KINETIC MODELLING OF COOKIE BROWNING DURING BAKING

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:
The modern food industry relies on the application of the Maillard reaction to produce many foods, e.g. coffee and bakery products that possess the colour and flavour demanded by the consumer. The aim of this study was kinetics modelling of cookie browning during 10 minutes of baking at 205°C in order to predict the cookie lightness variation during baking. Cookies were produced according to AACC Approved Method 10-50D from a commercial cookie plain white flour and wholegrain flour. Baking quality of used flours was determined using Alkaline water retention capacity (AWRC) and Solvent retention capacity (SRC) methods and by measuring width (W), thickness (T), W/T ratio (cookie spread factor) and volume of cookies. Both type of flour was used to make three types of mixing distinguished in water addition (standard-S; dry-D and wet-W formula). The colour of samples was measured using digital image analysis, and quantified using CIE*L*a*b colour model. Several mathematical model was proposed to predict the development of browning during baking (zero-, first- and second-order kinetics model). Lightness (*L**) variation were supposed to be representative of colour formation reaction. Comparing all the results of surface and bottom cookies lightness, the cookies with the plain white flour and standard addition of water had the lowest value of lightness change. The evolution of lightness appears to follow a second-order kinetic of cookies made from wholegrain flour, and evolution of lightness of cookies made from plain white flour followed zero-order kinetic. According to obtained results, all tested kinetics model can be used for modelling of cookie browning. Kinetic model is also suitable to suggest how baking profiles should be changed in order to obtain products with a different final lightness.**

KEYWORDS: cookies, colour, lightness, digital image analysis, kinetics model

INTRODUCTION

The colour is the first sensation that the consumer perceives. The overall appearance of any object is a combination of its chromatic and geometric attributes. Both of these attributes should be accounted for when making visual or instrumental assessment of appearance. Some of the instruments commonly used for colour determination are colorimeters, spectrophotometers, comparator charts or colour discs which proved to be useful tools for colour measurement. Colour measurement is an important tool for determining and monitoring quality of the bakery product[1]. Changes in bakery product colour can be associated with its previous heat treatment history. Various reactions such as pigment destruction (carotenoids and chlorophylls) and non-enzymatic browning reactions can occur during heating and therefore affect its colour[2]. The yellow-gold colour formation during baking is often called browning, and is the results of sugar degradation. Formation of coloured compounds during baking is product of chemical reactions specifically caramelisation and Maillard reactions. These reactions are activated by the higher temperature and lower water content in cookies during baking[3]. Direct heating of carbohydrates produces complex reactions namely as caramelisation reactions, were at high temperature sugars decompose into furfural compounds. Maillard reactions involve reducing sugar (glucose and fructose), protein (aminic compound) and some water. The Maillard reaction is influenced by temperature, pH, moisture content, presence or absence of metallic cations, and inner sugar structure. Particularly, the reaction is accelerated at medium moisture level and high temperature[2].

In recent years significant changes have occurred in objective colour measurement methods with advancements in computer hardware and software and digitalization technology. Image processing and image analysis are recognized as being the core of computer vision. This system known as computer vision has proven to be successful for objective measurement of various agricultural and food products. Computer vision includes the capturing, processing and analysing images[4]. Flatbed scanners, cameras and various software are finding increased applications for colour measurement and monitoring. Scanner is a device that optically scans object and converts it to a digital image, which is then transferred to a computer. The scanner head (includes mirrors, lens, filter and Charge Coupled Device (CCD array) move over the document line by line by belt attached to steeper motor. Each line is broken down into "basic dots" which correspond to pixels. A captor analyses the colour of each pixel. The colour of each pixel is broken down into 3 components (red, green, blue). Each colour component is measured and represented by a value. For 8-bit quantification, each component will have a value between 0 and 255 (28-1=255). Scanners typically read red-green-blue colour (RGB) data from the array. The scanned result is a non-compressed RGB image. Flatbed scanning is fast, easy to use, cheap, robust, independent of external light conditions, and with good accuracy. Computer vision and image analysis, are non-destructive and cost-effective techniques for sorting and grading of agricultural and food products during handling processes and commercial purposes. Therefore, the objective of this research study was the mathematical modelling of cookie browning (made of different recipes) during baking in order to apply it for optimization of baking process.

MATERIAL AND METHODS

COOKIE BAKING AND EVALUATION OF BAKING QUALITY OF FLOUR

Cookies were produced according to AACC Approved Method 10-50D[5] from commercial cookie plain white flour (Belje d.d. Beli Manastir, Croatia) and wholegrain flour (Podravka d.d., Koprivnica, Croatia). The other ingredients were shortening, dextrose, sucrose, sodium chloride and sodium bicarbonate from a local market.

Cookie flour quality evaluation was conducted using Alkaline water retention capacity (AWRC) and Solvent retention capacity (SRC) methods (AACC Methods 56-10[6] and 56-11[7]). Sodium bicarbonate (5%) was used for AWRC determination and four solvents were independently used to produce four SRC values: water SRC, 50% sucrose SRC, 5% sodium carbonate SRC, and 5% lactic acid SRC.

The cookie doughs were prepared by weighing the appropriate mass of each constituent and mixing the ingredients using an electronic mixer (Gorenje MMC800W, Slovenia) with a flat beater. Three different amounts of water were used: standard (S) with 16 g water/225 g of flour (AACC Method 10-50D), dry (D) with 12 g water/225 g of flour and wet (W) with 20 g water/225 g of flour.

Baking process was conducted in a convection oven (WiesheuMinimat Zibo, Wiesheu GmbH, Germany) during 10 minutes at 205°C with the precision of ±1°C.

Baking quality of cookie flour was determined in six cookies (AACC Method 10-50D) by width (W), thickness (T), and W/T ratio (cookie spread factor). Cookie volume was measured with the use of Volscan Profiler (Stable Micro Systems, UK).

IMAGE ACQUISITION OF COOKIES

Computer vision (CV) was used to evaluate cookies browning variation during baking. The method was based on scanning cookies samples using a flatbed scanner, processing the colour images using ImageJ software, and representing results in CIE$L^*a^*b^*$ colour space as a function of the flour type, cookie recipe and baking time respectively. Acquisition is the first step in colour sample measuring. Images can be acquired by scanners and cameras etc. Appropriate lighting and high-quality optics and electronic circuitry are critical in acquiring high quality images. In this paper flatbed scanner (Epson V500 photo) was used for image acquisition. To avoid external light conditions, scanner were placed in black box. After acquiring image, the process of converting pictorial images into numerical form is called digitisation. For this purpose *ImageJ* software were used to analyse image file created after digital scanning for colour parameters. Since digital images are acquired in the RGB colour space, colour parameter were transformed from RGB to CIE$L^*a^*b^*$ parameters as reported by León et all.[8]. All data were presented as mean values of at least three replicates.

MATHEMATICAL MODELLING OF BROWNING KINETICS

The kinetic parameters (browning rate constant, k) are determined by least-square method implemented in *Mathcad* based on the experimental data of baking of cookies during 10 minutes at 205°C. The model which have the smallest RMSE and the highest R values were chosen for prediction of cookies browning during baking.

In this paper three kinetic models were used based on cookie lightness changes and determined corresponding kinetic parameters (reaction rate constant). We have use approach of applying simple kinetics zero-, first-, and second-order kinetics for browning, represented by the variation of cookies lightness L^* during cookies baking. In the form of a zero-order kinetics for browning, represented by the variation of surface lightness L^* following equation is:

$$L^* = L_0^* - kt$$

With L_0^* the initial lightness of the sample, k the reaction rate constant (rate of browning), and t time.

Zero-order reactions are rather frequently reported for changes in foods, especially for formation reactions when the amount of product formed is only a small fraction of the amount of precursors present[9]. A frequently reported example of a zero-order reaction is the formation of brown colour in foods as a result of the Maillard reaction.

Another frequently used equation is first-order equation:

$$L^* = L_0^* \cdot exp(-kt)$$

or in its logarithmic form:

$$\ln L^* = \ln(L_0^* - kt)$$

and finally a second-order equation is sometimes encountered:

$$\frac{1}{L^*} = \frac{1}{L_0^*} + kt$$

Second-order reactions are sometimes reported for changes of amino acids involved in the Maillard reaction.

RESULTS AND DISCUSSION

Alkaline water retention capacity (AWRC) and Solvent retention capacity (SRC) are frequently used methods for determining cookie flour quality, especially when we need quick results, if there is a lack of equipment for determination of dough rheological properties, or if only a small amount of sample is accessible. These methods are used to determine flour capacity of holding different solutions after centrifugation. Lactic acid SRC is associated with gluten characteristic, sodium carbonate SRC is associated with levels of damaged starch, sucrose SRC is associated with pentosane characteristics while water SRC and Alkaline Water Retention Capacity (AWRC) are influenced by all of those flour constituents combined[6, 7].

Table 1. Alkaline water retention capacity (AWRC) and Solvent retention capacity (SRC) of flour

Wheat flour	AWRC (%)	SRC (%)			
		Water	Sucrose	Sodium carbonate	Lactic acid
Plain white flour	61.6±0.4[b]	62.6±0.6[b]	141.0±3.9[a]	70.3±0.6[b]	140.2±0.5[a]
Wholegrain flour	70.1±0.4[a]	65.5±0.3[a]	134.3±0.6[b]	78.7±0.9[a]	131.2±1.8[b]

Values are means ± SD of five measurements. Values in the same column with different superscripts are significantly different ($p < 0.05$)

Results showed that AWRC, water and sodium carbonate SRC values increased and sucrose and lactic acid SRC decreased when wholegrain flour was used instead of commercial cookie plain white flour (Table 1). This can be explained with the higher water absorption and weaker gluten of the wholegrain flour. Also, use of wholegrain flour significantly increased width and spread factor of cookies while volume and thickness were not affected (Table 2) which can be also explained by higher water absorption and weaker gluten. These results are in accordance with previous studies conducted by several investigators[10,11].

Table 2. Baking quality of cookie flour

Wheat flour	Volume (cm^3)	Width (cm)	Thickness (cm)	Cookie spread factor W/T*10
Plain white flour	49.5±0.7[a]	6.79±0.13[b]	1.31±0.02[a]	51.8±0.6[b]
Wholegrain flour	49.0±0.9[a]	7.02±0.24[a]	1.31±0.07[a]	53.6±1.1[a]

Surface browning is a common phenomenon for cookies during baking. Colour development only begins when sufficient amount of drying has occurred in cookies and depends also on the drying rate and the heat transfer coefficient during the different stages of baking.

Three colour models can be used to define colour; those are RGB (red, green, and blue) model, the CMYK (cyan, magenta, yellow and black) model, and the CIE$L^*a^*b^*$ model. The $L^*a^*b^*$ model is an international standard for colour measurement developed by the CIE in 1976. Among the three models, the $L^*a^*b^*$ model has the largest gamut encompassing all colours in the RGB and CMYK gamut's, and $L^*a^*b^*$ values are often used in food research studies. Unlike the RGB and CMYK colour models, CIE$L^*a^*b^*$ colour is designed to approximate human vision. It aspires to perceptual uniformity, and itsL^* component closely matches human perception of lightness. The $L^*a^*b^*$ colour space is perceptually uniform and the most complete model, device-independent, absolute model to be used as a reference. L^* is the luminance or lightness component, which ranges from 0 to 100, and parameters a^* (from green to red) and b^* (from blue to yellow) are the two chromatic components, which range from –120 to 120.

Formation of colour has been measured by computer vision, indirect method which quantify the amount of reflected light by the surface of the cookies and results are given in the CIE*L*a*b** colour space[8]. 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[12].

In this study CIE*L*a*b** colour model was used to quantitatively describe the colour change of the cookies during baking[13]. Lightness is a good descriptor of the browning progress since it represents the intensity of images, and is decoupled from colour changes denoted by *a** and *b** values[13].

Table 3. Variation of cookie surface lightness (*L**) during baking

*L**	Plain white flour			Wholegrain		
Baking time [min]	**D**	**S**	**W**	**D**	**S**	**W**
0	78.28	77.06	78.12	51.30	55.05	57.81
1	72.39	71.86	72.74	49.16	52.14	53.43
2	74.03	75.26	75.46	51.84	54.98	55.73
3	75.79	76.77	77.57	58.41	57.14	60.59
4	76.88	78.19	78.93	60.77	61.63	61.76
5	78.02	77.83	77.94	61.16	62.13	61.36
6	74.27	72.96	73.80	60.02	59.94	60.08
7	71.86	68.01	68.96	58.84	58.22	56.79
8	65.93	63.83	65.21	55.56	55.49	54.21
9	64.55	59.11	61.05	53.90	53.39	53.39
10	61.39	56.37	57.99	52.06	50.67	52.40

Water addition: standard (S) with 16 g water/225 g of flour, dry (D) with 12 g water/225 g of flour and wet (W) with 20 g water/225 g of flour

Table 4. Variation of cookie bottom lightness (*L**) during baking

*L**	Plain white flour			Wholegrain		
Baking time [min]	**D**	**S**	**W**	**D**	**S**	**W**
0	76.71	77.58	79.33	50.83	55.05	52.40
1	74.24	73.87	75.06	49.36	52.14	56.34
2	75.92	76.31	75.61	57.13	54.98	54.20
3	75.36	73.18	70.06	57.53	57.14	58.41
4	74.12	67.03	62.71	55.09	61.63	58.20
5	63.09	61.37	58.31	52.48	62.13	56.01
6	58.12	55.70	55.52	50.82	59.94	54.84
7	56.78	52.96	52.86	49.39	58.22	50.75
8	53.45	51.57	50.15	47.62	55.49	49.51
9	52.99	49.57	48.71	46.24	53.39	47.98
10	51.35	47.10	46.61	45.30	50.67	46.49

Water addition: standard (S) with 16 g water/225 g of flour, dry (D) with 12 g water/225 g of flour and wet (W) with 20 g water/225 g of flour

Table 3 and Table 4 show the variation of lightness of cookies during baking. It can be seen that the colour intensity of samples increased with baking time, as is expected. Comparing results of plain white flour and wholegrain cookie samples, the cookies with wholegrain flour became darker during baking for all water additions (D, S and W). Similar results were reported byGökmenet all.[14, 15].

Experimental recordings of plain flour and wholegrain cookies surface lightness during baking showed first an enlightenment and subsequently a darkening phase. The darkening phase is initiated in 6th min of baking. The darkening phase of bottom lightness during baking is initiated in 2nd min of baking.

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[16].

With the aim of predicting and controlling the development of browning during baking, it is necessary to quantify the advance of browning reactions. The best approach to model the browning development would be to consider the actual mechanisms of non-enzymatic reactions and transport phenomena occurring in products during baking. The kinetic approach is widely used for modelling browning.Kinetic modelling establishes that a process can be mathematically described by means of kinetic parameters with the aim of understanding, predicting and controlling the quality changes in food processing[17].

Kinetics parameters should be estimated from experiments close to actual baking conditions. Based on these concept, and selecting cookie lightness ($L*$) as browning index, a general model and related kinetic parameters (reaction rate constant) for colour development during baking can be stated. In order to describe the colour change during cookie baking, several kinetics model were used. Model validation can be seen in Tables 5 and 6.

Generally, the resulting modelled lightness profiles are in good agreement with the experimental results. The ability of the kinetic model to predict final lightness (important in terms of cookie sensory evaluation) values are given. Evolution of lightness of cookies surface and bottom made from plain white flour followed zero-order reaction. Browning rate constant k, varied from 1.2045 to 1.4072 min^{-1}. Prediction of lightness during baking was best described by zero-order kinetic model for plain flour cookies with standard water addition (S). Meanwhile, second-order kinetic model is more suitable for browning prediction of wholegrain cookies during baking.

Table 5. Variation of the browning rate of plain flourcookie samples

Sample	**Cookie surface**			**Cookie bottom**		
Water content	**D**	**S**	**W**	**D**	**S**	**W**
	Zero-order					
k_{CVS}**[min^{-1}]**	1.2045	1.5723	1.4072	2.5863	3.1462	3.5726
R	**0.7809**	**0.8045**	**0.7925**	**0.9357**	**0.9725**	0.9824
RMSE	3.3827	4.4443	4.2477	3.5537	2.5730	2.1155
	First-orderlinear					
k_{CVS}**[min^{-1}]**	1.6900E-02	2.2800E-02	2.0200E-02	3.9700E-02	4.9300E-02	5.5500E-02
R	0.7804	0.8007	0.7898	0.9350	0.9707	0.9883
RMSE	0.0485	0.0665	0.0623	0.0559	0.0430	0.0280
	First-order					
k_{CVS}**[min^{-1}]**	1.6300E-02	2.1600E-02	1.9100E-02	3.8500E-02	4.8200E-02	5.5400E-02
R	0.7689	0.7879	0.7774	0.9240	0.9642	0.9863
RMSE	3.4624	4.6073	4.3808	3.8512	2.9302	1.8651
	Second-orderlinear					
k_{CVS}**[min^{-1}]**	2.3799E-04	3.3341E-04	2.9182E-04	6.1681E-04	7.8401E-04	8.7832E-04
R	0.7795	0.7960	0.7867	0.9330	0.9652	**0.9878**
RMSE	6.9994E-04	1.0054E-03	9.2318E-04	8.9769E-04	7.7273E-04	4.7201E-04
	Second-order					
k_{CVS}**[min^{-1}]**	2.2054E-04	2.9533E-04	2.5987E-04	5.7058E-04	7.3291E-04	8.5052E-04
R	0.7573	0.7721	0.7630	0.9094	0.9503	0.9800
RMSE	3.5365	4.7547	4.5021	4.1892	3.4432	2.2515

Table 6. Variation of the browning rate of the wholegrain cookiesamples

Sample	Cookie surface			Cookie bottom		
Water content	**D**	**S**	**W**	**D**	**S**	**W**
	Zero-order					
k_{CVS}**[min^{-1}]**	0.0654	-0.1591	0.1544	0.1972	0.6749	0.9136
R	0.0728	0.0728	0.1829	0.2894	0.7256	0.8393
RMSE	3.9863	3.9863	4.7848	3.7740	3.0079	2.4786
	First-order linear					
k_{CVS}**[min^{-1}]**	1.2741E-03	-2.5334E-03	2.8300E-03	4.3404E-03	1.3400E-02	1.7700E-02
R	0.1219	0.1219	0.2128	0.3342	0.7393	0.8426
RMSE	0.0590	0.0590	0.0720	0.0722	0.0569	0.0475
	First-order					
k_{CVS}**[min^{-1}]**	9.6388E-04	-2.8063E-03	2.3094E-03	3.8552E-03	1.2700E-02	1.7100E-02
R	0.0718	0.0718	0.1811	0.2863	0.7163	0.8283
RMSE	3.9866	3.9866	4.7863	3.7777	3.0502	2.5539
	Second-order linear					
k_{CVS}**[min^{-1}]**	2.3643E-05	-3.9540E-05	5.0422E-05	9.4637E-05	2.6700E-04	3.4537E-04
R	**0.1576**	**0.1576**	**0.2395**	**0.3736**	**0.7501**	**0.8447**
RMSE	8.7606E-04	8.7606E-04	1.0895E-03	1.3888E-03	1.0885E-03	9.1886E-04
	Second-order					
k_{CVS}**[min^{-1}]**	1.4202E-05	-4.9522E-05	3.4555E-05	7.5379E-05	2.4063E-04	3.1928E-04
R	0.0708	0.0708	0.1794	0.2832	0.7072	0.8174
RMSE	3.9869	3.9869	4.7878	3.7813	3.0903	2.6259

CONCLUSIONS

During baking, complex chemical reactions take place in cookies, leading to the formation of heat-generated toxicants such as acrylamide. Comparing all the results of surface and bottom cookies lightness, the cookies with the plain flour and standard addition of water had the lowest value of lightness change. Several mathematical model was proposed to predict the development of browning during baking (zero-,first- and second-order kinetics model). The evolution of lightness appears to follow a second-order kinetic of cookies made from wholegrain flour, and evolution of lightness of cookies made from plainflour followed zero-order kinetic. Our experimental measurements also allowed us to use a kinetic model in order to predict colour formation (represented by lightness variations) of a cookies made by different recipes. According to obtained results, all tested kineticsmodel can be used for modelling of cookie browning. Kinetic model is alsosuitable to suggest how baking profiles should be changed in order to obtain products with a different final lightness. Advances in digital photography, flatbed scanners, and software for processing colour images provide a rapid, unbiased, and automated method for estimating the colorimetric parameters of coloured samples. With the developments in hardware and software for image analysis/processing, the applications of computer vision have been extended to the quality evaluation of diverse and processed foods, which has illustrated great advantages of using the technology for objective, rapid, non-contact and automated quality inspection and control.

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