CHARACTERISING THE KINETICS OF HIGH TEMPERATURE BROWNING IN FOODS

A Thesis Presented In Partial Fulfilment Of The Requirements For The Degree Of Doctor Of Philosophy In Food And Bioprocess Engineering

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ABSTRACT

Kinetic models for describing the Maillard reaction have been developed extensively but a versatile model has not been obtained because this reaction is very complex. The objective of this research was to develop a kinetic model to describe and predict the Maillard browning reaction occurring at the surface of foods during high temperature cooking. Commercial frozen pastry dough and processed potato product were used as the model food in this study. The progress of brown colour development was determined using image analysis methods in the CIE colour space ($L^*a^*b^*$ scale). The lightness (L^*) was found to be the best parameter to represent the browning reaction in these products. The lightness-time curve followed first order kinetics.

The effects of temperature and moisture content on the Maillard browning reaction between amino acids and reducing sugars were studied. The effect of moisture content was investigated by baking pastry samples at five different initial moisture contents (44.55, 33.89, 22.92, 10.95 and 9.18 wt% of d.b.) on a hot temperature controlled pan at 160°C for 60 minutes. The lightness-time curve was fitted with a first order kinetic model by non linear regression using the recorded surface temperature history as an input to obtain the initial lightness (L^*_0), endpoint or final lightness (L^*_∞) and kinetic rate constants (k). Statistical analysis (ANOVA) was used to test the effect of moisture content on these parameters. The result showed that the moisture content had no significant effect on the browning kinetics of pastry at the 95% confidence level ($P<0.05$). The moisture content had the most influence on the initial lightness ($P<0.005$), whereas the final lightness was moderately affected ($P<0.05$). Consequently, the effect of moisture content on the lightness was not considered as a major factor for browning reaction and was not included in the model for this study. Moisture content

did however influence the time-temperature history at the food surface due to evaporation.

The effect of temperature was studied by baking pastry samples (44.55 %MC; wt% d.b.) at six different temperatures (120, 130, 140, 150, 160 and 170˚C) for 60 minutes. The temperature dependence of the Maillard browning reaction of pastry baking was found to follow the Arrhenius law. The kinetic parameters: the activation energy (E_a), the kinetic rate constant at 150ºC (k_{150}) and the initial and final lightness (L^*_0 and L^*_∞) were obtained from the model fitting. The parameters were fitted using both isothermal and non-isothermal methods. As the baking temperature conditions were controlled to a constant temperature so an isothermal model fitting was reasonable to use for a first approximation. The minimization of the residual sum of square errors by non-linear regression with the Levenberg-Marquardt algorithm function *lscurvefit* was applied for this fitting. The activation energy (E_a) and the kinetic rate constant at 150ºC (k_{150}) values were obtained at 65.93 kJ·mol^{-1} and 0.017 min^{-1}, respectively. The initial and final lightness (L^*_0 and L^*_∞) were estimated at 91.78 and 65.24, respectively. The goodness of this fit (R^2) was calculated as 0.91.

However, experimentally it was found that the temperature of the pastry surface was not absolutely constant, and hence isothermal fitting was probably not justified. Therefore, the experimental data for lightness change and time-temperature histories were re-fitted to estimate the kinetic parameters. The MATLAB® function *lsqnonlin* was used to optimise the kinetic parameters using a non-isothermal model. The activation energy (E_a) and the kinetic rate constant at 150ºC (k_{150}) values were estimated at 71.90 kJ/mol and 0.025 min^{-1}, respectively. The initial and final lightness (L^*_0 and L^*_∞) were obtained as 91.21 and 67.54, respectively. The goodness of this fit (R^2) was calculated as 0.92.

Experimental trials were carried out to validate the model using the kinetic parameters obtained from the non-isothermal model fitting. The time-temperature histories for non-isothermal baking conditions were generated using several different scenarios of pan and oven baking, which provided conductive and convective heat transfer. The validation results showed the model gave good predictions with absolute relative errors (e_{abs}), of 1.93% (n = 50) and 0.38% (n = 8) for pan and oven baking, respectively.

In addition, the developed model was shown to be applicable for use in another food type, processed potato products. The same method as the pastry baking was used for fitting the model for processed potato product baking. The kinetic parameters of E_a, k_{150}, L^*_0 and L^*_∞ were obtained as 55.99 kJ·mol^{-1}, 0.025 min^{-1}, 82.90 and 49.78, respectively. They were different to the kinetics of pastry baking because of the different composition of the processed potato product. The validation of the model against separate processed potato product baking experiments gave an absolute relative error (e_{abs}) of 1.95% (n = 20) which shows that the predictions were good.

The key to achieving good predictions of colour change was in basing the model on the experimentally recorded surface temperature history, rather than assuming the surface is at the cooking temperature as was done in many literature studies. The model could be accurately fitted if it were possible to measure both surface temperature and colour simultaneously during cooking. To achieve this, an oven was modified by installing a thermal camera and infrared (IR) window for observing the temperature and colour values at the same time during the cooking process.

It was found that the surface of the pastry rose up during the cooking process as water evaporation created a bubble inside the pastry. This causes some variation in colour between samples. Moreover, the kinetics of the browning reaction were affected by the cooking condition, which changed the mechanism of the reaction. More than one browning kinetic was found when the different cooking conditions were applied. From the results of this study, it was hypothesied that the heating rate of the cooking had an influence on the pathway of the reaction mechanism. The fission pathway appears to be dominant when the pastry sample was baked under high temperature conditions, which produced a fast rate of the browning reaction with higher brown colour intensity than the alternatives. A lower intensity of brown colour was found on the pastry sample when baked under a slower heating rate suggesting that many intermediate compounds, such as aroma and volatile compounds, were generated in the reductones mechanism pathway. Following this, it was suggested that to develop a powerful kinetic model, the real cooking conditions for each food need to be indentified and used to characterise the reaction rate.

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แด่พ่อและแม่

ผู้ที่เป็นกำลังใจสำคัญที่สุดในชีวิต
ที่เล็งเห็นความสำคัญของการศึกษาและเป็นแรงบันดาลใจให้ลูกได้เดินทางมาถึงจุดนี้
สิ่งที่ลูกรับรู้มาตลอดชีวิต คือ พ่อกับแม่มักบอกเสมอว่าให้ตั้งใจเรียน เพราะท่านทั้งสองไม่มีโอกาสนี้
พ่อ เป็นบุคคลที่ถือได้ว่าเป็นผู้มีปัญญา
ทุกคำพูด ทุกคำสอนของพ่อ ไม่ได้มาจากความรู้หรือจากตำราเล่มไหนๆ
แต่ล้วนมาจากพื้นฐานของความดีที่มีอยู่ในตัวพ่อทั้งสิ้น
สิ่งเหล่านี้ทำให้ลูกคนนี้รักดี และดำรงตนอยู่ในทางที่ถูกเสมอมา
แม่ คือต้นแบบของความอดทนและความเข้มแข็ง
ถึงแม้ว่าลูกจะทำได้ไม่ถึงครึ่งของแม่
แต่ทุกครั้งที่ท้อถอยหรืออ่อนแอ คำพูดของแม่จะช่วยดึงให้ลูกลุกขึ้นสู้เสมอ
ขอบคุณทุกคำสอนของพ่อและแม่ที่บ่มเพาะให้เป็นอย่างทุกวันนี้
ลูกโชคดีมากที่ได้เกิดมาเป็นลูกพ่อกับแม่ค่ะ

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