

KINETIC STUDY ON NON ENZYMATIC BROWNING IN PASTRY BAKING

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ABSTRACT

A kinetic model for non enzymatic browning in pastry was obtained by baking pastry on a hot pan at six different temperatures (120, 130, 140, 150, 160 and 170°C) for 60 minutes. The development of brown colour at the surface of the sample was determined using image analysis methods in the CIE Lab colour parameters ($L^*a^*b^*$ scale) as physical parameters. The lightness (L^*) was found to be the best parameter to illustrate the browning reaction in high temperature pastry processes. The results showed that the intensity of brown colour increased and the lightness of the pastry surface decreased with rising temperature and as time progressed. The lightness-time curve was fitted to a first order kinetic model by minimising the residual sum of squared errors by non linear regression. The kinetic rate constant (k) of non enzymatic browning reaction of pastry baking has been found to follow an Arrhenius type dependence on temperature. The activation energy (E_a) and the initial kinetic rate constant (k_0) values are 65 kJ/mol and 2,397,000 s⁻¹, respectively.

INTRODUCTION

Non enzymatic browning is an important reaction occurring in food, which causes the colour change into golden brown. The reaction is complex, and normally happens in food during high temperature processing. The Maillard reaction is the main pathway for non-enzymatic browning (Ames & Benjamin, 2003). If controlled appropriately, non enzymatic browning is seen as being positive by consumers and is considered a good indicator of quality in bakery products. Therefore, monitoring and controlling the browning reaction is a key process for obtaining a good quality product (Sakla, 2001).

The Maillard reaction rate is affected by process conditions including the type and availability of reactant and processing factors such as temperature, time of heating, pH, and water activity (Ellis, 1959; Lopez & Pique, 1997; Ames, 1998; Fayle & Gerrard, 2002 and Ames & Benjamin, 2003). The reaction is also affected by metals, oxygen, and the presence of inhibitory agents, e.g., sulphite (Ames, 1990; deMan, 1999; Martins et al., 2000; Fayle & Gerrard, 2002).

The influence of temperature and time on browning kinetics has been studied for many foods and in many different cooking processes. For example browning kinetics have been studied in maize grits with an extrusion process (Ilo & Berghofer, 1999), in hazelnut roasting (Saklar et al., 2001 and Demir et al., 2002), sesame seed roasting (Kahyaoglu & Kaya, 2006), potatoes frying (Nourian & Ramaswamy, 2003 and Krokida et al., 2001), coffee bean roasting (Heyd et al., 2007) and crackers baking (Broyart et al., 1998), cookies (Shibukawa et al., 1989) and bread (Zanoni et al., 1995 and Zhang & Datta, 2006). In each case process parameters of temperature and time both affected the rate or extent of the browning reaction.

Most studies developed the browning kinetics by assuming isothermal conditions. However, in food processes phenomena such as water evaporation in baking or frying processes cause a thermal dynamic across the food surface. In many cases it is difficult to measure the surface temperature during experimentation and most often, the surface is simply assumed to be at the cooking medium. This makes using these systems unsuitable for isothermal studies of the browning kinetics. Therefore, the objective of this study was to develop a food and cooking system that resulted in uniform and constant conditions at the surface of the product so that accurate browning kinetics could be measured.

MATERIAL AND METHODS

1. Food system

High temperature browning occurs in many food systems but variations are likely due to compositional or surface differences. Therefore a model food system that allows reproducible measurement and defined experimentation was required. A number of potential model food samples were studied for this purpose. For the propose of research in evaluating browning kinetics under isothermal conditions a uniform colour is a preferred property to provide an uncomplicated colour evaluation, so the surface of sample should be smooth, remain flat and in good contact with the cooking surface. The composition of the model food should be homogenous. A low level of moisture content was needed to avoid heat transfer effects where a temperature plateau occurs at 100°C as the water at the surface is evaporated. The model food ought to include both sugar and protein in its composition because they are the browning reactants. A commercial frozen pastry brand of “Edmonds” was selected as the suitable 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), flavour.

2. The pan baking system design

The heating pan for pastry samples cooked in the study was developed by adapting a deep frying cooker (Fig. 1). The pan system consists of the deep fryer (ANViL model FFA 3001-TEU), the non stick teflon pan sheet, the stirrer and the aluminium weight that was put on top of the pastry to make complete contact between the pastry samples and the pan sheet (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 sheet 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 and it was heated by a 3 kW 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 sheet and to make it uniform.

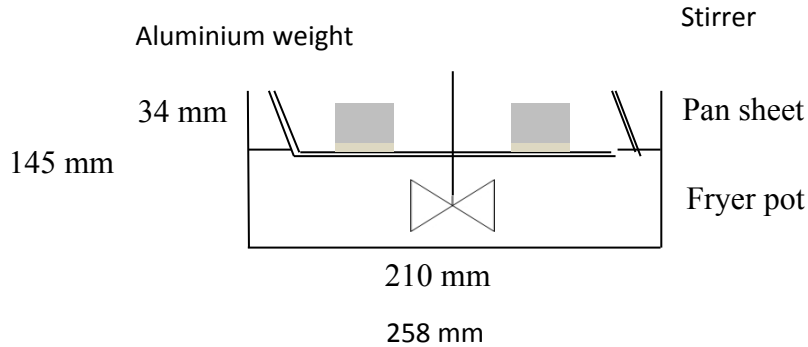


Figure 1: The prototype of cooking system by using a deep fryer

3. Temperature measurement

The temperature of oil, surface of pan and pastry in each experiment were measured by using type J thermocouples (20 gauge, accuracy $\pm 0.5^{\circ}\text{C}$) and logged by a data logger (Measurement ComputingTM: USB DAQ data acquisition) connected to a computer PC. Three temperature profiles were plotted and compared. The temperature was controlled to be stable at the set point by a PID controller (model CAL 3200).

4. Colour measurement: image processing

The image 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 the distance of 420 mm from 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°) and 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 picked up to take a photo with the resolution 480×640 pixels for measuring 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).

5. Experimental trials

The frozen pastry was purchased from the local supermarket and left at room temperature (20°C) until thawed then cut by a cookie cutter into circle with a diameter of 50 mm. The thickness of the pastry was 2 mm. The experiments consisted of 5

replications at 10°C temperature intervals from 120°C-170°C. Samples were randomly removed from four different baking positions after 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55 and 60 minutes. The removed samples were suddenly cooled down with ice in a stainless steel tray to stop the cooking process. All samples were photographed for analysis using the image system.

RESULTS AND DISCUSSION

The temperature history of the oil, pan and pastry surface during the cooking process were recorded and plotted as shown in figure 2. There was about 2°C difference in temperature between the oil and the pan at steady state. This shows the potential errors that can occur if it is assumed that the surface is at the same temperature as the heating mediums. The pastry samples were placed on the hot pan after the temperature of the pan was constant. After placing the samples, their temperature rapidly increased and took 8 minutes to come up temperature to be the same temperature as the pan temperature. After this short period, the pastry surface temperatures show a constant profile throughout the process. The constant temperature was a very long period when compared with the short initial heating period. Therefore it can be assumed that this system provided an isothermal condition.

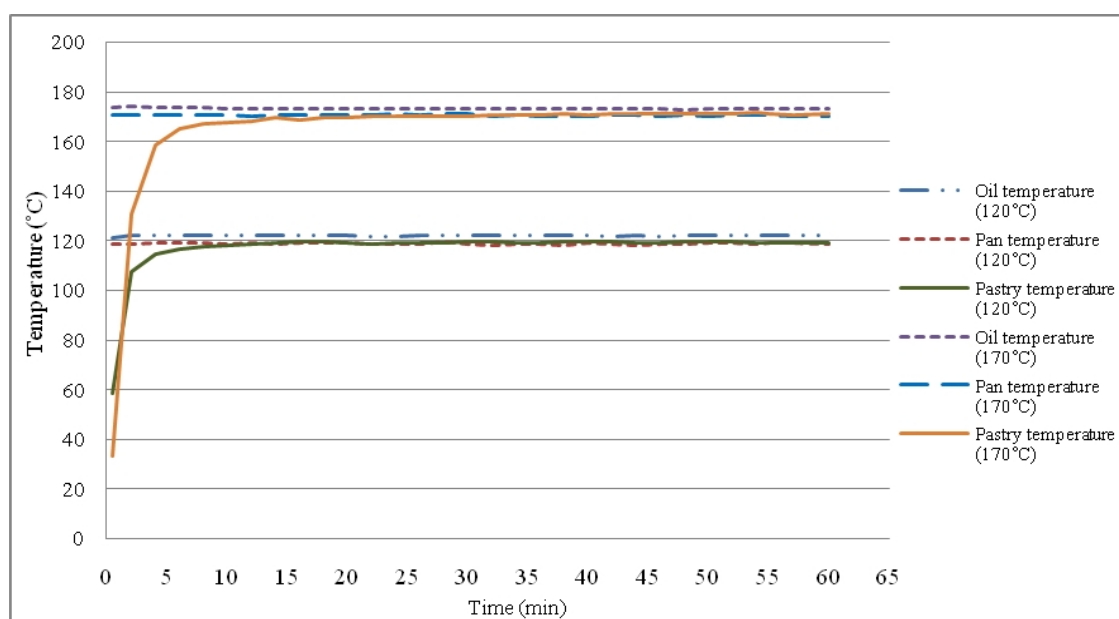
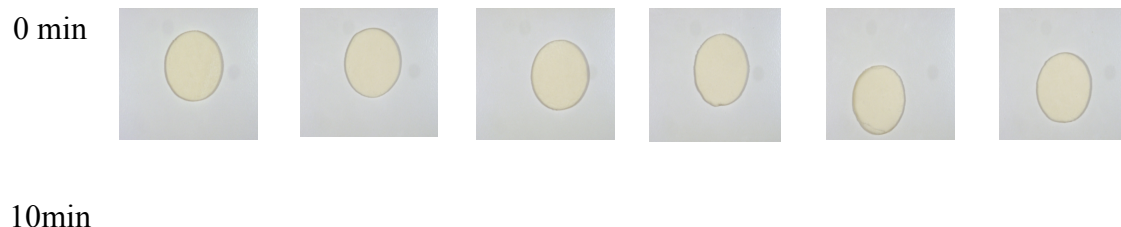


Figure 2: temperature profile of oil, surface of pan and pastry at two different cooking conditions (120°C and 170°C)

Fig. 3 shows the photos of pastry cooking at six difference temperatures (120 to 170°C) for a variety of times from 0 min (not baked) up to 60 min, it can be seen that the intensity of colour of the pastry's surface increases with time and increasing temperature.



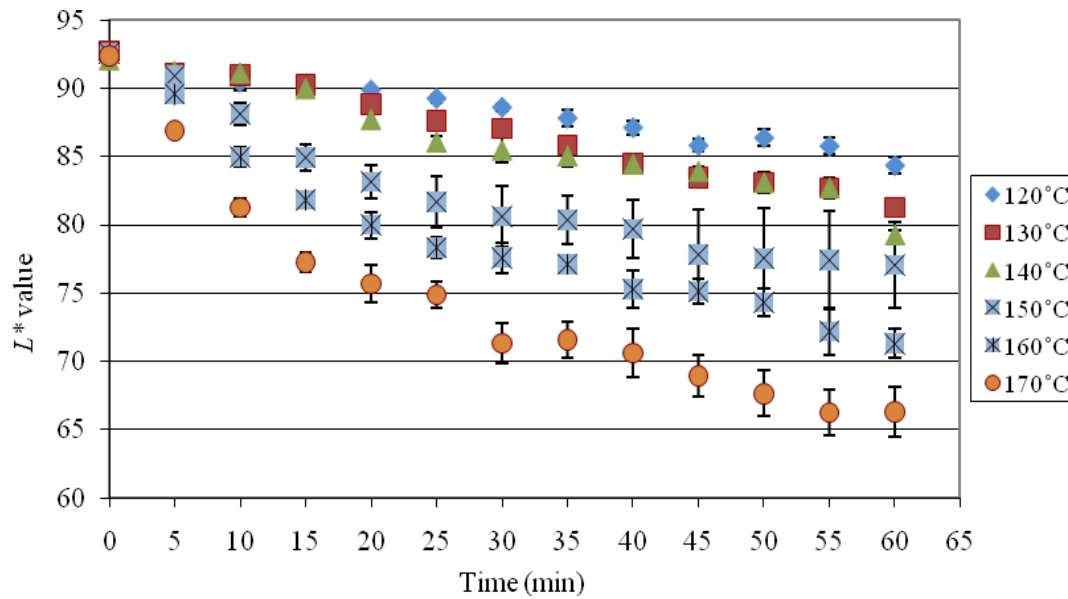


Figure 4: Variation of lightness (L^*) at pastry surface as a function of baking time.

During the first ten minutes of the study at low temperatures (120 and 130°C), the lightness rapidly dropped and an increased again when the process reached fifteen minutes. This was due to the slow evaporation of water in the sample. After that the lightness continuously decreased with time. This observation was found in other bakery products such as bread (Purlis & Salvadori, 2009; Zhang & Datta, 2006), buns (Wählby & Skjöldebrand, 2002), cookies (Shibukawa, Sugiyama & Yano, 1989; Gökmen et al., 2008) and crackers (Broyart, Trystram & Duquenoy, 1998). The extreme conditions at the surface are responsible for the very dark appearance and low lightness values for the samples baked at 170°C (Figs. 3 and 4).

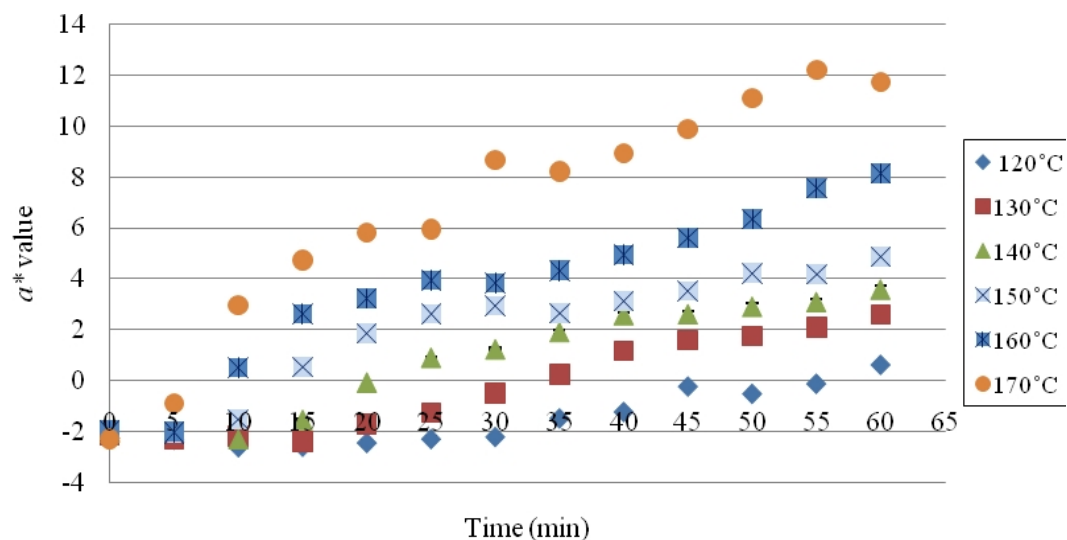


Figure 5: Variation of redness (a^*) at pastry surface as a function of baking time.

It can be seen from Fig. 5 that the redness values (a^*) of the pastry surface increased with increasing cooking temperature and time during the cooking process. It can be assumed that this redness was due to the Maillard reaction. Even so, the variation is quite small, especially at lower temperature. The same result was discovered by Ilo & Berghofer (1999) who studied the kinetics of colour change during extrusion cooking of maize grits.

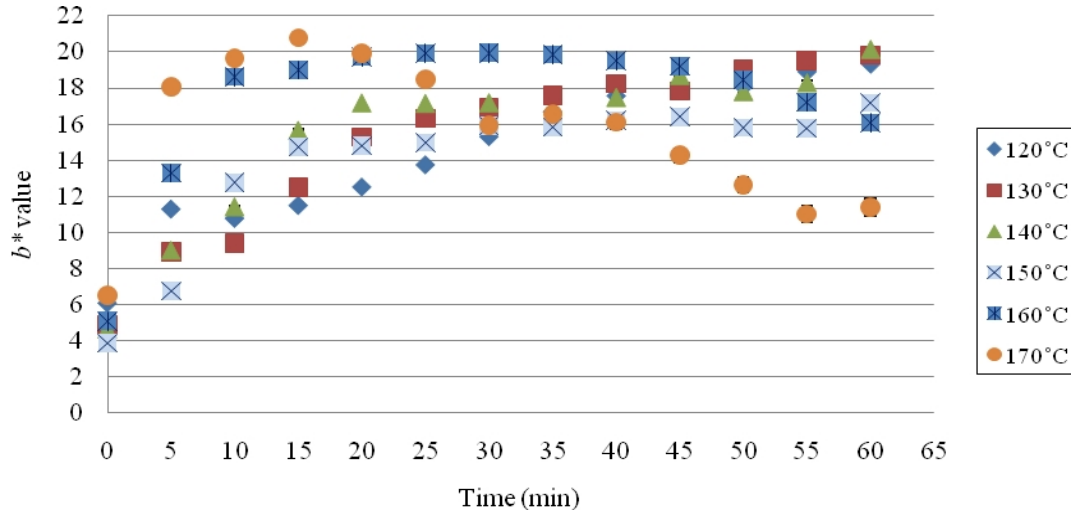


Figure 6: Variation of yellowness (b^*) at pastry surface as a function of baking time.

There is no trend of the yellowness values (b^*) of pastry changing, the graph shows the random pattern (Fig. 6). It cannot be concluded that the cooking conditions (time and temperature) have an influence on the yellowness value (b^*) for pastry cooking. Therefore the data of yellowness cannot be fitted with any kinetics model.

Kinetic Fitting

Even though the temperature heating changed in the first 5 minutes, the heating was much faster than the browning rate so the approximation of assuming isothermal conditions is justified.

Many other researchers found first order kinetics apply to browning reactions; for example bread baking (Zanoni et al., 1995 and Pulis & Salvadori, 2009), dough baking (Zuckerman & Miltz, 1997), cracker baking (Broyart et al., 1998) and potato frying (Krokida et al., 2001). After prolonged heating, a steady state colour (L_{∞}^*) is reached, which was also observed by Demir et al. (2002) who developed the browning kinetics in hazelnuts roasting at the temperature of 120°C and 180°C for a long time period and assuming isothermal condition.

For this case first order kinetics was used to describe the lightness - time curves and are given by;

$$\frac{dL^*}{dt} = -k(L^* - L_{\infty}^*) \quad \frac{dL^*}{dt} = -k(L^* - L_{\infty}^*) \quad (1)$$

where k is a first order rate constant (s^{-1}), which varied according to a temperature dependence that is described by the Arrhenius equation (Eq. 2) and t is time (s).

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

where k_0 is the Arrhenius constant (s^{-1}); E_a is the activation energy (J/mol); R is the universal gas constant (8.3145 J/mol·K) and T is absolute temperature (K). In isothermal conditions this can be integrated to give an equation for L^* as a function of time.

$$\int_{L^*_0}^{L^*} \frac{dL^*}{(L^* - L^*_{\infty})} = -k \int_0^t dt \quad \int_{L^*_0}^{L^*} \frac{dL^*}{(L^* - L^*_{\infty})} = -k \int_0^t dt \quad (3)$$

$$\ln\left(\frac{L^* - L^*_{\infty}}{L^*_0 - L^*_{\infty}}\right) = -kt \quad \ln\left(\frac{L^* - L^*_{\infty}}{L^*_0 - L^*_{\infty}}\right) = -kt$$

(4)

Then Eq. (4) can be rearranged and expressed as;

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

$$L^*_{predicted} = L^*_0 - (L^*_0 - L^*_{\infty}) * (1 - \exp(-kt)) \quad (5)$$

The L^*_0 , L^*_{∞} are the initial and infinity of L^* value, respectively. The parameters L^*_0 , k_0 and E_a in equation 2 and 5 were fitted to all the data simultaneously by minimizing the residual sum of squared errors by non-linear regression with a Levenberg-Marquarat algorithm function *lsqcurvefit* in MATLAB. The model fitting profile with the experimental data points of L^* values of pastry baked at six difference temperatures are shown in Fig. 7.

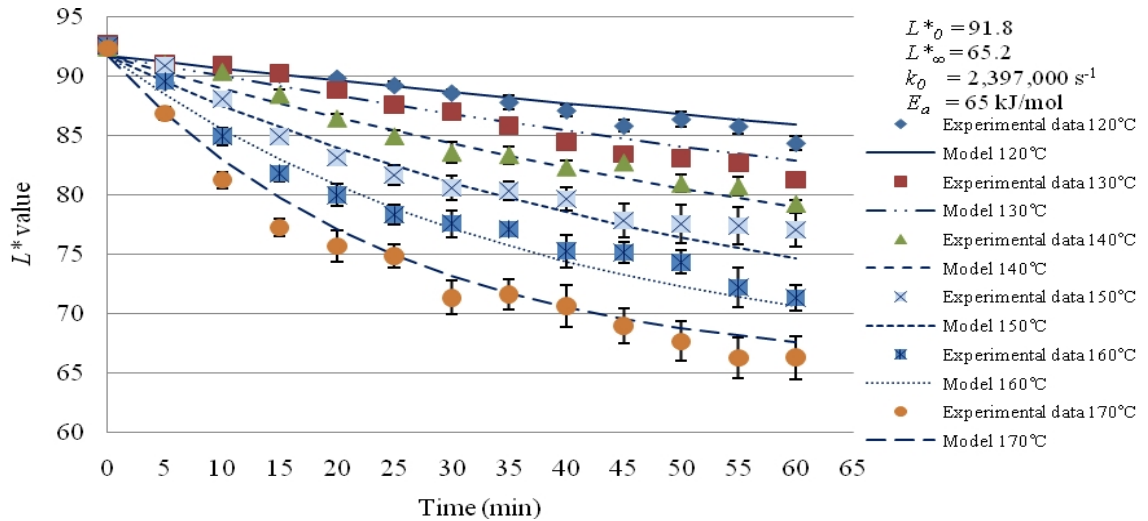


Figure 7: Fitted profile of the first order kinetic model with the experimental data point of the lightness values (L^*) for pastry baking at six different temperatures.

The initial L^* value (L^*_0) was measured as 92.58. As can be seen from these figure there is good agreement between the experimental results and the theoretical predictions of 91.8. It can be concluded that colour change was successfully modelled as a first order process, the temperature effect in rate constant being predicted by the Arrhenius equation. The kinetics parameters (k_0 and E_a) were obtained as 2,397,000 s⁻¹ and 65 kJ/mol, respectively. In general the activation energies for non-enzymatic browning in foods are between 37 and 167 kJ/mol (Heldman & Lund, 1992 and Villota & Hawkes, 1992). This calculated activation energy for L^* value in this work is similar to the values reported in bread based food product (45 and 70 kJ/mol) (Zanoni et al., 1995; Broyart et al., 1998; Zuckerman & Miltz, 1997 and Zhang & Datta, 2006).

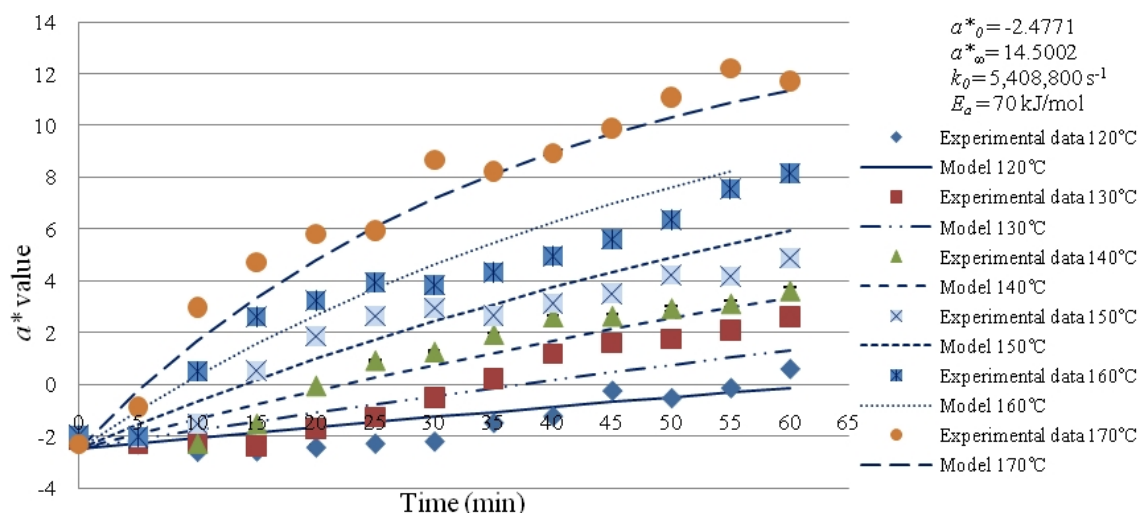


Figure 8: Fitted profile of the 1st order kinetic model with the experimental data point of the redness values (a^*) for pastry baking at six different temperatures.

Fig 8 shows a similar first order model can explain the kinetics of change in the colour parameter ' a^* ', they were fitted using the same model as for L^* (Eq. 2 and 5). An activation energy of 70 kJ/mol was found. This is of similar magnitude as found for intensity (L^*) (65 kJ/mol) suggesting both physical colour parameters reflect changes in browning product formation (melanoidins). Ilo and Berghofer (1999) reported similar comparative activation energy for a change in L^* (65 kJ/mol) and a^* (74 kJ/mol) during extrusion of maize grits.

In this work a significant effect was made to obtain very fast and uniform heat transfer. In spite of this there was a period of transient heating and there was a colour distribution across the surface of the pastry samples (Fig. 3). This suggests that future analysis should be carried out to incorporate the temperature history in characterising the kinetics of browning and the cause of variation on the sample surface. This will be the focus of future research.

CONCLUSION

The browning development can be easily monitored by image analysis and the L^* parameter suitably indicated the browning on pastry surfaces cooked at isothermal temperatures. The results of this study showed that the effect of both cooking temperature and time was significant for the pastry surface. Colour change was analysed as a first order kinetic and the browning reaction kinetics for pastry cooking sensitivity to temperature was described well by the Arrhenius equation, giving k_0 of 2,397,000 s⁻¹ and E_a of 65 kJ/mol for L^* value and k_0 of 5,408,800 s⁻¹ and E_a of 70 kJ/mol for a^* value.

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