Methodology for extracting an observable reaction pathway for the simulation and control of Maillard reaction during baking of sponge-cake like products

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ABSTRACT

There is an increasing demand from the food industry for complex products with controlled nutritional and sensorial properties (vitamins, antioxidants or flavour compounds contents). Many of these properties result from chemical reactions induced in food by the technological treatments. The conception of foods and the reappraisal of the products and processes require strategies allowing the appearance and the protection of valuable compounds to be controlled.
The reactions in a food system are described as a complex network of many chemical reactions. But only a small part of all the molecules consumed or synthesized by these reactions can be experimentally observed. A major stake of this study was to propose a methodology to extract a simplified (so-called apparent) identifiable reaction pathway which could give a reliable representation of the complex reaction system occurring during cooking of a bakery product. Such a methodology was based on theoretical knowledge of the system, taking into account the experimental constraints and the available information. A limited number of observable chemical markers were selected according to their ability to point out different advancement steps of the reactions (Maillard reaction, caramelization, lipid oxidation). The use of statistical methods made it possible to extract an apparent reaction pathway from available information. The representation of the reaction system as a stoichio-kinetic model, combined with mass balance and enthalpy equations, can provide a better knowledge of the transfer-reaction coupling and its consequences on the final products characteristics.

Keywords: Reaction kinetics; baking; identifiable reaction pathway; Maillard reaction; stoichio-kinetic model.

INTRODUCTION

The development of a complex food with controlled nutritional and organoleptic properties (like flavour compounds contents) requires the development of strategies allowing the appearance and the protection of valuable compounds to be controlled. Moreover, the development of food properties, either desirable (from organoleptic or functional point of view) or undesirable (off-flavours or potential toxicity), often results from chemical reactions initiated by technological treatments.
This study is part of the project REACTIAL "Prediction and control of the appearance or disappearance of reactional markers during food process and conservation ", carried out with the financial support of the ANR-The French National Research Agency. The objective was to develop rational strategies in order to preserve as well as possible the integrity of the nutritional compounds of a food and to optimize the production of positive newly-formed compounds. The project aimed at analysing the impact of formulation and heat and mass transfers on the reaction kinetics in order to understand how the processes act on reactions, and can favour the appearance, disappearance or preservation of such newly-formed compounds. Synchronous experimental data on heat and mass transfer phenomena and reactions on a sponge-cake like product were used as inputs in a methodological thinking. The latter aimed at creating a tool for integrating knowledge and decision-making aid in order to propose new technological pathways or new operating conditions for existing technologies.
Maillard reaction is among the main reactions occurring during thermal processing of food. This reaction concerns a complex network of different pathways producing a huge number of newly-formed compounds at variable amounts and lead to important changes in food flavour, colour, and nutritional value, with positive and negative consequences. The role of the Maillard reaction on food quality has been a matter of interest for years, but only few studies are dealing with the simultaneous effect of physical and chemical variables on the development of Maillard products. Studies of Maillard reaction have been performed in aqueous solutions

containing carbohydrates and amino acids. These simplified model systems have given useful information, but bakery products are complex and heterogeneous solids in which the development of Maillard reaction is certainly very different from the one observed in aqueous model systems. The added value of studying a real solid food like a bakery product lays in the complexity of the reactional system, with numerous possible reactants evolving in the heterogeneous, multiphasic structure. Moreover, the quantification of all reactants and products in a precise way remains a real analytical challenge.

The objective of the present work is to propose a methodological approach to apprehend the product-process interactions starting from measurable experimental information in order to analyse the impact of formulation and heat and mass transfers on reaction kinetics. It is based on a comprehensive "chemical engineering" approach which aims at supplementing and making reliable the knowledge on mechanisms and reaction kinetics, in order to formalize them into models for optimizing the product/process system.

The development of an instrumented pilot oven equipped with a dynamic on-line measurement of volatile compounds and a sampling system made it possible to obtain synchronous physical and chemical kinetic experimental data. The obtained knowledge on transfers and reactions on such a solid food during baking was thus used to contribute to a methodological reflexion onto the ways in which the matter, the reaction, and the coupled transfer-reaction system can be represented.

MATERIALS & METHODS

A sponge–cake like product was formulated, containing flour (25%, moisture content 13% w/w), monohydrate dextrose (25%), palm oil (4%), sodium chloride (1%), and pasteurized liquid eggs (45%; 76% w/w moisture content). The mixing and forming protocols are detailed in [1]. A semi-industrial pilot oven was designed to perfectly characterize and control baking conditions, insuring thermal homogeneity, sampling of products during processing, and continuous trapping of the volatile fraction above the product. An on-line extraction device was used for monitoring the release of newly-formed volatile compounds generated during baking [1].

Extraction and analysis methods have been developed for non-volatile markers such as HMF (hydroxymethylfurfural), free amino groups as precursors for Maillard reaction, and reducing sugars. For volatile markers, monitoring of aldehydes issued from lipid oxidation and products from Strecker degradation, caramelization and Maillard reaction was performed by dynamic SPME-GC-MS. Quantification of volatile compounds was performed through the evaluation of vapour/fibre partition coefficients from equilibrium measurements between gas and liquid phases.

RESULTS & DISCUSSION

The reaction system can be described as a complex network of many chemical reactions. But only a small part of all the molecules produced by these reactions can be assessed by analytical means. A major stake of this work was to extract a simplified reaction pathway which can give a reliable representation of the complex reaction system based on measurable compounds. It has been necessary to determine exhaustively the reactions which really take place in the product and to specify the occurrence of these reactions during the baking process. The theoretical knowledge of the system and the analysis of available information made it possible to extract an apparent reaction pathway. The methodological approach could be summarized as follows: "pose the problem in all its complexity starting from data of the literature, simplify it on the basis of realistic assumption in relation to the actual knowledge of the system and to the accessible experimental information, and capitalize this knowledge in the form of a model". It is drawn as a diagram in Figure 1 corresponding to the following steps:

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. Three types of reactions were focussed on: Maillard, lipid oxidation, and caramelization reactions.
ii) Selection of relevant chemical markers to follow the selected reactions pathways.
iii) Extraction of an apparent but identifiable reaction scheme from the exhaustive set of theoretical reactions by considering the experimental available information and making as few assumptions as possible.
iv) Acquisition of experimental data taking into account the key-variables likely to influence the reaction.
v) Identification of the reaction rates of the apparent reaction scheme from the experimental data.
vi) Development of a knowledge based model in order to determine the influence of process parameters on the final quality.

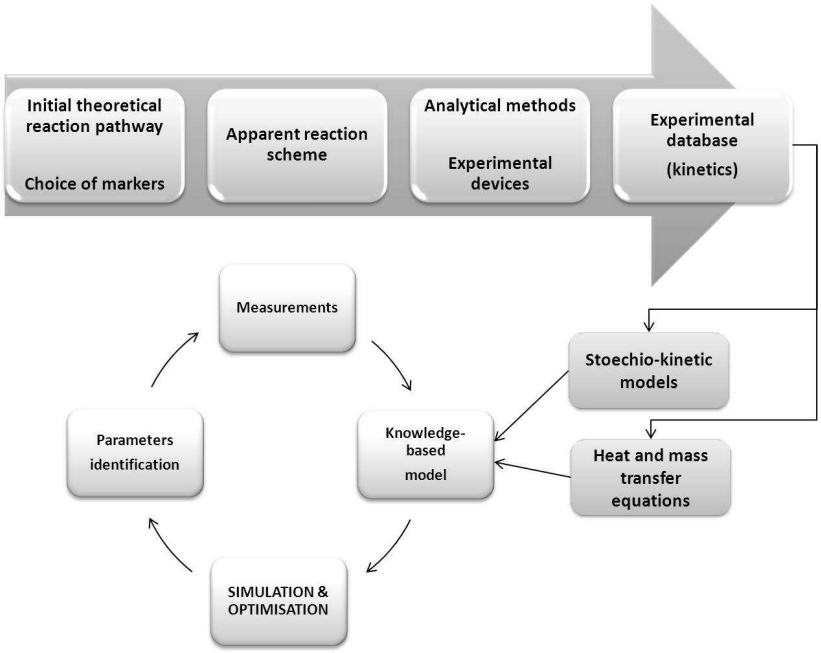

Figure 1. Methodological approach.

This representation of the reaction system combined with the involved physical laws can provide a better knowledge on the transfer-reaction coupling and the consequences on the final products characteristics. Reaction markers were selected according to their ability to point out different advancement steps of the reactions (Maillard reactions, lipids oxidation and caramelization), taking into account the availability of reliable methods of analysis. A relevant reaction marker can either be a substrate or a product of a reaction pathway, possibly with a sensorial or nutritional interest.

Initial theoretical reaction pathway and choice of markers

The following reaction scheme first produced from the literature (Figure 2) was considered:

- Maillard reaction, resulting from the non-enzymatic addition reaction between a carbonyl group (from sugar essentially) and a free amino group ($R\text{-}NH_2$ from amino acids or proteins), with 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;
- caramelization reaction, with the formation of α-dicarbonyl (3-deoxyosones and 1-deoxyosones) from sugars; such α-dicarbonyl can also be produced by Maillard reaction;
- lipid autoxidation reactions;
- interactions between Maillard reaction and lipid oxidation (formation of alkylpyrazines).

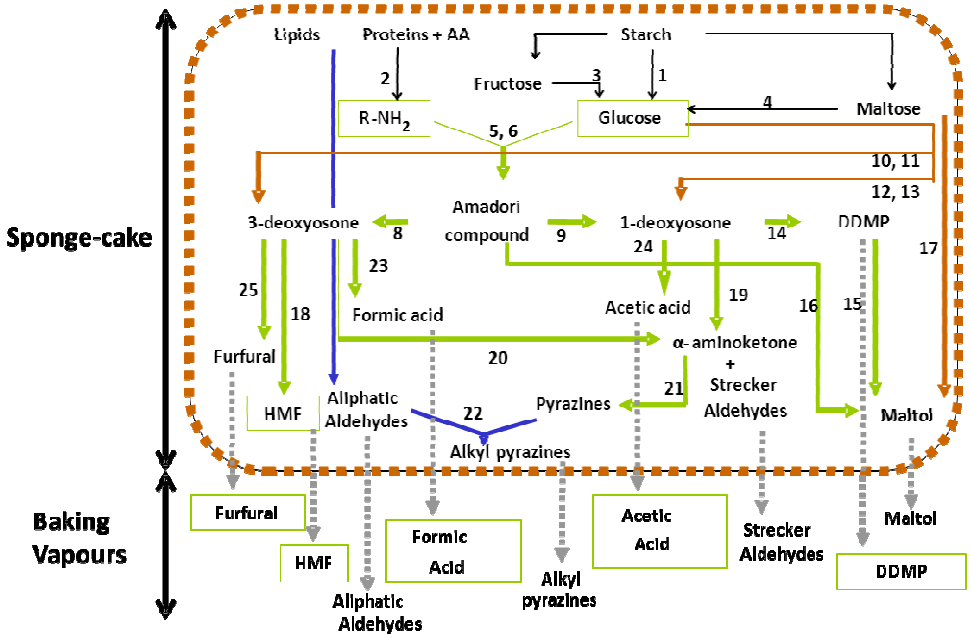

Figure 2. Theoretical reaction pathway.

A list of markers was chosen allowing the reactions to be followed during baking (Table 1). The choice was based on a survey of the literature and preliminary studies [2], and it consisted in precursors (glucose and free amino groups (RNH_2) supplied by amino acids, peptides and proteins), possible markers of the main reaction pathway and molecules mainly associated with organoleptic properties (aroma compounds). In the case of such a complex solid, it appears clearly that the extraction and analytical techniques currently available do limit the number of possible markers.

Table 1. List of possible markers (**finally retained markers**)

Reaction pathway of interest	**Localization**	**Chemical compound**
Maillard reaction and caramelization*	In the sponge cake	**Glucose***, Maltose, Fructose
		Free-amino groups ($R\text{-}NH_2$)
		Furosine
		5-hydroxymethylfurfural (HMF)*
	In the baking vapours	**2,3-dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one (DDMP)**
		Maltol
		Furfural*
		2,5-dimethylpyrazine
		HMF*
		Strecker's aldehydes (2- and 3-methylbutanal)
		Formic acid*
		Acetic acid*
Lipid oxidation	In the sponge-cake	Conjugated dienes
	In the baking vapours	Hexanal
Interactions between Maillard reaction and lipid oxidation	In the baking vapours	Alkylpyrazines

Observable reaction pathway

The type and amount of detected markers depend on the product formula and applied analytical tools. Maltol, Strecker's aldehydes, 2,5 dimethylpyrazine, and any alkylpyrazines could not be detected within the limits of detection of the analytical methods, and this list was finally reduced to a set of 8 markers (= species in a rectangle in Figure 2). Fructose was lower than the limit of quantification, making the isomerization reaction impossible to observe. Due to the absence of alkylpyrazines, the global route from lipid oxidation to interaction with Maillard reaction disappeared from the reaction pathway. Moreover, as furosine was not measured, and no pyrazine was detected, the Maillard and caramelization reactions were pointed out by the same markers making it not possible to completely differentiate the two pathways. According to the number of observable chemical markers, the initial reaction pathway was therefore updated and simplified to an observable apparent reaction scheme with only 6 chemical reactions (Figure 3). This number is the maximum number of independent reactions corresponding to the rank of the matrix of stoichiometric coefficients [3].

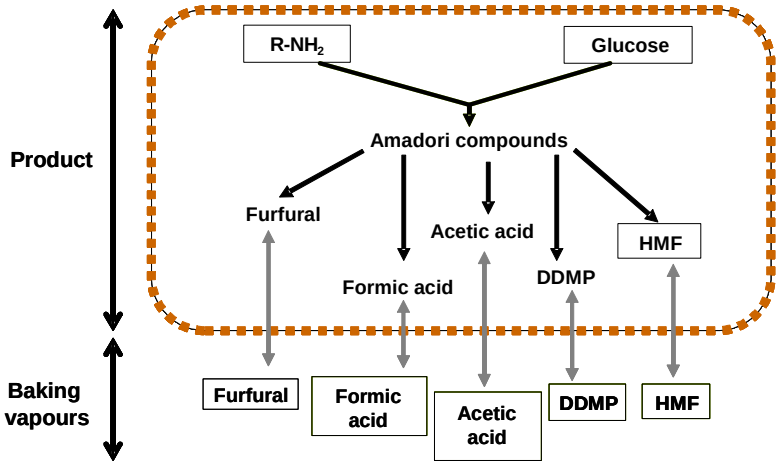

Figure 3. Apparent reaction scheme.

This reaction scheme is much less exhaustive than the first one, but it can make it possible to identify kinetic parameters on a real product baked under realistic operating conditions and to analyse the impact of the process parameters.

Identification of the reaction rates

A semi-industrial convective oven was designed and characterized in order to generate reliable kinetic data on thermal reactions occurring during the transformation of bakery products under real processing conditions [1]. It provided precise and reproducible thermal conditions on a large uniform baking area. The oven was also equipped with two original sampling devices enabling to acquire synchronous kinetic data on reaction products in the food matrix as well as in the vapors emitted by the product during baking and this, without disturbing the thermal environment.

A stoichio-kinetic model was implemented for the simulation of reaction kinetics as a function of temperature and initial concentrations. Partial orders of all reactions were assumed equal to one, and temperature effects were described using the Arrhenius equation. Kinetic constants were identified on a set of experimental data obtained for 3 levels of air temperature (140 – 170 – 200 °C) and 2 levels of convection. Temperature and moisture profiles in the products were predicted by heat and mass transfer balance equations taking into account internal moisture evaporation and vapour migration within the open porosity of the product during heating as well as apparent liquid moisture migration described by Fick's law. Internal heat transfer phenomena were described using Fourier's law and apparent thermal heat conductivity. External heat and mass transfer phenomena taken into account were convective drying, convective and radiative heat transfer for both heating product and baking tray [4].

As a first approach, the optimal values of unknown kinetic parameters were determined using a trial and error methodology. Experimental measurements were relatively well described by this model, except glucose consumption which was largely overestimated by the model (Figure 4). Such a result is certainly due to the

lack of specific markers of caramelization in the apparent reaction scheme. The values of the identified kinetic parameters must nevertheless be used with caution in extrapolated conditions and a study of sensibility on parameters has to be done before any further interpretation.

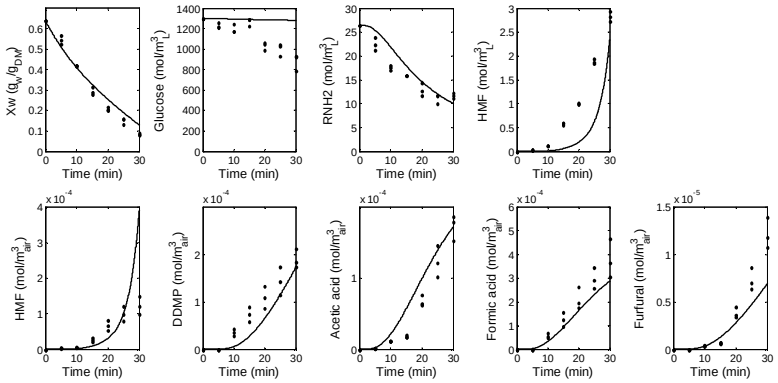

Figure 4. Comparison between experimental (dots) and predicted (continuous lines) concentrations for water and chemical species during baking at 170°C (maximum ventilation).

CONCLUSION

The proposed methodology enabled a qualitative analysis of the studied system, and is expected to lead to a quantitative formalization of the observed phenomena. It is based on various stages of formalization and modelling of the matter, reaction system and physical phenomena, essential to pass from an industrial system to an experimental system. These stages of formalization and modelling necessarily involve a “degradation” of the real system and the results can only give a partial representation of the real process. But the resulting models are structurally identifiable and can be used for new formulating and processing food strategies and for a cognitive purpose of interpretation of reaction pathway. It must be outlined that a careful process of discussion between multidisciplinary actors (chemists, process specialists, model makers…) is necessary for this partial view to be as realistic as possible, and to make sure that the experimental data acquired are in agreement with the objectives of modelling.
Such a "chemical engineering" approach is innovative for food processing, and offers interesting perspectives for controlling processes and the sensorial and nutritional properties of the products.

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