Reaction Engineering for Sponge Cake Baking: Development of a Methodology to extract an Apparent Identifiable Reaction Scheme

S. Fehaili[1,2], B. Rega[1], M. Courel[2], P. Giampaoli[1], C. Brandam[3], X. Meyer[3], C. Bonazzi[2]

[1] UMR 1211 Sciences de l'Aliment et de l'Emballage, AgroParisTech,Cnam,INRA ,1, av. des Olympiades, F-91300 Massy.
[2] UMR 1145 Génie Industriel Alimentaire, AgroParisTech,Cemagref,INRA, 1 av. des Olympiades, F-91300 Massy
UMR 5503 Laboratoire de Génie Chimique, CNRS/UPS/INPT, 5 rue Paulin Talabot, F-31106 Toulouse, France

Abstract: The food properties often results from a set of complex chemical reactions initiated by technological treatments. The ultimate objective of this work is to develop rational operating strategies for foods in order to preserve the integrity of the nutritional compounds or to enhance the production of positive newly formed compounds. A "reaction engineering" approach will allow building robust and reliable knowledge on the mechanisms and on the reaction kinetics and then formalizing them into models to optimize the product/process system. The present paper describes the first stage of this approach. It consists in extracting an apparent identifiable reaction scheme on the basis of theoretical knowledge of the system and observable experimental data and on the use of statistical methods.

1. Introduction

The role of the Maillard reaction in building food quality has been a matter of interest for years. Despite abundant literature, few studies are dealing with the simultaneous effect of physical and chemical variables on the development of Maillard reaction products; in papers dealing with thermal treatment, the latter is merely considered as a mass and energy transfer operation and the link with the chemical variables is not approached [1]. One of the main objectives of this project is to understand how the processes act on reactions and can favour the appearance, disappearance or preservation of newly formed compounds during the baking of sponge cake. The reaction system can be described as a complex network of many chemical reactions. But only a small part of all the molecules synthesized by these reactions are observable. A major stake of this work will be to extract a simplified reaction pathway which can give a reliable representation of the complex reaction system based on observable compounds. It will be necessary to determine the reactions which really take place and to specify the occurrence of these reactions during the process. The theoretical knowledge of the system and the use of statistical methods should make it possible to extract an apparent reaction pathway from available experimental information. The methodological approach is as follows:

i) Selection of the key-reaction pathways related to previously defined organoleptic and nutritional qualities of the sponge cake and the links occurring between the different reaction pathways [2]. Three types of reactions will be focussed on: Maillard, lipid oxidation and caramelization reactions.
ii) Definition and selection of relevant chemical markers to follow the reactions pathways.
iii) Extraction of an apparent but identifiable reaction scheme regarding the observable components from the complete set of theoretical reactions by making as little assumptions as possible.
iv) Acquisition of experimental data taking into account the key-variables likely to influence the reaction.
v) Validation of the reaction scheme from experimental data.
vi) Development of a knowledge based model and selection of the right assumptions to be made: which physical phenomena have to be integrated in the unit operation model and which reactions are to be taken into account and with which kinetic model?

Only the first three points will be developed in this paper.

2. State of the art on the kinetics of Maillard reaction

The majority of the published work dealing with the kinetics of the Maillard reaction rely on simple kinetic models to describe either loss of reactants (sugars, amino acids, amino acid residues in proteins) or formation of products (Amadori, HMF...). On the use of this approach, van Boekel concluded that the results are very much dependent on experimental conditions and on the extent of the reaction [3]. To better understand reaction mechanisms, an advanced approach is necessary, considering reaction pathways in more detail. Kinetic modelling using multiresponse models has proven to be a useful tool to enable further unravelling of reaction mechanisms in the Maillard reaction [4, 5]. A first proposed reaction mechanism is tested by the multiresponse analysis where the degradation of the reactants is analysed simultaneously with the formation of the intermediates [6]. It is a very interesting approach which makes it possible to identify the mechanisms of formation/disappearance of the compounds. The multiresponse approach has already been validated for acrylamide formation in model solutions of glucose and asparagines [7] and on Maillard reaction in milk [8]. However, this method is not easily applicable in a real food system like sponge cake: first, it is a complex formulated solid where reaction compounds do not react in the same way as in a simple model solution; second, only a small part of all the molecules that can be synthesized by thermal reactions are observable and it would be almost impossible to identify the whole reaction scheme.

3. Selection of key reaction pathways

The early Maillard reaction consists of the non-enzymatic formation of a covalent bond between the carbonyl group (sugar) and the free amine group ($R\text{-}NH_2$). The occurring chemical reactions can be broadly divided into three main stages: (i) the early stage, consisting of the formation of the Amadori product; (ii) the advanced stage, comprising degradation of the Amadori product, and (iii) the final stage, typified by the production of brown polymers and co-polymers, the melanoidins. The degradation of the Amadori product depends on the pH of the system. At pH 7 or below, it mainly undergoes 1,2-enolisation with the formation of 3-deoxyosones. At pH above 7 the degradation of the Amadori compound is thought to involve mainly 2,3 enolisation, where 1-deoxyosones are formed. The key intermediate compounds of this reaction are the α-dicarbonyl (3-deoxyosones and 1-deoxyosones) which are also formed by the caramelization reaction [9]. Thus, the compounds derived from the degradation of the 1- and 3-deoxyosones are indistinctly generated either by the caramelization or by the Maillard reaction (Fig.1).

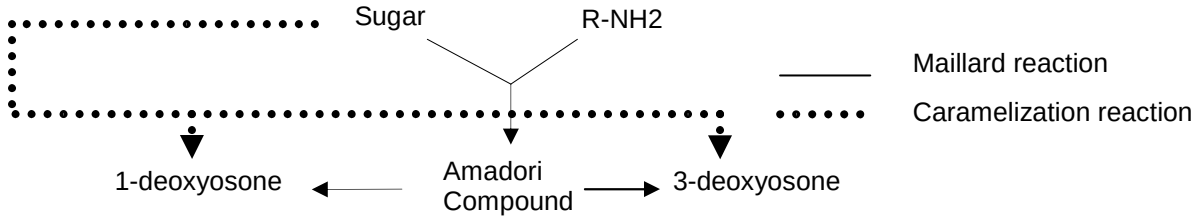

Fig.1: Interaction between Maillard and caramelization reactions

3.1 Compounds derived from the degradation of the deoxyosones

The 3-deoxyosone will undergo successive dehydrations and a displacement of the double bond to form hydroxymethylfurfural (HMF) [9], while the 1-deoxyosone generates the 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one (pyranone) as a typical marker of this reactive pathway [10]. Pure 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one was found to be converted into

maltol, hydroxymaltol, and isomaltol [11]. Maltol can also be formed directly from the Amadori compound and from disaccharides [11]. The deoxyosones are also degraded by the Strecker reaction. This reaction puts in presence the deoxyosones on the one hand and the amino acids on the other hand. This is an autocatalytic reaction, which occurs in food with high concentrations in amino acids and strong temperatures or under pressure [12]. The formed α-aminoketone can induce the genesis of pyrazines.

3.2 Compounds derived from the interaction between Maillard reaction and lipid oxidation

Lipid autoxidation reactions generate a multitude of new compounds, in particular, a great number of aliphatic aldehydes. Nevertheless these aldehydes can further react with heterocyclic compounds formed by Maillard reaction. For instance aliphatic aldehydes may react with pyrazines and result in the formation of compounds with long alkyl chains, the alkylpyrazines [13].

3.3 Schematic overall reaction

A first scheme of the main reaction pathways involved in the three studied reactions and their interactions is proposed in Fig 2. The concentration of the products as well as various processing variables are likely to influence the advancement of the Maillard, lipid oxidation and caramelization reactions. Manipulating these variables can affect the balance of the various chemical pathways making up the three reactions of interest.

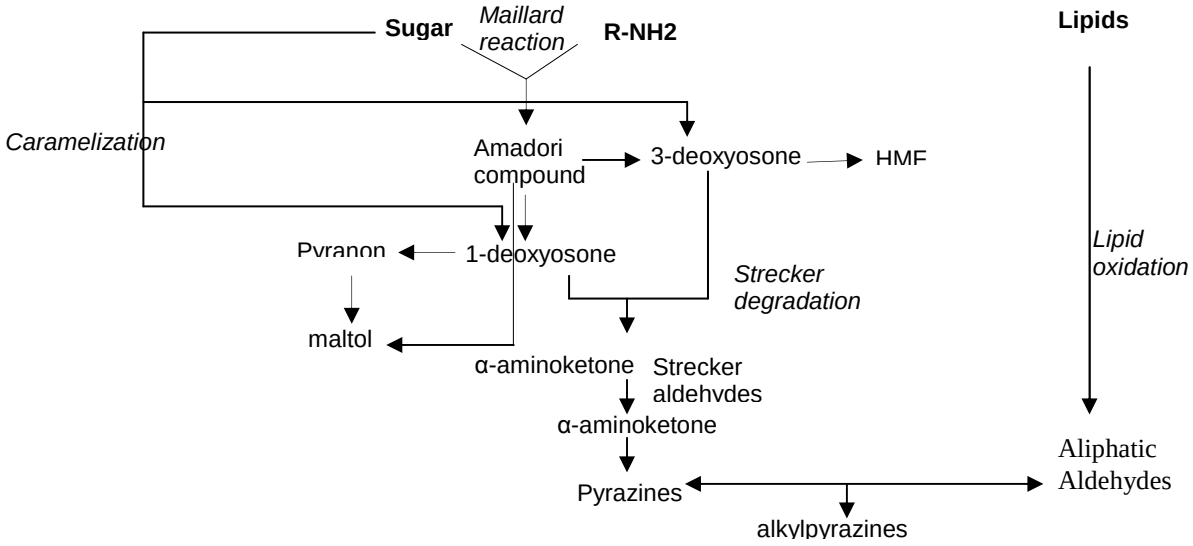

Fig.2: Proposal of a first scheme of the main pathways involved in the three studied reactions and their interactions, *i.e.* Maillard, lipid oxidation and caramelization reactions

4. Selection of relevant markers to follow the reaction pathways

The reaction markers are selected according to their ability to point out different advancement steps of the chemical reactions, taking into account the availability of reliable methods of analysis. A reaction marker can be either a substrate or a product of a reaction pathway, possibly with an organoleptic interest. The Amadori compound and aliphatic aldehydes were chosen as Maillard reaction and lipid oxidation markers respectively. No marker has been selected for the

caramelization reaction since the deoxyosone formation intermediates are unstable and therefore difficult to analyse. HMF et 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one were selected as typical markers of 3-deoxyosone and 1-deoxyosone degradation [10] and maltol, because of its organoleptic interest. To track the Strecker degradation and alkylpyrazine formation, two Strecker aldehydes and pyrazines were chosen.

5. Extraction of observable reaction pathways

The available reaction markers do not permit observing all the reaction pathways presented in the initial scheme (Fig. 2). The reaction scheme at the current state is not identifiable. To reach observable reaction pathways, a stoichiometric matrix is built. The matrix rank indicates the number of independent reactions. An identifiable reaction system is a system which matrix rank equals the number of total reactions [14, 15].

5.1 Construction of the stoichiometric matrix

The construction of the stoichiometric matrix requires that both the reaction scheme and the values of the stoichiometric coefficients are known. For example, if we assume that A, B, C, D and E components obey to the following reaction scheme:

$A + B \rightarrow C + D$ (I)
$D \rightarrow B + E$ (II)
$A \rightarrow E$ (III)

Then the matrix of stoichiometric coefficients is:

A	B	C	D	E
-1	-1	1	1	0
0	1	0	-1	1
-1	0	0	0	1

The matrix constructed from the initial reaction scheme consists of 21 lines corresponding to the chemical reactions pathways and 13 columns corresponding to selected reaction markers.

5.2 Extraction of an observable reaction pathways

The obtained stoichiometric matrix has a rank of 8, which means that only 8 out of the 21 reactions are linearly independent, and therefore observable. Consequently, the building of an *observable* reaction scheme requires reducing the initial one by: i) eliminating the unlikely reactions based on literature and ii) searching linear dependencies. For instance, in the previous example, reaction III is the sum of reactions I and II; as these reactions are linearly dependent and cannot be distinguished, they must be condensed into reaction III.
This implies that some assumptions must be drawn *a priori* and validated *a posteriori*.
The observable system obtained (Table 1) is less exhaustive than the overall reaction scheme but it should give a reliable representation of the real and complex reaction system.

Table 1: Observable reactions issued from the stoichiometric matrix of rank 8

1	Sugar + RNH_2 ↔ Amadori compound + H_2O
2	2 Amadori compounds → 4 H_2O + Maltol + HMF
3	Sugar → 2 H_2O + pyranone
4	Sugar → 3 H_2O + HMF
5	Disacharide → 2 H_2O + Maltol + monosacharide
6	RNH_2 + deoxyosone → Strecker aldehyde + α-aminoketone + CO_2
7	2 α-aminoketone → Pyrazines + 2 H_2O
8	Pyrazines + Aliphatic aldehyde → alkylpyrazine + H_2O

6. Conclusion

The successful implementation of such an approach is highly dependent on the quality of the experimental data that will be obtained. Appropriate experimental tools have been designed to guaranty the reliability of the kinetic models that will be derived from experiments: i) reliable analytical methods giving access to reaction products ii) A discontinuous lab-scale baking oven was specially designed to achieve a good reproducibility of the baking conditions. Hence, the model of heat and mass transfer has to be associated to the kinetic model in order to relate the control variables of the process to the building of the quality through chemical reactions.

7. Acknowledgment

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8. References

1. Broyart, B. and G. Trystram, *Modelling heat and mass transfer during the continuous baking of biscuits.* J. Food Eng., 2002. **51**(1): p. 47-57.
2. Rega, B.; Guerard, A.; Maire, M. and Giampaoli P. (2006) Searching the missed flavour: chemical and sensorial characterisation of flavour compounds released during baking. Proceedings of the 11th Weurman Flavour Research Symposium, Copenhagen, (in press).
3. van Boekel, M.A.J.S., *Kinetic aspects of the Maillard reaction : a critical review.* Nahrung 2001. **45**: p. 150-159.
4. Mundt, S. and B.L. Wedzicha, *A kinetic model for the glucose-fructose-glycine browning reaction.* J. Agric Food Chem., 2003. **51**: p. 3651-3655.
5. Martins, S.I.F.S. and M.A.J.S. van Boekel, *A kinetic model for the glucose/glycine Maillard reaction pathways.* Food Chemistry, 2005. **90**: p. 257-269.
6. Martins, S.I.F.S., A.T.M. Marcelis, and M.A.J.S. van Boekel, *Kinetic modelling of Amadori N-(1-deoxy-D-frucyos-1-yl)-glycine degradation pathways. Part I-Reaction mechanism.* Carbohydr. Res., 2003. **338**: p. 1651-1663.
7. Knol, J.J., et al., *Toward a kinetic model for acrylamide formation in a glucose-asparagine reaction system.* J. Agric Food Chem., 2005. **53**: p. 6133-6139.
8. Boekel, M.A.J.S.v., Acta Horticulturae, 1998. **476**: p. 149-155.
9. Kroh, L.W., *Caramelisation in food and beverages.* Food chemistry, 1994. **51**: p. 373-379.
10. Davidek, T., et al., *Simultaneous quantitative analysis of Maillard reaction precursors and products by high-performance anion exchange chromatography.* J. Agric Food Chem., 2003. **51**: p. 7259-7265.
11. Yaylayan, V.A. and S. Mandeville, *Stereochemical control of maltol formation in Maillard reaction.* J. Agric. Food Chem., 1994. **42**: p. 771-775.
12. Cremer, D.R., M. Vollenbroeker, and K. Eichner, *Investigation of the formation of Strecker aldehydes from the reaction of amadori rearrangement products with alpha-amino acids in low moisture model systems.* Eur food Res Technol, 2000. **211**: p. 400-403.
13. Shi, H. and C.-T. HO, *The flavour of poultry meat.* ,In *Flavour of meat and meat Products*, F. Shahidi, Editor. 1994, Chapman & Hall: New York. p. 52-70.
14. Fillon M., M. Meyer, H. Pingaud, X. Joulia (1995) Data reconciliation based on elemental balances applied to batch experiments. 5th European Symposium on Computer Aided Process Engineering, ESCAPE 5, Bled, Slovenia, 11 - 14 June 1995, Supplement to Computers & Chemical Engineering, 19, pp S293-S298, (1995)
15. Moreau A., Truong-Meyer X.M., Pingaud H., Strehaiano P. (1999) Metabolic engineering of *Brevibacterium linens* at a macroscopic level. 9th European Congress of Biotechnology 9 (ECB9), 12-15 juillet 1999, Bruxelles, Belgique.