Modelling the browning of bakery products during baking: a review

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Keywords:

Bakery
Baking
Browning
Colour
Caramelization
Maillard
Kinetic

Article history:

Received 29.03.2022
Received in revised form 18.08.2022
Accepted 2.09.2022

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DOI: 10.24263/2304-974X-2022-11-2-3

Abstract

Introduction. It was reviewed the results of scientific studies on the presence of non-enzymatic browning compounds in bakery products, the mechanism and factors influencing their formation, as well as the prediction and control of the development of browning in baked goods using mathematical modelling.

Materials and methods. Analytical studies on the mechanism of browning on the surface of bakery products and the prediction and control of the development of browning in bakery products using mathematical modelling based on already available research articles.

Results and discussion. The formation of colour in bakery products during the baking phase is commonly known as browning. The brown colour on the surface of bakery products comes from melanoidins (an insoluble brown pigment) and caramel, which are products of non-enzymatic browning reactions (Maillard reactions and caramelization). These reactions can also form undesirable products with potentially mutagenic effects (acrylamide, hydroxymethylfurfural and furfural), resulting in a loss of nutritional value of the product. The change in the colour of the surface of the product is considered an essential parameter for determining the end of the baking process of bakery products. Efforts should be made to develop a fast, inexpensive, automated, reasonable and objective method to track colour change during baking. The development of a mathematical model of browning is essential to predict and control this phenomena during baking as a function of operating conditions and the product recipe. Kinetic models for the colour change of bakery products are divided into two groups. The first group consists of kinetic models of colour change where the independent variable is time. This group includes kinetic models of zero, first and second order reactions and the exponential empirical model. The second group consists of kinetic models of colour change where the independent variable is mass loss.

Conclusion. Since browning affects the overall quality of food and leads to changes in sensory and nutritional properties (reduction in bioavailability of proteins and amino acids, formation of acrylamide, hydroxymethylfurfural, and formation of substances with antioxidant activity), it is a topic of great interest to food technologists.

Introduction

Bakery products include foods whose main ingredient is flour and which undergo a baking process, such as bread, various pastries, cakes, crackers, pies, croissants, and many other products. The external appearance is the first characteristic of the quality of bakery products that the consumer perceives. Controlling the development of colour on the surface of bakery products directly affects their acceptance or rejection by consumers. The formation of colour on the surface of bakery products during baking is considered a desirable characteristic and is the result of non-enzymatic browning reactions (Hodge, 1953). By monitoring and controlling these reactions, it is possible to influence the desired colour of the final product.

The brown colour on the surface of bakery products comes from melanoidins (an insoluble brown pigment) and caramel, which are products of non-enzymatic browning reactions (Maillard reactions and caramelization). These reactions can also form undesirable products with potentially mutagenic effects (acrylamide (AA), hydroxymethylfurfural (HMF) and furfural), resulting in a loss of nutritional value of the product.

During baking of bakery products, a crust is formed and the change in the initial colour of the crust starts with the appearance of light yellow dextrins when a temperature of 110 to 120 °C is reached on the surface of the product (Wahlby and Skjoldebrand, 2002). A further increase in temperature leads to the formation of products of the Maillard reaction and caramelization (melanoidins and caramel) and then to the combustion of the products and the formation of a black porous mass. The speed of colour development on the surface of bakery products depends on the process conditions such as temperature and baking time. However, apart from the process conditions, colour development is also influenced by the amount of water, water activity, pH, amount of reducing sugars, etc.

Numerous researchers have developed various direct and indirect methods for measuring colour on the product surface. Direct methods aim at quantitative monitoring of the products of Maillard reactions and caramelization (AA, HMF and furfural) (Ramirez-Jimenez et al., 2000). While indirect methods are based on the principle of measuring the amount of light reflected from the surface of the analysed sample using devices such as colorimeter, chromameter (Gokmen et al, 2008a-b; Purlis and Salvadori, 2007), and a computer image analysis system (Brosnan and Sun, 2004, Du and Sun, 2004, 2005; Shahin and Symons, 2001).

All reactions proceed at a certain rate, which depends primarily on the temperature and concentration of the reacting substances. The rate of chemical reactions (chemical kinetics) is an area of interest for many scientists (Montgomery and Runger, 2003; Purlis and Salvadori, 2007, 2009a-c; Purlis 2010, 2011; van Boekel, 2008), whose research is related to the colour change of bakery products during baking (kinetic modelling). Furthermore, a good understanding of the kinetics of non-enzymatic browning reactions can inform how to improve the food product, preserve existing nutritional components during processing or minimise the occurrence of undesirable degradative changes. Therefore, the purpose of developing mathematical models is often to predict the behaviour of food ingredients during processing and storage and to optimise the process to obtain the highest quality product.

Considering that the external appearance is the most striking feature of the quality of bakery products, monitoring the kinetics of colour change during baking is important for optimising the quality of the final product. Good management of all processes in the production and distribution chain in the market leads to high quality food that is safe for the health of consumers. Among other things, it is necessary to prevent non-enzymatic browning reactions to reduce colour and flavour changes when these changes have a negative impact on the quality of the final product. Changes caused by non-enzymatic browning may be desirable in some cases when a specific flavour is to be achieved during a thermal treatment such as baking, roasting or drying. Enzymatic browning reactions can contribute to the general acceptability of foods such as tea, coffee, cocoa and dried fruits. Despite much research on non-enzymatic browning, with a focus on Maillard reactions, the means to control these reactions during processing are not yet fully understood.

The change in the colour of the surface of the product is considered an essential parameter for determining the end of the baking process of bakery products. The development of a mathematical model of browning is essential to predict and control this phenomenon during baking as a function of operating conditions and the product recipe. Kinetic models for the colour change of bakery products are divided into two groups. The first group consists of kinetic models of colour change where the independent variable is time. This group includes kinetic models of zero, first and second order reactions and the exponential empirical model (Pedreschi et al., 2006; van Boekel, 2008). The second group consists of kinetic models of colour change where the independent variable is mass loss (Purlis and Salvadori, 2007).

The aim of this article is to present, based on the available literature, the results of scientific studies on the presence of non-enzymatic browning products in bakery products, the mechanism of their formation and the factors influencing their formation, as well as the prediction and control of the development of browning in bakery products using mathematical modelling.

Materials and methods

The review is based on already available research articles on the presence of non-enzymatic browning products in bakery products, the mechanism of their formation and the factors influencing their formation, as well as on the use of kinetic models of browning, which are essential for predicting and controlling this phenomenon during baking depending on the operating conditions and product formulation.

Literature referenced in this review article was obtained from bibliographic information in Google Scholar, Web of Science, Science Direct, Scopus, Springer Link, EBSCO host, Wiley online library, PubMed, DOAB (directory of open access books), Ovid SP database and CAB abstracts.

Results and discussion

Changes in bakery products during heat treatment

Products in which flour is the main ingredient and which undergo a baking process are called bakery products. Bakery products include bread, pastries, croissants, pies, cookies, cakes, and many other products, all of which differ in their composition and production methods. Baking is a heat treatment process in which heat is applied directly to the food and temperatures of up to 260 °C are reached. Due to the high temperatures used in baking and the low moisture content, the heat treatment of bakery products triggers a series of chemical reactions between food ingredients that affect the quality of the final product. The consequences of these chemical reactions are mainly improvements in the textural and organoleptic properties of the food. However, undesirable consequences may also occur, such as the natural formation of potentially toxic products, which may also affect the final taste and appearance of the food. Baking can be defined as a process that transforms a base of flour and water or a dough into a food product with unique sensory characteristics. Therefore, the appearance and the colour of the surface of bakery products in general are very important quality parameters on which the consumer's decision to accept the product depends, as it is related to the taste and the degree of satisfaction (Pedreschi et al., 2006). As for the quality of bakery products, although the typical characteristics depend on the product itself, the surface colour, together with texture and taste, is the most important characteristic for consumer preference, so they can be used to evaluate the baking result (Abdullah, 2008). In addition, legal regulations may also set certain parameters for this aspect. For example, in Argentina, bread crust must have a uniform golden yellow colour (ANMAT, 2004). Therefore, understanding the evolution of colour on the product surface is a very important factor for the bakery industry.

Chemical processes that influence the colour development of bakery products

Baking is a complex process that involves a number of physical, chemical, and biological changes, such as water evaporation, creation of porous structures, volume expansion, denaturation of proteins, gelatinization of starch, crust formation, and others (Mondal and Datta, 2008). The consequence of the above changes is the development of certain characteristics of bakery products – colour, shape, size and texture, where the colour of the product surface has a significant impact on the evaluation of the quality of the food itself. During baking, a brown colour develops on the surface of bakery products, which is the result of non-enzymatic chemical reactions of the colorants present (Purlis, 2010).

Non-enzymatic browning reactions include several types of reactions: dehydration, degradation, fragmentation, condensation, and polymerization, whose chemistry and kinetics are complex. In many cases, non-enzymatic browning is a negative phenomenon that leads not only to a change in colour, but also to other changes such as the degradation of food components (amino acids, ascorbic acid), a decrease in protein digestibility and, in some cases, the formation of toxic compounds. Non-enzymatic browning involves a whole series of reactions that lead to the formation of brown pigments. However, non-enzymatic browning is not always a negative phenomenon, and work is often done to create the conditions for its occurrence. Non-enzymatic browning products are compounds with a certain colour and flavour, which in some cases are desirable and very important for consumer acceptance of some products (bakery products, roasted meat, roasted coffee, French fries, etc.).

When non-enzymatic browning reactions occur without the presence of nitrogen compounds, these reactions are called caramelization reactions, and when they occur in the presence of nitrogen compounds, they are called carbonyl-amine reactions or Maillard reactions. Maillard reactions and caramelization reactions are the main processes involved in the colouration of bakery products (Capuano et al., 2008).

The brown products of Maillard reactions, melanoidins, are formed when reducing sugars and amino acids, proteins, and/or other nitrogenous compounds are heated at specific temperatures. The process of caramelization involves complex groups of reactions that result from the direct heating of carbohydrates, particularly sucrose and reducing sugars (Bemiller et al., 1996). Maillard reactions occur under conditions corresponding to an average moisture content, a temperature above 50 °C, and a pH between 4 and 7 (Kroh, 1994).

Caramelization and Maillard reaction

Caramelization, which depends on direct degradation of sugar, requires stronger conditions, such as temperatures above 120 °C, pH between 3 and 9, and low water activity (Kroh, 1994). During baking, starch and sucrose can be hydrolysed to reduce sugars, which can then participate in both reactions, usually allowing the Maillard reaction and the caramelization reaction to occur simultaneously (Villota and Hawkes, 2007). In caramelization reactions in many cases, although not necessarily, sugars are the main reactants. These reactions involve the conversion and degradation of sugars without the presence of amino compounds. The process of caramelization includes the following reactions: enolization, isomerization, dehydration, fragmentation and polymerization, forming light yellow to black pigments. During caramelization of sucrose at 200 °C, three endothermic processes were observed:

- After melting of sucrose, foaming of the mass begins and there is a loss of one molecule of water per molecule of sucrose, resulting in the formation of isosucrose.
- Further heating with loss of mass produces caramel ($C_{24}H_{36}O_{18}$). The isolated caramel dissolves in water and ethyl alcohol and has a bitter taste.
- The third stage occurs after foaming, with prolonged heating, and the caramel pigment is formed.

Further heating of sucrose leads to the formation of humin, i.e. caramelin, a dark substance with high molecular weight. The mechanism of caramel pigment formation involves a polymerization reaction that produces coloured polymers with high molecular mass, in which the number of C atoms increases in proportion to the degree of dehydration, i.e. the temperature and duration of their exposure. In systems subject to caramelization reactions, this leads to further parallel reactions with a very complex mechanism and to the formation of red, brown and dark brown pigments of different composition and properties, which differ significantly from Aldo-caramel in structure, composition and properties (Nursten, 2005).

Maillard reactions are named after the French chemist Louis-Camille Maillard, who was the first to describe the changes in flavour and colour when reducing sugars are heated with amino acids (Nursten, 2005). These reactions are of great importance in food technology and chemistry, as well as in medicine and nutrition (Tomasik, 2004). Maillard reactions are one of the main reactions that cause protein degradation during food processing and storage. They can also cause other undesirable nutritional changes, such as loss of essential amino acids (lysine, arginine, cysteine, and methionine) or reduction of protein digestibility and amino acid availability or changes in flavour. The whole process of forming Maillard reaction products can be divided into three main stages depending on the colour formation (Figure 1). In the first stage, sugars and amino acids condense, and after condensation, the Amadori rearrangement and 1-amino-1deoxy-2-ketose are formed. In the second stage, the product may be slightly yellow or colourless, and dehydration and fragmentation of the sugar molecules occur. Amino acids are also broken down at this stage. In this intermediate stage, HMF cleavage products such as pyruvaldehyde and diacetyl are formed. In the last stage, aldol condensation takes place and finally the heterocyclic nitrogenous compounds, the melanoidins, which are strongly coloured, are formed (Nursten, 2005).

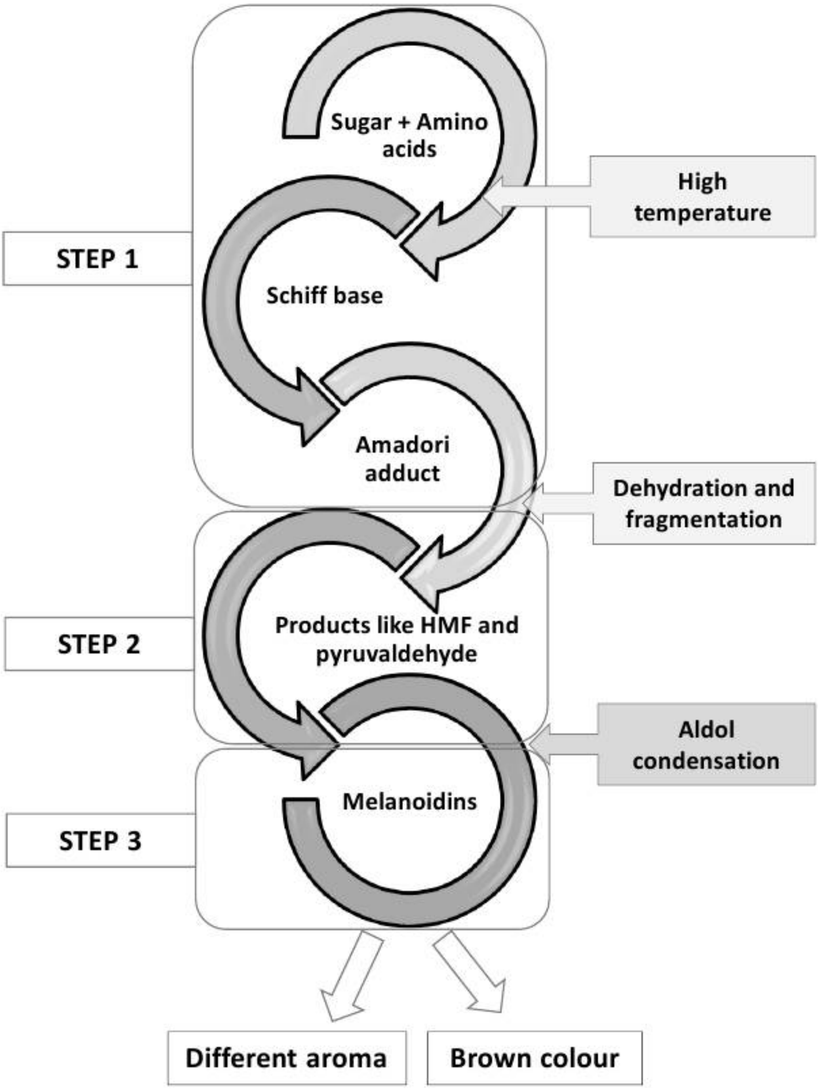

Figure 1. The process of Maillard reaction products formation

The Maillard reaction is the main reaction for colour formation. The formation of melanoidins by the Maillard reaction follows a zero order kinetic (Bates et al. 1998; Martins and van Boekel, 2003; Morales and van Boekel, 1998). The formation of melanoidins in biscuits is faster than in bread. The low water content and small size cause the water to evaporate quickly and the product to dry out faster. The nature of these reactions and the nature of the resulting products are influenced by the properties of the medium itself, more specifically the food (e.g. water activity, pH, chemical composition of the food, temperature). The type of reducing sugar is also very important, for example, pentoses react much faster than hexoses, monosaccharides faster than disaccharides (Tomasik, 2004; Hui et al., 2006).

Because of the chemical characteristics (i.e., reactants and products) of the Maillard and caramelization reactions, the importance of colour development during roasting is not only related to sensory characteristics such as the formation of a desirable hue and flavour, but also to changes in nutrient composition. In this sense, Maillard reactions affect the content and bioavailability of amino acids and proteins (Morales et al., 2007), which is associated with the formation of harmful compounds such as AA and HMF (Stadler et al., 2016). The formation of AA begins with the condensation of reducing sugars and the amino acid asparagine in the first stage of Maillard reactions (De Vleeschouwer et al., 2009). The formation of AA correlates strongly with the temperature and duration of the baking process, the amount of asparagine and reducing sugars, and starts at a temperature of 120 – 130 °C (Ahrné et al., 2007). The formation of AA is also related to the development of surface colour of bakery products (Gökmen et al., 2008a, b; Mesias and Morales, 2016).

Factors influencing the non-enzymatic browning reaction of bakery products

Important parameters in non-enzymatic browning reactions are temperature, pH of the environment, water activity, type and concentration of reactants, reaction time and water content. Depending on these factors, the reaction proceeds with different qualitative changes and at different rates.

The **temperature** dependence of the reaction is often expressed by the activation energy. Activation energy data for Maillard reactions range from 10–160 KJ/mol, depending on which effect of which reaction was measured. The activation energy is highly dependent on pH and reactant structure, making it difficult to isolate the effect of temperature as an independent variable. For all model systems, the rate of browning, as measured by colour development, increases two- to threefold for every 10 °C increase in temperature. As temperature increases, compounds are formed that may participate in or inhibit browning reactions. Sucrose is inert at relatively low temperatures, but when reaction conditions are suitable for its hydrolysis to glucose and fructose, the newly formed compounds are readily involved in caramelization reactions or in the carbonyl-amine reaction. Amino acids catalyse the reaction of sucrose at neutral pH, while formaldehyde formed by the Strecker degradation of glycine can effectively block the involvement of unreacted glycine or other amino acids in the non-enzymatic browning reaction.

Changing the **pH** of a model system results in qualitatively different browning reactions. The browning reactions show a decrease in reaction rate at low pH values, i.e., pH values with optimal stability of the reducing sugars present. The browning reactions themselves affect pH, making it difficult to assess the effect of pH on the overall system. Tests have shown that browning in aqueous solutions is a consequence of caramelization, while in the almost dry state of the reactants or at alkaline pH values, the Maillard reactions predominate.

Water and concentration of reactants (sugar and protein) – water catalyses the enolization of reducing sugars and the enol forms readily undergo fragmentation and dehydration reactions. At the beginning of the carbonyl-amine reaction, an aldose or ketose sugar reacts with a primary or secondary amine or amino acid to form a glycosylamine, and the reaction is reversible. The influence of water content is important for glycosylamine yield. At low water content, there is a significant accumulation of these compounds, which is why non-enzymatic browning of carbonylamine is pronounced in dehydrated and concentrated foods.

Mathematical model for browning of bakery products during baking

Determining the colour of bakery products

The first step in predicting and controlling the development of browning is its quantification. Numerous researchers have developed various methods to determine the colour on the surface of bakery products. Generally, methods can be classified in:

- Direct (chemical, objective) methods,
- Indirect (sensory, subjective) methods.

Direct methods aim at the quantitative monitoring of the products of Maillard reactions and caramelization (AA, HMF and furfural) (Ramirez-Jimenez, 2000), while indirect methods are based on the principle of measuring the amount of light reflected from the surface of the analysed sample with different measuring devices. Many different devices for indirect colour determination are available on the market. Most of them are designed in such a way that the colour determination is done by direct contact between the instrument and the sample. Instruments for indirect colour determination that are frequently used in practise are: Colourimeter, Chromameter, Spectrophotometer, Densiometer (Gokmen et al., 2008a; Purlis and Salvadori, 2007) and more recently a computer vision system (Brosnan and Sun, 2004; Zeng et al., 2007; Lukinac et al., 2018).

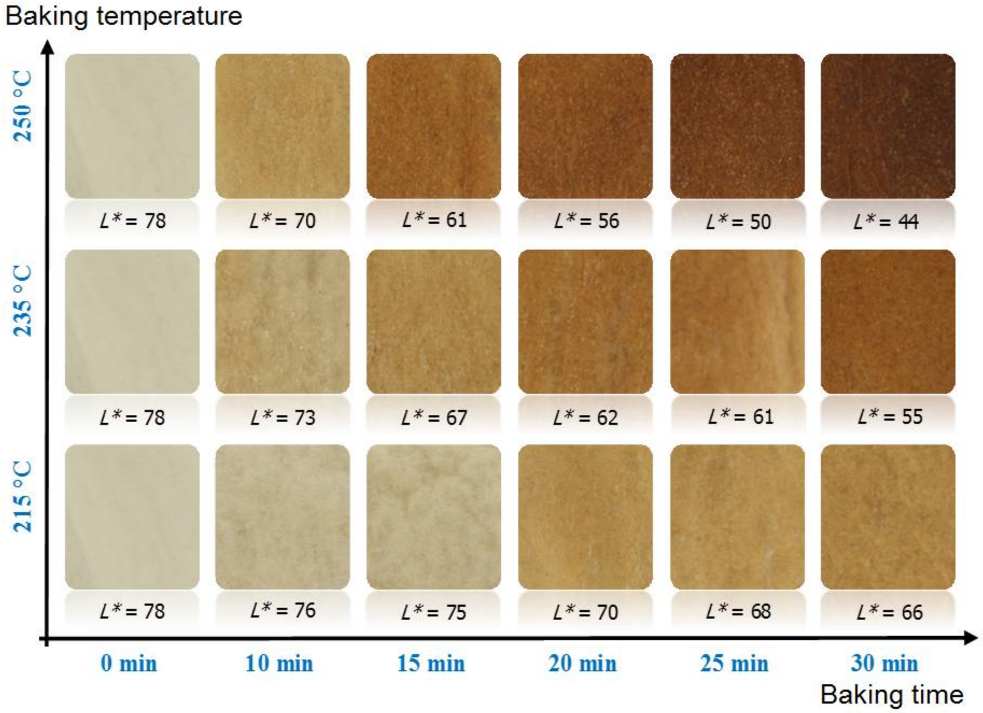

Figure 2. Browning development at surface of bakery products during baking at different baking temperatures

The computer vision system can cover the entire surface of the sample, making it a more objective and precise method, in contrast to the colorimeter, which analyses the surface of only a few centimetres (about 2 cm^2) (Mendoza et al., 2007a, b). This method of colour measurement can be used as a tool for automatic process control in industry (for a visual overview of the production process), improving the overall quality of the product. The advantage of the computer vision system over colour assessment with the human eye is the objectivity and continuity in colour assessment (Zheng et al., 2006).

In food research, colour is often represented using the CIE $L^*a^*b^*$ colour space, which is an international standard for colour measurement (Mendoza et al., 2007a, 2007b). The three parameters of this model represent the lightness of the colour (L^*), which is between 0 and 100 (0 = black, 100 = white), its position between red and green (a^*, values between -120 and +120) and its position between yellow and blue (b^*, values between -120 and +120) (Yam and Papadakis, 2004).

Some typical values of lightness (L^*) of the bread crust at different baking conditions are shown in Figure 2, where the influence of the oven temperature on the colour development can be clearly seen. The intensity of the colour of the samples increases with baking time, which is to be expected and is also confirmed by the lower values of L^*. In addition, increased temperatures and a low water content influence the formation of the yellow-brown colour of the bread crust. Browning occurs only after baking for 10 minutes at 250 °C, 15 minutes at 235 °C and 20 minutes at 215 °C oven temperature.

Modelling the crust browning of bakery products based on the measurement of lightness and total colour change

According to Haefner (2005), modelling has three goals: understanding, predicting and controlling the process, while other authors also mention optimisation (Montgomery and Runger, 2003). In terms of understanding, modelling is a tool in science that uses mathematical models to describe the physical and chemical changes that take place in food. The difference between prediction and control is that prediction is a quantitative prediction of the future properties of a food based on knowledge of the food and the processing it will undergo. Control, on the other hand, is about checking the process conditions during production with the aim of achieving the desired quality. It can be concluded that mathematical models can be used to predict and control the qualitative properties of food and other possible changes in these properties. Mathematical models are mostly linear, polynomial, and exponential or power expressions (van Boekel, 1996, 2008; Dolan, 2003).

Although a group of complex chemical reactions causes colour formation, it can be simplified for technological purposes by assuming a general mechanism of browning and then using colour models based on reflectance methods. It has been found in the literature that the development of browning during baking can be well described by a first-order kinetic model whose parameters depend on the local temperature and the water activity of the product. Moreover, the kinetic parameters should be estimated from experiments that are close to the actual baking conditions, i.e. a non-isothermal process occurring in a non-ideal system, to obtain better predictive performance (Dolan, 2003). The kinetic models used to describe the colour change of bakery products can be divided into two groups.

- The first group consists of kinetic models of colour change in which time is the independent variable (Eq. (2-14)), kinetic models of zero-, first- and second-order reactions and the empirical exponential model (Pedreschi, 2007; van Boekel, 2008).
- The second group consists of kinetic models of colour change of bakery products where the independent variable is mass loss (Eq. (15–18)) (Purlis and Salvadori, 2007).

Hermann and Nour (1977) studied the kinetics of surface browning in dough made of flour and water during baking at 150, 170 and 190 °C. They found that the surface browning of dough made of flour and water is due to Maillard reactions, which are described as sequential reactions Eq. (1):

$$A + K \ldots \overset{k_1}{\rightarrow} Z \overset{k_2}{\rightarrow} P \overset{k_3}{\rightarrow} M \qquad (1)$$

The reaction between amino acids (A) and reducing sugars (K) leads to intermediates (Z). These lead to water-soluble coloured products (P), which turn into insoluble coloured compounds, namely melanoidins (M). Experimental tests have shown that the kinetics of browning are characterised by three phases: a lag phase (found at 150°C), followed by an exponential phase (found at the three temperatures) and an asymptotic phase (found at 190°C). The browning reaction after the lag phase can be described by first order kinetics for the formation of compounds P (i.e. exponential phase) when $k_2 > k_3$, and then by the combination of kinetics for the formation of compounds P and M when $k_2 \sim -k_3$ (i.e. asymptotic phase).

Based on the general rate law, the disappearance of a compound in a closed system with only one compound reacting can be written in Eq. (2). By including the surface lightness (L^*) in Eq. (2) and choosing the surface lightness as the browning index, a general model for the colour development of the surface of bakery products during baking can be given as follows (Eq. (3)):

$$r = \frac{dc_A}{dt} = k \cdot c^n \qquad (2)$$

$$\frac{dL^*}{dt} = k \cdot (L^*)^n \qquad (3)$$

where r = reaction rate (mol/dm^3·s);
c_A = concentration of reactants A (mol/dm^3);
t = baking time (s);
k = reaction rate constant (s^{-1});
c = concentration (mol/dm^3);
n = order of reaction ($0 \leq n \leq 2$)
L^* = CIE colour component of surface lightness.

The temperature dependence of the reaction rate constant for browning is generally explained by the Arrhenius equation (Eq. (4)), and isothermal and non-isothermal methods have been used to determine the kinetic parameters.

$$k = k_0 \cdot exp\left(-\frac{E_a}{RT}\right) \qquad (4)$$

where k_0 = Arrhenius constant (s^{-1});
E_a = activation energy (J/mol);
R = universal gas constant (8.314 J/mol/K);
T = (absolute) temperature (K).

The kinetics of the browning reaction in food is generally considered to be a zero-order or first-order reaction, with first-order kinetics being the most commonly used in the literature. First order kinetics was frequently used for describing the browning reactions in terms of the colour change indicated in CIE$L^*a^*b^*$ colour model.

Shibukawa et al (1989) studied the effect of heating by convection and radiation in an oven at different baking temperatures (180 – 240 °C) on the surface colour of biscuits. This colour was compared to the browning of a model solution of monosodium glutamate and glucose, which followed first order kinetics. Mundt and Wedzicha (2007) proposed a first-order kinetic model based on the measurement of the surface colour of biscuits in R, G, B colour values during baking at temperatures of 105–130 °C. Ait Ameur et al., (2006, 2007) showed that the formation of HMF in cookies follows first-order kinetics, as does colour development, and that water activity strongly influences the production of coloured compounds. The rates of HMF formation during baking were 0.0028, 0.0067 and 0.0082 s^1 at 200, 250 and 300 °C, respectively. Furthermore, Hadiyanto et al. (2007) proposed a zero-order kinetic model for the formation of melanoidins (by the Maillard reaction) during the baking of bakery products, taking into account the influence of temperature and water activity.

To obtain a model for browning development, parameter estimation is required. If a non-isothermal approach is applied, the model will include the thermal history of the product during baking (the same analysis is valid for water activity or water content). To describe the dependence of rate constant (k) with temperature, the Arrhenius' law is commonly used (Eq. (5):

$$k = A \cdot exp\left(-\frac{E_a}{RT}\right) \tag{5}$$

where k = reaction rate constant (s^{-1});
A = pre-exponential factor;
E_a = activation energy (J/mol);
R = universal gas constant (8.314 J/mol/K);
T = (absolute) temperature (K).

The kinetic constants of the browning reaction during baking (k) are different for different products. They depend on the composition, especially on the concentration of reducing sugars and amino groups.

Zanoni et al. (1995) proposed a first-order kinetic reaction model for prediction of crust browning of bread during the baking process. The experimentally determined colour values of samples of grinded bread crust by heating in the range of 140 – 250 °C served as the basis for building the model. In this model (Eq. (6)); the reaction rate constant depends on surface temperature according to the Arrhenius equation:

$$k = k_0 \cdot exp\left(-\frac{E_a}{RT}\right) \tag{6}$$

with $k_0 = 42000\ (s^{-1})$, E_a= 64.151 (kJ/mol)

where k = reaction rate constant (s^{-1});
k_0 = pre-exponential factor;
E_a = activation energy (J/mol);
R = universal gas constant (8.314 J/mol/K);
T = (absolute) temperature (K).

He gave the relationship between the reaction rate constant and the baking temperature by applying the Arrhenius law. The proposed model was tested on bread samples, at baking temperatures at 200 and 250 °C. According to the results, the model was applicable at a baking temperature of 250 °C, given that the experiment was conducted in non-isothermal conditions (real conditions).

However, this expression (Eq. (6)) for temperature dependence is relevant to chemical compounds such as HMF where energy activation occurs in the context of a reaction. In the case of lightness or any other colour variable that represents the change in colour intensity and is not directly related to chemical compounds, the concept of activation energy may not be applicable (van Boekel, 2008). Instead of the Arrhenius equation, the following expression can be used to describe the dependence of the browning rate constant on temperature equally well (Eq. (7)):

$$c = c_0 \cdot exp\left[-A\,exp\left(-\frac{E_a}{RT}\right)\cdot t\right] \tag{7}$$

where c = concentration (mol/dm^3);
c_0 = initial concentration at t =0 (mol/dm^3);
A = pre-exponential factor;
E_a = activation energy (J/mol);
R = universal gas constant (8.314 J/mol/K);
T = (absolute) temperature (K);
t = time (s).

Because of the strong correlation between A and E_a, it is desirable to reparametrize the Arrhenius equation (van Boekel, 1996). A very simple reparametrization is the introduction of the reference temperature (T_{ref}) in the Eq. (5):

$$k_1 = A \cdot exp\left(-\frac{E_a}{RT_1}\right) \tag{8}$$

$$k_2 = A \cdot exp\left(-\frac{E_a}{RT_2}\right) \tag{9}$$

where k = reaction rate constant (s^{-1});
A = pre-exponential factor;
E_a = activation energy (J/mol);
R = universal gas constant (8.314 J/mol/K);
T = reference temperature.

Besides temperature and baking time, colour development on the surface of bakery products is also influenced by water activity (a_w), or the amount of water in the crust (X_b). Broyart et al. (1998) proposed to define the parameters of the browning rate constant (k_0 and E_a in their model) as a function of water content (Eq. (10–12)). The kinetic model developed is a first-order reaction and is based on monitoring the lightness of the cracker (L^*) as a function of product temperature and moisture. The model is applicable for predicting the brightness change within the temperature range 180–330 °C. The model is also suitable to suggest how baking profiles should be changed in order to obtain products with a different final lightness. The authors (Broyart et al., 1998) have proposed a model (two multiparameter equations) for prediction of lightness variations during baking as a function of time, temperature and water content, that differs for the lightening (Eq. (10)) and darkening (Eq. (11-12)) phases of the biscuit surface during baking:

$$\frac{dL^*}{dt} = +\, k_1 \cdot L^*$$
$$k_1 = k_1^0 \cdot exp\left(-\frac{E_{a1}}{RT_{b(t)}}\right) \tag{10}$$

$$\frac{dL^*}{dt} = -\, k_2 \cdot L^*$$
$$k_2 = k_2^0 \cdot exp\left(-\frac{E_{a2}}{RT_{b(t)}}\right) \tag{11}$$

$$k_2^0 = k_2^1 + \left(\frac{k_2^2}{X_{b(t)}}\right)$$
$$\frac{E_{a2}}{R} = k_2^3 + \left(\frac{k_2^4}{X_{b(t)}}\right) \tag{12}$$

where L^* = CIE colour component of surface lightness.
k_1 = reaction rate constant of enlightenment reaction (min^{-1});
k_2 = reaction rate constant of darkening reaction (min^{-1});
k_1^0 = kinetic constant of enlightenment reaction (min^{-1});
k_2^0 = kinetic constant of darkening reaction (min^{-1});
k_2^1, k_2^2, k_1^0, k_1^0, = Kinetic parameters of darkening reaction (respectively in min^{-1}, g water/100 g dry matter/min, K, g water/K/ 100 g dry matter);
E_{a1} = activation energy of enlightenment reaction (kJ/mol);
E_{a2} = activation energy of darkening reaction (kJ/mol);
R = universal gas constant (8.314 J/mol/K);
t = baking time (min);
$T_{b(t)}$ = cracker temperature (°C)
$X_{b(t)}$ = water content (g water/100 g dry matter).

In addition to the temperature and baking time, the water activity in the bread also has significant influence on the colour. Considering this fact, Purlis and Salvadori (2009c) proposed another model for monitoring the colour development of the crust of bread. This approach to define the parameters of an Arrhenius-like expression for the rate constant (k) as a function of water activity (a_w) (Eq. (13–14)):

$$k_0 = k_1 + \frac{k_2}{a_w} \tag{13}$$

$$Ar = k_3 + \frac{k_4}{a_w} \tag{14}$$

where a_w = water activity;
k_0, k_1, k_2, k_3, k_4 and Ar are fit parameters.

Kinetic models for the colour change during bread baking as a function of product weight loss and baking temperature were reported by Purlis and Salvadori (2007) and are represented by the equations Eq. (15-16). They proposed a colour prediction model where the total colour difference (ΔE) is a function of product mass loss (WL) and baking temperature (T_{oven}):

$$\Delta E = k \cdot WL \tag{15}$$

$$k = k_0 \cdot T_{oven} + k_1 \tag{16}$$

where ΔE = total colour difference;
k = reaction rate constant (s^{-1});
WL = product weight loss (%);
T_{oven} = baking temperature (°C);
k_0, and k_1 are fit parameters.

The experiment was conducted at temperatures of 180, 200 and 220 °C, with forced and natural convection, and the colour of the surface of the bread samples during baking was monitored by computer image analysis. The developed mathematical model predicted the colour change in non-ideal conditions, similar to the real conditions of bread production in the bakery industry. In this way, the evolution of browning was followed in a non-ideal system close to real baking conditions. Acceptable results for a general baking process were reported. Quevedo et al. (2017) investigated the browning kinetics of two types of pita bread based on computer vision colour measurement on the surface at four different baking temperatures (160, 180, 200 and 220 °C). They suggested that the fractal method can be used to record the browning of the pita bread and to calculate a fractal browning rate. In general, the fractal method can be considered as a new means to quantify the browning kinetics, where the formation of a heterogeneous colour on the surface is observed and where the traditional method is more difficult to apply. The method offers great potential for application not only to bread but also to other foods which show an inhomogeneous colour on the surface. Zhang et al. (2016) investigated the bread baking process using a miniature bread approach and modelled the browning kinetics of miniature bread during baking with spatial reaction engineering approach (S- REA). They found that the combination of S-REA and equations relating surface moisture content and temperature to overall colour changes modelled browning kinetics well. Golchin et al. (2020) developed a mathematical model for predicting the crust temperature and weight loss of toast bread at different oven temperatures and baking times. The predicted crust temperature and weight loss of the bread (control and with guar gum) agreed well with the experimental temperature with coefficients of determination of 0.98 and 0.99, respectively (Eq. (17–18)).

$$WL_{prc} = -0.0325 \cdot (WL_{Ex})^2 + 2.326 \cdot WL_{Ex} + 3.474 \tag{17}$$

$$WL_{prc} = -0.017 \cdot (WL_{Ex})^2 + 1.218 \cdot WL_{Ex} + 3.507 \tag{18}$$

where WL_{prc} = predicted weight loss of sample containing guar (%);
WL_{Ex} = Measured weight loss (%).

Conclusion

1. Chemically, non-enzymatic browning is mostly based on caramelization reactions and Millard reactions. Various factors such as temperature, concentration of reactants, water activity, pH and others influence the intensity of the colour change. These reactions occur when food is treated at elevated or high temperatures.
2. Efforts should be made to develop a fast, inexpensive, automated, reasonable and objective method to track colour change during baking. One possible approach would be to calibrate e.g. a computer vision system or a colorimeter) against a quantification of AA or HMF depending on the product recipe and finally express the colour in standardized units (e.g. using the CIE$L^*a^*b^*$ model).
3. The formation of colour in bakery products during the baking phase is commonly known as browning. Understanding browning development provides the opportunity to control, optimize and design processes and equipment for the bakery industry as it affects the overall quality of bakery products, including their sensory and nutritional properties. For this purpose, a mathematical model for browning development is useful.
4. The development of a mathematical model of browning is essential to predict and control this phenomenon during baking depending on the operating conditions and the product recipe. A browning model cannot be developed from the actual mechanisms of colour formation, as these have not yet been clarified. However, the kinetic approach is a helpful alternative to describe colour changes during baking.
5. Since browning affects the overall quality of food and leads to changes in sensory and nutritional properties (reduction in bioavailability of proteins and amino acids, formation of AA and HMF, and formation of substances with antioxidant activity), it is a topic of great interest to food technologists.

References

Abdullah, M.Z. (2008), Quality evaluation of bakery products. In: Sun D.W., ed., *Computer vision technology for food quality evaluation, 2nd edition,* pp. 481–522.

Ahrné, L., Andersson, C.G., Floberg, F., Rosén, J., Lingnert, H. (2007), Effect of crust temperature and water content on acrylamide formation during baking of white bread: steam and falling temperature baking, *LWT – Food Science and Technology,* 40(10), pp. 1708–1715.

Ameur, L., Mathieu, O., Lalanne, V., Trystram, G., Birlouezaragon, I. (2007), Comparison of the effects of sucrose and hexose on furfural formation and browning in cookies baked at different temperatures, *Food Chemistry*, 101(4), pp. 1407–1416.

Ameur, L.A., Trystram, G., Birlouez-Aragon, I. (2006), Accumulation of 5-hydroxymethyl-2-furfural in cookies during the backing process: Validation of an extraction method, *Food Chemistry*, 98(4), pp. 790–796.

ANMAT (2004), Código Alimentario Argentino (Food Code of Argentina, chapter IX). ANMAT – La Administración Nacional de Medicamentos, Alimentos y Tecnología Médica (The National Administration of Drugs, Foods and Medical Devices), http://www.anmat.gov.ar/codigoa/CAPITULO_IX_Harinas_actualiz_06-03.pdf (01.10.2022).

Bates, L., Ames, J. M., MacDougall, D. B., Taylor, P.C. (2006), Laboratory reaction cell to model maillard color development in a starch-glucose-lysine system, *Journal of Food Science*, 63(6), pp. 991–996.

Bemiller, J.N., Whistler, R.L. (1996), Carbohydrates. In: Fennema O.R., ed., *Food Chemistry, 3ed,* Marcel Dekker, New York, pp. 171–174.

Brosnan, T., Sun, D.W. (2002), Inspection and grading of agricultural and food products by computer vision system-a review, *Computers and Electronics in Agriculture*, 36, pp. 193–213.

Brosnan, T., Sun, D.W. (2004), Improving quality inspection of food products by computer vision-a review, *Journal of Food Engineering*, 61, pp. 3–16.

Broyart, B., Trystram, G., Duquenoy, A. (1998), Predicting colour kinetics during cracker baking, *Journal of Food Engineering*, 35, pp. 351–368.

Capuano, E., Ferrigno, A., Acampa, I., Alt–Ameur, L., Fogliano, V. (2008), Characterization of the Maillard reaction in bread crisps, *European Food Research and Technology*, 228, pp. 311–319.

De Vleeschouwer, K., Van der Plancken, I., Van Loey, A., Hendrickx, M.E. (2009), Modelling acrylamide changes in foods: from single-response empirical to multiresponse mechanistic approaches, *Trends in Food Science and Technology*, 20(3–4), pp. 155–167.

Dolan, K.D. (2003), Estimation of kinetic parameters for nonisotermal food processes, *Journal of Food Science*, 68, pp. 728-741.

Du, C.-J., Sun, D.-W. (2004), Recent developments in the applications of image processing techniques for food quality evaluation, *Trends in Food Science & Technology*, 15, pp. 230–249.

Du, C.J., Sun, D.W. (2005), Comparison of three methods for classification of pizza topping using different colour space transformations, *Journal of Food Engineering*, 68, pp. 277–287.

Gökmen, V., Açar, Ö.Ç., Arribas-Lorenzo, G., Morales, F.J. (2008a), Investigating the correlation between acrylamide content and browning ratio of model cookies, *Journal of Food Engineering,* 87(3), pp. 380–385.

Gökmen, V., Açar Ö.C., Serpen, A., Morales, F.J. (2008b), Effect of leavening agents and sugars on the formation of hydroxymethylfurfural in cookies during baking, *European Food Research and Technology*, 226, pp. 1031–1037.

Golchin, M.F., Movahhed, S., Eshaghi, M., Ahmadi Chenarbon, H. (2020), Mathematical modeling of weight loss and crust temperature of toast bread containing guar gum during baking process, *Food Science & Nutrition*, 9(1), pp. 272–281.

Hadiyanto, A.A., Straten, G., van Boom, R.M., Esveld, D.C., Boxtel, A.J.B. (2007), Quality prediction of bakery products in the initial phase of process design, *Innovative Food Science & Emerging Technologies*, 8(2), pp. 285–298.

Haefner, J.W. (2005), *Modeling biological systems: principles and applications*, Springer, New York.

Hermann, J., Nour, S. (1977), Modelluntersuchungen zur Bildung von Carbonylverbindungen und Brfiunung durch die Maillard-Reaktion beim Backprozess, *Nahrung*, 21, pp. 319-330.

Hodge, J.E. (1953), Chemistry of browning reactions in model systems, *Agricultural and Food Chemistry*, 15, pp. 928–943.

Hui, Y.H., Wai-Kit N., Nollet, L.M.L., Paliyath, G., Simpson, B.K. (2006), *Food Biochemistry and Food Processing,* Blackwell Publishing, USA.

Kroh, L.W. (1994), Caramelization in food and beverages, *Food Chemistry,* 51, pp. 373–379.

Lukinac, J., Jukić, M., Mastanjević, K., Lučan, M. (2018), Application of computer vision and image analysis method in cheese-quality evaluation: a review, *Ukrainian Food Journal*, 7(2), pp. 192-214.

Martins, S.I.F.S., van Boekel, M.A.J.S. (2003), Melanoidins extinction coefficient in the glucose/glycine Maillard reaction, *Food Chemistry*, 83(1), pp. 135–142.

Mendoza, F., Dejmek, P., Aguilera, J.M. (2007a), Calibrated color measurements of agricultural foods using image analysis, *Postharvest Biology and Technology*, 41, pp. 285–295.

Mendoza, F., Dejmek, P., Aguilera, J.M. (2007b), Colour and image texture analysis in classification of commercial potato chips, *Food Research International*, 40(9), pp. 1146–1154.

Mesias, M., Morales, F.J (2016), Acrylamide in bakery products. In: Gökmen V., ed., *Acrylamide in Food: Analysis, Content and Potential Health Effects, 1st edition*, pp. 131–157.

Mondal, A., Datta, A.K. (2008), Bread baking – A review, *Journal of Food Engineering*, 86, pp. 465–474.

Montgomery, D.C., Runger, G.C. (2003), *Applied statistics and probability for engineers,* John Wiley & Sons Inc., New York.

Morales, F.J., Açar Ö.Ç., Serpen, A., Arribas-Lorenzo, G., Gökmen, V. (2007), Degradation of free tryptophan in a cookie model system and its application in commercial samples, *Journal of Agricultural and Food Chemistry,* 55(16), pp. 6793–6797.

Morales, F.J., van Boekel, M.A.J.S. (1998), A Study on advanced Maillard reaction in heated casein/sugar solutions: Colour formation, *International Dairy Journal*, 8(10-11), pp. 907–915.

Mundt, S., Wedzicha, B.L. (2007), A kinetic model for browning in the baking of biscuits: Effects of water activity and temperature, *LWT – Food Science and Technology*, 40(6), pp. 1078–1082.

Nursten, H. (2005), The chemistry of nonenzymic browning, In: *The Maillard Reaction*. Royal Society of Chemistry, UK.

Pedreschi, F., León, J., Mery, D., Moyano, P. (2006), Development of a computer vision system to measure the colour of potato chips, *Food Research International*, 39(10), pp. 1092–1098.

Purlis, E., Salvadori, V.O. (2007), Bread browning kinetics during baking, *Journal of Food Engineering,* 80, pp. 1107–1115.

Purlis, E., Salvadori, V.O. (2009a), Bread baking as a moving boundary problem. Part 1: Mathematical modelling, *Journal of Food Engineering*, 91(3), pp. 428–433.

Purlis, E., Salvadori, V.O. (2009b), Bread baking as a moving boundary problem. Part 2: Model validation and numerical simulation, *Journal of Food Engineering,* 91(3), pp. 434–442.

Purlis, E., Salvadori, V.O. (2009c), Modelling the browning of bread during baking, *Food Research International*, 42(7), pp. 865–870.

Purlis, E. (2010), Browning development in bakery products – A review, *Journal of Food Engineering*, 99, pp. 239–249.

Purlis, E. (2011), Bread baking: Technological considerations based on process modelling and simulation, *Journal of Food Engineering*, 103(1), pp. 92–102.

Quevedo, R., Rojas, R., Pedreschi, F., Bastias, J. M., Siché, R., Uquiche, E., Díaz, O. (2017), Quantification of the browning kinetic on pita bread using fractal method, *Food and Bioprocess Technology*, 11(1), pp. 201–208.

Ramirez-Jimenez, A., Guerra-Hernandez, E., Garcia-Villanova, B. (2000), Browning indicators in bread, *Journal of Agricultural and Food Chemistry*, 48, pp. 4176–4181.

Shahin, M.A., Symons, S.J. (2001), A machine vision system for grading lentil, *Canadian Biosystems Engineering*, 43, pp. 7.7–7.14.

Shibukawa, S., Sugiyama, K., Yano, T. (1989), Effects of heat transfer by radiation and convection on browning of cookies at baking, *Journal of Food Science,* 54, pp. 621-624.

Stadler, R.H., Studer, A. (2016) Acrylamide formation mechanisms, In: Gökmen V., ed., *Acrylamide in Food: Analysis, Content and Potential Health Effects, 1st edition*, Elsevier, pp. 1–17.

Tomasik, P. (2004), *Chemical and Functional Properties of Food Saccharides*, CRC Press LLC.

van Boekel, M.A.J.S. (1996), Statistical aspects of kinetic modeling for food science problems, *Journal of Food Science*, 61, pp. 477–489.

van Boekel, M.A.J.S. (2008), Kinetic modeling of food quality: A critical review, *Comprehensive Reviews in Food Science and Food Safety*, 7(1), pp. 144–158.

Villota, R., Hawkes, J.G (2007), Reaction kinetics in food systems, In: Heldman D. R., Lund D. B., Sabliov C., ed., *Handbook of Food Engineering, 2nd edition*, pp. 125–286.

Wahlby, U., Skjoldebrand, C. (2002), Reheating characteristics of crust formed on buns, and crust formation, *Journal of Food Engineering,* 53, pp. 177–184.

Yam, K.L., Papadakis, S.E. (2004), A simple digital imaging method for measuring and analyzing color of food surfaces, *Journal of Food Engineering*, 61(1), pp. 137–142.

Zanoni, B., Peri, C., Bruno, D. (1995), Modelling of browning kinetics of bread crust during baking, *LWT – Food Science and Technology*, 28, pp. 604–609.

Zhang, L., Putranto, A., Zhou, W., Boom, R. M., Schutyser, M. A. I., Chen, X. D. (2016), Miniature bread baking as a timesaving research approach and mathematical modeling of browning kinetics, *Food and Bioproducts Processing*, 100, pp. 401–411.

Zheng, C., Sun, D. W., Zheng, L. (2006), Recent developments and applications of image features for food quality evaluation and inspection – a review, *Trends in Food Science and Technology*, 17, pp. 642–655.