture-related measurements as quality criteria, overlooking other important aspects, such as the occurrence of safety-related compounds, sensory properties, consumer acceptability, and the role that reactivity plays in these.

Clearly, there is a current need for developing mitigation strategies for furan in baked goods and heat-treated foods in general, while considering their sensory quality. Sponge cake is a suitable foodstuff for studying the relationship between reactivity and quality and further develop optimization strategies. Indeed, its complex chemical composition and structure resulting from diverse ingredients (i.e. sugar, egg, fat, flour, salt), which may undergo several reaction pathways during thermal treatment, make it an interesting product to study. In fact, it contains furan at the ppb level (Cepeda-Vázquez, Blumenthal, Camel, & Rega, 2017) and a number of aroma compounds typically found in bakery products (Cepeda-Vázquez, Rega, Descharles, & Camel, 2018; Maire, Rega, Cuvelier, Soto, & Giampaoli, 2013; Pozo-Bayón, Ruíz-Rodríguez, Pernin, & Cayot, 2007; Rega, Guerard, Delarue, Maire, & Giampaoli, 2009).

This paper deals with the effects of both formulation and baking conditions on sponge cake reactivity and quality and its further optimization. A holistic approach covering several aspects, including volatile generation, physical and physicochemical properties, sensory characteristics and consumer liking, is used for understanding the underlying phenomena, while a quality optimization strategy based on furan mitigation and liking is presented. This is achieved through experimental design for effectively studying the relationship between each factor and each of the variables (linear, quadratic) and interactions among factors themselves. The paper finally discusses whether optimization criteria are conflicting or not and hence, whether a trade-off must be considered.

2. Materials and methods

2.1. General

An experimental design considering both sponge cake formulation (sucrose, glucose, whole egg and egg white content) and baking conditions (time and temperature) was first carried out. Several responses were then acquired through four blocks of variables, namely: volatile compound analysis, physical and physicochemical measurements, sensory evaluation and consumer tests. All responses were used for studying the effect of formulation and baking conditions on sponge cake quality and gaining insight into its relationship with reactivity. Furan content and consumer liking were in particular used for optimizing sponge cake, both from a food safety and sensory quality point of view.

Sponge cakes studied here are slim in order to induce crust formation and enhance reaction pathways, making it possible to obtain a large variety of products having different properties (e.g. chemical, sensory).

2.2. Chemicals and standards

Furan (purity: 99%), furfural (purity: 99%), 2-methylbutanal (purity: 95%), 2,5-dimethylpyrazine (purity: 99.9%), benzaldehyde (purity: 99%), hexanal (purity: 98%), 2-

pentylfuran (purity: 97%), 1-hydroxy-2-propanone (purity: 90%) and d4-furan (purity: 98%) were supplied by Sigma-Aldrich. 3-Methylbutanal (purity: 98%) was obtained from Merck, 2,3,5-trimethylpyrazine was supplied by Acros (purity: 99%) and d4-furfural (purity: 99.7%) was obtained from CIL Cluzeau, CDN Isotopes (Pointe-Claire, Canada). Methanol (purity: 99.9%) was purchased from Carlo Erba (Val-de-Reuil, France). Ultrapure water (> 5 MΩ.cm) was produced using a Millipore Elix 3 System from Millipore SAS (Molsheim, France).

2.3. Ingredients

Flour was kindly provided by Grands Moulins de Paris (Ivry-sur-Seine, France). Caster sucrose was obtained from Tereos (Lille, France) and glucose (dextrose monohydrate) was kindly provided by Roquette Frères (Lestrem, France). Pasteurized whole egg and egg white were supplied by Agrodoubs (Flagey, France) and Ovoteam (Massy, France). Non-hydrogenated palm oil was obtained from Palva Celys (Rezé, France). NaCl was supplied by Salinor (Clichy, France). Sucrose, glucose and salt were stored at room temperature; flour, whole egg, egg white and palm oil were stored at -20°C. Flour, whole egg and egg white were thawed at 4°C and palm oil in a water bath at 50°C prior to use.

2.4. Sponge cake preparation

Sponge cakes were formulated in line with Cepeda-Vázquez et al., (2018) and according to the experimental design, using the following recipe: 125 g of flour, 125 g of sugar, 225 g of egg-based ingredient, 20 g of non-hydrogenated palm oil and 5 g of NaCl, where sugar refers to sucrose and/or glucose and egg-based ingredient to whole egg and/or egg white.

2.4.1. Batter preparation

Sponge cake batter (500 g) was prepared according to Cepeda-Vázquez et al., (2017) by mixing and beating the egg-based ingredient (whole egg and/or egg white), the sugar (sucrose and/or glucose) and salt using a kitchen appliance (Kenwood Chef, KM300, UK) for 10 min at maximum speed. Flour was gently added during 1.5 min at minimum speed and the whole was further beaten for 0.5 min. Palm oil was gently added during 15 s at minimum speed and the batter beaten for 1 min at the same speed. Formulations containing egg white-only were further battered for 120 s for proper incorporation.

2.4.2. Baking trials

Aliquots of 20 g of batter were poured into 21 aluminium molds (8.0 cm x 4.5 cm x 3.5 cm) and baked in an instrumented oven (Bongard, Wolfisheim, France), specifically designed to ensure thermal homogeneity (Fehaili, Courel, Rega, & Giampaoli, 2010). Baking temperature and time were set according to the design of experiments (DOE): 155-185°C for 15-25 min.

Resulting sponge cakes, of about 1.8 cm high, were sampled and stored according to the analysis for which they were bound. One sponge cake was sampled for colour measurements, while four were used for other instrumental analyses. These were put into hermetically sealed glass jars immediately after baking and then frozen at -20°C for further composite sampling (see 2.5). The remaining cakes, bound for sensory and consumer tests, were cut into bite-sized rectangular pieces of approximately 4.0 cm x 2.25 cm containing both crust and crumb, put into re-sealable zipper storage plastic bags, cooled at room temperature, sealed and then frozen at -20°C.

2.5. Composite sampling

For each row of the experimental design, four frozen sponge cakes were ground by means of a Grindomix GM200 knife mill, equipped with a stainless steel bowl and titan knifes (Retsch GmbH, Haan, Germany). Each batch was ground using the following conditions: 3,000 rpm for 10 s, then 6,000 rpm for up to 20 s. Composite samples were immediately put into hermetically sealed glass jars and stored at -20°C until analysis (adapted from Cepeda-Vázquez et al., (2017)).

2.6. Physical and physicochemical properties

Dry matter and pH determination were carried out as in previous studies (Cepeda-Vázquez et al., 2018). Colour measurement was performed on the upper face of a whole cake at 3 points by using a 6834 spectro-guide sphere gloss colorimeter (BYK-Gardner, Germany) and expressed in the CIELab colour space (adapted from Cepeda-Vázquez et al., (2018); Poinot et al., (2008)).

2.7. HS trap / GC-MS procedure

Several volatile compounds were studied according to Cepeda-Vázquez et al., (2018). While furan and furfural were defined as relevant furanic quality markers for safety and aroma, respectively, additional aroma compounds commonly found in baked goods were also considered. These compounds are representative of different classes (furans, aldehydes, pyrazines, etc.) and reaction pathways (mainly caramelization, Maillard reaction, lipid oxidation and Strecker degradation).

Quantitative analysis for furan and furfural and semi-quantitative analysis for additional key aroma markers (n=3) were performed simultaneously by means of a TurboMatrix Headspace Sampler HS 40 Trap (Perkin Elmer, Llantrisant, UK) equipped with an air monitoring trap containing a two-sorbent bed (Carbotrap and Carbosieve SIII, Perkin Elmer), and a Trace GC Ultra gas chromatography system coupled to an ISQ single quadrupole mass spectrometer (Thermo Scientific, Rodano, Italy) (Cepeda-Vázquez et al., 2017, 2018).

2.7.1. Standard solutions for furan and furfural quantification

Stock and standard solutions were prepared in a room at 18°C, while HS samples were prepared in a separate room to avoid any cross-contamination from the surrounding air. Stock solutions of d4-furan, d4-furfural, furan and furfural in methanol were prepared separately at a concentration of 2.5 g l^{-1}, put into hermetic amber glass bottles and stored at -20°C for up to one month. A standard solution of d4-furan at a concentration of 25 ng μl^{-1} was prepared daily by diluting the stock solution in ultrapure water. In order to adapt isotope concentration to different samples, six mixed standard solutions were prepared daily by diluting the standard solution of d4-furan and the stock solution of d4-furfural in ultrapure water (concentrations ranged from 0.03 to 4.1 ng μl^{-1} for d4-furan and from 1.2 to 735 ng μl^{-1} for d4-furfural). They were then kept at 4°C until use. All glassware was previously baked out at 55°C for at least 24 h to avoid any contamination prior to analysis (Cepeda-Vázquez et al., 2017).

2.7.2. HS sample preparation

During vial preparation, sponge cake composite samples were kept in an ice bath to avoid volatile loss. Aliquots of ground sponge cake (0.588 g, dry basis) and ultrapure water (9.412 g) were weighed into 20 ml vials for a 16 water / sample amount ratio (dry basis) and 10 g of total amount (water + sample amount, dry basis) (Cepeda-Vázquez et al., 2017). All amounts were exactly measured in mass. A volume of 40 µl of the corresponding d4-furan + d4-furfural standard solution was added according to the estimated furan and furfural concentration of each sample. Vials were capped with aluminium polytetrafluoroethylene coated silicone septa at each step of preparation and sealed immediately after labeled standards' addition to avoid loss of volatiles. Vials were then vortexed for 5 s at maximum speed. All HS vials were previously baked out in a muffle furnace at 350°C for at least 1 h to avoid any HS glassware contamination before analysis (Cepeda-Vázquez et al., 2017).

2.7.3. HS trap conditions

Conditions were set as previously described for the optimization of HS trap joint extraction of furan and furfural (Cepeda-Vázquez et al., 2017).

2.7.4. GC-MS analysis

GC-MS was adapted from Cepeda-Vázquez et al., (2018). A 100% polyethylene glycol column (ZB-WAX) was used for separation (60 m x 0.25 mm x 0.5 µm; Zebron, USA). Helium was used as carrier gas at a constant flow rate of 1.2 ml min^{-1}. Injection was done in split mode (split ratio of 1:8). The GC oven was programmed as follows: initial temperature 40°C (held for 4 min), then raised at 10°C min^{-1} until 150°C and then raised at 20°C min^{-1} until reaching a final temperature of 240°C (held for 8 min). MS transfer line and ion source temperatures were set to 230°C and 200°C, respectively. The ionization mode was electron impact (EI), 70 eV. Data acquisition was done in nine segments, including a full scan mode from 25 to 150 m/z at 0.2 s per scan and the corresponding selected ion monitoring (SIM) mode with a dwell time of 0.1 s each, except for furfural and d4-furfural 0.05 s each (furan, m/z 39, *68*; d4-furan, m/z 42, *72*; 2-methylbutanal, m/z 41, 44, *57*; 3-methylbutanal 41, *44*, 57; hexanal, m/z 44, *56*; 2-penylfuran, m/z *81*, 138; 1-hydroxy-2-propanone, m/z *43*, 74; 2,5-dimethylpyrazine, m/z 42, *108*; 2,6-dimethylpyrazine, m/z 42, *108*; 2,3,5-trimethylpyrazine, m/z 42, *122*; furfural, m/z 39, 95, *96*; d4-furfural, m/z 42, 98, *100*; benzaldehyde, m/z 77, *106* [quantifier ions in italics]). Chromatographic peak areas for each compound were calculated by extracting the quantifier ions from the SIM mode acquisition data using Quan Browser, Xcalibur 2.1.0 SP1, build 1160 (Thermo Fisher Scientific Inc., USA) and used both for quantitative and semi-quantitative analyses. Native molecules were confirmed by means of the Wiley 8 and NIST 08 mass spectra libraries, calculation of normal alkane retention index (RI) and comparison to NIST Chemistry WebBook SRD 69 (2017) indices, and analysis of pure standards (Cepeda-Vázquez et al., 2018).

The reported method performances for furan and furfural quantification are the following: repeatability (RSD: ≤ 3.3% for furan and ≤ 2.6% for furfural), intermediate precision (RSD: 4.0% for furan and 4.3% for furfural), linearity (R^2: 0.9957 for furan and 0.9996 for furfural), limit of detection (LOD; furan: 0.50 ng g^{-1} sample, dry basis; furfural: 10.2 ng g^{-1} sample, dry basis), limit of quantification (LOQ; furan: 0.99 ng g^{-1} sample, dry basis; furfural: 41.1 ng g^{-1} sample, dry basis) (Cepeda-Vázquez et al., 2017). Experimental reproducibility, from batter preparation to HS trap analysis, has been reported as 6.4 and 6.8% for furan and furfural quantitation, respectively, and ranged from 6 to 15% for the semi-quantitative analysis of selected markers (Cepeda-Vázquez et al., 2018).

2.8. Sensory description

Bite-sized frozen samples were thawed at room temperature 30 min prior to descriptive analysis by 5 panelists well aware of sensory descriptive methodologies (3 females, 2 males) for sensory description. Term generation was first carried out individually in 2 sessions of about 30 min each, as follows: 9 products were randomly presented per session and panelists were free to generate descriptors into 7 categories, namely appearance, texture, odour, mouthfeel, taste, aroma and persistence; a blank category was also provided for additional terms. A total of 179 terms were collected. Semantic consensus was then achieved in a discussion session where panelists were presented with a full set of samples. Synonyms were identified and a total of 18 terms were selected as appropriate for evaluation; protocols were defined accordingly. Evaluation of 18 samples was then carried out in 2 sessions in individual cabins, where water and napkins were available for panelists. Samples were put into plastic cups labeled with a 3-digit code randomly assigned and presented monodically (one by one), according to a XLSTAT-generated serving order. Nine products were assessed per session using the 18 previously selected descriptors and a rating-based variant of the check-all-that-apply and flash profile techniques. Evaluating sessions took about 30 min each.

2.9. Consumer tests

Consumers who volunteered to take the tests were recruited at AgroParisTech (Massy Center) in France (n=50). Tests were carried out at the Sensory Perception and Sensometrics Laboratory in individual cabins. Verbal and written information about the study was provided to participants and consent was given orally.

Samples were thawed, prepared and labeled as for the sensory description; a full set of 18 samples was presented to consumers in one session, monodically following a XLSTAT-generated serving order. Consumers were asked to select the corresponding 3-digit code and indicate overall liking using the ISO 9-point hedonic scale (where 1 = "extremely dislike", 5 = "neither like nor dislike" and 9 = "extremely like") (ISO, 2003). Water and napkins were available at each cabin. Average time for hedonic tests was around 15 min per participant.

Approval from an ethical board was not considered necessary for this study since sponge cake is a common foodstuff. Additionally, the furan content of our samples remained at a low level overall when compared to other widely consumed food products, such as baby-food, bread, cereal snacks or coffee (Zoller et al., 2007).

2.10. Optimization procedure

The step-by-step procedure, from selection of factors to optimization, is briefly described below.

2.10.1. Selection of factors

Formulation and baking conditions were considered at once for studying reactivity and optimizing sponge cake quality. Previous studies showed that sugar and egg are the two most impacting categories of ingredients on key quality marker generation in sponge cake, including furan, furfural and other selected aroma markers (Cepeda-Vázquez et al., 2018). Hence, two variables related to recipe were selected: sucrose content (S, %, within sugar category) and whole egg content (E, %, within egg-based ingredient category). In other words, a mixed approach was considered within each of these variables, making it possible to study both sucrose and glucose, and also whole egg and egg white. Among process conditions, only baking variables were taken into account since these are likely the most important factors influencing the extent of reaction pathways leading to safety and quality-related compounds in baked goods (mainly through caramelization, Maillard reaction and lipid oxidation). Baking time (t) and temperature (T) were thus selected.

2.10.2. Optimal design of experiments

An optimal, tailor-made experimental plan consisting of 18 rows was designed to study and optimize sponge cake quality (Table 1). Response surface models were postulated including all quadratic and linear terms, as well as second order interactions.

The experimental plan was designed considering orthogonality among all factors, meaning that the effects of the formulation and baking variables could be differentiated from one another.

The following low (-1), middle (0) and high (+1) levels were selected for each factor: *S*, 0/50/100% (within sugar category); *E*, 0/50/100% (within egg-based ingredient category); *t*, 15/20/25 min; *T*, 155/170/185°C. Sucrose and whole egg levels were set according to previous formulation studies (Cepeda-Vázquez et al., 2018), while screening trials were carried out for setting time and temperature levels. In these, the extreme formulations were studied (i.e. glucose-based and also egg white-containing sponge cakes, which were reported to have the highest and lowest furanic compound content and darkest and lightest colour, respectively) (Cepeda-Vázquez et al., 2018). During such trials, batters were baked at 140, 170 and 200°C for 10, 15, 20, 25 and 30 min, yielding a wide range of samples. Sensory acceptability and analytical sensitivity were the criteria to narrow the baking boundaries for the experimental design. Unbaked and burnt products were left out since they were out of the acceptability range. Such unbaked cakes were also likely to be below the furan detection limit, based on the results by Cepeda-Vázquez et al., (2018).

2.10.3. Model fitting and multivariate optimization

Multiple linear regression (MLR) was performed by standard least squares (SLS) for each response (5% for type I error). For volatile compounds, responses were defined as logarithmic functions (ln) of furan content, furfural content and chromatographic peak areas for the additional aroma compounds to respect homoscedasticity hypothesis of MLR. Thirty-five models were obtained accordingly (11 on volatiles, 5 on physicochemical properties, 18 on sensory descriptors and 1 on consumer preference) in order to study the main effects and interactions.

A sponge cake optimization strategy was then generated by means of a prediction profiler based on the resulting models for mean consumer preference and furan content, using desirability functions. The model for furfural content was also added for illustrative purposes. Terms in the furan reduced model were considered into the joint profiler. Desirabilities were defined as the maximum value for liking, the minimum value for furan and none for furfural. As a result, single values for each factor were obtained by maximizing overall desirability.

2.11. Additional data treatment

To visualize and interpret our results, we performed a Principal Component Analysis (PCA) on mean values for each set of experiments (individually): for volatile compounds, physical and physicochemical properties, sensory data (correlation method), as well as for consumer data (covariance method) (Greenhoff & MacFie, 1999). Factors of the DOE were added as supplementary variables in all PCA to identify their potential linear links to volatile compound generation, sponge cake properties and consumer liking.

To identify the discriminating variables (i.e. the ones that enable us to differentiate the set of experiments), two-way ANOVA (Product, Panelist) was carried out on sensory data (one per descriptor). To identify the differences in terms of liking for the experiments, two-way ANOVA (Product, Consumer) was carried out on hedonic scores. Agglomerative Hierarchical Clustering (AHC) was also performed on consumer data (standardized by consumer - using Euclidean distance for dissimilarities and Ward's method for agglomeration) to identify potential clusters of consumers in terms of liking.

Formulation and baking experimental design, MLR and optimization by means of desirability functions were done in JMP 10.0.0 (SAS Institute Inc.). Sensory and consumer experimental set-up, ANOVA, AHC and PCA were carried out in XLSTAT 2014.5.04 (Addinsoft SARL).

3. Results and discussion

3.1. Furan and furfural content

Furan content was low in most samples and remained at a ng g^{-1} level, while that of furfural ranged from ng g^{-1} to µg g^{-1}. Interestingly, furan and furfural reduced models show that their contents are affected by sponge cake formulation, baking and their interactions in very similar ways (all linear terms, most quadratic effects and interactions, R^2: 0.965 for furan and 0.991 for furfural, P > F: < 0.0001 for both variables) (Table 2). This suggests that predominant pathways in furan generation are those common to furfural (i.e. caramelization and Maillard reaction) when coupling sponge cake formulation to baking conditions. This result confirms previous findings showing that changes in fat leading to mild lipid oxidation did not exert a significant effect on furan content (Cepeda-Vázquez et al., 2018). Differences in content levels do suggest however, that furfural's generation is favoured over that of furan regardless of the formulation or baking conditions. Similar results were observed when studying sponge cake formulation alone (Cepeda-Vázquez et al., 2018) and in a kinetic study in cake models specifically designed to follow furan and furfural's formation via caramelization and Maillard reaction (Srivastava et al., 2018). Overall, this suggests that furfural (less volatile and easier to analyze than furan), could indeed be a proper marker of furan generation in this type of product or reaction system.

3.2. Reactivity in sponge cake

Furan, furfural and selected key markers, as well as physical and physicochemical properties were considered for studying reactivity. According to the PCA on responses of all markers, principal components 1, 2 and 3 account for 95.8% of variability (Figure 1a and b).

Even though the DOE was built considering orthogonality among the effects under study, both loading plots depicting them as supplementary variables show that these are no longer orthogonal, meaning that interactions among some DOE factors do take place (Figure 1a and b). This was also confirmed by the corresponding response surface models, where not only the main effects but also several interactions were observed for all compounds ($R^2 \geq 0.911$ and $P > F$: < 0.0001 for all models). This clearly suggests that the generation of volatile compounds in sponge cake is due to formulation and baking conditions, as well as their interactions.

Moreover, in the PC1 vs PC2 plot, DOE factors follow two axes: sugar type is highly related to PC2 (25.2%), i.e. sucrose (+), glucose (-), while whole egg (+), time (+) and temperature (+) relate to PC1 (51.4%) to a minor extent. However, in the PC2 vs PC3 plot, whole egg appears to be anticorrelated to time and temperature, forming a new axis strongly related to PC3 (19.2%) (Figure 1a and b).

Furan, furfural and 1-hydroxy-2-propanone, all found in one cluster, contribute positively to PC1 and PC3 and negatively to PC2. This means that sugar, egg-based ingredients as well as baking time and temperature, all contribute to their formation, either directly or through their interactions. Pyrazines, all grouped into another cluster, would be predominantly affected by sugar (related to PC2) and by whole egg to a much lower extent, baking time or temperature (related to PC1 and PC3). More importantly, these clusters exhibit different behaviours when considering PC2 (highly related to sugar category): furan, furfural and 1-hydroxy-2-propanone correlate to glucose (-), while pyrazines correlate to sucrose (+) (Figure 1a and b). These important findings suggest that, when considering the nature of sugar, furan, furfural and 1-hydroxy-2-propanone are predominantly formed from glucose, a reducing sugar, either via caramelization or Maillard reaction, while pyrazines are majorly formed from sucrose, a non-reducing sugar, via hydrolysis and further Strecker degradation (often considered into the Maillard reaction pathway).

Other aroma compounds are found in a third cluster: hexanal, 2-pentylfuran and Strecker aldehydes (benzaldehyde, 3-methylbutanal, 2-methylbutanal) (Figure 1a and b). While 2-pentylfuran can be formed through lipid oxidation from polyunsaturated fatty acids (PUFAs) and also via the interaction of lipid oxidation products and amino groups (Adams, Bouckaert, Van Lancker, De Meulenaer, & De Kimpe, 2011; Belitz, Grosch, & Schieberle, 2009; Grein, Huffer, Scheller, & Schreier, 1993; Hidalgo, Gallardo, & Zamora, 2005; Perez Locas & Yaylayan, 2004; Whitfield, 1992), hexanal can only be formed via lipid oxidation. Hence, a high correlation between hexanal and Strecker aldehydes was initially unexpected, but their high correlation to whole egg (mostly related to PC3) might explain it. Indeed, whole egg is an important source of both PUFAs and free amino acids (U.S. Department of Agriculture (USDA), 2016), which are precursors of hexanal and Strecker aldehydes, respectively. As of 2-pentylfuran, previous studies on sponge cake formulation showed that it was somewhat correlated to hexanal and also to Strecker aldehydes (Cepeda-Vázquez et al., 2018). Hence, its correlation to them in this work, that is, when considering baking time and temperature in addition to formulation, is not surprising.

Another interesting result is the finding that Strecker aldehydes and pyrazines are not grouped into one cluster, although they both depend on free amino acids and sugar degradation products (dicarbonyls for Strecker aldehydes, and aminoketones or 1-hydroxy-2-propanone along with NH_3 and hexanal for pyrazines).

Physical and physicochemical properties are adequately represented in the PC1 and PC2 plot (PC1: 77.9%, PC2: 13.4%) (Figure 1c). Although DOE factors are less well represented in the same plot, again two axes are visible: the first relating to sucrose content and the second one partially to temperature and whole egg content to a much lower extent. Baking time appears to be correlated to both axes. Clearly, all properties are dependent on all formulation and baking variables, since they are not aligned to the axes. Overall, long baking times, high temperatures, and formulations with whole egg and glucose, that is more advanced thermal reactions, all relate to low lightness (L*) and pH values, as expected. These two properties are indeed the best indicators of browning progression according to modeling (R^2: 0.976 and 0.928, respectively, and P > F: <0.0001 for both variables).

3.3. Sponge cake sensory quality

Regarding sensory data, most descriptors were found useful for discriminating sponge cake samples, except for caramel odour (P > F for product: 0.151) and nut aroma, which was close to the set significance level (P > F for product: 0.055). All the discriminating sensory terms, along with nut aroma, were further analyzed by PCA.

Most descriptors are well represented in the PC1 vs PC2 plot, accounting for 73.0% of variability of sensory data (Figure 2). Interestingly, while some descriptors are scattered, two clusters are clearly visible (lower left and lower right) and differentiated by PC1. The first one groups variables related to “typical” descriptors for sponge cake, such as sponge cake and egg aroma and odour, as well as sweet taste. The second one includes descriptors related to “severe” thermal reactions, like caramel and burnt notes, colour, bitter taste and is opposite to spongy mouthfeel and sticky texture. The "typical" cluster is highly related to sucrose content, and to short time and low temperatures (or their interaction) to a minor extent, while the "severe" group is related to long baking time and high temperature (or their interaction), and to glucose to some extent. A very important finding is that whole egg is highly correlated to both “typical” and “severe” descriptors, since it is negatively correlated to PC2.

Firmness and crusty mouthfeel are both related to time and temperature, which is not surprising, but they also are to whole egg; chewy mouthfeel interestingly relates to glucose and egg white (Figure 2).

Concerning hedonic scores, AHC resulted in two clusters of 21 and 29 participants, respectively (supplementary figure A). According to ANOVA results, consumers in cluster 1 rank products higher (P > F: 0.001), yet clusters seem to have similar class profiles (supplementary figure B). PCA on liking also shows that consumers are mostly grouped into one cluster, both in the PC1 vs PC2 (59.2%) and PC1 vs PC3 plots (54.9%) (Figure 3a and b). Liking appears to be highly related to sucrose, opposite to baking time and temperature, and influenced by whole egg to a minor extent. A response surface model considering preference scores for all participants (n=50) confirms that all formulation and baking factors, as well as some interactions, impact liking (R^2: 0.987, P > F: < 0.0001). Sponge cakes with a high sucrose and whole egg content, baked during a short time at low temperature are preferred overall.

3.4. Linking reactivity and sponge cake quality

Results discussed in previous sections prove that formulation (sucrose, glucose, whole egg and egg white content) and baking conditions (time and temperature) do have an effect on the reaction pathways occurring in sponge cake and its quality. Furthermore, interactions among formulation and baking factors were identified and quantified. More importantly, these factors impact volatile generation, physical, physicochemical and sensory properties as well as liking differently, that is to say they interact in different ways. These findings underline the need of using a holistic approach by studying several factors and also several aspects of the product at once. In this regard, gaining further insight might be achieved by applying sensometric or chemometric tools to study the relationship between different blocks of variables or variables from different blocks, together or aside from factors. For instance, it would be interesting to determine how the selected aroma markers correlate to preference, how the latter is impacted by texture or to define how "typical" sponge cake or "severe" heat treatment descriptors, L* and pH relate to preference and furan content.

3.5. Optimizing sponge cake: liking and furan mitigation

Furan mitigation and consumer preference, here defined as food safety and sensory quality criteria, are both affected by formulation and baking factors as explained before. More importantly, they exhibit opposite behaviours in relation to most factors and furan content level remains low overall despite changes in these. Consequently, there is enough room for finding optimal sponge cakes with low furan content that fall within consumers' preference.

A set of optimal sponge cake formulation and baking conditions was found, considering both quality criteria simultaneously, based on desirability function maximization (Figure 4a). High sucrose content (with respect to glucose), low temperature and short baking time, all contribute to maximizing liking and minimizing furan, within the studied ranges. These quality criteria are however conflicting with respect to whole egg content, since they are both positively influenced by such factor. A trade-off would naturally be considered, as depicted in Figure 4a, yet the predicted furan content remains below LOD (0.50 ng g^{-1} sample, dry basis) along the boundaries of these factor, when keeping the rest of them at their optimal values. This means that amino acids and lipids in whole egg would not favour furan generation as much as sugar type, and that whole egg would do more for liking than for furan generation, when keeping the remaining variables at optimal values. As a result, increasing whole egg content for maximizing liking alone might as well be considered (Figure 4b).

Also, the fact that the optimal values are reached at the low boundaries for time and temperature suggests that there might be greater room for optimization if setting even lower values for these two variables. However, it must be noted that lower values could also lead to unbaked products reducing hedonic score and hence, a quadratic form might therefore be observed for these factors. Finally, prediction profiler depicts similar curves for furan and furfural for both optimization scenarios (Figure 4a and b), confirming that these compounds behave in similar ways.

4. Conclusions

Furan content and consumer liking, selected as food safety and sensory quality criteria for sponge cake optimization respectively, are influenced in opposite ways by most formulation and baking factors. Overall, high sucrose content (in relation to glucose), low temperature and short baking times yield sponge cakes with a minimal furan content and a maximal consumer liking score, while whole egg content may be set according to preference only, since furan level would remain around LOD levels. It must also be noted that other optimization strategies could be used instead, such as defining a threshold for furan content and/or preference, once regulations on furan content are defined, and depending on the criteria set for meeting consumer needs.

Regarding reactivity, several reaction pathways seem to occur when considering both formulation and baking conditions in sponge cake, according to the study of key markers. Furan, furfural and 1-hydroxy-2-propanone would be predominantly produced from glucose via caramelization and/or Maillard reaction, while pyrazines would be mainly generated from sucrose via sugar hydrolysis and further Strecker degradation. The latter, as well as lipid oxidation would also occur and be highly related to egg yolk (in whole egg). Moreover, furfural, whose analysis might be easier than that of furan, could indeed be a proper marker of furan generation in this type of products given their close relationship.

This work contributes to the development of quality-driven design strategies adapted for heat-treated food, based on safety and sensory criteria. It also advances the understanding of the link between reactivity and quality through a holistic approach. This strategy could also be broadened to other quality aspects (e.g. loss of nutritional value, antioxidant content, etc.) or easily applied to thermally-treated products with different properties (e.g. sensory, chemical composition, structure, dimensions, etc.). It could be further explored by applying sensometric or chemometric tools as well, for gaining further insight into how different quality aspects relate to each other (e.g. sensory description and consumer liking), or how variables from different aspects also relate (e.g. aroma markers from GC-MS analysis and aroma descriptors from sensory tests; furfural content and both colour measurements and as perceived by panelists, etc).

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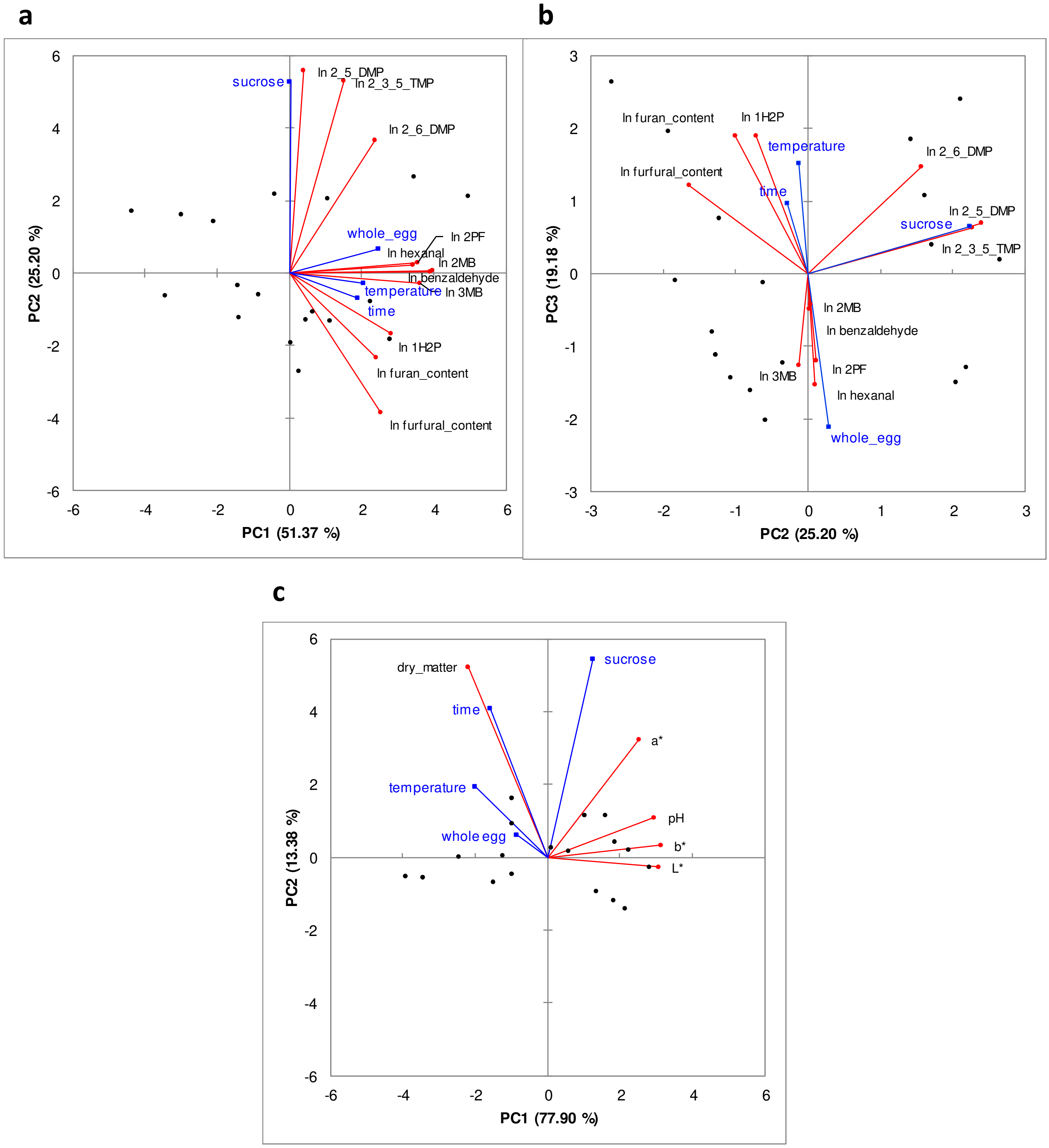


Figure 1 PCA biplots on selected volatile markers and physical-physicochemical properties.
ln: logarithmic functions; 2MB: 2-methylbutanal; 3MB: 3-methylbutanal; 2PF: 2-pentylfuran; 1H2P: 1-hydroxy-2-propanone; 2,5 DMP: 2,5-dimethylpyrazine; 2,6 DMP: 2,6-dimethylpyrazine; 2,3,5 TMP: 2,3,5-trimethylpyrazine; L*: lightness, a*: green (-) to red (+); b*: blue (-) to yellow (+); variables for PCA (•); supplementary variables (▪)

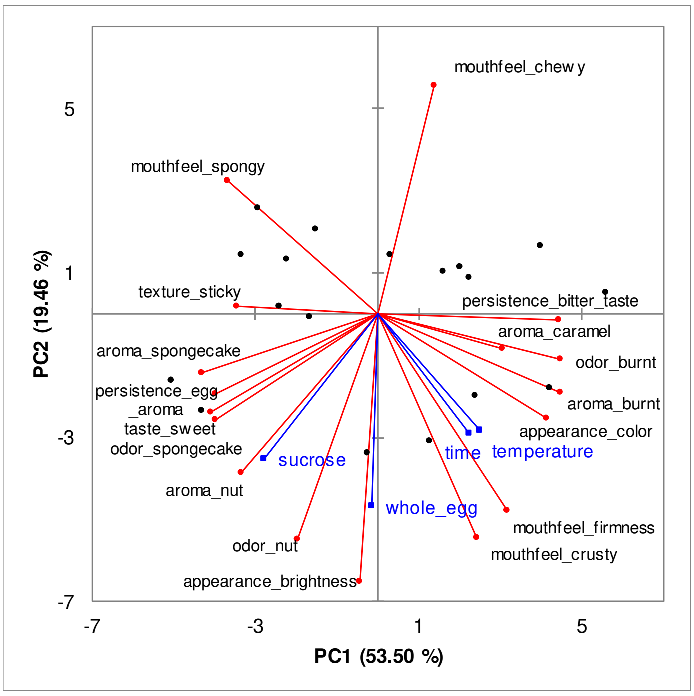
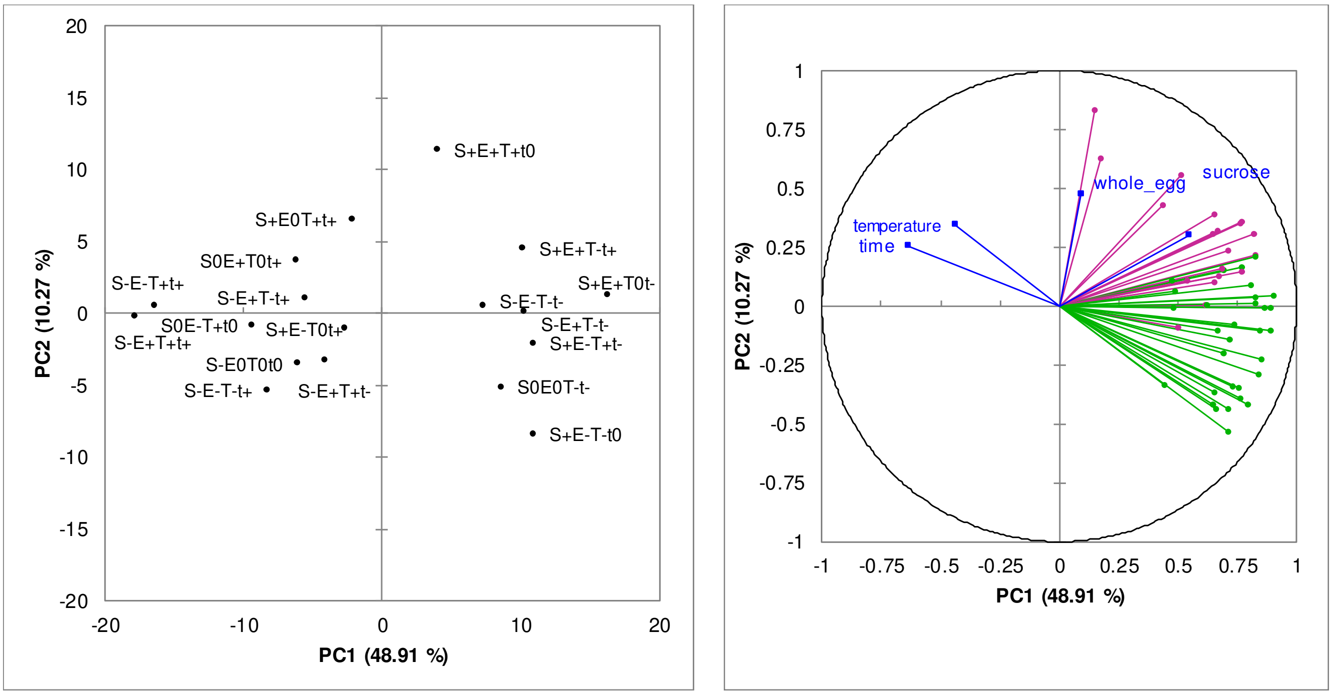


Figure 2 PCA biplot on sensory descriptors.
Variables for PCA (•); supplementary variables (▪)

a



b

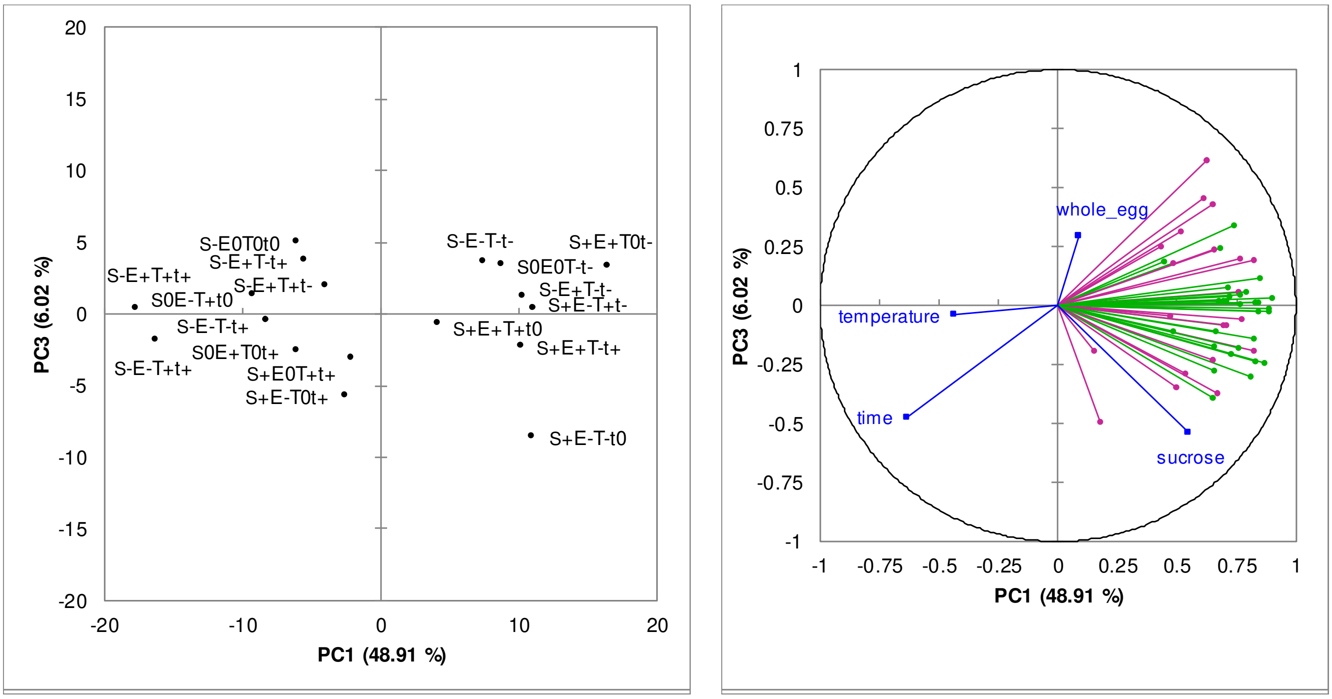


Figure 3 PCA score and loading plots on consumer liking.
S: sucrose, E: whole egg; T: baking temperature; t: baking time; low level (-); mid-level (0); high level (+); variables for PCA, cluster 1 (•); cluster 2 (•); supplementary variables (▪)

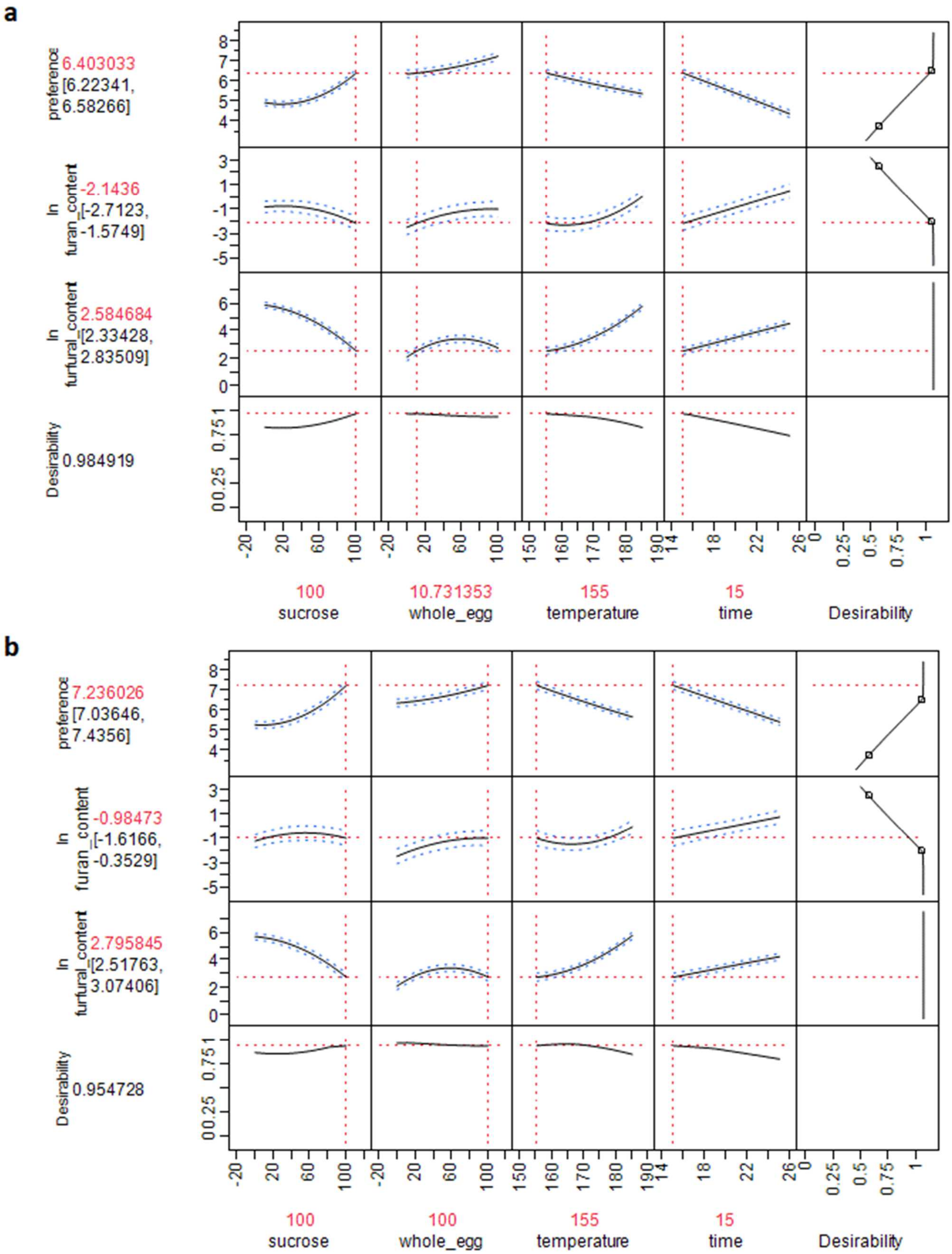


Figure 4 Prediction profilers with desirability functions.

Response surface models for preference, logarithmic functions (ln) of furan and furfural content, and desirability function according to factors; desirabilities are defined as the maximum value for preference, minimum value for furan content and none for furfural content; (a) set of optimal formulation and baking conditions; (b) set of optimal values for sucrose, temperature and time and maximal value for whole egg.

Table 1 Optimal response surface design on sponge cake formulation and process conditions

Run	Sucrose *S (%)* [a]	Whole egg *E (%)* [b]	Baking temperature *T (°C)*	Baking time *t (min)*
1	1	0	1	1
2	-1	1	1	-1
3	-1	1	-1	1
4	1	1	1	0
5	1	1	0	-1
6	1	-1	1	-1
7	-1	-1	-1	1
8	0	0	-1	-1
9	1	-1	0	1
10	1	1	-1	1
11	-1	-1	-1	-1
12	-1	0	0	0
13	1	-1	-1	0
14	-1	-1	1	1
15	-1	1	-1	-1
16	-1	1	1	1
17	0	1	0	1
18	0	-1	1	0

[a] within sugar category; [b] within egg-based ingredient category

Table 2 Furan and furfural content according to experimental design along with response surface models

	Run		*Furan*	*Furfural*		*Parameter estimate*	*Furan* [a]	*Furfural* [a]
content (ng g^{-1} sample, dry basis)	1		179.5 ± 31.1	12297.5 ± 669.3	**modeling**	*Intercept*	1.E+02	7.E+01
	2		1.7 ± 0.2	3107.4 ± 53.9		*sucrose*	6.E-02	-5.E-02
	3		1.7 ± 0.3	1634.1 ± 12.1		*whole_egg*	1.E-01	5.E-02
	4		4.0 ± 0.2	877.2 ± 26.1		*temperature*	-1.E+00	-8.E-01
	5		0.5 ± 0.0	53.3 ± 58.4		*time*	-9.E-01	-2.E-01
	6		0.6 ± 0.1	168.2 ± 31.5		*sucrose*sucrose*	-2.E-04	-3.E-04
	7		7.1 ± 1.6	1687.3 ± 72.1		*sucrose*whole_egg*	2.E-04	4.E-05
	8		0.4 ± 0.0	218.8 ± 96.3		*whole_egg*whole_egg*	-2.E-04	-4.E-04
	9		4.2 ± 0.5	272.9 ± 14.0		*sucrose*temperature*	-3.E-04	3.E-04
	10		2.4 ± 0.2	70.8 ± 6.5		*whole_egg*temperature*	-5.E-04	-
	11		0.4 ± 0.1	296.2 ± 16.0		*temperature*temperature*	4.E-03	3.E-03
	12		4.7 ± 0.4	3751.4 ± 185.8		*sucrose*time*	-	-
	13		0.4 ± 0.1	26.3 ± 3.3		*whole_egg*time*	-1.E-03	-6.E-04
	14		721.3 ± 43.0	43861.8 ± 1749.3		*temperature*time*	7.E-03	3.E-03
	15		0.3 ± 0.0	279.3 ± 19.8		*time*time*	-	-
	16		155.6 ± 4.3	25781.7 ± 958.4				
	17		4.8 ± 0.5	1606.8 ± 20.4				
	18		176.8 ± 16.7	8710.8 ± 215.6				

means and 95% confidence intervals (n=3)

[a] ln of content