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# Modelling the Maillard reaction during the cooking of a model cheese

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ABSTRACT

During processing and storage of industrial processed cheese, odorous compounds are formed. Some of them are potentially unwanted for the flavour of the product. To reduce the appearance of these compounds, a methodological approach was employed. It consists of: (i) the identification of the key compounds or precursors responsible for the off-flavour observed, (ii) the monitoring of these markers during the heat treatments applied to the cheese medium, (iii) the establishment of an observable reaction scheme adapted from a literature survey to the compounds identified in the heated cheese medium (iv) the multi-responses stoichiokinetic modelling of these reaction markers. Systematic two-dimensional gas chromatography time-of-flight mass spectrometry was used for the semi-quantitation of trace compounds. Precursors were quantitated by high-performance liquid chromatography. The experimental data obtained were fitted to the model with 14 elementary linked reactions forming a multi-response observable reaction scheme.



## 1. Introduction

Processed cheese derives from the transformation of dairy (Gouda, Cheddar, Emmental, butter and various milk powder) and non dairy (emulsifiers, texturizing agents, aroma) ingredients into one homogenous generally spreadable product with a long shelf life (Caric, 2000; Kapoor & Metzger, 2008).

The mechanical and thermal settings necessary to get a microbiologically safe product with both colour and texture desirable for consumers are well known and could readily be modelled. For instance, the thermal settings necessary to get a microbiologically safe processed cheese could readily be calculated from the parameters of Bigelow and Weibull (van Boekel, 2002). Colour defects promoted by the application of inadequate thermal settings in relationship with the composition of the cheese medium and linked to the Maillard reaction have been extensively studied (Bley, Johnson, & Olson, 1985a, 1985b). The rearrangement of caseins by emulsifying salts giving rise to a creamed texture has been the topic of much research (Lee, Buwalda, Euston, Foegeding, & McKenna, 2003; Panouille, Durand, Nicolai, Larquet, & Boisset, 2005).

In fact consumers request a microbiologically safe product with optimal colour, texture and taste. However it is very unlikely that these four responses reach their optimal properties for the same formulations and processing parameters. Therefore the best compromise has to be found. Methods for an accurate quantitation of colour, texture and microbiological safety exist. However this is not the case for taste and flavour and their accurate quantitation remain a major analytical challenge. For this reason, there is still

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a need to integrate the development of flavour into the multimodal strategies for the optimisation of processed cheese quality.

Control and optimisation of flavour properties has been recently described as "the ultimate challenge for the food and flavour industry" (Parker, 2013). Up to now the multi-response stoichiokinetic models of the Maillard reaction have been mostly applied to model systems (Brands & van Boekel, 2001) but rarely to real food products (Parker et al., 2012). In contrast to model systems, that are usually buffered and exposed at a single temperature, the pH of the food matrix is susceptible to decrease as weak acids such as formic or acetic acids are formed. In addition, the temperature of the cheese medium varies in order to stick to the thermal parameters that are usually applied during the elaboration of industrial processed cheese. Moreover most of the multi-response stoichiokinetic model studies do not focus on the formation of the odorous volatile compounds. (Brands & van Boekel, 2002, Martins & Van Boekel, 2005). Indeed, the formation of these volatiles and odorous compounds is a crucial step in the Maillard reaction and many elementary reactions are combined, as has been shown by studies using stable isotopes labelling (Yaylayan, 1997, 2003). Finally, the quantitation of volatile compounds in complex multiphasic food matrices, whose desorption properties potentially vary during their mechanical and thermal elaboration remains until now, a major analytical challenge (Samavati, 2013).

In a previous study (Bertrand et al., 2011), we determined from a qualitative point of view that lipid oxidation, caramelisation and Maillard reaction are responsible for most of the changes occurring in the volatile fraction during the thermal treatments applied to processed cheeses. Some of the molecules originating from these reactions are already known as responsible for "off flavour" defects. In particular, we identified two molecules, maltol and furaneol, produced during the Maillard reaction as the main contributors to "overcooked" defects.

The aim of this work is to move from a qualitative approach toward a quantitative model that could be integrated into multicriteria optimisation strategies for the prediction of processed cheese quality. Therefore, this study is focused on the Maillard reaction, as it was found to be the main source for off-flavour identified during cooking (Bertrand et al., 2011). We were led (i) to extract an observable reaction scheme from the data contained in the volatile fraction of the processed cheeses and the literature available, (ii) and to model the evolution of the key compounds using a multi-responses stoichiokinetic model. Such a model consists of an intricate network of reactions. A detailed guideline concerning the establishment and the resolution of a multi-response stoichiokinetic model can be found for instance in the book of Van Boekel (2009a, chap. 8, 2009b, chap. 14).

The present work must not be seen as a fundamental work (generally conducted in a simplified binary mixture with perfectly controlled pH and temperature) aiming at the removal of theoretical and analytical locks for a better understanding of the Maillard reaction, but as an attempt to get the best of the current knowledge available in order to improve the flavour quality of industrially processed cheeses. This is consequently the first step of a sequential design aiming at a better understanding of the processed cheese system.

## 2. Material and methods

### 2.1. Composition, formulation and cooking of the cheese

#### 2.1.1. Composition and formulation

Micellar casein native and milk permeate were purchased from Ingredia (St-Pol-sur-Ternoise, France). Anhydrous milk fat was from Campina (Amersfoort, The Netherlands). Sodium chloride and citric acid were purchased from Sigma-Aldrich (St. Louis, MO) and were of analytical grade. Deionised water and a mixture of sodium polyphosphates (Pitkowski, Nicolai, & Durand, 2008) were also used. The final composition per 100 g of cheese was approximately 60 g of water, 20 g of fat, 12 g of protein, 6 g of lactose and some other minor constituents. More details about the manufacturing process are provided in our previous study (Bertrand et al., 2011).

#### 2.1.2. Cooking system

A cooking system was designed for heating a cheese sample of about 10 g to a final temperature of 80–150 °C as quickly as possible and to maintain this temperature for a given time. It is possible to reach 150 °C in about 3 min and 30 s. The specifications of the system, its operational parameters and performances are also described in Bertrand et al. (2011). The temperature was measured by using a type-K thermocouple placed at the core of the cheese medium in a set of preliminary experiments. It was removed during the experiments in order to prevent any contamination of the volatile fraction by the probe.

Cooking conditions used for this study are shown in Fig. 1. Each point corresponds to a triplicate run including formulation, cooking and analysis steps. As the device is conceived to withstand the pressure for cooking at temperature above 100 °C, it is not possible to regularly take a sample during a single backing and only one sample, corresponding to the final stage of a single experiment could be taken out. Because of this, the number of samples taken is necessarily reduced. In order to get the most information possible, the times intervals were reduced when working at higher temperatures.

### 2.2. Assay of non-volatile compounds

The method used to quantify the sugar content (lactose and galactose) was adapted from Rocklin and Pohl (1983). Two grams of processed cheese were dissolved in 100 mL of deionised water; 2 mL of acetic acid (10%v/v) were added and the pH of the solution was adjusted to 4.6 with about 2 mL of 1 M sodium acetate. The sugar content was quantified by ion exchange HPLC and detected by amperometry. The quantitation limits for the two products were in the range of 10 mg for 100 g of processed cheese.

The free amino acid contents were measured chromatographically according to French standards (AFNOR XP V 18-113, January 1998 and AFNOR XPV 18-114, January 1998 for tryptophan).

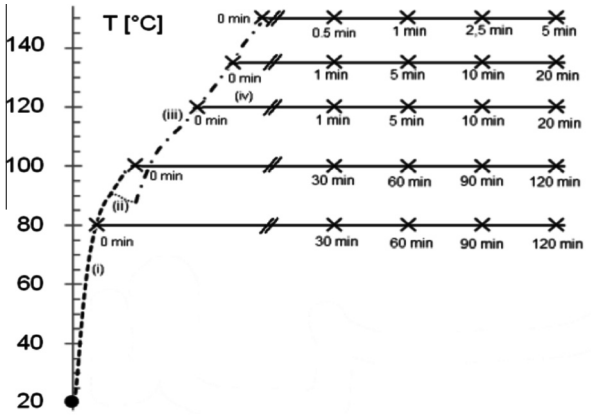


**Fig. 1.** Overview of the experimental design. Numbers represent the time spent at the selected temperature (warm up period excluded). The thermal treatments were carried out according to the methodology described in Bertrand et al. (2011). Processed cheese samples were analysed by solid-phase microextraction associated with comprehensive gas chromatography–time of flight mass spectrometry.