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Bread as a Chemical Reactor: Triggering the Aroma Production through Chemical Kinetics

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Recent studies address the structural modifications occurring in the thermal processing of food to interact with the development of aroma and taste compounds. Food sensory science is often related to statistical analysis of panel tests and subjective human responses. From a chemical engineering perspective, food can be treated like a chemical reactor. Bread can be one example of “food chemical reactor”, which enormously changes its density (from high to low depending on the leavening process), its aroma (driven from Maillard and other reactions involving carbohydrates, proteins and fats), its color (caramelization and Maillard), its structure (starch gelatinization, gluten hardening), etc. Indeed, transport phenomena and chemical kinetics are consistently involved in this process. A detailed study on the chemical kinetics of bread aroma development can be helpful to achieve an objective quality marker, which can be monitored and controlled dynamically through the process conditions and variables. The identification of the most relevant aroma compounds and the relative production paths description is the key to the kinetic approach. This would be beneficial for industrial purposes: the result of the research is the scientific description of a quantitative-sensorial aspect. This feature can be useful for further integration with physical/phenomenological models and texture models, to achieve an innovative holistic viewpoint for the product development and process control on the industrial scale breadmaking.

1. Introduction and scope

During baking, bread can be considered as a chemical reactor, since a large number of chemical reactions, including Maillard Reaction, starch gelatinization, proteins denaturation, etc. take place in the evolving food matrix. In particular, Maillard reaction is a very complex reaction scheme that, starting from proteins and carbohydrates, can develop a large number of compounds (more than 300) in solid, liquid and gas phases. Some of those compounds are responsible of the aroma and colour development.

Depending on the starting amino acid (derived from proteins) and sugar (from carbohydrates), on the water content and the medium pH, Maillard reaction can form very different compounds: some of these are characteristic of baked bread, and particularly interesting for this study.

All proteins start reacting with a sugar, forming a glycosyl-amine, then the glycosyl-amine reacts to form a Schiff base, in equilibrium with the relative Amadori compound: Amadori compouds decompose into a rearranged sugar (deoxyglucosone) and an amino acid residue (different from each other depending on the startingamino-acid) (Ledl and Schleicher, 1990).

The rearranged sugars are highly reactive and fundamental for the advanced-stage Maillard products formation, including some reference aroma compounds. According to literature (Schieberle and Grosch, 1989), two main compounds responsible for the bread aroma were identified: 2-acetyl-2-thiazoline (AT) and *2*-5-hydroxymethylfurfural (HMF) are potent odorants with a relatively low perception threshold (Fuganti et al.,

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2007). These compounds have been selected as aroma makers for the current study. The description of their development is the main target of this work, which involves the modelling of the bread crust region as the most reactive part, where the production of bread mainly occurs.

2. Materials and methods

The modelling activity of food matrices is an ongoing activity for the authors, that successfully developed and implemented models for bread baking (Papasidero et al., 2015a) and meat roasting processes (Papasidero et al., 2015b). Those models included the dynamic description of temperature and weight loss, validated with experimental data. In particular, the bread model has been also applied to the energy optimization case (Papasidero et al., 2016), where different heating sources have been the optimization variable towards the minimization of the energy needed for cooking, under selected quality constraints (e.g. crust colour and starch gelatinization). In that case, one single optimization step needed for the solution of a PDE system with a finite elements approach and about 1,000 elements in the mesh domain consisted in about 5 minutes of computational time. A previous application (Papasidero et al., 2014) dealt with the implementation of a general Maillard kinetic model (Jousse et al., 2002) coupled with a thermal balance needed to describe the cooking temperature affecting the reaction kinetics and the model of the oven where experimental tests were performed (including the oven thermo-fluid dynamics). In that case, the aim of the work was to study the tools and the possibility to implement the oven-food-kinetics coupling for a future study. The chosen model needed about 25 - 30 minutes of computational time to be solved.

Due to the necessity to get shorter computational times with the aim of a future kinetic parameters regression, further simplifications have been chosen for the current study, including the limitation of the modelling domain to the only bread crust.

To model a complex food matrix such as bread crust, it has been necessary to make some assumptions:

- Maillard reaction occurs mostly in the crust, due to its higher temperature and lower water content. The high water content and the maximum inner temperature of 100 °C (depending on the evaporation temperature boundary) limit the impact of the Maillard reaction in the bread core. Therefore, only the crust is modelled
- Volatile compounds diffuse only in one direction, from inside of the bread to ambient air, due to forced air convection affecting the bread surface
- Effective Diffusion coefficients are calculated based on a gas mixture composed by water, carbon dioxide and ethanol. Its value include a correction for bread porosity and tortuosity
- Bread crust matrix is considered as a homogenous medium, to avoid the impact on the computational effort of mathematical models for physical pores formation and evolution during baking
- The bread crust is assumed to have a constant thickness and the same temperature in all the computational domain. This assumption can be easily removed assuming a crust development and a temperature gradient, perhaps from parallel bread models. Nonetheless, it would make the calculations much slower
- The chemical paths leading to the selected aroma markers are either taken from literature or hypothesised based on analogies with similar reactions, not necessarily including all the elementary steps
- The kinetic steps are associated to the kinetic scheme presented by Jousse et al. with some modifications. That scheme was proposed as a general Maillard reaction scheme, many reaction steps can be seen as specific cases of the proposed reaction classes

2.1 Markers identification and kinetic pathways

According to the literature (Adams and De Kimpe, 2006) two compounds have a relevant contribution to the bread aroma: 2-Acetyl-2-Thiazoline (AT) and 5-hydroxymethylfurfural (HMF).

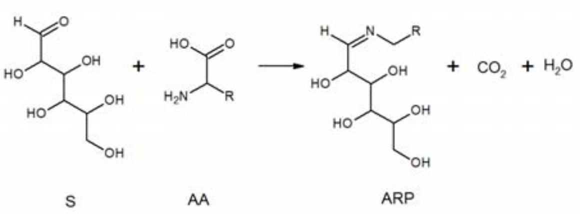

Figure 1 Initial step of Maillard Reaction

Their perception threshold is only 0.01 µg/kg$_{bread}$ (Cerny, 2008). As advanced products of Maillard's reaction, the formation of these markers starts from a rearranged amino acid (1-pyrroline and cisteamine, respectively) with a rearranged sugar (1-deoxyosone and its derived decomposition product piruvaldehyde).
After the fast formation (and rearrangement) of few intermediates, the final product can finally diffuse to the ambient air (in the oven).
The hypothesised chemical reactions for the formation of the two markers are reported in Figure 3 and Figure 4, where only a part of the overall specific mechanism is shown for conciseness (Maillard initial steps in Figure 1 and Figure 2).

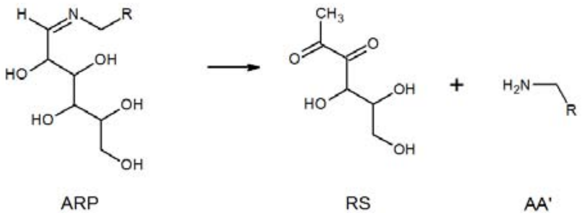

Figure 2 Second step of the Maillard reaction, formation of rearranged sugar and amino-acid residue

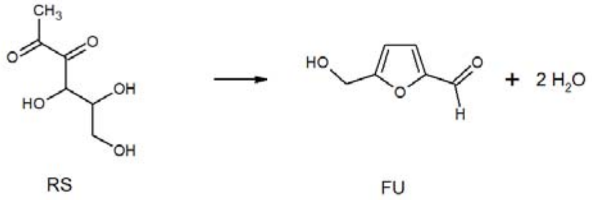

Figure 3 Chemical path for the formation of 5-Hydroxymethylfurfural (Capuano and Fogliano, 2011)

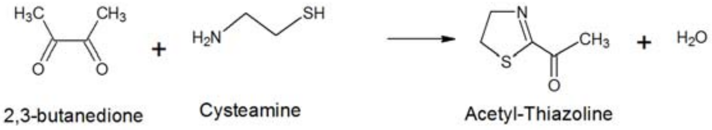

Figure 4 Chemical path for the formation of 2-Acetyl-Thiazoline from Cysteamine and 2,3-butanedione

As specified before, the presented pathways can be identified in a general Maillard scheme where different amino-acids and reducing sugar can react (in principle with different kinetics) following common paths until the intermediate Maillard product are formed (being very specific on the initial compounds).

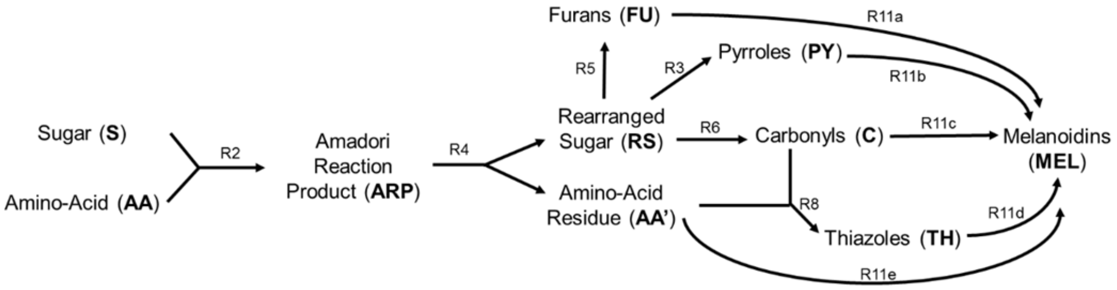

Figure 5 Proposed kinetic scheme

From this perspective, 2-Acetyl-2-Thiazoline comes from the reaction of one amino-acid residue (Cysteamine, **AA'**) with a "Carbonyl" compound (Pyruvaldheyde, formed from rearranged sugar degradation, **RS**). 2-Acetyl-1-Pyrroline is one of the "Pyrroles" compounds. Some other compound classes, such as "Furans", are included in the presented scheme to favour a multi-response modelling perspective (Van Boekel, 2008), thus including the possible effect of parallel reactions, going to the detriment of the markers formation.

The inclusion of the class “Melanoidins” is needed to include the compounds formed in the last stage of the Maillard reactions, remaining in solid phase and being responsible of the “browning” phenomena (Purlis, 2010). It is relevant to underline that the exact structure and molar weight of melanoidins is not completely known. Its concentration is usually measured measuring the absorbance at a specific wavelength, but the unknown molar weight makes it difficult to relate that data to those for compounds to which quantitative techniques can be applied (Fogliano and Morales, 2011).
The proposed kinetic scheme is reported in Figure 5.

2.2 Kinetic constants

The kinetic constants are based on literature in analogy with the original scheme. It is worth to mention that those constants have been evaluated on a model system and in homogeneous media with a limited number of reactants. The impact of the huge variety of reactants and products (often intermediates to further reactions) is still not taken into account due to the extreme complexity of an appropriate experimental characterization, needing for many and many crossed techniques or many more studies on both model systems and food systems. For this reason, the kinetic constant for the initial step has been divided by a factor 500. Further studies and detailed experimental data on aroma development will allow to perform parametric regression and model discrimination to get appropriate (apparent) kinetic constants and alternative pathways.

$$k_j = k_j^0 \exp\left(-\frac{E_a}{RT}\right) \qquad (1)$$

The considered kinetic constants follow the Arrhenius law, Eq(1). Table 1 reports the kinetic constants and activation energies for the kinetic model:

Table 1: Kinetic constants

Reaction	k0 (1/s or L/mol/s*)	Ea (kJ/mol)
R2*	5.0×10^{10}	120.5
R3	6.0×10^{1}	35.1
R4	1.5×10^{5}	52.9
R5	2.0×10^{11}	109.3
R6	5.0×10^{5}	66.5
R8*	5.0×10^{11}	83.1
R11 (a,b,c,d,e)	1.0×10^{10}	99.7

2.3 Transport model with diffusion and reaction

As mentioned before, we assume that Maillard reaction occurs only in bread crust.
This assumption can be made because of reaction temperature: in bread core, the temperature reaches a plateau at 100 °C, because of the water evaporation. The crust is that part of bread where water evaporation mostly already occurred. In principle, an evaporation front generates a coloured crust of few mm, depending on the bread kind and process.

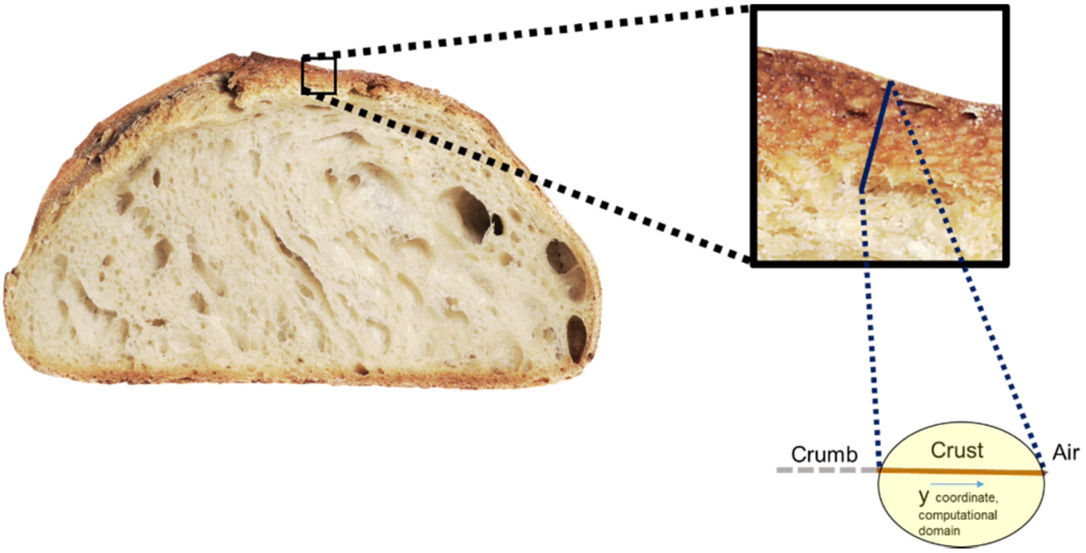

Figure 6 Schematic of the computational domain (crust region)

The crust temperature can increase up to and sometimes over 140 °C at the end of baking. Despite Maillard reaction can take place even at ambient temperatures with very long reaction times, to get a visible reaction rate the surface temperature needs at least 130 °C for times in the order of decades of minutes.

A PDE system including reaction and diffusion of the compounds considered in the kinetic scheme is written in a modelling software with finite element approach (Eq(2), applied to each compound):

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i + \sum_{j=1}^{NR} R_{i,j} \tag{2}$$

where $R_{i,j}$ is the reaction rate related to the selected compound.

The diffusivity of solid species (AA, S, RS, ARP, MEL) is set to zero, while the other (gaseous) species (FU, PY, C, TH) can diffuse with a diffusion coefficient of 10^{-9} m^2/s. No flux boundary condition is set in the crumb direction, while convection is set from the crust. The mass transfer coefficient (gas species) is $K_{mat} = 10^{-2}$ m^2/s. The temperature trend is taken from an experimental baking test as one example trend. It is inserted in the modelling program through the use of an exponential expression (Eq(3).

$$T_{oven} = T_{\min} + (T_{\max} - T_{\min}) \cdot \left(1 - \exp\left(-\frac{t}{\tau}\right)\right) \tag{3}$$

The implementation and the solution of the PDE system is achieved using the finite element approach, and the numerical integration is entrusted to COMSOL Multiphysics 5.0 (COMSOL-AB, 2014).

3. Results and discussion

The greater part of the reactants is consumed to give the intermediate products Figure 7. Since the amino-acid residues (AA') react with the low concentration carbonyl containing compound (C) and to give melanoidins (MEL), its concentration gets high values, comparable to that of the terminal product. Figure 8 reports the concentration of two relevant aroma compound classes, furans (FU) and thiazoles (TH) in the inner and surface layers. In this case, the concentration is very low compared to many other compounds but still reasonable for aromas. The effect of the diffusion and convection that lowers the aroma concentrations between the two layers can be highlighted from the chart.

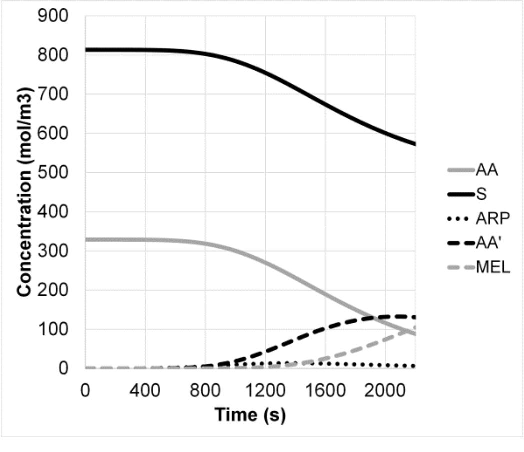

Figure 7 Concentration profile for the major compound classes included in the model

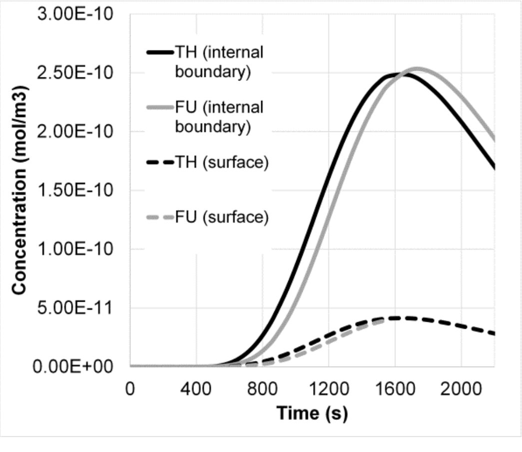

Figure 8 Concentration profile for the aroma compound classes included in the model

The degradation of proteins is comparable to that in the paper from Singh (2005), which reports a decrease in the extractable proteins with baking due to the polymerization (responsible for melanoidins formation).

Melanoidins formation is here also considered as an easy way to describe the possible compounds that cannot react anymore nor diffuse.

The solution of the problem took about 2 s of computational time. This is a good result in the viewpoint of a kinetic parameters regression. Further details on the possible mechanisms underlying the production of aromas, new reaction paths and appropriate data in both the gas and solid phases can allow to take advantage of this approach, assuming that the measured aroma concentrations are those on the surface.

4. Conclusions and future work

The presented work analyses the phenomena involved in bread aroma formation, focusing on the development of Maillard reaction compounds with particular reference to two selected markers and their compound classes. The developed model can be useful to perform parametric regression, taking advantage of experimental data collected on bread baking tests. This tool is detailed enough to consider the reaction and diffusion of the products, as well as very easy to solve computationally (solution time about 2 s). The kinetic scheme is rather simple to avoid the extreme complexity of the reaction network, needing for a very big effort on the data collections, with many different experimental techniques. Apparent kinetic rates are supposed to be appropriate for this initial stage of modelling, to avoid multicollinearity and large solution times.

The developed kinetic scheme can be easily coupled with physical models including water evaporation and crust formation, to use the information related to water content (or activity) in the kinetic constants.

Future work will include this step, after the above mentioned kinetic parameters regression based on volatile compounds profile, obtained by using a PTR-TOF-MS (Makhoul et al., 2015) during a cooking test in a properly equipped oven. Further computational tools can be provided to assess the sustainability of the food treatments as seen, for instance, for beer (De Marco et al., 2016) and oil (Busset et al., 2015) production.

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