Analysis of the Color Change in Fish during the Grilling Process

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Samples of red sea bream (Pagrus major), a white-meat fish, were grilled under an infrared heater, and the temperature and color of the sample surface was measured. For the change in color, brightness component \( L^* \) and two chromatic components \( a^* \) (from green to red) and \( b^* \) (from blue to yellow) were measured. As the browning reaction proceeded, \( L^* \) decreased monotonously and \( a^* \) and \( b^* \) varied in a complex way; however, \( a^* \) and \( b^* \) were correlated with \( L^* \). The browning reaction was treated as a first-order reaction and it was assumed that \( L^* \) decreased in proportion to the reactive product. The reaction rate constant of the diminution rate of \( L^* \) was determined to be in agreement with the values obtained from the experiment in which sample temperatures were maintained at a certain level. The estimated values of \( L^* \), \( a^* \), and \( b^* \) were in good agreement with experimental values.

Keywords: kinetic analysis, browning, fish, color

Introduction

Grilled fish is a popular dish used in prepared meals and boxed lunches. Moderately browned, delicious-looking fish is generally preferred; thus, color plays an important role in the appeal of the fish. In actual cooking processes in the food industry, the degree of grilling is often determined empirically. If the cooking process, including the browning process, can be predicted, then heating equipment able to grill fish optimally could be developed. This study aimed to carry out a kinetic analysis of the color change in grilled fish in order to quantify the grilling process.

Color plays an important role in quantifying the degree of grilling in fish. Further, color is also widely used to evaluate many other foods. Several reports have clarified the relationship between color change and the factors that cause it, allowing the optimum conditions for food storage and processing to be determined.

Using a color difference meter, a sensor makes contact with the food, and the color is determined on the basis of the reflection of light from the sensor. Using this method, Yan et al. (2008) measured the color of bananas in storage, and analyzed the relationship between the color temperature and humidity of the storage environment. Kaida et al. (1999) determined the optimum brown color for pan-fried beef fillet on the basis of the relationship between frying temperature and frying time.

Some reports have used computer vision (CV) methods, which involve capturing and digitizing images of food in order to determine the color. Purlis and Salvadori (2007) studied the relationship between the color of the surface of bread, weight loss of bread, and the oven temperature during baking in order to show that the development of bread surface browning can be predicted. Pedreschi et al. (2006) investigated the relationship between the color of potato chips and the temperature of the oil used in deep frying. The study reported a quick color change when the potato chips were fried at a high temperature. They also described a method to convert the RGB data into \( L^* \), \( a^* \), and \( b^* \) units. Kong et al. (2007) evaluated the quality of thermally processed salmon by heating salmon samples sealed in aluminum containers at constant temperatures to investigate color, heating time, heating temperature, weight loss, texture, and thiamine content. Based on heating experiments at temperatures ranging from 100°C to 131.1°C, the study calculated the rate constants for \( L^* \), \( b^* \), and the activation energy \( E_a \) in the Arrhenius equation, and showed 70 to 100 kJ/mol of \( E_a \). Niamnuy et al. (2008) established the relationship between the color loss of boiled

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and dried shrimp during storage and the storage temperature, storage period, and astaxanthin content.

Although there are many reports similar to those described above, there are no reports on the analysis of fish browning during the grilling process. This study analyzed the browning color of fish samples during grilling on the basis of the relationship between the color, sample surface temperature, and grilling time.

**Materials and Methods**

Red sea bream (*Pagrus major*), a white-meat fish, was used for the samples. Raw fillets of red sea bream (cultivated in Ehime Prefecture) were purchased on the day of the experiment. The skin and bones were removed, and the fish were cut into pieces of 4 cm × 5 cm × 2 cm (width × length × thickness). The samples were wrapped with wrapping film and refrigerated (5°C) until use in experiments. The initial water content of the samples was approximately 75% w/w (wet basis).

Figure 1 shows a schematic diagram of the experimental apparatus. An infrared heater (100 V/750 W, Sakaguchi E. H. VOC Corp., Tokyo, Japan) was used as the heat source. The heater was cylindrical in shape (10 mm in diameter × 200 mm in length). The infrared energy was irradiated in a down direction from the heater, owing to the installed reflection hood. The temperature of the heater could be varied by controlling the voltage, and the heater responded quickly. The samples were placed on an electronic balance and positioned approximately 7 cm below the heat source. The irradiation energy, which was measured by the radiation sensor (RF30, Captec, Villeneuve d’Ascq, France) at the sample position, was 1.8 × 10⁴ W/m² when the heater was applied at 100V. The surface center temperature of the samples was measured using a K-type thermocouple (ø = 0.5 mm). When the temperature of the same point was measured with the infrared radiation thermometer, both were in close agreement; the validity of the measurement with the thermocouple was verified. Heating experiments were performed at room temperature.

Color is frequently represented using the $L^∗a^∗b^*$ color space as mentioned in the Introduction. In the $L^∗a^∗b^*$ color space, $L^∗$ is the luminance or lightness component, and $a^∗$ and $b^∗$ are the color degree which show the hue and the chroma. $+a^∗$ and $−a^∗$ indicate the direction of red and green, respectively. $+b^∗$ and $−b^∗$ indicate the direction of yellow and blue, respectively.

The color of sample surfaces was measured by contacting the sample with a spectro-photometric color difference meter (NF333, Nippon Denshoku Industries Co., Ltd., Tokyo, Japan), just after turning off the power supply of the heater. $L^∗$, $a^∗$, and $b^∗$ were measured with a D65 light source with a view field angle of 2°. The color of the temperature measurement point on each sample was measured at least five times; a mean value, excluding the maximum and minimum values, was then calculated.

To verify whether a browning reaction takes place at 100°C, a heating experiment in steam was performed using a pan heated by an electric heater as follows. The wire net...
was set in the pan, and water was poured under the net and boiled. After the pan was capped and filled with steam, the sample was put on the wire net and steamed. Additionally, a heating experiment using a temperature-controlled oven maintained at 100°C was performed under a non-humidified condition, where drying of the sample takes place.

Results and Discussion

Surface color change of samples To investigate color change during grilling, each sample was grilled using a heater with a constant voltage, from its raw state until the surface temperature reached approximately 200°C. Figure 2 shows the surface temperature change, and Fig. 3 shows the color change in the sample during grilling. Identical samples were used for this experiment, and the color was measured and photographs were taken after turning the heater off at nearly constant time intervals. The temperatures presented in Fig. 3 show the temperature immediately before the color measurement. This operation caused a fluctuation in the temperature, as shown in Fig. 2; the temperature declined when the heater was turned off and rose again during grilling. Figure 4 shows the color change caused by grilling. The surface temperature of the samples during grilling is also described in Fig. 4.

In general, color change is considered to comprise four steps: (1) protein denaturation, (2) water evaporation, (3) browning reaction, and (4) carbonization reaction. The experimental results showed that up to a surface temperature of approximately 80°C, the sample color was white and bright due to the denaturation of proteins, and \( L^* \) reached its maximum value. \( L^* \) subsequently decreased gradually because of water evaporation. As the temperature of the sample surface reached approximately 130°C, the browning reaction became more remarkable, and \( L^* \) decreased significantly. When \( L^* \) was approximately 40 to 50, chroma \( C^* (= \sqrt{a^2 + b^2}) \) was large because \( b^* \) had a maximum value and \( a^* \) was in-

![Image](image1.png)

Fig. 2. The temperature at the surface of the sample during grilling.

![Image](image2.png)

Fig. 3. The color change at the sample surface during grilling.

![Image](image3.png)

Fig. 4. The change in the color and temperature of the sample surface during grilling.

\([\square L^*, \blacktriangle a^*, \blacklozenge b^* + \text{sample surface temperature}]\)
creasing, and the sample appeared to be bright brown in color. When the temperature of the sample surface reached 180°C, the sample burnt, turning black in color and emitted smoke when $a'$ took the maximum value, that is to say, when $L^*$ was approximately 30. After that, as the temperature of the sample surface rose, $L^*$, $a'$, and $b'$ declined. This was considered to be the carbonization phase.

**Color change caused by browning reaction** To determine whether drying or browning caused the color change when the sample was grilled at 100°C, an experiment was carried out with a constant oven temperature. The experiment involved making a comparison between a sample heated at 100°C in a constant temperature oven and a sample exposed to saturated steam at 100°C. While the steamed sample showed no color change, the sample in the constant temperature oven showed weight loss and color change; the color change at 100°C likely results from drying. Because the surface temperature does not exceed 100°C in the presence of enough moisture, it is thought that a browning reaction takes place after the moisture dries and the temperature rises. Then, it was assumed that the color change caused by browning starts at 110°C.

To investigate the color change caused by the browning reaction in detail, an experiment was performed in which samples were grilled after being steamed. Samples were steamed for approximately 15 min to eliminate the color change caused by protein denaturation and were then grilled. The color of the samples was measured just after steaming, and the samples were then grilled for approximately 30 min at given constant temperatures (110−150°C), which are kept constant by regulating the voltage of the heater, and the color of the samples was measured at intervals. The heater was turned off to measure the color, and was turned on again to continue grilling.

Figure 5(A) shows the change in $L^*$, when the surface temperature of the samples was kept at given temperatures. From this figure, it was found that $L^*$ decreases monotonously as the heating time increased, and that the diminution rate of $L^*$ rises with the temperature of the sample surface. Figure 5(B) and (C) show the change in $a'$ and $b'$, respectively, when the surface temperature of the samples were kept at given temperatures, as in Fig. 5(A). From Fig. 5(B), $a'$ was shown to decrease slightly once, increase afterwards, and then decrease with the heating time. On the other hand, from Fig. 5(C), $b'$ was shown to increase first with time, and decrease afterwards. Thus, $a'$ and $b'$ varied in a complicated way with time, and it is difficult to determine the change rate of $a'$ and $b'$ directly from these figures.

Next, we considered the trajectory through color space as the browning reaction proceeds. The color space is represented by orthogonal coordinates ($L^*$, $a'$, and $b'$), and is also represented by cylindrical coordinates ($L^*$, hue angle, and chroma). In this study, we used $L^*$, $a'$, and $b'$ coordinates as the color space, because the orthogonal coordinate system more conveniently represents three dimensions.

Figure 6 shows a three-dimensional graph that represents...
the color space. In this figure, all the experimental points are plotted. The plotted points followed almost the same trajectory through color space, regardless of the sample surface temperature. This result demonstrates that the surface browning color developed in the same way, regardless of heating temperature and heating rate. Therefore, if $L^*$ declines, $a^*$ and $b^*$ change in accordance with it.

To understand the three-dimensional trajectory, two-dimensional projection drawings of the $L^*-a^*$, $L^*-b^*$, and $a^*-b^*$ planes are shown in Fig. 7(A-C). Fig. 7(A) and (B) show the correlations between $a^*$ and $L^*$, and between $b^*$ and $L^*$, respectively. The correlations with $L^*$ are determined with empirical equations from the following cubic functions:

$$a^* = 4.84 \times 10^{-4} \times (L^*)^3 - 8.7 \times 10^{-2} \times (L^*)^2 + 4.48 \times (L^*) - 54.2 \quad \text{at} \quad 28 < L^* < 90 \quad (1)$$

$$b^* = 4.76 \times 10^{-4} \times (L^*)^3 - 1.14 \times 10^{-1} \times (L^*)^2 + 8.02 \times (L^*) - 141.4 \quad \text{at} \quad 28 < L^* < 90 \quad (2)$$

When the value of $L^*$ decreases, $a^*$ and $b^*$ change simultaneously according to eqs. (1) and (2), respectively. This means the color point moves within the color space. As a result, the relation between $a^*$ and $b^*$, which is calculated from eqs. (1) and (2), is shown as the solid line in Fig. 7(C).

**Kinetic analysis of the browning reaction** The browning process is a type of Maillard reaction, and is considered to involve a series of complex reactions, including an amino-carbonyl reaction. It is difficult to identify the elementary reaction and formulate the rate equation to obtain the rate constant. Therefore, this study simplified the reaction as follows.

Assuming that an original substance A (reactant A) is
transformed into a browning substance P by heating, and that the producing rate of P is proportional to the concentration of remaining A, the reaction rate equation can be expressed by the following equation:

\[ \text{A} \rightarrow \text{P} \quad (3) \]

\[ \frac{dC_A}{dt} = -\frac{dC_P}{dt} = kC_A \quad (4) \]

Initial condition

\[ C_A = C_{A_0}, C_P = 0 \quad (5) \]

where \( C_A \) and \( C_P \) are the concentrations of A and P, respectively, and \( k \) is the rate constant.

Assuming that there is no browning substance initially and that all of A finally changes into P, the initial and final concentrations are represented as follows:

\[ C_{A_i} = C_{P_i} = 0 \]
\[ C_{A_f} = C_{P_f} = C_0 \]

Equation (4) shows the change in \( L^* \). Temperature dependence of the rate constant is assumed to follow the Arrhenius equation.

\[ \ln Y = -kt \quad (12) \]

However, as shown in Fig. 8, the condition in which temperature is constant did not hold because it took time to reach a given temperature and the temperature fluctuated during measurement. Then, we evaluated the frequency factor and the activation energy in eq. (11) as follows.

When eq. (11) is substituted into eq. (9), the next equation is obtained.

\[ \frac{dY}{dt} = -k_0 \exp\left(-\frac{E_a}{RT}\right) Y \quad (13) \]

If the frequency factor and the activation energy are provided, and using the experimental temperature history, \( Y \) could be calculated by numerical integration of eq. (13). This calculation used the Runge-Kutta-Gill (RKG) method. Therefore, we assumed the initial value of the activation energy \((E_a)_1\). Subscript 1 of \((E_a)_1\) represents the value used for the first trial. Then, frequency factor \((k_0)_1\) corresponding to \((E_a)_1\) was evaluated to generate good agreement between the measured \(L^*\) and the calculated values. In this calculation, the Golden section method, which is a kind of search method, was used to minimize the difference between the measurements and the calculation value. One frequency factor \((k_0)_1\) was obtained from this calculation for the assumed activation energy \((E_a)_1\).

Activation energy \((E_a)_2\) was then adjusted for the second trial, and the frequency factor \((k_0)_2\) corresponding to \((E_a)_2\) was obtained in the same manner. Using this iterative process, the error values for the variables were minimized, resulting in the determination of the set of \((E_a)m, (k_0)m\), which were selected as the activation energy and the frequency fac-

![Fig. 8. Y and temperature history when temperature is controlled at 150℃.](image-url)
Good agreement between these measured values and the calculated ones was observed. Therefore, if temperature history of a sample surface is obtained, values for $L^*$, $a^*$, and $b^*$ or values for $L^*$, hue, and chroma can be calculated and the color change caused by grilling can be predicted.

Conclusions

The objective of this study was to quantify the color change in fish during grilling. A kinetic analysis of the color changes in grilled fish was carried out using red sea bream ($Pagrus major$), a representative white-meat fish, and the following results were obtained:

1. As the browning reaction proceeded, $L^*$ decreased monotonously and $a^*$ and $b^*$ varied in a complex way. However, the three-dimensional graph of $L^*$, $a^*$, and $b^*$ showed that the plotted points followed almost the same locus, re-

Table 1. Activation energies and frequency factors at each temperature.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$E_a$ [kJ/mol]</th>
<th>$k_0$ [1/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>130°C</td>
<td>50</td>
<td>$5.69 \times 10^3$</td>
</tr>
<tr>
<td>140°C</td>
<td>47</td>
<td>$2.41 \times 10^3$</td>
</tr>
<tr>
<td>150°C</td>
<td>55</td>
<td>$3.76 \times 10^4$</td>
</tr>
<tr>
<td>Average</td>
<td>50.7</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Frequency factors when the activation energy is 50.7 kJ/mol.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$E_a$ [kJ/mol]</th>
<th>$k_0$ [1/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>130°C</td>
<td>50.7</td>
<td>$6.98 \times 10^3$</td>
</tr>
<tr>
<td>140°C</td>
<td>50.7</td>
<td>$7.40 \times 10^3$</td>
</tr>
<tr>
<td>150°C</td>
<td>50.7</td>
<td>$1.01 \times 10^4$</td>
</tr>
<tr>
<td>Average</td>
<td>50.7</td>
<td>$8.16 \times 10^3$</td>
</tr>
</tbody>
</table>

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1. As the browning reaction proceeded, $L^*$ decreased monotonously and $a^*$ and $b^*$ varied in a complex way. However, the three-dimensional graph of $L^*$, $a^*$, and $b^*$ showed that the plotted points followed almost the same locus, re-
gardless of the surface temperature of the sample. This result demonstrated that the browning color on the surface developed in the same way.

(2) To quantify the browning reaction, a dimensionless parameter $Y$ was defined, and the browning reaction was expressed by a first-order equation. Assuming that the rate constant $k$ follows the Arrhenius equation, $L^*$ was calculated and the frequency factor and activation energy were determined, as they were in agreement with the measured values in the grilling experiment with controlled temperature.

(3) On the basis of the history of the surface temperature of samples in the experiment, the change in $L^*$ was calculated from the frequency factor and the activation energy. In addition, the values of $a^*$ and $b^*$ were also evaluated from their relationship with $L^*$. The calculated values for $L^*$, $a^*$, and $b^*$ were in good agreement with the corresponding measured values. These results demonstrated that the color change caused by grilling can be predicted on the basis of the change in surface temperature.

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References