THE STUDY OF THE EFFECT OF WATER ACTIVITY ON THE BROWNING KINETICS OF PASTRY AT HIGH PROCESS TEMPERATURES

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ABSTRACT

The influence of water on the rate of non-enzymatic browning reactions in food is unclear. A maximum browning rate has been reported in many foods between water activities (a_w) of 0.6 and 0.7, but other studies report either increasing or decreasing rates with increasing water activity (a_w). The effect of water activity (a_w) on the browning kinetics of pastry samples was investigated in this study. Pastry samples with five different water activities (a_w) at 0.97, 0.93, 0.85, 0.58 and 0.48 were baked on a hot temperature controlled pan at 160°C for 60 minutes. The browning on the pastry surface was measured by image analysis using the L^* a^* b^* colour space. The lightness-time curve was fitted with a first order kinetic model by using non linear regression to obtain the initial lightness (L^*_0), endpoint or final lightness (L^*_∞) and kinetic rate constants (k). The effect of water activity (a_w) on these parameters was determined by ANOVA. The result showed that the water activity (a_w) had no significant effect on the browning kinetics of pastry at the 95% confidence level ($P<0.05$). The water activity (a_w) had the most influence on the initial lightness ($P<0.01$), whereas the final lightness was moderately effected ($P<0.01$).

INTRODUCTION

Non-enzymatic browning reactions, such as Maillard reactions, that occur during high temperature food processing, cause the colour to change into golden brown. This reaction is greatly influenced by process temperature. However some literature report that water activity (a_w) also affects the rate of formation of browning products (Franzen, Singh, & Okos, 1990).The Maillard reaction is sometimes considered as undesirable in some foods such as concentrated, intermediate moisture and dried foods because it results in off colours (Eskin, 1990). To avoid this problem the appropriate conditions for this reaction need to be understood. In baked products this browning is desirable and therefore is important to understand how to control the rate during baking.

A maximum browning reaction rate occurs in most foods at certain values of water activity (a_w) depending on the type of food (Toribio, Nunes, & Lozano, 1984) or its composition. For example, the maximum rate of non-ezymatic browning reaction in general foods was reported at a water activity (a_w) of 0.6-0.7 (Eskin, 1990 and Vaikousi et al., 2008) and 0.5-0.8 (Labuza & Baiser, 1992). In apple juice maximum browning was reported to occur between the a_w of 0.53 and 0.55 (Toribio, Nunes , & Lozano, 1984). Some studies reported the rate as a function of the moisture content. The maximum rate of reaction was found at a moisture content of 7% (dry weight) for skim milk (Franzen et al., 1990), 15% for potatoes (Hendel et al., 1955) and 14% for L-cystein/D-glucose model in a microwave irradiation system (Yeo & Shibamoto, 1991). Nevertheless, most studies refer to water activity (a_w) rather than the moisture content for the reason that water activity is a measure of the available water for reaction (Franzen et al 1990). Therefore this study focused on the effect of the water activity (a_w) on the browning kinetics.

The rate of Maillard browning reactions change considerably with increasing water activity (a_w) (Labuza et al., 1970; Eichner & Karel, 1972 and Singh et al., 1983). Labuza and Baiser (1992) reported that the Maillard reaction starts to occur at a water activity (a_w) of 0.2-0.3 for most foods. The rate increases with increasing water activity (a_w) and then decreases at higher water activities (a_w) as the browning reactants becoming diluted (Labuza et al., 1970; Cuzzoni et al., 1988 and Vaikousi et al., 2008). Opposing trends are also reported however. The rate increases with an increase of water activity (a_w) in some studies (e.g. Labuza and Baizer, 1992) but in others a decrease in moisture content, resulted in an increasing rate of the browning reaction (Eichner & Karel, 1972).

The decreasing rate of browning reaction at very low value of water activity (a_w) is due to its high viscosity, so this decreases the molecular mobility of the reactants and slows down the browning reaction rate (Labuza et al., 1970). This phenomena was also found in apple juice (Toribio, Nunes , & Lozano, 1984), and in a glucose-glycine-glycerol-water system (Eichner& Karel, 1972).

It can be concluded from the literature review above that the moisture or water activity in the food has an effect on the non-enzymatic browning reaction but there is a lot of variation in observations. Therefore this study aims to investigate the effect of water activity (a_w) on the non enzymatic browning kinetics in a model pastry system undergoing high temperature cooking.

MATERIAL AND METHODS

1. Food system

A commercial frozen pastry (“Edmonds” brand), was selected as a model food for this study. The ingredients consist of wheat flour, water, animal and vegetable fats and oils, salt, emulsifiers (soy lecithin, 471), colour (160a), acidity regulators (330, 500), antioxidant (320) and flavour. The frozen pastry was thawed by leaving it at room temperature for 15 minutes. After thawing the pastry was cut into circular shapes using a cookie cutter with a diameter of 50 mm. All samples were weighed on a four digit balance (Sartorius CPA22 4S) and the data recorded. The pastry samples were placed in vacuum desiccators which contained moist silica gel with a water activity (a_w) of 0.45±0.001 S.E.) for 9, 20, 40 and 65 hrs. After that, all samples were heat sealed into aluminium foil pouch bags for 24 hrs to ensure that the moisture content of the pastry was uniform. The water activity (a_w) of the pastry samples were measured prior to cooking using an AquaLab Water Activity Meter model 4TE.

2. The design of pan baking system

The heating pan for cooking pastry samples in the study was developed by adapting a deep frying cooker (Fig. 1). The pan system consists of a deep fryer (ANViL model FFA 3001-TEU), a non stick teflon pan, a stirrer and an aluminium weight (325 gram) placed on top of the pastry to ensure complete contact between the pastry samples and the pan (Fig. 1). The dimensions of the deep fryer pot were 258 mm wide, 317 mm long and 145 mm deep and the dimensions of the pan were 210 mm wide and long and 34 mm deep. The deep fryer pot contained the oil which was used to heat the pan. Heat transfer oil (CALTEX Chevron: REGAL R&O 46) was selected for use in this study. It was heated by a 3000 watt heating coil and the oil's temperature was controlled by a PID controller (model CAL 3200). A stirrer was applied to increase the heat transfer from the oil to the pan and to make the temperature uniform.

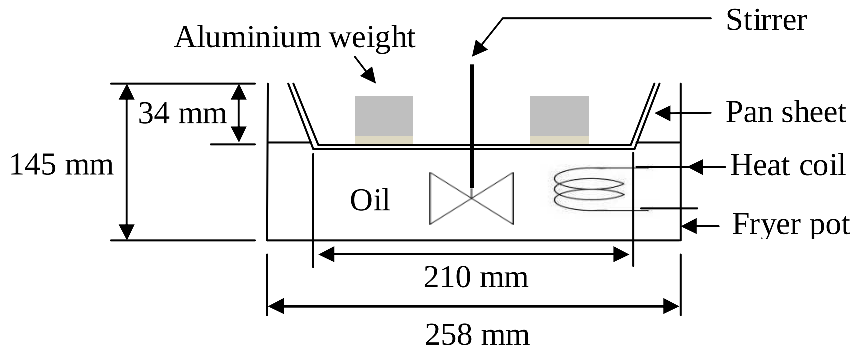

Figure 1: The deep frying based cooking system

3. Temperature measurement

The temperature of oil and the surface of the pan and pastry in each experiment were measured using type J thermocouples (20 gauge, accuracy ±0.5˚C) and logged with a data logger (Measurement Computing^{TM}: USB DAQ data acquisition) connected to a computer.

4. Colour measurement: image processing

The imaging system was set up in a dark room to avoid light and reflection from the environment. The system consisted of a digital camera (SONY DFW-SX 900) which was located vertically at a distance of 420 mm above the sample. The camera was connected to a PC on which the VIPS (Visual Image Processing System) software was installed. The lighting system included two light bulbs (OSRAM 100 W with a beam angle of 80˚) placed at an angle of 45˚ with respect to the camera. Prior to operating the image system, the white balance was set by capturing an image of a uniform white tile. After every 5 minutes of cooking, a pastry sample was removed from the pan to take a photo with the resolution 480*640 pixels to measure the brown colour on the pastry surface. The VIPS software program was used to analyse the brown colour and convert to the *L*a*b** colour space. Where *L** refers to the lightness, which ranges from 0 to 100 (black to white) (Gilchrist et al., 1999), *a** is the position between green (-100) and red (+100) and *b** is the position between yellow (-100) and blue (+100). The intensity of colour of the pastry's surface was generally determined by the colour parameters of *L*a*b** (CIE food colour system). Lightness (*L**) 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 (Gonzalez & Woods, 2002).

5. Experimental trials

Pastry samples with five different water activities (a_w) (0.97, 0.93, 0.85, 0.58 and 0.48) were baked on the hot pan at a temperature of 160°C, with two replications. Pastry samples were removed from the hot pan and the brown colour development on the surface of the pastry was measured by image processing every five minutes until 60 minutes. The lightness-time curve was fitted with a first order kinetic model by using the CurveExpert software program to obtain the initial lightness, final lightness and kinetic rate constants. The effect of water activity (a_w) on the browning kinetics was determined by comparing the kinetic rate constants and statistical analysis was used to analyse for significant differences between the kinetic rate values.

RESULTS AND DISCUSSION

The lightness (*L**) of the pastry surface is shown in figure 2. It can be seen from the graph that the lightness of the surface colour at all water activity (a_w) levels decreased as process time increased. The effect of the water activity (a_w) on the non-enzymatic browning reaction was tested by kinetic model fitting. The lightness-time curve was fitted with a first order kinetic model (eq. 1) using CurveExpert software program.

$$L^*_{predicted} = L^*_0 - (L^*_{0-} L^*_\infty) * (1 - \exp(-kt)) \qquad (1)$$

The L^*_0, L^*_∞ are the initial and final values of *L**, respectively and k is a kinetic rate constant (min^{-1}). The L^*_0, L^*_∞ and k parameters obtained are presented in table 1.

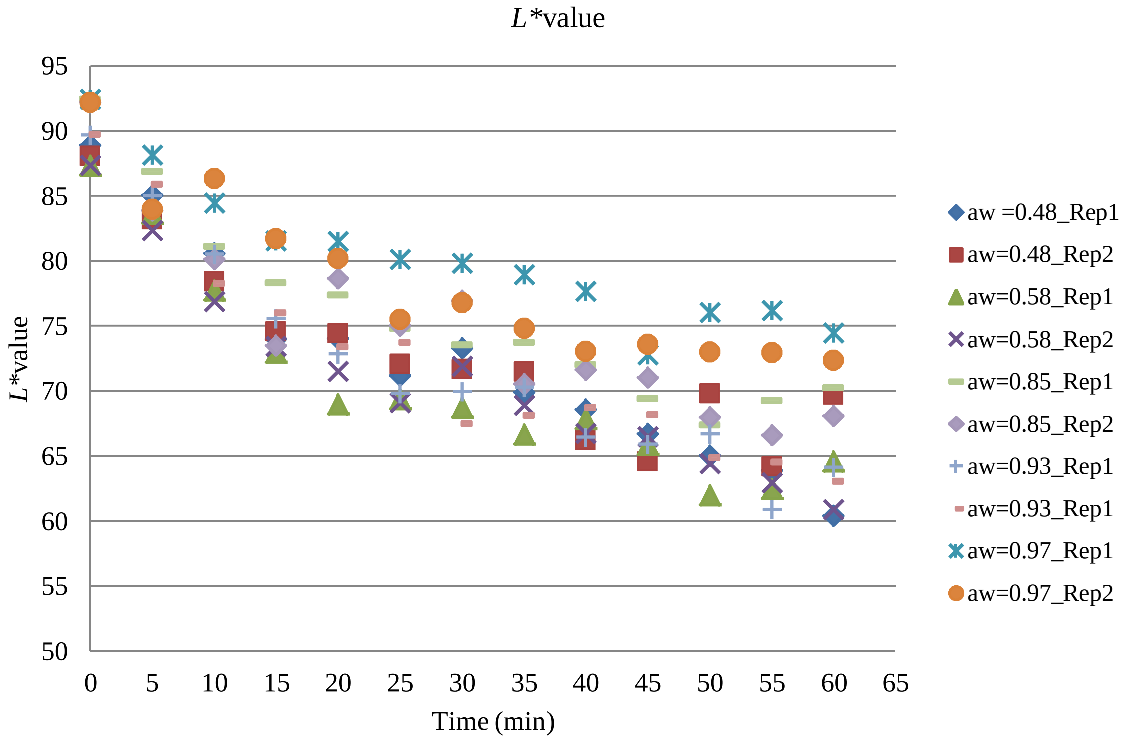

Figure 2: the lightness-time curve of the pastry surface

Table 1: The predicted parameters obtaining from model fitting

%MC (dry wt)	a_w of sample	Replication	L^*_0	L^*_∞	k (min^{-1})	R^2
8.77	0.48	Rep 1	88.20	56.99	0.028	0.98
		Rep 2	88.06	65.95	0.053	0.96
14.30	0.58	Rep 1	88.05	62.66	0.059	0.98
		Rep 2	86.40	60.44	0.040	0.98
17.89	0.85	Rep 1	87.60	65.18	0.032	0.98
		Rep 2	87.47	64.76	0.033	0.94
30.55	0.93	Rep 1	89.88	61.45	0.033	0.98
		Rep 2	89.85	62.42	0.044	0.98
50.62	0.97	Rep 1	91.86	73.83	0.042	0.97
		Rep 2	91.33	70.80	0.045	0.97

From Table 1, it can be concluded that the experimental data was fitted well with the first order kinetic model because the goodness of fit (R^2) are very high (0.94-0.98). The kinetic rate constant varies in the range from 0.028 to 0.059 min^{-1}. The effect of water activity (a_w) of the pastry on the browning kinetics can be compared by comparing the kinetic rate parameter (k) among all samples by statistical analysis. The MINITAB software program was used in this study. The ANOVA (analysis of variance) is given in Table 2.

Table 2: ANOVA for effect of water activity (a_w) on the kinetic rate (k) of pastry baking

Variance	DF	SS	MS	F	P
Factor	4	0.000232	0.000058	0.63	0.663^{ns}
Error	5	0.000463	0.000093		
Total	9	0.000696			
R-sq	33.45%				

*, **, *** = Significant at P<0.05, P<0.01 and P=0.001, respectively.
ns = Not significant at P = 0.05 level.

Table 2 shows that the P-value was greater than 0.05, meaning the kinetic rate constant (k) was not significantly different at the 95% level confidence. Therefore it can be assumed that the water activity (a_w) of the pastry has no significant effect on the browning kinetics of pastry. The effect of water activity (a_w) on the initial and final lightness of the pastry sample was also investigated and the statistical values are shown in Table 3.

Table 3: ANOVA for effect of water activity (a_w) on the initial and final lightness (L^*initial and L^*final) of pastry baking

	Effect of a_w on L^*_0					Effect of a_w on L^*_∞				
Variance	DF	SS	MS	F	P	DF	SS	MS	F	P
Factor	4	26.932	6.733	21.95	0.002**	4	171.4	42.86	4.49	0.065^{ns}
Error	5	1.534	0.307			5	47.71	9.54		
Total	9	28.466				9	219.2			
R-sq	94.61%					78.23%				

*, **, *** = Significant at P<0.05, P<0.01 and P=0.001, respectively.
ns = Not significant at P = 0.05 level.

The water activity (a_w) has most influence on the initial lightness (P<0.01), whereas the final lightness was moderately effected by water activity (a_w) (P>0.05). The mean values and standard error of the initial and final lightness are shown in Table 4. The differences among mean values of all data were also tested by MINITAB software program using Tukey's method at 95% confidence intervals. A significant difference in an initial lightness among pastry sample study is indicated by the superscript letters a, b and c over the mean values. Table 4 shows that there were significant difference between the initial lightness (L^*_0) for samples at different water activity, although it is not an obvious function of water activity (a_w).

Table 4: Mean and standard error of the initial and final lightness (L^*_0 and L^*_∞) of pastry baking

a_w	L^*_0			L^*_∞		
	N	Mean	S.E.	N	Mean	S.E.
0.48	2	88.13[bc*]	0.03	2	61.47 [a]	1.58
0.58	2	87.22[c]	0.30	2	61.55 [a]	0.39
0.85	2	87.54[c]	0.02	2	64.97 [a]	0.07
0.93	2	89.86[ab]	0.00	2	61.94 [a]	0.17
0.97	2	91.60[a]	0.09	2	72.32 [a]	0.53

*The letters a, b and c mean that samples that do not share a letter are significantly different at the 95% confidence level, using a Tukey Method.

CONCLUSION

This study showed that the water activity (a_w) has no significant influence on the kinetic rate parameter (k) for the browning reaction but it affected the initial lightness (L^*_0) and final lightness (L^*_∞). Heat transfer rates to the pastry surface were very fast in these experiments. As a result there was no significant delay in the pastry surface reaching the pan temperature. In some heating systems however (e.g. baking), it is likely that a delay in temperature rise would occur due to evaporation. This effect could potentially explain the apparent slower rate at higher water activity (a_w) reported in some studies.

REFERENCES

Cuzzoni, M. T., Stoppini, G., Gazzani, G., & Mazza, P. (1988). Influence of water activity and reaction temperature of ribose-lysine and glucose-lysine Maillard systems on mutagenicity, absorbance and content of furfurals. *Food and Chemical Toxicology, 26* (10), 815-822.

Eichner, K., & Karel, M. (1972). Influence of water content and water activity on the sugar-amino browning reaction in model systems under various conditions. *Journal of Agricultural and Food Chemistry, 20* (2), 218-223.

Eskin, N. (1990). Biochemistry of food spoilage: enzymatic browning. *Biochemistry of foods. 2nd ed. New York: Academic Press. p,* 401–432.

Franzen, K., Singh, R. K., & Okos, M. R. (1990). Kinetics of nonenzymatic browning in dried skim milk. *Journal of Food Engineering, 11* (3), 225-239.

Gilchrist, A., Nobbs, J., & John, L. (1999). Colorimetry, Theory *Encyclopedia of Spectroscopy and Spectrometry* (pp. 380-385). Oxford: Academic Press.

Hendel, C. E., Silveira, V. G. & Harrington, W. O. (1955). Rates of non-enzymatic browning of white potato during dehydration. *Food Technol*., 9, 433-438.

Labuza, T., Tannenbaum, S. R., & Karel, M. (1970). Water content and stability of low-moisture and intermediate-moisture foods. *Food Technology, (24)*, 543–550.

Labuza, T. P., & Baiser, W. M. (1992). The kinetics of nonenzymatic browning. In H. G. Schwartzberg & R. W. Hartel (Eds.), *Physical chemistry of foods* (pp. 595-649). New York: Marcel Dekker.

Singh, R. K., Lund, D. B., & Buelow, F. H. (1983). Storage Stability of Intermediate Moisture Apples: Kinetics of Quality Change. *Journal of Food Science, 48*(3), 939-944.

Toribio, J. L., Nunes, R. V., & Lozano, J. E. (1984). Influence of Water Activity on the Nonenzymatic Browning of Apple Juice Concentrate during Storage. *Journal of Food Science, 49* (6), 1630-1631.

Vaikousi, H., Koutsoumanis, K., & Biliaderis, C. G. (2008). Kinetic modelling of non-enzymatic browning of apple juice concentrates differing in water activity under isothermal and dynamic heating conditions. *Food Chemistry, 107* (2), 785-796.

Yeo, H., & Shibamoto, T. (1991). Effects of moisture content on the Maillard browning model system upon microwave irradiation. *Journal of Agricultural and Food Chemistry, 39* (10), 1860-1862.