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PII: S0260-8774(10)00117-2
DOI: 10.1016/j.jfoodeng.2010.03.008
Reference: JFOE 6053

To appear in: *Journal of Food Engineering*

Received Date: 30 October 2009
Revised Date: 25 February 2010
Accepted Date: 7 March 2010

Please cite this article as: Purlis, E., Browning development in bakery products – A review, *Journal of Food Engineering* (2010), doi: 10.1016/j.jfoodeng.2010.03.008

Browning development in bakery products – A review

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Abstract

This paper presents a review regarding several aspects of the development of browning during baking of bakery products, mainly from an engineering point of view. During baking, the formation of colour is due to the Maillard reaction, and caramelization of sugars. Besides the major influence of this phenomenon on the initial acceptance of products by consumers, it is the responsible for other relevant changes occurring in food during baking, i.e. production of flavour and aroma compounds, formation of toxic products (e.g. acrylamide), and decrease of nutritional value of proteins. As well as baking, the development of browning in bakery products is a simultaneous heat and mass transfer process that occurs mostly in a non-ideal system under non-ideal conditions. In addition, the mechanisms of chemical reactions involved are still not elucidated completely, so the process is difficult to control and represents a major challenge for food engineers. Effects of browning on properties of products and experimental, modelling and technological aspects of colour formation during baking are reviewed.

Keywords: Non-enzymatic browning; Maillard reaction; Caramelization; Baking; Crust; Acrylamide; Colour; Kinetic modelling.

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1. Introduction

Baking of bakery products can be defined as the process which transforms dough, basically made of flour and water (other ingredients such as sugars, fat, egg, leavening agent, and other additives will depend on each specific product), in a food with unique sensorial features. In this way, the aspect and colour of food surface is generally the first quality parameter evaluated by consumers and is critical in the acceptance of the product, since it is associated with flavour and level of satisfaction (Pedreschi et al., 2006). Respect to bakery products, although typical (and diverse) quality features are related to each product, surface colour together with its texture and flavour are the main features considering preference of consumers, and thus can be used to judge the completion of baking (Abdullah, 2008). Moreover, regulation can also establish certain parameters in this aspect; e.g. in Argentina, bread crust must present a uniform yellow-gold colour (ANMAT, 2004). Therefore, understanding the development of colour at product surface is a very important issue for the bakery industry.

The formation of colour in bakery products during baking is widely known as browning. Browning is the result of non-enzymatic chemical reactions which produce coloured compounds during the baking process; such reactions are the Maillard reaction and caramelization. The Maillard reaction takes place where reducing sugars and amino acids, proteins, and/or other nitrogen-containing compounds are heated together, while caramelization is a term for describing a complex group of reactions that occur due to direct heating of carbohydrates, in particular sucrose and reducing sugars (Fennema, 1996). Because of chemical features (i.e. reactants and products) of the Maillard reaction and caramelization, the importance of browning development during baking is not only related to sensorial aspects such as colour formation and flavour generation, but also to nutritional issues. In this sense, the Maillard reaction impairs the content and bioavailability of amino acids and proteins (Fennema, 1996; Morales et al., 2007), and it is related to the formation of harmful compounds such as acrylamide and hydroxymethylfurfural (HMF) (Gökmen et al., 2007, 2008a; Mottram et al., 2002; Stadler et al., 2002). On the other hand, Maillard reaction products are also associated with some positive nutritional properties like antioxidant activity (Morales et al., 2009; Yoshimura et al., 1997).

The occurrence of browning should not be decoupled from transport phenomena taking place in products during baking. In fact, browning reactions mainly depend on temperature and water activity, as represents the availability of water for chemical reactions in food. During the baking process, simultaneous heat and mass transfer occurs within the product producing several physical, chemical, and biochemical changes besides browning, i.e. volume change (expansion and shrinkage), water evaporation, dough/crumb transition due to protein denaturation and starch gelatinization, and formation of a crust (Mondal and Datta, 2008; Sablani et al., 1998; Yin and Walker, 1995). So, knowledge about transport phenomena of baking is also essential to study the development of browning during the process. In particular, the crust formation and its influence on baking have received much attention recently (Jefferson et al., 2006; Vanin et al., 2009; Zhang et al., 2007). This clearly contributes to a better understanding of colour formation, which mostly happens at surface of bakery products.

During baking of bread and other products such as cake, the formation and progressive advancing of an evaporation front towards the core are responsible of generating the crust (Lostie et al., 2002a, 2002b, 2004; Purlis and Salvadori, 2009a, 2009b; Zanoni et al., 1993, 1994). In the outer region of the product, the water content continuously decreases down to 5-10% (wet basis), while temperature rapidly increases above 100 ºC, tending to the oven temperature asymptotically. These variations in moisture and temperature give certain structural characteristics to the crust which avoids dehydration of inner regions by restricting the water vapour diffusion to the oven ambient (Hasatani et al., 1991; Wählby and Skjöldebrand, 2002). Regarding thin products like biscuit, internal mechanisms of transport may differ from previous description, but similar changes occur at surface giving the same characteristics (Ait Ameur et al., 2007; Gökmen et al., 2008a).

In conclusion, browning development in bakery products is related to various research areas of food science, and has implications to sensorial, nutritional, and industrial (design, control and optimization) aspects, and therefore, it represents a major challenge for food engineers. Table 1 presents a summary of the most relevant studies on the reviewed subject, regarding several aspects. The main objective of this paper was to review the published literature on browning development in bakery products from an engineering point of view. In this way, this review seeks to contribute to a better understanding of this subject from a comprehensive perspective, considering sensorial and nutritional aspects, measurement, modelling, and technological features that are important for the baking industry.

2. Effects of browning on properties of bakery products

The development of browning in bakery products is the result of the Maillard reaction and caramelization of sugars. Ingredients of baked foods such as bread, cake, and biscuit, i.e. carbohydrates, proteins and water, are actually the reactants for these chemical reactions, which are catalyzed by a low-medium moisture level and high temperature obtained at the product surface during baking (Fennema, 1996). Though the objective of this paper was not to review the browning process from a chemical but from an engineering point of view, a brief description of browning reactions will be given in order to have an adequate background to better understand the effects of browning on properties of bakery products. It is worth to note that the Maillard reaction and caramelization have been extensively studied in the (food) chemistry field; for a detailed discussion about this subject, the reader should be referred to specific literature (Baltes, 1982; Fennema, 1996; Hodge, 1953; Kroh, 1994; Martins et al., 2001; Namiki, 1988).

The Maillard reaction is actually a complex network of various reactions involving reactants and products with high reactivity, and its mechanism is still a controversial issue; therefore the reaction is difficult to control (Martins et al., 2001; Namiki, 1988). Basically, the reaction begins with a condensation between a reducing sugar (e.g. glucose) and a compound having a free amino group of an amino acid or mainly the ε-amino group of lysine in proteins. The condensation product (N-substituted glycosylamine) is then rearranged to form the Amadori product (1-amino-1-deoxy-2-ketose) which is subsequently degraded into different compounds depending on the pH of the system. At low-medium pH (4-7), HMF or furfural (when hexoses or pentoses are involved, respectively) are formed via enolization, which are highly reactive compounds that take part in further reactions (i.e. condensation and polymerization) leading to the formation of melanoidins and other brown polymers, and aromatic substances (Martins et al., 2001). A simplified scheme of the Maillard reaction is shown in Figure 1, where only the pathway corresponding to the formation of colour via HMF or furfural is depicted. This is the route commonly associated with browning development in bakery products because of the pH range, and experimentally followed by HMF quantification. Other reaction pathways (pH>7) involve sugar dehydration and fragmentation, amino acid degradation (Strecker degradation), and finally polymerization and formation of melanoidins. Corresponding (intermediate) reaction products include reductones, fission products (acetol, pyruvaldehyde and diacetyl), aldehydes, aldols and N-free polymers, and aldimines (Hodge, 1953).

Caramelization is also a complex group of reactions, and occurs by strongly heating (i.e. temperature greater than 120 ºC) of reducing carbohydrates without a nitrogen-containing compound (Fennema, 1996). Kroh (1994) described a principal sequence of sugar degradation reactions as follows: initial enolization, dehydration, dicarbonyl cleavage, retro aldolization, aldolization, and finally, radical reaction. From these principal reactions, the key intermediates are the osuloses (α-dicarbonyl compounds) obtained after enolization and dehydration, which lead to the formation of products with double bonds or unsaturated rings such as derivatives of furan, e.g. HMF, and polymers (Fennema, 1996; Kroh, 1994). During baking, starch and sucrose can be hydrolyzed leading to reducing sugars that can participate in both browning reactions, thus the Maillard reaction and caramelization may take place simultaneously (Capuano et al., 2008). Browning reactions are fundamental for the bakery industry because they produce changes in colour, flavour and nutritional value of products during baking.

2.1. Quality aspects

In bakery products, the surface colour is an important quality feature associated with aroma, taste, and appearance characteristics relevant from the consumers' viewpoint. In this sense, browning can be defined as the formation of typical colour, i.e.

yellow-gold or brown, depending on each particular product (i.e. ingredients, operating conditions, product specifications). The development of browning in bakery products is a dynamic process mainly influenced by temperature and water activity of the system, and results from the production and accumulation of coloured compounds during baking, i.e. principally HMF and melanoidins. Then, browning can be followed by measuring the reaction products concentration, or alternatively, the reactants consumption. On the other hand, the concept of lightness is commonly used to describe the variation of colour during baking, since lightness is a parameter of the CIE $L^*a^*b^*$ colour space (L^*, which ranges from 100 to 0 – white to black –), an international standard for colour measurement widely used in food science (Yam and Papadakis, 2004). Aspects related to measurement of browning development are discussed in the next section.

Before baking, dough presents values of lightness between 80 and 95 (Purlis and Salvadori, 2009c; Ramírez-Jiménez et al., 2000b; Shibukawa et al., 1989), although lower values can be measured depending on ingredients, e.g. high amount of egg and/or sugar generates a darker dough (Broyart et al., 1998); note that this discussion does not include products containing chocolate or similar coloured ingredients. In a chemical sense, HMF cannot be detected in raw dough since it is a product of browning reactions and therefore it is not present in untreated foods (Ait Ameur et al., 2006).

Then, one or two stages could be distinguished in the variation of product lightness during baking. The first stage is characterized by an enlightenment of the surface during the first minutes of baking. This phenomenon seems to be absurd since it is against browning chemistry; however, it was detected by some authors. In biscuit baking, Shibukawa et al. (1989) measured a slight increase of lightness (ca. 2.7%) at the early stage of heating (first 5-10 min) and suggested the drying of the surface to be responsible. Broyart et al. (1998) also observed this phenomenon (between 7.9% and 11.8%) during cracker baking and suggested the initial increase of product thickness (cracker spring) to explain it; a similar reason was proposed by Purlis and Salvadori (2007, 2009c), who observed 1.2-3.5% more of surface lightness in bread at 5 min of baking. Probably, this first enlightenment is only due to physical changes occurring at the product surface at the beginning of the process. Before baking, i.e. after dough preparation (and proving), the surface of dough is wrinkled, irregular, but after a few minutes of heating, it turns considerably smooth due to volume increase. This change in surface texture may be the reason of the observed initial enlightenment, since a smooth regular surface can reflect more amount of light than a wrinkled irregular one. In this sense, this first stage is related to the method used for measuring browning development. Certainly, reflectance or visual techniques such as colorimeter or computer vision system can detect this (physical) change in contrast to chemical methods, i.e. from a chemical point of view this first stage is a lag phase where the food system conditions (temperature and water activity) are not sufficient for allowing the formation of browning reactions products.

Indeed, there exist certain minimum requirements for the initiation of colour formation during baking of bakery products. In general, browning is detected since water activity decreases to 0.4-0.7 and temperature surpasses 105-120 ºC (Table 2). Under such conditions, only the surface (or crust) can show a significant change in colour during baking. Actually, in bread, HMF is detected almost exclusively in the crust (Capuano et al., 2008; Ramírez-Jiménez et al., 2000b). In conventional or traditional processing, temperature in inner regions (or crumb) does not exceed 100 ºC and water content (and activity) remains almost constant until the end of baking, though biscuit baking could be an exception when high oven temperature (>200-250 ºC) is used due to product thinness (Ait Ameur et al., 2007; Sablani et al., 1998). Temperature requirement is related to energy necessary to start chemical reactions, i.e. activation energy. In addition, the production of coloured compounds such as HMF always needs at least one dehydration step during the Maillard reaction (Figure 1) and caramelization (Kroh, 1994), so too much water induces an inhibition of browning reaction by the products (Ait Ameur et al., 2006; Martins et al., 2001).

In this way, low water activity favours the formation of colour during baking, which is consistent with reported high on-set temperatures, and transport phenomena involved in baking. In other words, as baking proceeds, temperature increases and water activity decreases at product surface (Figure 2), and therefore, browning development is accelerated leading to the formation and accumulation of colour compounds (Figure 3). Product formulation is also a critical factor for browning development. In bakery products, sugars content and the type of sugar are the main variables affecting colour formation. In general, HMF formation is increased with sugars content, but depending on baking conditions, sugars degradation proceeds in different ways. For instance, at oven temperatures below 300 ºC, sucrose presents stability and then glucose and fructose produce more HMF (Ait Ameur et al., 2007; Gökmen et al., 2007). Inversely, for more drastic baking conditions, sucrose can be totally hydrolyzed, and fructose and glucose released appear more reactive than pre-existing hexose in glucose and fructose formulated products in producing HMF (Ait Ameur et al., 2007). On the other hand, fructose can generate more HMF than glucose in any baking condition (Ait Ameur et al., 2007). Another important ingredient is the type of (chemical) leavening agent; the use of ammonium bicarbonate reduces the pH of dough and then accelerates the degradation of sucrose and consequently the formation of HMF during baking (Gökmen et al., 2008b).

It is difficult to suggest standard or target values for lightness or HMF concentration since there exist a great diversity of bakery products and operating conditions, besides consumers' preference is involved, but typical values are given in Table 3 in order to help establishing a general reference for conventional baking. Finally, when temperature is very high and low water activity is achieved at product surface, caramelization takes place producing more coloured compounds in addition to Maillard reaction products; this drastic condition is responsible for a burnt appearance characterized by low lightness of products. This can be seen in Figures 2 and 3 for bread baking; from 15-20 min under 220 ºC oven temperature, surface temperature surpasses 160 ºC and water activity decreases below 0.2, thus producing lightness values lower than 60 (Purlis and Salvadori, 2009c). Some authors reported values of total colour change (ΔE^*) between 50 and 60 as unacceptable condition for consumption regarding bread baking (Ahrné et al., 2007; Zanoni et al., 1995).

In addition to colour development, browning reactions produce compounds that contribute to flavour and aroma attributes of bakery products, which are also essential in the initial judgment of consumers. In the Maillard reaction, the type of flavour compound formed depends on the type of sugars and amino acids involved, while temperature, time, pH and water content of the system influence the reaction kinetics (Martins et al., 2001; van Boekel, 2006). Degradation (i.e. deamination and decarboxylation) of amino acids by dicarbonyls (Strecker degradation) is of major importance to flavour formation by the Maillard reaction, though other pathways are also possible (van Boekel, 2006). Sugars degradation in absence of amino acids, i.e. caramelization, also gives flavour compounds, especially related to caramel flavour (Fennema, 1996; Kroh, 1994). Some characteristic (desired) compounds are 2-acetyl-1-pyrroline, 4-hydroxy-2,5-dimethyl-3(2H)-furanone, methional, methylpropanal, 2,3-

butanedione, maltol and isomaltol (Fennema, 1996; Rychlik and Grosch, 1996; Vanin et al., 2009).

2.2. Nutritional aspects

The development of browning also produces important effects on the nutritional properties of bakery products. In the beginning of Maillard reaction, the condensation between reducing sugars and amino acids certainly destroys the amino acids, as well as melanoidins formation (Figure 1). This is of particular importance in the case of lysine, an essential amino acid whose ε-amino group is the major source of primary amines in proteins and therefore suffers a significant loss of bioavailability when the Maillard reaction occurs (Fennema, 1996). Furthermore, during browning occur oxidation and destruction of other essential amino acids (methionine and tryptophan) and cross-linking of proteins (also related to crust formation and setting), thus impairing digestibility of proteins involved and reducing the nutritional quality of bakery products (Morales et al., 2007). For instance, Tsen et al. (1983) reported a decrease in protein efficiency ratio (PER) of bread dough from 1.34 to 0.92 due to baking, and availability of lysine of 75% for bread crust in contrast to 90% for crumb, showing the negative effect of browning on the nutritional value of products.

The Maillard reaction is also associated with the formation of acrylamide, a probably carcinogenic compound (Mottram et al., 2002; Stadler et al., 2002). In 2002, significant amounts of acrylamide (150-4000 μg kg^{-1}) were found during cooking of carbohydrate-rich foods (Tareke et al., 2002). Actually, bakery products, together with potato products and coffee, are the most important sources of acrylamide (Claus et al., 2008). Reported values for acrylamide concentration in bread crust range between 85 and 230 µg kg^{-1}, for conventional baking at 200-270 ºC during 10-20 min (Ahrné et al., 2007; Surdyk et al, 2004); in the case of biscuits, average content of acrylamide is between 150 and 229 µg kg^{-1}, approximately (Gökmen et al., 2008a). Therefore, acrylamide formation during baking has been the focus of numerous studies with the aim of understanding the reaction mechanisms involved in order to predict and control its occurrence.

Acrylamide formation is initiated by the condensation of reducing sugars and amino acid asparagine in the first stage of the Maillard reaction (De Vleeschouwer et al., 2009; Mottram et al., 2002; Stadler et al., 2002; Zyzak et al., 2003). Production of acrylamide is strongly correlated with baking temperature and time, asparagine and reducing sugars content, and apparently starts at 120-130 ºC, so it could be only found in the crust of bakery products (Ahrné et al., 2007; Becalski et al., 2003; Bråthen and Knutsen, 2005; Surdyk et al., 2004). In addition, acrylamide formation is highly correlated with colour development (Ahrné et al., 2007; Amrein et al., 2004; Gökmen et al., 2008a; Surdyk et al, 2004). Mitigation strategies have been proposed to reduce the concentration of this toxic compound in baked foods: the use of sucrose instead of reducing sugars (Gökmen et al., 2007), and sodium hydrogencarbonate instead of ammonium hydrogencarbonate as leavening agent (Amrein et al., 2004; Graf et al., 2006); the addition of asparaginase (Capuano et al., 2008); steam and falling temperature baking (Ahrné et al., 2007). On the other hand, HMF is also suspected to be a harmful compound, so its presence is also undesired in bakery products (Gökmen et al., 2008b).

On a positive note, some products of browning reactions are health promoting substances. Reductones and melanoidins formed in browning reactions present antioxidative activity based on reducing power and metal chelating capability (Baltes, 1982; Fennema, 1996; González-Mateo et al., 2009; Morales et al., 2009; Yoshimura et al., 1997), and desmutagenic effects have been reported in the Maillard reaction (Martins et al., 2001).

3. Measurement of browning development

With the aim of predicting and controlling the development of browning during baking, it results necessary to quantify the advance of browning reactions. In this way, the formation of colour has been measured by different experimental techniques, which can be divided into two main categories: direct and indirect techniques. The first group involves chemical methods that aim to measure the concentration of browning reactions products (or alternatively the consumption of reactants). Conversely, the indirect approach is focused on registering the variation of colour produced by the Maillard reaction and caramelization, i.e. it is related to technological applications.

Direct or chemical techniques are mostly intended to measure the concentration of HMF and furfurals in products during baking. The general procedure consists in an extraction method, and subsequent quantification by HPLC-UV; UV detection is carried out at 280 or 284 nm (Ait Ameur et al., 2006, 2007; Ramírez-Jiménez et al., 2000b). A similar protocol is used for furosine determination, which is a compound formed at early stages of Maillard reaction (Ramírez-Jiménez et al., 2000b). Development of browning can also be followed by measuring the reactants consumption. In this sense, Ait Ameur et al. (2007) quantified the degradation of sugars in biscuit baking with a HPLC-RI (refractive index) detection method, after a water-ethanol extraction.

Indirect techniques are based on a technological or sensorial approach. The traditional way of measuring the variation of colour has been the use of a colorimeter or colour sensor (Ahrné et al., 2007; Ait Ameur et al., 2007; Baik et al., 2000; Broyart et al., 1998; Keskin et al., 2004; Mundt and Wedzicha, 2007; Ramírez-Jiménez et al., 2000a, 2000b; Shibukawa et al., 1989; Zanoni et al., 1995; Zareifard et al., 2009), while computer vision systems represent a very promising tool for industrial applications (Abdullah, 2008; Gökmen et al., 2008; Purlis and Salvadori, 2007, 2009c; Wählby and Skjöldebrand, 2002). Basically, indirect methods quantify the amount of reflected light by the surface of the food, i.e. reflectance measurement, and results are given in a certain colour space. In food science, colour is mostly represented by the CIE $L^*a^*b^*$ colour space, which is an international standard for colour measurement adopted by *Commission Internationale de l'Eclairage* (CIE) in 1976 (León et al., 2006). The three parameters of this model represent the lightness of colour (L^*), its position between red and green (a^*), and its position between yellow and blue (b^*) (Yam and Papadakis, 2004). The CIE $L^*a^*b^*$ colour system is based on the spectral sensitivity of human sight and its adaptation to prevailing lighting conditions (Mendoza et al., 2007).

Main advantages of chemical techniques are objectivity, since a compound concentration is being measured, and sensibility (Ramírez-Jiménez et al., 2000b). On the other hand, such methods are destructive, laborious and time consuming. Inversely, indirect techniques are automated, rapid and non-destructive, although they have a sensorial basis. At present, computer vision is preferred over colorimeter or colour sensor devices in food engineering applications, especially in the research field. This is because computer vision based on image processing is a low-cost technique. In addition, computer vision does not imply any contact with samples for measurement, which is essential in the case of deformable materials such as dough. A major advantage of this technique with respect to a conventional colorimeter is the measured area in a single determination. By means of computer vision a great amount of data could be processed in one step, e.g. the whole top surface of a product (see Figure 3b), while colorimeters give information about much smaller areas, e.g. 0.95 cm^2 for Minolta CR-300 (Japan). Moreover, other important quality properties besides colour can be assessed by using this method, i.e. size, shape, and texture of products (Zheng et al., 2006), and also can be used to evaluate nutritional properties such as acrylamide formation during baking (Ahrné et al., 2007; Gökmen et al., 2008a). For further information about computer vision and its applications for food quality evaluation, the reader should be referred to specific reviews and literature (Brosnan and Sun, 2004; Gunasekaran, 1996; León et al., 2006; Sun, 2008; Zheng et al., 2006).

4. Mathematical modelling of browning

Once the browning process has been characterized in terms of product properties and operating conditions, it becomes essential for food technologists to develop a mathematical model with the aim of predicting and therefore controlling the browning development during baking, which not only affects sensorial attributes but also the nutritional value of food. However, modelling this process in bakery products is a major challenge, since browning reactions involve complex mechanisms that are still not well elucidated, and moreover occur in a non-ideal system where simultaneous heat and mass transfer takes place, producing continuous changes in temperature and water activity.

Undoubtedly, the best approach to model the browning development would be to consider the actual mechanisms of reactions and transport phenomena occurring in products during baking, but this is not possible so far. Instead, the kinetic approach is widely used for modelling browning. Kinetic modelling establishes that a process can be mathematically described by means of rate constants and activation energies (i.e. kinetic parameters) with the aim of understanding, predicting and controlling the quality changes in food processing (van Boekel, 2008). In addition, the kinetic approach is a powerful tool since it is based only on the rate-determining steps of the reaction, which provide control points (Martins et al., 2001). In this way, colour formation is usually simplified by assuming a general mechanism of browning including both the Maillard reaction and caramelization (Zanoni et al., 1995). On these concepts, some efforts have been made to predict the development of browning during baking. Mostly, browning models have been developed for bread and biscuit, assuming first-order kinetics with the browning rate constant dependent on temperature.

In the case of bread, Zanoni et al. (1995) firstly proposed a mathematical model to predict the browning of crust during baking. The model was set up by using ground, dried bread crumb as a model system for crust. Flat and compressed discs of milled crumb were dried until reaching constant weight and then heated at constant temperature with a refractory plate. Several browning experiments were performed at different temperatures (140 to 250 ºC). A first-order kinetic model for total colour difference was proposed, and the reaction rate constant was found to be temperature dependent following the Arrhenius' equation. Then, Zanoni et al. (1995) applied the proposed model to predict crust browning during bread baking at 200 and 250 ºC, but results were only acceptable for 250 ºC. The authors concluded that kinetic parameters obtained from isothermal experiments cannot be used for practical baking conditions, and also remarked on the influence of water content on browning.

Purlis and Salvadori (2007) reported an expression for colour development during bread baking as a function of product weight loss and baking temperature. Experimental data were obtained for 180, 200 and 220 ºC oven temperature under natural and forced convection baking modes, and colour was measured directly from bread samples by using a computer vision system. In this way, the development of browning was followed in a non-ideal system, close to a real baking condition. Acceptable results were reported for a general baking process. More recently, these authors proposed another model for browning of bread during baking, but depending on local temperature and water activity (Purlis and Salvadori, 2009c). This model was based on a non-isothermal kinetic approach, since bread surface heating (and drying) and thus browning are non-isothermal processes. So, the variation of temperature and water activity during baking (obtained by numerical simulation) was included in the browning model. Good results for kinetic parameter estimation and description of colour development according to heat and mass transfer processes were reported.

Regarding biscuit baking, Broyart et al. (1998) developed a first-order kinetic model to predict the lightness variation during the process. For parameter estimation and model validation, baking experiments were carried out at 180-330 ºC oven temperature, and colour of cracker surface was measured by a reflectance method. In addition, average temperature and water content of samples were registered in each baking test. In this way, the variation of bulk temperature and moisture of biscuit during baking could be included in the browning model. Prediction errors for lightness were between 1% and 24% at the end of baking, which were partially attributed to imprecision of colour measurements at high surface temperatures. Moreover, Broyart et al. (1998) emphasized the limitation of the model since average parameters (i.e. temperature and water content) are used to predict a surface property (i.e. lightness).

Also for baking of biscuit, Mundt and Wedzicha (2007) proposed a first-order kinetic model based on an approach commonly used in colour-using industry (e.g. textile) to relate reflectance measurements (R, G, B colour values) to concentration of coloured compounds produced by browning reactions. The authors reported that water activity has no effect on the kinetics of browning, though experimental data were obtained at low temperature (105-130 ºC). Conversely, from a chemical viewpoint, Ait Ameur et al. (2006, 2007) showed that formation of HMF in biscuit follows first-order kinetics, as well as colour development, and that water activity highly influences the production of coloured compounds. Finally, Hadiyanto et al. (2007) proposed a zero-order kinetic model for the formation of melanoidins (due to Maillard reaction) during baking of bakery products, where the influence of temperature and water activity was taken into account. Table 4 presents some values of kinetic parameters reported in literature for browning development.

4.1. A general model for browning

So far, it has been demonstrated that development of browning during baking can be well described by a first-order kinetic model, with parameters depending on local temperature and water activity of the product. In addition, although colour formation is caused by group of complex chemical reactions, it can be simplified by assuming a general mechanism of browning, and followed by using colour models related to reflectance methods, for technological purposes. Finally, kinetics parameters should be estimated from experiments close to actual baking conditions, i.e. a non-isothermal process occurring in a non-ideal system, in order to obtain a better prediction performance (Dolan, 2003).

Based on these concepts, and selecting surface lightness (L^*) as browning index, a general model for colour development during baking can be stated as follows:

$$\frac{dL^*}{dt} = -kL^* \qquad (1)$$

To describe the dependence of rate constant (k) with temperature, the Arrhenius' law is commonly used:

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

where k_0 is the pre-exponential factor, E_a is the activation energy, T is (absolute) temperature, and R is the universal gas constant. However, this expression for temperature dependence has significance for chemical compounds such as HMF, which involves an energy activation related to a reaction. In the case of lightness or other colour variable representing the change of colour intensity, not directly involving chemical compounds, the activation energy concept may not be applicable (van Boekel, 2008). Instead of Arrhenius' equation, the following expression can be used to describe equally well the dependence of browning rate constant with temperature:

$$k = k_0 \exp\left(-\frac{A}{T}\right) \tag{3}$$

where k_0 and A are fit parameters without physical meaning.

On the other hand, the influence of water activity (or water content) of the product surface can be incorporated in different ways. For instance, Broyart et al. (1998) proposed to define the parameters of browning rate constant expression (k_0 and E_a in their model) as a function of water content. Then, Purlis and Salvadori (2009c) adopted this approach to express the parameters of an Arrhenius-like expression for rate constant k (Eq. (3)) as a function of water activity:

$$k_0 = k_1 + \frac{k_2}{a_w} \tag{4}$$

$$A = k_3 + \frac{k_4}{a_w} \tag{5}$$

Finally, parameter estimation is required to obtain a model for browning development. It is not the intention to review here the available numerical methods for computing the kinetic parameters, but it would be helpful to make some considerations with respect to the kinetic approach selected to develop a mathematical model. If a non-isothermal approach will be applied, the model will include the thermal history of the product during baking (the same analysis is valid for water activity or water content). So, let us consider that the browning development is described by Eqs. (1) and (3), and the variation of temperature during baking has been registered. Then, an analytical expression for lightness variation can not be obtained, since *k* depends on temperature that also changes with time. Therefore, Eq. (1) must be evaluated numerically in order to estimate kinetic parameters. For instance, Broyart et al. (1998) applied the Euler-Cauchy method, and Purlis and Salvadori (2009c) used a medium order Runge-Kutta routine.

5. Technological aspects of browning

After understanding the browning process, i.e. chemical reactions involved and their effects on both sensorial and nutritional properties of products, and knowing about how to measure and predict its development during baking, it would be interesting and useful to analyze such phenomenon from a technological point of view. In this way, the formation of colour has been correlated with other changes occurring during baking. The major advantage of this approach is that colour development is usually easier to monitor than other processes or reactions taking place in bakery products during baking, especially nowadays with the existence of rapid detection devices such as computer vision systems or colour sensors. Furthermore, surface colour is highly associated with the overall quality of food, and certainly has an important effect on the consumer judgment and therefore the acceptability of bakery products, since colour influences the anticipated oral and olfactory sensations because of the memory of previous eating experiences (Abdullah, 2008). In addition, if a computer vision system is used to measure browning development, other features can be extracted simultaneously, i.e. size, shape, and texture (Brosnan and Sun, 2004; Zheng et al., 2006). Computer vision can be coupled to learning techniques such as fuzzy logic and artificial neural networks for quality evaluation. In this way, assessment of quality attributes can be achieved automatically, improving production performance besides increasing evaluation accuracy (Du and Sun, 2006).

In particular, fuzzy logic and artificial neural networks appear as very interesting tools for food process control based on browning development, since the reasoning and linguistic terms of operators, experts, and consumers can be taken into account (Allais et al., 2007; Perrot et al., 2006). For bread baking, Kim and Cho (1997) developed neural networks models and a fuzzy controller to reduce the cost for heating the oven and to perform an intelligent control of the process. For the case of biscuit baking, Perrot et al. (1996, 2000) applied fuzzy methods for real time quality evaluation and feed-back control of the process. Another contribution to the field was made by Ioannou et al. (2004a, 2004b): they presented a browning process control system that gives the operator a diagnosis of the state of the product/process and proposes actions on process parameters based on a decision model. As well, browning can be part of an overall procedure developed for process design and optimization (Hadiyanto et al., 2007, 2008a, 2008b; Therdthai et al., 2002), and management of baking ovens (McFarlane, 1990). For these purposes, it can be useful to have a mathematical model for describing colour development during baking as a function of process variables.

Finally, the variation of nutritional properties of products could be followed through browning during baking. For instance, acrylamide formation is of major concern in food processing, but its experimental determination requires a (destructive) chemical and non-fast method that cannot be applied in a continuous production line. Fortunately, a good correlation between browning development and acrylamide formation was found in baking of biscuit (Gökmen et al., 2008) and bread (Ahrné et al., 2007). In this way, combining a correlation between colour and acrylamide formation, and a computer vision system, a process control tool could be developed for both safety and quality evaluation purposes.

6. Conclusion

The development of browning in bakery products during baking is a subject of major interest for food technologists. Browning affects the overall quality of food, producing changes in sensorial attributes such as colour, flavour and aroma, global acceptance, and in nutritional properties, i.e. decrease of bioavailability of proteins and amino acids, formation of toxic compounds (e.g. acrylamide and HMF), and generating substances with antioxidative capability. Browning is the result of the Maillard reaction and caramelization, and its development depends on product formulation (amino compounds, sugars and leavening agents) and operating conditions (temperature and water activity). In this way, the use of real food systems instead of model systems is necessary for better understanding and controlling of browning in bakery products.

Colour development is correlated with several changes occurring during baking, which represents a major advantage for food engineers. In this way, formation of colour has been measured by chemical and sensorial methods, both providing good results.

Nevertheless, it would be useful to develop a standard or universal procedure to follow colour variation during baking. A possible approach would be to calibrate a sensorial method (e.g. computer vision system or colorimeter) against a chemical technique (e.g. HMF quantification), as a function of product formulation, and finally to express the colour in standardized units (e.g. using CIE $L^*a^*b^*$ model). In other words, an effort should be made to develop a rapid, low-cost, automated, sensible and objective method for the baking industry.

Finally, it has been shown that understanding the browning development gives the possibility of managing the baking process in an overall way; it can be used to control, optimize, and design processes and equipment for the bakery industry. For these aims, it will be useful to have a mathematical model for browning development. A browning model cannot be developed from the actual mechanisms of colour formation due to they are not elucidated yet, but the kinetic approach is a helpful alternative to describe colour changes during baking. An adequate model should include the influence of temperature and water activity (or water content) on browning development, and kinetic parameters should be obtained under conditions close to real baking situations (non-isothermal mostly) by using appropriate measurement techniques, experimental designs, and numerical methods.

Acknowledgements

Author would like to thank to Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), and Universidad Nacional de La Plata (UNLP) for financial support.

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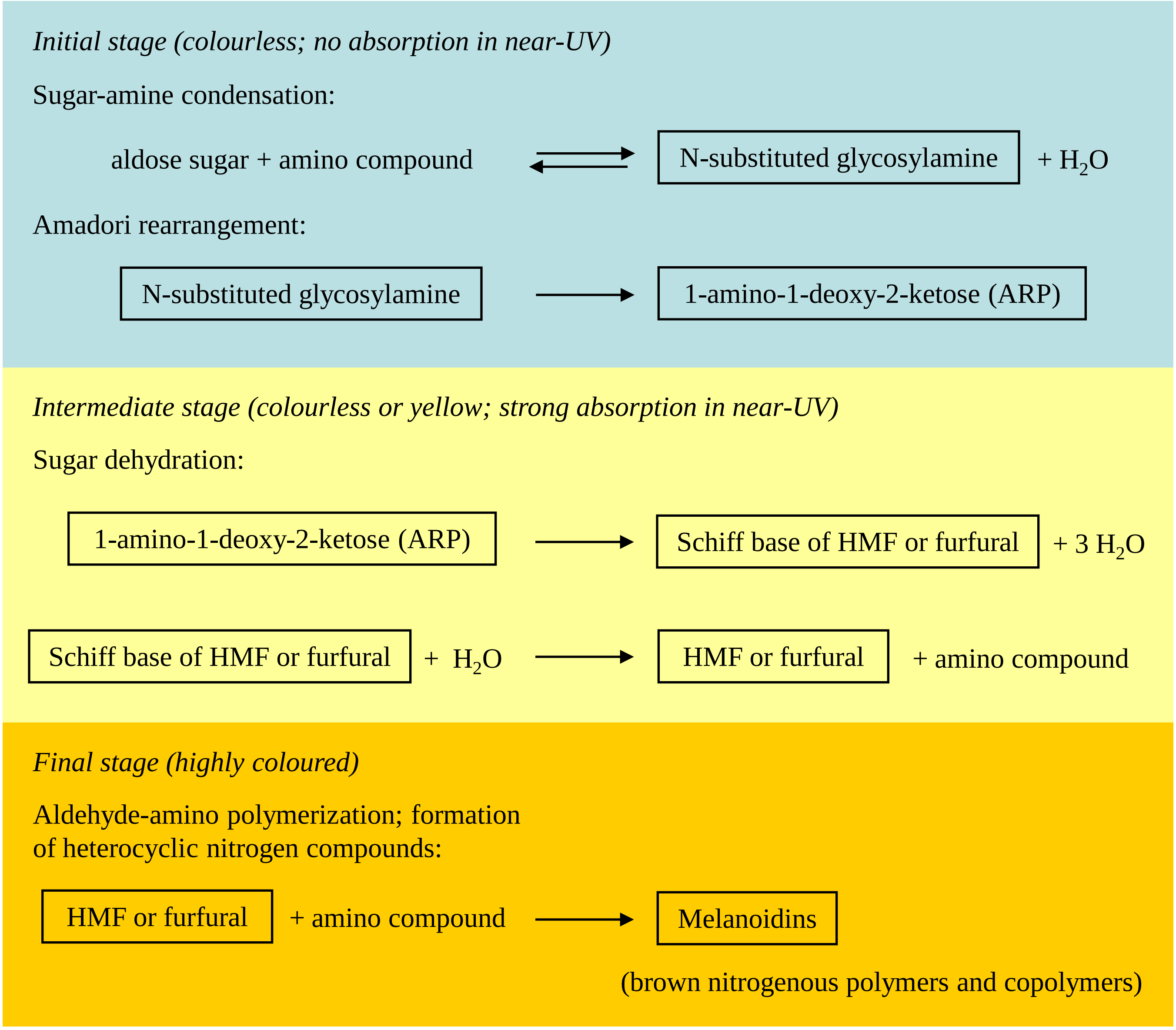
Figure captions

Figure 1. Simplified scheme of the Maillard reaction (pH≤7), adapted from Hodge (1953), and Martins et al. (2001). ARP: Amadori rearrangement product; HMF: hydroxymethylfurfural.

Figure 2. Temperature (a) and water activity (b) at bread surface during baking at 180 ºC (squares), 200 ºC (triangles), and 220 ºC (circles), obtained by numerical simulation (Purlis and Salvadori, 2009c).

Figure 3. (a) Variation of lightness of bread surface during baking at 180 ºC (squares), 200 ºC (triangles), and 220 ºC (circles). (b) Image gallery of samples corresponding to (a) (Purlis and Salvadori, 2009c).

Figure 1 – Purlis



Initial stage (colourless; no absorption in near-UV)

Sugar-amine condensation:

aldose sugar + amino compound ⇌ N-substituted glycosylamine + H_2O

Amadori rearrangement:

N-substituted glycosylamine → 1-amino-1-deoxy-2-ketose (ARP)

Intermediate stage (colourless or yellow; strong absorption in near-UV)

Sugar dehydration:

1-amino-1-deoxy-2-ketose (ARP) → Schiff base of HMF or furfural + 3 H_2O

Schiff base of HMF or furfural + H_2O → HMF or furfural + amino compound

Final stage (highly coloured)

Aldehyde-amino polymerization; formation of heterocyclic nitrogen compounds:

HMF or furfural + amino compound → Melanoidins

(brown nitrogenous polymers and copolymers)

Figure 2 – Purlis

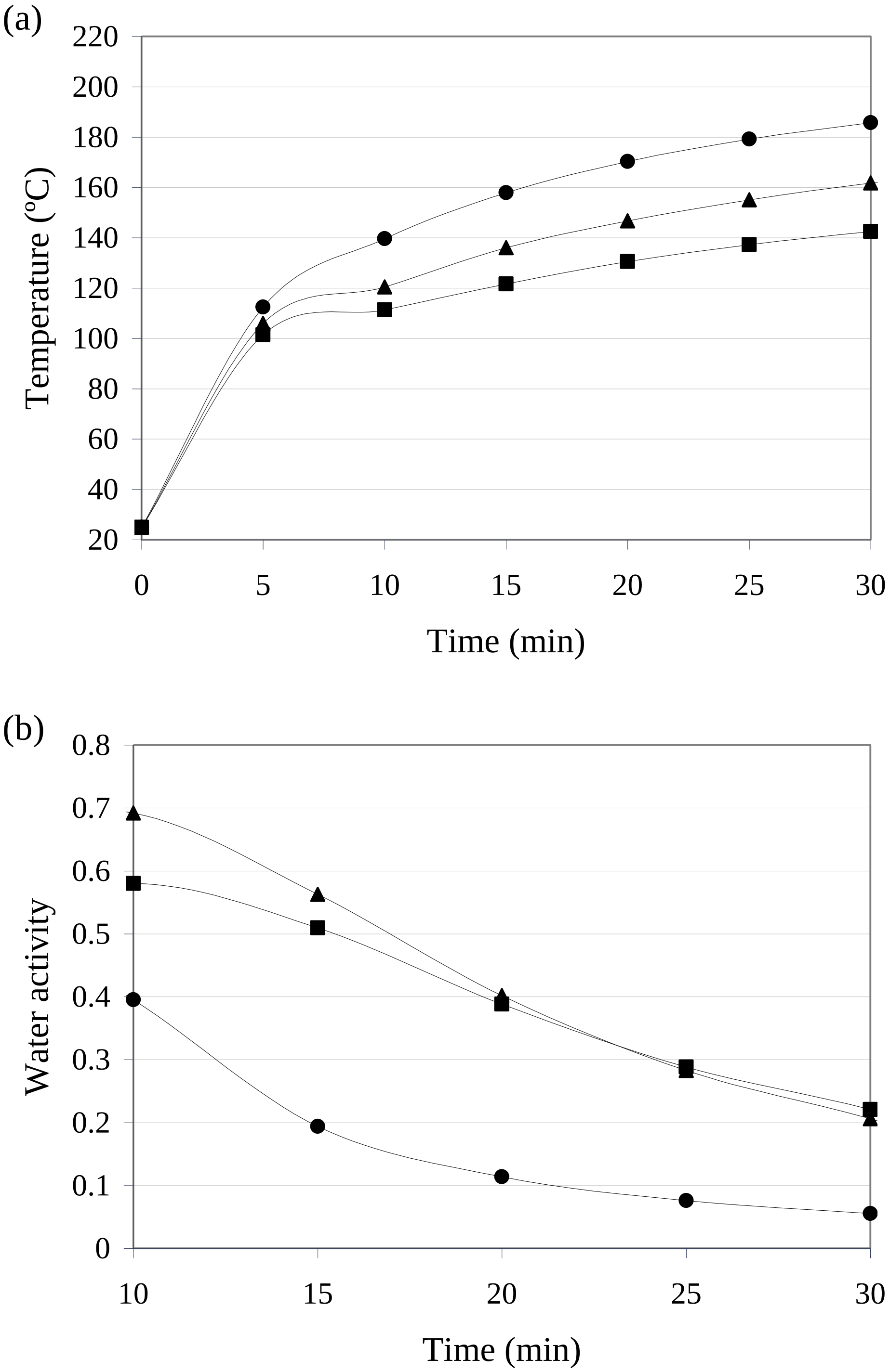


Figure 3 – Purlis

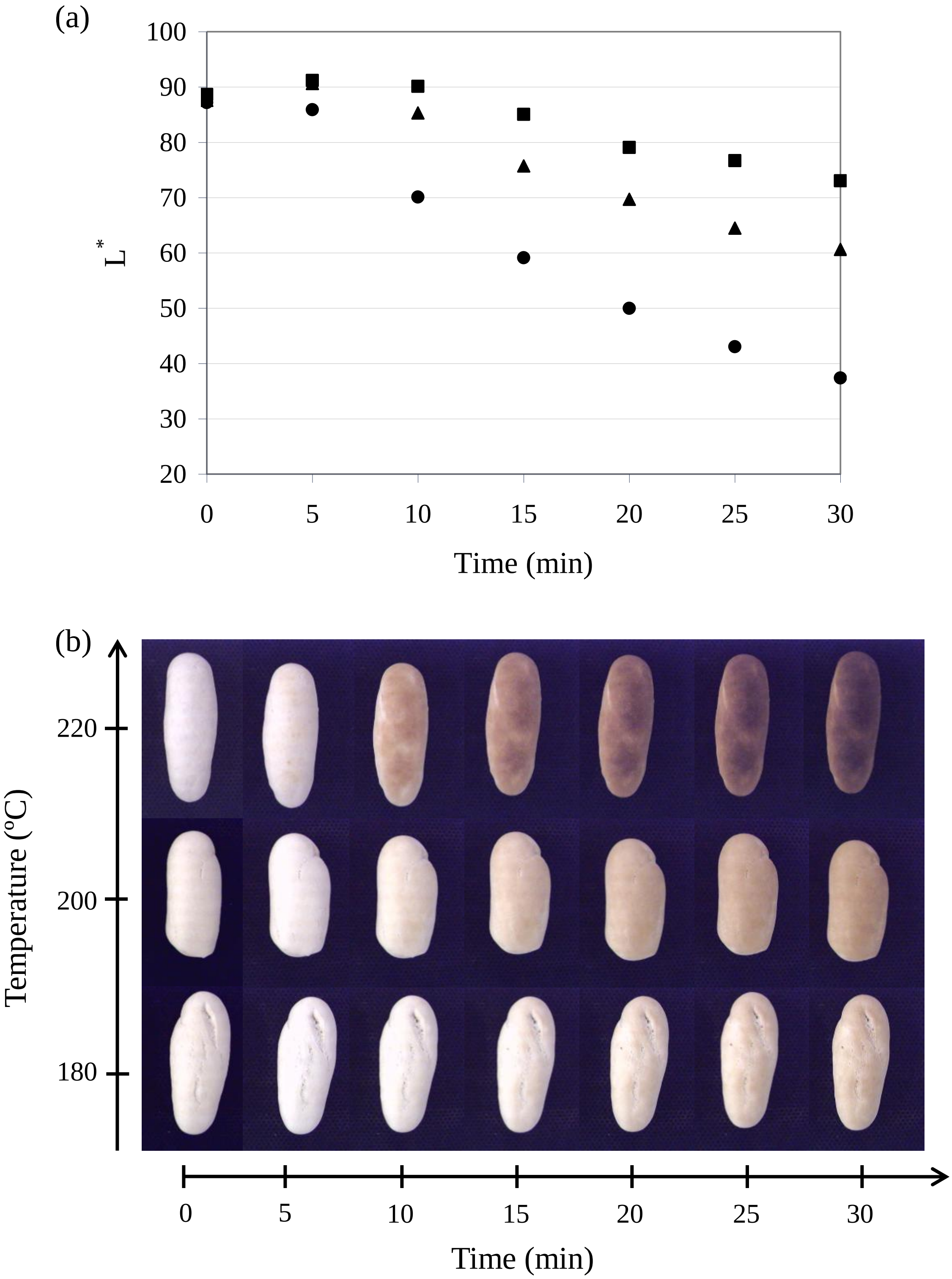


Table 1

Principal aspects of browning development in bakery products and most relevant studies.

Aspect of browning development	Reference
Chemistry of the Maillard reaction and caramelization	Hodge (1953), Kroh (1994), Martins et al. (2001), van Boekel (2006)
Study of the Maillard reaction and caramelization in bakery products	Ait Ameur et al. (2006, 2007), Capuano et al. (2008), Gökmen et al. (2007, 2008b), Ramírez-Jiménez et al. (2000b)
Chemistry of acrylamide formation	De Vleeschouwer et al. (2009), Mottram et al. (2002), Stadler et al. (2002), Tareke et al. (2002), Zyzak et al. (2003)
Acrylamide formation in bakery products	Ahrné et al. (2007), Amrein et al. (2004), Becalski et al. (2003), Bråthen and Knutsen (2005), Gökmen et al. (2007, 2008a), Surdyk et al. (2004)
Kinetic modelling	Broyart et al. (1998), Dolan (2003), Purlis and Salvadori (2009c), van Boekel (2008)

Table 2

Temperature and water activity values for initiation of browning for different bakery products.

Product	Temperature (ºC)	Water activity	Reference
Biscuit 100% flour 50% sugar 20% margarine ~20% milk 5% eggs	>120		Shibukawa et al. (1989) L^* determination
Biscuit 100% flour 37% sugars 17.5% water 16% fats	>105-115		Broyart et al. (1998) L^* determination
Biscuit 100% flour 50% sugar syrup 17% palm fat		<0.4-0.7	Ait Ameur et al. (2006, 2007) HMF determination
Biscuit 100% flour 44% sugars 40% shortening 22% water 1.5% leavening agents 1.25% salt		<0.4	Gökmen et al. (2008b) HMF determination
Bun 100% flour ~57% skimmed milk 11.4% margarine 9.7% sugar 5.7% fresh yeast	>110		Wählby and Skjöldebrand (2002) L^* determination
Bread 100% flour 54.1% water 1.6% salt 1.6% sugar 1.6% margarine 1.2% dry yeast	>120	<0.6	Purlis and Salvadori (2009c) L^* determination

Table 3

Some typical values of lightness (L^*) and HMF concentration (mg kg^{-1} dry matter) in bakery products for various baking conditions. Ranges of L^*, HMF and/or operating conditions are ordered respectively.

Product	L^* or HMF	Operating conditions	Reference
Biscuit	L^* = 40-50	19 min, 200 ºC	Shibukawa et al. (1989)
	L^* = 55.7-14.4	6 min, 240-330 ºC	Broyart et al. (1998)
	L^* = 57.1	90 min, 180 ºC	Ramírez-Jiménez et al. (2000a)
	HMF = 15.6		
	HMF = 0.49-74.6	(Commercial, unknown)	Ait Ameur et al. (2006)
Fermented dough, ~10% sucrose	L^* = 65.6	8-10 min, 220 ºC	Ramírez-Jiménez et al. (2000a)
	HMF = 151.2		
White bread	L^* = 84.1, 77.2	50 min, 200 ºC	Ramírez-Jiménez et al. (2000b)
	HMF = 11.8, 68.8		
	L^* = 81.6	60 min, 200 ºC	
	HMF = 40.1		
	L^* = 81.9, 82.1	30 min, 210 ºC	
	HMF = 3.4, 15.7		
	L^* = 83.0	16 min, 235 ºC	
	HMF = 21.8		
Bread crisp	L^* = 80.73	40 min, 140 ºC	Capuano et al. (2008)
	HMF = 2.53		
	L^* = 72.40	34 min, 160 ºC	
	HMF = 14.63		
	L^* = 63.48	25 min, 180 ºC	
	HMF = 47.02		
Bun	L^* = 52.13	8 min, 225 ºC	Esteller et al. (2006)
Muffin	L^* = 83.9 ± 2.8	(Commercial, unknown)	González-Mateo et al. (2009)

Table 4

Kinetic models for browning development in bakery products. More details can be found in the text (Section 4).

Product	Model description	Reference
Biscuit	First order for L^*; Arrhenius-like equation for rate constant $k = k_0 \exp\left(-\frac{A}{T}\right)$ (min^{-1}) $k_0 = 2.40 \times 10^8 + \frac{1.56 \times 10^7}{X_w}$ $A = 8.13 \times 10^3 + \frac{3.90 \times 10^2}{X_w}$	Broyart et al. (1998)
	First order for HMF; E_a = 10.63 kJ mol^{-1} (Arrhenius) k = 0.0028 s^{-1} for 200 ºC baking k = 0.0067 s^{-1} for 250 ºC baking k = 0.0082 s^{-1} for 300 ºC baking	Ait Ameur et al. (2006)
Bread	First order for ΔE; Arrhenius equation for rate constant k_0 = 42000 s^{-1}, E_a = 64151 J mol^{-1}	Zanoni et al. (1995)
	$\Delta E = (k_0\, T_{oven} + k_1)\, WL$, k_0 = 0.0266 ºC^{-1}, k_1 = -3.4991	Purlis and Salvadori (2007)
	First order for L^*; Arrhenius-like equation for rate constant $k = k_0 \exp\left(-\frac{A}{T}\right)$ (min^{-1}) $k_0 = 7.9233 \times 10^6 + \frac{2.7397 \times 10^6}{a_w}$ $A = 8.7015 \times 10^3 + \frac{49.4738}{a_w}$	Purlis and Salvadori (2009c)

k: constant rate. E_a: activation energy. ΔE: total colour change. WL: weight loss (%). T_{oven}: oven temperature (ºC). T: temperature (K). a_w: water activity. X_w: water content (dry basis).