Modelling kinetics of thermal degradation of colour in peach puree

I.M.L.B. Ávila, C.L.M. Silva *

Abstract

Optimisation of thermal processes relies on adequate degradation kinetic models for food safety and quality. In order to use peach puree as a model food to further validate calculated optimal conditions, isothermal experiments, using peach puree, were performed between 110°C and 135°C. Colour was quantified using the \( L, a, b \) system. Two combinations of these parameters, \( La/b \) and Total Colour Difference (TCD), were used to evaluate the total colour change. A one-step non-linear regression was performed on all data using the Arrhenius model. The changes in the \( L \) and \( b \) values followed a first-order reaction with activation energies of 107 ± 7 and 109 ± 8 kJ/mol, respectively. The fractional conversion model was applied to \( a, La/b \) and TCD resulting in activation energies of 106 ± 13, 106 ± 10 and 119 ± 9 kJ/mol, respectively. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Peach puree; Colour degradation; Kinetics; Modelling; Model food

1. Introduction

Thermal treatment is one of the most important methods of food preservation (Lund, 1975). However, excessive heating produces considerable losses in the quality and particularly in the organoleptic properties of foods (Hayakawa & Timbers, 1977). Kinetic models of thermal destruction are essential to design new processes assuming a safe food product and giving a maximum retention of quality factors (Lund, 1975; Teixeira, Dixon, Zahradnik & Zinsmeister, 1969). Moreover, information available on reaction kinetics is still quite limited (Holdsworth, 1990).

The first quality impact by which the consumers take the decision to acquire a product is its visible appearance. The colour of products can be specified by three co-ordinates in the colour space which can be obtained directly with a tristimulus colorimeter. The \( L, a \) and \( b \) system is the more frequently used scale to measure the colour of food products (Francis & Clydesdale, 1975). The \( L \)-value is a measure of the lightness, the \( b \)-value indicates the change of the colour from blue to yellow, and the \( a \)-value the change from green to red (Hutchings, 1994).

Changes in food colour can be associated with its previous heat treatment history. Various reactions such as pigment destruction (carotenoids and chlorophylls) and non-enzymatic browning (Maillard) reactions, can occur during heating of fruits and vegetables and therefore affect its colour (Reyes & Luh, 1960; Abets & Wrolstad, 1979; Resnik & Chirife, 1979; Cornwell & Wrolstad, 1981). The retention of total colour can be used as a quality indicator to evaluate the extent of deterioration due to thermal processing (Shin & Bhowmik, 1995). Several researchers have published work on modelling of thermal degradation kinetics of colour in the temperature range of sterilisation conditions. Silva and Ignatiadis (1995) presented a literature review on this subject. Table 1 reviews kinetic data on colour thermal degradation of some fruits and vegetables. The majority of the published work report first order or zero order degradation reaction kinetics. Only Steet and Tong (1996) described the thermal degradation kinetics of green colour in peas, applying the fractional conversion model (also known as reversible first order model – Levenspiel, 1972).

The palatability and quality of fresh peach products depends on the variety and maturity index of the fruit itself (Delwiche & Baumgardner, 1985). The processing of peach fruits to pulp, nectar, compote or to dried products is commercially established. The processing method is also very important because it can hardly damage peach colour, flavour, and texture (Askar, Abdel-Fadeel, Ghonaim, Abd El-Gaied & Ali, 1996a,b).

Some works have been published about the use of colour
Table 1
Published data for kinetics of colour thermal degradation of some fruits and vegetables

<table>
<thead>
<tr>
<th>Reference</th>
<th>Product</th>
<th>Temperature range (°C)</th>
<th>Equipment</th>
<th>Colour parameter</th>
<th>Kinetics</th>
<th>D_{10,°C} (min)</th>
<th>z (°C)</th>
<th>(k_0) (s(^{-1}))</th>
<th>E(_a) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hayakawa and Timbers (1977)</td>
<td>Asparagus</td>
<td>79.4–149</td>
<td>Gardner AC-1</td>
<td>(a/b)</td>
<td>First order</td>
<td>41.7</td>
<td>38.9</td>
<td>75.6</td>
<td>82.8</td>
</tr>
<tr>
<td></td>
<td>Green beans</td>
<td></td>
<td></td>
<td></td>
<td>First order</td>
<td>39.4</td>
<td>63.5</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Green peas</td>
<td></td>
<td></td>
<td></td>
<td>First order</td>
<td>21</td>
<td>28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ohlsson (1980)</td>
<td>Vegetables</td>
<td>110–134</td>
<td>HunterLab</td>
<td>(L)</td>
<td>First order</td>
<td>38.9</td>
<td>82.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tomato sauce</td>
<td></td>
<td></td>
<td></td>
<td>First order</td>
<td>39.4</td>
<td>63.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rao, Lee, Katz and Cooley (1981)</td>
<td>Peas</td>
<td>98.9–126.7</td>
<td>Hunter D25-3</td>
<td>(a/b)</td>
<td>First order</td>
<td>13.2</td>
<td>38.3</td>
<td>73.15</td>
<td></td>
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<tr>
<td>Aguerre and Suárez (1987)</td>
<td>Corn</td>
<td>57–100</td>
<td>HunterLab LS-5000</td>
<td>TCD</td>
<td>Zero order</td>
<td></td>
<td></td>
<td>71.06</td>
<td></td>
</tr>
<tr>
<td>Merin, Gagel, Popel, Bernstein and Rosenthal (1987)</td>
<td>Prickly pear fruit (conc. solution)</td>
<td>50–90</td>
<td>Spectrophotometer</td>
<td>Absorvance at 535 nm</td>
<td>First order</td>
<td>4.19</td>
<td>24.5</td>
<td>3.30 x 10^4</td>
<td>44.85</td>
</tr>
<tr>
<td>Rhim, Nunes and Jones (1989)</td>
<td>Grape juice</td>
<td>60–95</td>
<td>Spectroguard Colour system</td>
<td>(L)</td>
<td>First order</td>
<td>1.30 x 10^2</td>
<td>114.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shin and Bhowmik (1995)</td>
<td>Pea puree</td>
<td>110–125</td>
<td>Hunterlab LS-5400</td>
<td>(L_{ab})</td>
<td>First order</td>
<td>31.10</td>
<td>42.9</td>
<td>1.29 x 10^6</td>
<td>67.9</td>
</tr>
<tr>
<td>Steet and Tong (1996)</td>
<td>Peas</td>
<td>70–90</td>
<td>Minolta CR-210</td>
<td>(a)</td>
<td>Fract. conv.</td>
<td>9.75 x 10^6</td>
<td>76.08</td>
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<tr>
<td>Barreiro, Milano and Sandoval (1997)</td>
<td>Double concentrated tomato paste</td>
<td>70–100</td>
<td>Gardner XL-23</td>
<td>(L) (1st phase)</td>
<td>First order</td>
<td>4.85 x 10^6</td>
<td>48.07</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(L) (2nd phase)</td>
<td>First order</td>
<td>2.16 x 10^5</td>
<td>23.95</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(a)</td>
<td>First order</td>
<td>5.37 x 10^7</td>
<td>40.92</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(b)</td>
<td>First order</td>
<td>2.63 x 10^7</td>
<td>85.69</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(E)</td>
<td>First order</td>
<td>6.43 x 10^7</td>
<td>42.22</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(a/b)</td>
<td>First order</td>
<td>1.09 x 10^4</td>
<td>28.67</td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TCD</td>
<td>Zero order</td>
<td>2.40 x 10^7</td>
<td>42.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lozano and Ibarz (1997)</td>
<td>Apple pulp</td>
<td>56–94</td>
<td>Hunterlab D25L-2</td>
<td>(L)</td>
<td>First order</td>
<td>1.37 x 10^0</td>
<td>66.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Peach pulp</td>
<td></td>
<td></td>
<td>(L)</td>
<td>First order</td>
<td>1.35 x 10^7</td>
<td>45.02</td>
<td></td>
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<tr>
<td></td>
<td>Plum pulp</td>
<td></td>
<td></td>
<td>(L)</td>
<td>First order</td>
<td>1.74 x 10^7</td>
<td>67.72</td>
<td></td>
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<tr>
<td></td>
<td>Apple pulp</td>
<td></td>
<td></td>
<td>TCD</td>
<td>Fract. conv.</td>
<td>1.97 x 10^0</td>
<td>28.51</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Peach pulp</td>
<td></td>
<td></td>
<td>TCD</td>
<td>Fract. conv.</td>
<td>1.12 x 10^1</td>
<td>39.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Plum pulp</td>
<td></td>
<td></td>
<td>TCD</td>
<td>Fract. conv.</td>
<td>3.43 x 10^1</td>
<td>35.95</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a k_0\) is the reaction rate constant at infinite temperature.

\(^b\) Fract conv. is the fractional conversion model.

\(^c\) SI is the saturation index (SI = \(\sqrt{a^2 + b^2}\)).
measurement of peaches to evaluate their maturity indices (Delwiche & Baumgardner, 1983, 1985) or on the quality control for canned peach halves (Duran, Rodriguez & Alcedo, 1979), peach compote, pulp and nectar (Askar et al., 1996b).

The pH value of peach puree is in the range of 3.6–4.0 (Lund, 1976). Therefore, a relatively mild thermal treatment, such as pasteurisation, is adequate to stabilise it at room temperature (Fellows, 1988). Colour thermal degradation of apples, peaches and plums pulp was studied by Lozano and Ibarz (1997) in the temperature range of 56–94. However, due to its easy availability and sensitivity to heat treatment, this product has great potential to be used as a quality indicator for sterilisation processing conditions. At these processing temperatures (over 100°C) peaches can only be used as a model food product.

Therefore, the objective of this research study was the mathematical modelling of colour peach puree thermal degradation kinetics, in order to apply it as an indicator for sterilisation thermal processing conditions impact on quality.

2. Kinetic considerations

Numerous research studies apply zero- (Eq. (1)) or first-order (Eq. (2)) models to describe the degradation of colour in food products:

\[ C = C_0 - kt, \]
\[ C = C_0 \exp(-kt), \]

where \( C \) is the measured colour scale value, or a combination of the colour scale values, \( C_0 \) the initial \( C \), \( t \) the heating time and \( k \) the reaction rate constant.

Also the fractional conversion model can be used to describe the colour degradation (Levenspiel, 1972):

\[ \frac{C - C_f}{C_0 - C_f} = \exp(-kt), \]

where \( C_f \) is the final equilibrium value of the colour parameter.

Colour concentration can be translated in the \( L_a \) and \( b \) parameters of the colour system, or by a combination of these three values, such as \( \text{La} \) and TCD:

\[ \text{TCD} = \sqrt{\Delta L^2 + \Delta b^2 + \Delta a^2}. \]

\( \text{La} \) and TCD express a total colour change of the food product (Shin & Bhowmik, 1995).

The Arrhenius equation is usually applied to evaluate the reaction rate constant temperature dependence:

\[ k = k_{\text{ref}} \exp \left( -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right), \]

where \( T \) is the absolute temperature, \( T_{\text{ref}} \) the reference absolute temperature, \( k_{\text{ref}} \) the reaction rate constant at the reference temperature, \( E_a \) the activation energy and \( R \) the universal gas constant.

3. Materials and methods

Peaches of the Roubidoux cultivar were purchased in the local market, peeled, destoned and pureed. After being homogenised with a spoon, the peach puree was separated into small dark plastic bags and frozen stored at \(-20 \pm 1°C\).

For each experiment, the required amount of peach puree was thawed at ambient temperature and introduced into glass vials (Chrompack/Cat.N°10202/Vial 2 ml) which were closed and kept out of daylight. These small vials were used to reduce the existence of sample temperature gradient during heating.

Six isothermal experiments were performed at 110°C, 115°C, 120°C, 125°C, 130°C and 135°C in an oil bath (Tempunit TU-16D Techne) with temperature control. The vials were placed in the oil bath after its temperature had reached the specified value. At pre-specified time intervals, the samples were cooled in an ice–water mixture immediately after withdrawal from the oil bath. After cooling the samples, the colour measurements were carried out in a room with controlled light. A Petri dish (normax 60×15 mm) was filled with the puree contained in four vials (≈12 g) and placed directly over the Colorimeter (Minolta Chroma Meter Cr-300). The \( L \), \( a \) and \( b \) colour system was used to evaluate the colour.

Statistical analysis of the data was performed using the STATA program version 4.0 (Stata Corporation, 1995). Both two-step and one-step non-linear regressions (Arabshahi & Lund, 1985) were performed and also regression analysis of residuals was examined (Box, Hunter & Hunter, 1978).

4. Results and discussion

With the increase of heating temperature and time, peach puree becomes darker. This corresponds to a decrease in the \( L \)-value of the colour scale (Fig. 1). Peach puree also loses its yellowness and becomes more red when heated. This change is translated by a decrease of the \( b \)-value (Fig. 2) and an increase of the \( a \)-value (Fig. 3).

Enzymatic browning is a serious problem when dealing with peaches because the oxidative enzymes, such as peroxidase and polyphenolase, may cause browning accompanied by changes in colour, flavour and nutritive value during frozen storage and thawing of the product (Reyes & Luh, 1960). During the thermal
treatment of peaches, those enzymes are inactivated, but many other reactions can take place affecting colour. Carotenoids degradation and non-enzymatic browning (Maillard) reactions are the most common.

In order to find the kinetic model that better fits the obtained experimental data points, the two-step method was used as a first approach (Arabshahi & Lund, 1985). Considering each colour parameter, a regression analysis was applied, in a first step, for each isothermal experiment to calculate the corresponding reaction rate constant. Figs. 1 and 2 show the first order reaction model (Eq. (2)) applied to the $L$ and $b$ values, respectively. The fractional conversion kinetics (Eq. (3)) was used to model the thermal degradation of the $a$, $L_{ab}$ and TCD parameters (Figs. 3–5, respectively). In the second step, the Arrhenius equation (5) was used to describe the temperature dependence of the reaction rate constant.

In order to make a better estimate of the kinetic parameters, a one-step non-linear regression was applied to all data (Arabshahi & Lund, 1985). Based on the examination of the residuals, these proved to be the most adequate models, once the distribution of residuals has no visual tendency (were randomly distributed around zero). One example of these plots is showed in Fig. 6 for the $L_{ab}$ parameter.

Estimated activation energies and rate constants at the reference temperature of 122.5°C and corresponding 95% confidence intervals are reported in Table 2. These values are within those published in the literature.
5. Conclusions

The objective measurement of colour using the L, a and b system can totally translate the real behaviour of canned peach puree when submitted to heat treatment. The Lab and TCD parameters proved to be good indicators of the total colour change of heat treated peach puree.

The Arrhenius model described well the temperature dependence of the reaction rate constant for all the colour parameters considered. The peach puree colour thermal degradation followed a first-order reaction kinetics for the L and b values with activation energies of 107±7 and 109±8 kJ/mol, and rate constants at reference temperature (122.5°C) of 2.9×10^{-3}±2×10^{-4} and 4×10^{-3}±3×10^{-4} min^{-1}, respectively. The a, Lab and TCD parameters were modelled using the fractional conversion equation. The activation energies obtained were 106±13, 106±10 and 119±9 kJ/mol, and the reaction rate constants at reference temperature of 122.5°C were 0.03±8×10^{-3}, 0.026±6×10^{-3} and 0.0085±3×10^{-3} min^{-1}, respectively. Therefore, retention of peach puree total colour may be used as a quality indicator for sterilisation processing conditions.

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References


