Effect of Heat Treatment on Oxidation of Hazelnut Oil
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Abstract: Thermal processing, a common processing method of vegetable oil in daily life, is accompanied by the formation of some harmful substances. This study determined the peroxide value, anisidine value, total peroxide value, polar compound content, fatty acid content, and core aldehyde content of hazelnut oil under different thermal processing conditions. The oxidation kinetics equation of fatty acid and temperature of hazelnut oil was established, and the correlation between the contents of fatty acid and core aldehyde and four oxidation indexes was analyzed. The results showed that the TPC of hazelnut oil exceeds 24% when heated for 10 min at 210ºC, indicating that hazelnut oil is not suitable for high temperature and long-time heating. The contents of linoleic acid and oleic acid in hazelnut oil varied significantly at different thermal processing temperatures (p ≤ 0.01). The change of linoleic acid was more consistent with the first-order oxidation kinetics model. Two core aldehydes were detected in hazelnut oil, aldehyde 9-oxo and aldehyde 10-oxo-8. The core aldehyde 9-oxo content changed most obviously with the heating temperature, and it was the main non-volatile aldehydes of hazelnut oil thermal oxidation. Correlation analysis showed that the heating temperature of hazelnut oil had a significant effect on the oxidation index (p ≤ 0.01), and linoleic acid had the strongest correlation with the oxidation index, which could reflect the overall oxidation of hazelnut oil. The total amount of core aldehyde and the content of core aldehyde 9-oxo strongly correlated with the oxidation index (p ≤ 0.01), which can be used as one of the indicators to evaluate the oxidation degree of hazelnut oil. This study is of great significance for promoting the application of hazelnut oil in daily cooking and processing.

Key words: hazelnut oil, thermal oxidation, core aldehydes, kinetic model

1 Introduction
As people’s living standards rise, hazelnut oil is gradually used in daily cooking. Hazelnut oil has a high content of unsaturated fatty acids. Unsaturated fatty acids react with oxygen in the air, producing a short carbon chain of aldehyde, ketone, and acid with a pungent and peculiar smell, causing the hazelnut oil quantitative change or even losing its edible value. Therefore, it is very important to study the thermal oxidation of hazelnut oil. The thermal oxidation of vegetable oils is a very complex process. Compared with self-oxidation at normal temperature, complex chemical reactions will occur, including hydrolysis and thermal oxidation1–5. The thermal oxidation reaction can lead to hydroxyl fatty acids, TAG oxide monomers, polymerization products, trans-fatty acids, sterol derivatives, and other substances6–11.

Hazelnut oil has a high content of unsaturated fatty acids, which is easy to oxidation and metamorphism under high-temperature heat treatment. Therefore, it is necessary to establish the oxidation kinetic equation of hazelnut oil. In previous studies, the kinetic models of lipid oxidation were mostly established based on the relationship between fatty acids and oxidation time12. This study, for the first time, established the kinetic models of thermal oxidation between temperature change and fatty acid composition change under different heat treatment times and obtained the thermal oxidation mechanism of hazelnut oil.

The deterioration of frying oil is commonly monitored with total polar compounds (TPC) content. Based on the regulations or laws of frying oil, the maximum value of TPC has been set at 27% in Switzerland, Australia, and China, 25% in Spain, Portugal, Italy, France, and Belgium, and 24% in Germany, respectively13. TPC can be divided into oxidation compounds, including triacylglycerol dimer, triacylglycerol oligomer, and oxidized triacylglycerol and hydrolysis compounds, including triacylglycerol hydrolysates and free fatty acids. Triacylglycerol dimer and triacylglycerol oligomer were harmless, due to their low hydrolysis rate, while the lymphatic absorption of oxidized triacylglycerol was up to 93%14. Compared with other TPC frac-
tions, oxidized triacylglycerol potentially had more negative biological effects\(^{(15)}\). The distributions of polar compounds could be significantly different even at the same TPC value, so it is necessary to measure the distribution of TPC in frying oil\(^{(16)}\).

Fatty acids are important nutritional components of vegetable oil and determine its quality. Fatty acids are important structural and functional components of cells in a biological system. However, such substances are easy to be oxidized in various ways. The oxidation stability of vegetable oil decreased with increased free fatty acid content\(^{(17)}\). During high-temperature heating, the fatty acids in vegetable oil are oxidized, and a series of chemical reactions occur. The total fatty acids in the oil decrease, and the content of unsaturated fatty acids gradually decreases, such as oleic acid, linoleic acid, and linolenic acid are destroyed, resulting in the loss of their nutritional value\(^{(18)}\).

The primary oxidation products of oils are volatile and easily oxidized to form a series of secondary oxidation products, including core aldehydes, during thermal processing\(^{(19)}\).

Core aldehydes \(\text{(GCAs)}\) are non-volatile higher aldehydes formed during lipid oxidation. As aldehydes, although there is no direct report on their toxicity, they have the same common carbonyl compounds as other aldehydes. Since the \(\alpha\)-amino group of lysine is the target group of saturated aldehydes and the thiol group of cysteine is the target group of unsaturated aldehydes in proteins, if these susceptible amino acids are involved in protein function, aldehyde modification will lead to the inactivation of the protein, thereby exerting cytotoxic effects\(^{(20)}\). Unsaturated aldehydes are more dangerous because they are more lipophilic and can destroy biofilms with the intake of oils into the body\(^{(21)}\). \(\alpha,\beta\) oxidized unsaturated aldehydes are a kind of free aldehydes produced by the degradation of hydroperoxides of unsaturated fatty acids\(^{(22)}\), which are active in nature, of which 4-hydroxy-2-trans-nonenal (HNE) is suspected to be associated with atherosclerosis, liver disease, Parkinson’s disease, Alzheimer’s disease, and Huntington’s syndrome\(^{(23)}\). It can also cause DNA and mitochondrial damage, affecting the expression of cancer-related proteins\(^{(24)}\).

Therefore, this study aims to start with the thermal oxidation of hazelnut oil, establish the kinetic model of thermal oxidation, and study the formation rule of core aldehydes, to lay a foundation for further control of hazelnut oil oxidation.

2 Materials and Methods

2.1 Materials

Hazelnut oil, was made by cold pressing.

2.2 Oil sample hot processing

To systematically study the effects of different heat treatment temperatures and thermal processing on the oxidation and nutritional quality of hazelnut oil in daily life and production practice, the temperature was set at 20°C as a control, and isothermal heating was carried out at 30°C intervals starting at 60°C. Hazelnut oil was heated at 60, 90, 120, 150, 180, and 210°C for 5 min and 10 min. This temperature range includes hot processing temperatures in daily life, and production practices, such as cold mixing, micro heat treatment, slight heating, and frying. The physical and chemical indexes of hazelnut oil after different hot processing were analyzed and determined. A total of 14 treatments were performed, with 3 replicates per treatment\(^{(25)}\).

Fifty milliliters of hazelnut oil were placed in a 250 mL beaker, heated in a water bath at the appropriate temperature and time, and the processed samples were stored at \(-20°C\).

2.3 Determination of peroxide value

Two grams of the hazelnut oil sample were weighed accurately to 0.001 g and placed in a 250 mL iodine flask. Thirty milliliters of chloroform:glacial acetic acid solution (2:3) was added to the iodine flask, and the sample was dissolved completely by shaking gently. One milliliter of saturated potassium iodide solution was added to the hazelnut oil sample, and the cover of the iodine flask was fastened. The flask was shaken gently for 0.5 min, placed in the dark for 3 min, then dissolved in 100 mL water. A standard solution of 0.01 mol/L sodium thiosulfate was immediately used to titrate the iodine precipitate. When the precipitate was titrated to light yellow, 1 mL of a starch indicator was added, and the titration was continued with strong shaking until the blue in the solution disappeared. The volume of 0.01 mol/L sodium thiosulfate solution consumed for the blank test did not exceed 0.1 mL. The peroxide value is expressed by the mass fraction of peroxide equivalent to iodine, given by the formula:

\[
X = \frac{(V - V_0) \times C}{2 \times m} \times 100
\]

where \(X\) is the peroxide value \((\text{nmol/kg})\), \(V\) is the volume of sodium thiosulfate standard solution consumed \((\text{mL})\), \(V_0\) is the volume of sodium thiosulfate standard solution consumed in the blank test \((\text{mL})\), \(C\) is the sodium thiosulfate standard solution concentration \((\text{mol/L})\), \(m\) is the sample’s mass \((\text{g})\). 0.1269 is the mass of iodine equivalent to 1.00 mL of standard titration solution of sodium thiosulfate, and 100 is the conversion factor.

2.4 Determination of \(p\)-anisidine value

The appropriate amount of oil sample \((0.2 \text{ g - 3 g})\) was accurately weighed and placed in a 25 mL bottle. Hazelnut oil was dissolved with isooctane, and the final volume was...
fixed accordingly. The absorbance range was 0.2 - 0.8 within the measurement range of the spectrophotometer. The dosage is large in the early oxidation stage and gradually decreases in the later stage.

Five milliliters of sample solution were removed from the plugged test tube, 1 mL of p-Anisidine reagent was added, the plug was replaced, and the solution fully mixed. The solution was reacted in the dark for 8 min, the mixed solution was immediately transferred to the spectrophotometer colorimetric dish, and the absorbance at 350 nm was measured as $A_1$.

Five milliliters of sample solution were removed from the plugged test tube, 1 mL glacial acetic acid was added to the remaining solution, the plug was replaced, and the solution was fully mixed. The solution was reacted in the dark for 8 min, the mixed solution was immediately transferred to the spectrophotometer colorimetric dish, and the absorbance at 350 nm was measured as $A_2$.

Five milliliters of isooctane were removed from the plugged test tube, 1 mL p-anisidine reagent was added to the remaining solution, the plug was replaced, and the solution was fully mixed. The solution was reacted in the dark for 8 min, the mixed solution was immediately transferred to the spectrophotometer colorimetric dish, and the absorbance at 350 nm was measured as $A_3$.

If the Blank sample exceeds 0.2, the p-anisidine reaction was reprocessed. The p-anisidine value was calculated by the formula:

$$p-\text{AnV} = \frac{1000QV}{m} \times (A_1 - A_2 - A_3) \times 1.2$$

where $p$-AnV is the p-anisidine value of the sample (no unit), $Q$ is the sample concentration of the test solution (g/mL), $V$ is the volume of the dissolved sample (mL), $m$ is the mass of the sample (g), $A_1$ is the absorption value of the reacted solution, $A_2$ is absorption value of the unreacted solution, $A_3$ is absorption value of the blank solution, 1.2 is the correction factor for diluting the solution with 1 mL of p-anisidine reagent or glacial acetic acid solution.

2.5 Calculation of total oxidation value (TOTOX)

TOTOX was calculated according to the formula:

$$\text{TOTOX} = 2 \text{POV} + p-\text{AnV}$$

where TOTOX is the total oxidation value of the sample (no unit), POV is the peroxide value of the sample (g/100 g), and $p$-AnV is the p-AnV of the sample (no unit).

2.6 Determination of total polar component (TPC)

Twenty-five grams of silica gel 60 were weighted and dissolved in 80 mL of non-polar eluent (petroleum ether: diethyl ether = 87:13), and stirred to make silica gel suspended. Immediately the suspension was poured into a vertically placed glass chromatography column (inner diameter 21 mm, length 450 mm) through a funnel. The beaker was washed with an appropriate amount of non-polar eluent so that all silica gel was transferred into the glass chromatography column. The valve was open to release the eluent until the level of the eluent in the column was 10 mm higher than the top of the silica gel. Then, the valve was closed, and 4 g of sea sand was added into the glass chromatography column through a funnel. The valve was open again, and the eluent in the column was released until the eluent level was less than 10 mm below the top of the sea sand sedimentation layer.

The oil sample was accurately weighted from 2.4 g to 2.6 g (accurate to 0.001 g) using a 50 mL glass beaker. Twenty milliliters of non-polar eluent were added to the weighed sample to dissolve the sample completely. The sample was diluted to a 50 mL final volume with a non-polar eluent.

A clean 250 mL flask was baked in a constant temperature drying oven at 103°C ± 2°C for 1 h, allowed to cool in a dryer to room temperature, then weighed ($m_0$, accurate to 0.001 g). The flask was then placed at the eluent outlet directly below the glass chromatography column to collect the eluent. Twenty milliliters of sample solution were removed and slowly added to the glass chromatography column. Open the valve at the lower end of the glass chromatography column and release the eluent until the level descends to the top of the sea sand layer. A total of 200 mL of non-polar eluent was added to the glass chromatography column 2-3 times. The eluent was collected in a single flask, and the valve was adjusted to make the 200 mL eluent pass through the glass chromatography column in 80-90 min. At the end of elution, the non-polar eluent was drawn from the dropper to wash the substance attached to the solvent outlet at the lower end of the glass chromatography column, and the eluent was incorporated into the same flask.

The flask was placed in a rotary evaporator with a water bath temperature of 60°C. Under normal pressure, most of the solvent evaporated, and under negative pressure, the remaining solvent was evaporated by rotation until nearly dry. Then the flask was removed, and the water on the outer wall of the flask was dried. The flask was placed into a vacuum constant temperature drying oven at 40°C and baked for 20-30 min under negative pressure of 0.1 Mpa. Afterward, the flask was placed in a glass dryer, allowed to cool to room temperature, and then weighed ($m_1$, accurate to 0.001 g).

The content of polar components in oil samples is calculated according to the following formula:

$$X = 100 - \frac{m_1 - m_0}{m} \times 100$$

where $X$ is the content of polar components of the oil sample, %; $m_0$ is the Blank sample, the mass of 250 mL in g, $m_1$ is the total mass (g) of the 250 mL flask and non-polar components after drying the solvent, $m$ is the mass of the
the rate equation of the reaction follows:

\[ k_0 t = \frac{kT}{e^{Ea/RT}} \]

where, \( k \) is the reaction rate constant at temperature \( T \), \( R \) is the molar gas constant /J/K/mol; \( T \) is the absolute temperature in K, \( k_0 \) is the Arrhenius constant, and \( Ea \) is the activation energy of oxidation reaction divided by J/mol. 

The Arrhenius equation was used to describe the relationship between oil oxidation rate and temperature:

\[ \ln k = \ln k_0 - \frac{Ea}{RT} \]

where, \( k \) is the reaction rate constant at temperature \( T \), \( R \) is the molar gas constant /J/K/mol; \( T \) is the absolute temperature in K, \( k_0 \) is the Arrhenius constant, and \( Ea \) is the activation energy of oxidation reaction divided by J/mol.

Suppose the oxidation of fatty acids with time follows the zero-order reaction kinetics. In that case, the change of fatty acid content is independent of its initial content, and the rate equation of the reaction follows:

\[ -\frac{df}{dt} = k_0t \]

and after integration:

\[ f_0 - f_t = k_0t \]

If the oxidation of fatty acids with time follows the first-order reaction kinetics, the rate equation of the reaction follows:

\[ -\frac{df}{dt} = k_0F \]

and after integration:

\[ \ln (F_t) = -kt + \ln (F_0) \]

If the oxidation of fatty acids with time follows the second-order reaction kinetics, the reaction rate equation follows:

\[ -\frac{df}{dt} = k_0F^2 \]

and after integration:

\[ \frac{1}{F_t} - \frac{1}{F_0} = kT \]

Combined with the kinetic model and Arrhenius formula, the kinetic model of storage temperature and fatty acid content changing with storage time was established (Table 1).

### Table 1 Kinetic equation of grease oxidation.

<table>
<thead>
<tr>
<th>Order</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>( F_0 - F_t = \frac{k_0t}{e^{Ea/RT}} )</td>
</tr>
<tr>
<td>First</td>
<td>( \ln (F_t) = -\frac{k_0t}{e^{Ea/RT}} + \ln (F_0) )</td>
</tr>
<tr>
<td>Second</td>
<td>( \frac{1}{F_t} - \frac{1}{F_0} = \frac{k_0t}{e^{Ea/RT}} )</td>
</tr>
</tbody>
</table>

2.7 Fatty acid composition

For fatty acid methyl esterification, 50 mg of fat was weighed and placed in a 10 mL volumetric flask. Two milliliters of petroleum ether and benzene mixed solvent (V/V = 1:1) were added and gently shaken to dissolve it. Then 2 mL 0.4 mol/L potassium hydroxide-methanol solution was added, mixed well, and allowed to stand at room temperature for 1 h. Then, distilled water was added to make all organic methanol solution rise to the upper part of the bottleneck, and the supernatant was absorbed for testing after clarification.

An HP-FFAP (30 m \( \times \) 0.250 mm \( \times \) 0.25 \( \mu \text{m} \)) elastic quartz capillary column was used for gas chromatography. The heating procedure consisted of an initial temperature of 50\( ^\circ \text{C} \), then rising to 250\( ^\circ \text{C} \) at 10\( ^\circ \text{C} \)/min for 5 min, the vaporization temperature was 260\( ^\circ \text{C} \), The carrier gas was helium at a 0.4 MPa pressure, and an injection volume of 1 \( \mu \text{L} \). The area normalization method was used for quantitative analysis. Each component’s relative contents were obtained, and the contents of total unsaturated fatty acids, monounsaturated fatty acids, and polyunsaturated fatty acids were calculated.

2.8 Kinetic equation of thermal oxidation of hazelnut oil

The Arrhenius equation was used to describe the relationship between oil oxidation rate and temperature:

\[ \ln k = \ln k_0 - \frac{Ea}{RT} \]

The contents of total unsaturated fatty acids, monounsaturated fatty acids, and polyunsaturated fatty acids were calculated.

2.9 Determination of core aldehyde

Three hundred milligrams of the sample were weighed into a 50 mL capping centrifuge tube, and 100 \( \mu \text{L} \) internal standard solution (1 mg/mL), 3 mL tert-butylmethyl ether, and 2 mL sodium methoxide solution (0.2 M) were added. The centrifuge tube was closed and oscillated on the vortex oscillator for 1 min, then stood at room temperature (25\( ^\circ \text{C} \)) for 2 min. Then 0.1 mL sulfuric acid-methanol solution (0.5 M) was added to neutralize the base generated in the system, and vortexed for 5 s. Then 3 mL ultrapure water was added, and the vortex oscillated for 10 s at a speed of 3500 r/min, centrifuged for 5 min. The upper organic layer was transferred into a 5 mL pressure-capped centrifugal tube, and the volatile solvent was used with a nitrogen blower (45\( ^\circ \text{C} \)) for separation. After the solvent was volatilized, it was redissolved in 1 mL HPLC grade \( n \)-hexane, anhydrous sodium sulfate was added, and vortex oscillated for 2 s. The sample solution was absorbed with a 1 mL disposable syringe, through 0.22 \( \mu \text{m} \) organic filter membrane, injected into 2 mL brown sample bottle to prepare it for testing.

GC conditions: the heating procedure is: the initial temperature was 90\( ^\circ \text{C} \) for 2 min, the temperature was raised to 240\( ^\circ \text{C} \) at 6\( ^\circ \text{C} \)/min, and the temperature was maintained for
10 min. The temperature of the detector and injector was 250°C. The injection volume was 1.0 μL. The split injection had a split ratio of 1:40. The carrier gas was high purity He. The flow rate was 1.2 mL/min. The MS conditions were 250°C transmission line temperature, the ion source temperature was 200°C, the ionization mode was electron spray ionization (ESI), and the electron bombardment energy was 70 eV. The scanning range m/z is 40-240, the scanning speed is 0.2 scan/s, and the scanning mode was full scan. The chromatographic peaks of each target component were automatically integrated, and their contents were calculated by the internal standard method. The quantitative formula is as follows:

\[ m_i = \frac{A_i}{A_{is}} \times \frac{f_i}{\alpha} \times \delta \]

where \( m_i \) is the GCAs content (mg), \( A_i \) is the methyl aldehyde esters (core methyl aldehyde esters peak area), \( A_{is} \) is the peak area of the internal reference material, \( m_i \) is the mass of the internal standard added to the sample (0.1 mg), \( f_i \) is the relative correction factor of 1, \( \alpha \) is the conversion factor of methyl aldehyde ester into GCAs content, \( \alpha (9\text{-}oxo) = 4.16 \) and \( \alpha (10\text{-}oxo\text{-}8) = 3.96 \).

2.10 Data collation and analysis

Excel 2016 was used for data collation, Origin2021 Pro was used for graphs, and SPSS 23 was used for one-way ANOVA and Pearson correlation analysis of data. Each group of tests was repeated three times and parallel three times.

3 Results

3.1 Effects of different thermal processing conditions on oxidation index of hazelnut oil

The changes in the samples’ peroxide values were measured after heating the hazelnut oil at different temperatures for 5 and 10 min (Fig. 1). A significant decrease in the peroxide values occurred at 180°C mainly due to the instability of the oil’s primary hydrogen peroxide oxidation products. From 20°C to 150°C, the peroxide value did not increase significantly. At 180°C, the peroxide value is significantly reduced. This indicates that 180°C is the mark for hazelnut oil to enter the secondary oxidation stage. When heated for 5 min at 210°C, the peroxide value continued to decrease. In comparison, when heated for 10 min, the peroxide value increased, indicating that with the extension of heating time, the thermal oxidation rate of hazelnut oil also increased.

The p-AnV is usually used to evaluate the content of secondary oxidation products such as aldehydes and ketones. As shown in Fig. 2, when the temperature was lower than 60°C after heating for 5 min, the p-AnV of hazelnut oil did not change significantly. However, increased slightly from 90°C to 120°C, and the most significant increase was from 150°C to 180°C, and then tended to be gentle after 180°C. When heated for 10 min, p-AnV began to rise starting at 90°C, with the largest increase at 150°C to 180°C, indicating that with the increase in heating temperature, the increasing rate of p-AnV increased at first and then decreased. The main generation stage of aldehydes and ketones is 180°C.

TOTOX is commonly used to assess lipids’ overall oxidation degree and combines primary oxidation products (hydroperoxides) with secondary oxidation products (aldehydes). As shown in Fig. 3, the total peroxide value showed a gradual upward trend, consistent with the p-AnV.
indicating that with the increase in temperature and the heating time extension, the hazelnut oil's overall oxidation degree showed a gradual upward trend, which mainly depended on the p-AnV.

The TPC is one of the most reliable indexes to evaluate heating oil quality. Changes in TPC at different temperatures were measured (Fig. 4). With the increase in heating temperature, the TPC of hazelnut oil shows a gradual rise trend, indicating that heating temperature significantly affected TPC. According to the standards of various countries, the average TPC in edible oil should not exceed 24-30; however, when heating hazelnut oil at 210°C for 10 min, the TPC exceeds 24, so hazelnut oil is not suitable for high temperature, long time heating.

3.2 Fat acid composition

As shown in Table 2, hazelnut oil is mainly composed of five fatty acids, palmitic acid, palmitoleic acid, stearic acid, oleic acid, and linoleic acid. Among them, palmitic acid and stearic acid are saturated fatty acids, while palmitoleic acid, oleic acid, and linoleic acid are unsaturated fatty acids. During the thermal processing of hazelnut oil, the palmitic acid, palmitoleic acid, and stearic acid contents did not change significantly. However, the oleic acid content was always upward, while the linoleic acid content showed a downward trend.

3.3 Establishment of oxidation kinetic equation

Arrhenius curves corresponding to heating for 5 and 10 min were established with reciprocal temperature (1/T) as the abscissa and logarithmic value (lnk) of reaction rate constant k as the ordinate. The results are shown in Fig. 5. According to the intercept and slope of the Arrhenius curve in Fig. 5, k₀ and Ea in Table 1 can be calculated to...

### Table 2 Composition and changes of fatty acids (%).

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Molecular formula</th>
<th>Heating time/min</th>
<th>20°C</th>
<th>60°C</th>
<th>90°C</th>
<th>120°C</th>
<th>150°C</th>
<th>180°C</th>
<th>210°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic acid</td>
<td>C16:0</td>
<td>5</td>
<td>4.93 ± 0.11a</td>
<td>5.15 ± 0.18a</td>
<td>5.04 ± 0.12a</td>
<td>5.10 ± 0.06a</td>
<td>5.06 ± 0.29a</td>
<td>4.99 ± 0.11a</td>
<td>5.31 ± 0.06a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>4.93 ± 0.11a</td>
<td>5.15 ± 0.18a</td>
<td>5.10 ± 0.15a</td>
<td>5.14 ± 0.16a</td>
<td>5.17 ± 0.15a</td>
<td>5.02 ± 0.20a</td>
<td>5.21 ± 0.06a</td>
</tr>
<tr>
<td>Palmitoleic acid</td>
<td>C16:1</td>
<td>5</td>
<td>0.18 ± 0.06a</td>
<td>0.15 ± 0.10a</td>
<td>0.19 ± 0.08a</td>
<td>0.15 ± 0.08a</td>
<td>0.19 ± 0.06a</td>
<td>0.16 ± 0.06a</td>
<td>0.17 ± 0.08a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>0.18 ± 0.06a</td>
<td>0.16 ± 0.04a</td>
<td>0.18 ± 0.08a</td>
<td>0.17 ± 0.08a</td>
<td>0.17 ± 0.08a</td>
<td>0.16 ± 0.07a</td>
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<tr>
<td>Stearic acid</td>
<td>C18:0</td>
<td>5</td>
<td>1.96 ± 0.10a</td>
<td>1.86 ± 0.08a</td>
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<td>1.93 ± 0.08a</td>
<td>1.89 ± 0.11a</td>
<td>1.94 ± 0.07a</td>
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<td></td>
<td></td>
<td>10</td>
<td>1.96 ± 0.10a</td>
<td>1.90 ± 0.06a</td>
<td>1.98 ± 0.10a</td>
<td>1.95 ± 0.02a</td>
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<td>1.97 ± 0.04a</td>
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<tr>
<td>Oleic acid</td>
<td>C18:1</td>
<td>5</td>
<td>81.08 ± 0.06d</td>
<td>81.09 ± 0.09d</td>
<td>81.55 ± 0.06cd</td>
<td>81.61 ± 0.05cd</td>
<td>81.69 ± 0.08c</td>
<td>81.75 ± 0.08b</td>
<td>81.88 ± 0.09a</td>
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<tr>
<td></td>
<td></td>
<td>10</td>
<td>81.08 ± 0.06e</td>
<td>81.13 ± 0.06de</td>
<td>81.63 ± 0.06de</td>
<td>81.70 ± 0.09d</td>
<td>81.82 ± 0.10c</td>
<td>81.86 ± 0.06b</td>
<td>81.92 ± 0.05a</td>
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<tr>
<td>Linoleic acid</td>
<td>C18:2</td>
<td>5</td>
<td>7.42 ± 0.02a</td>
<td>7.34 ± 0.01b</td>
<td>7.29 ± 0.02c</td>
<td>7.28 ± 0.02c</td>
<td>7.26 ± 0.02d</td>
<td>7.24 ± 0.03de</td>
<td>7.23 ± 0.02de</td>
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<tr>
<td></td>
<td></td>
<td>10</td>
<td>7.42 ± 0.02a</td>
<td>7.33 ± 0.02b</td>
<td>7.26 ± 0.03c</td>
<td>7.20 ± 0.02d</td>
<td>7.16 ± 0.04e</td>
<td>7.13 ± 0.06f</td>
<td>7.10 ± 0.05f</td>
</tr>
</tbody>
</table>

Data are presented as mean ± SD (n = 10). Mean values with different superscript letters are statistically different (p ≤ 0.05) among the groups. a-f Values with different superscripts in the same row are significantly different (p ≤ 0.05).
Fig. 5  Heat for 5 and 10 minutes corresponding to the Arrhenius curve.

Table 3  Equation, rate constant and correlation coefficient $R^2$.

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Heating time/min</th>
<th>Equation</th>
<th>$k$</th>
<th>$R^2$</th>
</tr>
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<tr>
<td>Linoleic acid</td>
<td>5</td>
<td>$7.42 - F_t = \frac{0.0172}{e^{14.718/T}}$</td>
<td>0.0239</td>
<td>0.973</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\ln(F_t) = -\frac{0.0172}{14.718} + 2.0042$</td>
<td>0.1757</td>
<td>0.988</td>
</tr>
<tr>
<td></td>
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<td>$\frac{1}{F_t} - 0.1348 = \frac{0.0172}{e^{14.718/T}}$</td>
<td>1.0663</td>
<td>0.972</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>$7.42 - F_t = \frac{0.0324}{e^{16.430/T}}$</td>
<td>0.0228</td>
<td>0.976</td>
</tr>
<tr>
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<td>$\ln(F_t) = -\frac{0.0324}{16.430} + 2.0042$</td>
<td>0.1665</td>
<td>0.981</td>
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<tr>
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<td></td>
<td>$\frac{1}{F_t} - 0.1348 = \frac{0.0324}{e^{16.430/T}}$</td>
<td>0.8483</td>
<td>0.963</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>5</td>
<td>$81.08 - F_t = \frac{0.0172}{e^{14.718/T}}$</td>
<td>-0.0035</td>
<td>0.957</td>
</tr>
<tr>
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<td></td>
<td>$\ln(F_t) = -\frac{0.0172}{14.718} + 4.3991$</td>
<td>-0.2771</td>
<td>0.957</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\frac{1}{F_t} - 0.0123 = \frac{0.0172}{e^{14.718/T}}$</td>
<td>-4.7499</td>
<td>0.961</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>$81.08 - F_t = \frac{0.0324}{e^{16.430/T}}$</td>
<td>-0.0068</td>
<td>0.961</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\ln(F_t) = -\frac{0.0324}{16.430} + 4.3991$</td>
<td>-0.5354</td>
<td>0.961</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\frac{1}{F_t} - 0.0123 = \frac{0.0324}{e^{16.430/T}}$</td>
<td>-4.3577</td>
<td>0.972</td>
</tr>
<tr>
<td>Palmitoleic acid</td>
<td>5</td>
<td>$0.18 - F_t = \frac{0.0172}{e^{14.718/T}}$</td>
<td>-0.0138</td>
<td>0.069</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\ln(F_t) = -\frac{0.0172}{14.718} - 1.7148$</td>
<td>-0.0025</td>
<td>0.070</td>
</tr>
</tbody>
</table>
obtain the fitting equation in Table 3.

Table 3 shows that among the main fatty acid compositions of hazelnut oil, only the reaction rate constant $k$ value of linoleic acid increases gradually with the heating time, from 63.162 to 67.671, indicating that the oxidation rate of oil is closely related to the heating time, and the longer the heating time, the faster the oxidation rate. The $R^2$ between the linoleic acid content and the first-order kinetic equation was the largest, which was 0.988 and 0.981, regardless of the heating time, indicating that the change of linoleic acid could best reflect the thermal oxidation law of hazelnut oil, and was following the first-order

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Heating time/min</th>
<th>Equation</th>
<th>$k$</th>
<th>$R^2$</th>
</tr>
</thead>
</table>
| Palmitic acid | 5
| $1/F_t - 5.5556 = \frac{0.0172}{e^{14.738}}$ | $0.0529$ | 0.078 |
| $\ln(F_t) = -\frac{0.0324}{e^{16.430}} - 1.7148$ | $-0.0050$ | 0.069 |
| $1/F_t - 0.2028 = \frac{0.0172}{e^{14.738}}$ | $0.0132$ | 0.005 |
| $\ln(F_t) = -\frac{0.0324}{e^{16.430}} + 1.5953$ | $0.0020$ | 0.006 |
| $1/F_t - 0.2028 = \frac{0.0172}{e^{14.738}}$ | $0.0006$ | 0.006 |
| $\ln(F_t) = -\frac{0.0324}{e^{16.430}} + 1.5953$ | $0.0022$ | 0.001 |
| Stearic acid | 5
| $1/F_t - 5.5556 = \frac{0.0172}{e^{14.738}}$ | $-0.0094$ | 0.260 |
| $\ln(F_t) = -\frac{0.0324}{e^{16.430}} + 0.6730$ | $-0.0181$ | 0.260 |
| $1/F_t - 0.5102 = \frac{0.0172}{e^{14.738}}$ | $-0.0341$ | 0.261 |
| $\ln(F_t) = -\frac{0.0324}{e^{16.430}} + 0.6730$ | $-0.0184$ | 0.052 |
| $1/F_t - 0.5102 = \frac{0.0324}{e^{16.430}}$ | $-0.0095$ | 0.052 |
Analysis of Thermal Oxidation Constituents of Hazelnut Oil

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3.4 Changes in core aldehyde content

The aldehydes produced during heating can be divided into volatile and non-volatile aldehydes. Most studies focus on volatile aldehydes, and the non-volatile aldehydes are rarely reported and often ignored. However, non-volatile aldehydes will remain in the heating oil and can be absorbed by food, which will harm human health.

Two kinds of GCAs were detected in hazelnut oil, 9-oxo and 10-oxo-8, as shown in Fig. 6. The species and variation trend correspond to the existing research results. Under heating conditions for 5 and 10 min, the types and quantities of GCAs generated were similar. Hazelnut oil 10-oxo-8 accounted for the highest proportion, about 80%, and the rest were mainly 9-oxo. The 9-oxo content increased significantly with the increase in temperature (Fig. 7), while the core aldehyde 10-oxo-8 had little effect with the increase in temperature (Fig. 8). The main core aldehyde in hazelnut oil at normal temperature is 10-oxo-8, and 9-oxo is gradually produced with the increase of heating temperature.

3.5 Correlation between oxidation index of hazelnut oil and heating temperature

As shown in Table 4, the total amount of fatty acids (C18:1, C18:2), TOTOX, TPC, 9-oxo, 10-oxo-8, and GCAs of all samples showed a significant linear correlation with heating temperature when $p \leq 0.01$, and p-AnV showed a significant linear correlation with heating temperature when $p \leq 0.05$. POV value did not correlate in this study because hydroperoxide, the primary oxidation product of lipids, was unstable and easy to decompose under heating conditions. The results show that the heating temperature directly affects the thermal stability of hazelnut oil.

3.6 Correlation between fatty acid and oxidation index of hazelnut oil

Pearson correlation coefficient was obtained by bivariate correlation analysis between fatty acid and POV, p-AnV,
the correlation intensity is divided into very strong correlation, strong correlation, moderate correlation, and only weak or no correlation existed. Linoleic acid (C18:2) shows a strong correlation with TOTOX and TPC, with correlation coefficients of 0.931 and 0.864, both at the 0.01 level. Moreover, p-AnV established a strong correlation with a correlation coefficient of 0.796. The correlation coefficients between oleic acid (C18:1) and TOTOX and TPC were 0.863 and 0.831, respectively, at the 0.01 level. The correlation coefficient between p-AnV was 0.745. However, the correlation coefficient of oleic acid was lower than that of linoleic acid, so the content of linoleic acid was the best evaluation of the oxidation degree of hazelnut oil.

3.7 Correlation between GCAs and oxidation index of hazelnut oil

As shown in Table 6, Pearson correlation coefficients between total GCAs and POV, p-AnV, TOTOX, and TPC were 0.530, 0.956, 0.879, and 0.935, respectively, and were significantly strongly correlated at the 0.01 level except for peroxide value which correlated at the 0.05 level. The correlation coefficients between GCAs (9-oxo) content and P-AnV, TOTOX, and TPC were 0.625, 0.954, 0.867, and 0.933, respectively, showing a significantly strong correlation at 0.01 level except for peroxide value which correlated at the 0.05 level. The correlation between GCAs (10-oxo-8) content and four oxidation indexes were weak. POV mainly represents hydroperoxides in oils, while TPC can comprehensively reflect oxidation, hydrolysis, cracking, and polymerization. The correlation between the GCAs contents and the oil deterioration index was different. In conclusion, GCAs strongly correlate with pyrolysis and oxidation reactions and can be used as an indicator for evaluating lipid oxidation.

3.8 Formation mechanism of GCAs

The formation mechanism of GCAs is shown in Fig. 9. Unsaturated fatty acids on triglyceride molecules undergo free radical chain reactions to generate hydroperoxides. Under certain conditions, the O-O bond of hydroperoxides splits to generate alkoxy and hydroxyl free radicals. The C-C bonds on both sides of the alkoxy free radicals are broken by β-shearing. The alkoxy free radical fragments generated by pathway A break away from the glycerol framework and form free aliphatic aldehydes with different carbon chain lengths (mainly volatile small molecule aldehydes) in subsequent oxidative cracking. However, the β-shearing of the B pathway keeps the alkoxy radicals on the glycerol framework, and these fragments form the core aldehydes in subsequent free radical reactions.

At present, the research on thermal oxidation of oil is mainly explained according to the heating time. In this study, according to the characteristics of high saturated fatty acids of hazelnut oil, the influence of temperature on the thermal oxidation law of hazelnut oil was mainly studied. However, the heating time was not deeply dis-
Analysis of Thermal Oxidation Constituents of Hazelnut Oil

4 Conclusion

This study established the kinetic equation of thermal oxidation of hazelnut oil, and determined the changes in peroxide value, anisidine value, total peroxide value, polar compounds, fatty acids, and core aldehydes contents in the thermal oxidation. It is concluded that the first-order kinetic equation of linoleic acid better reflects the thermal oxidation law of hazelnut oil, and the mass of the GCAs (9-oxo) increases significantly with the heating temperature, indicating that 9-oxo is the main core aldehyde product of hazelnut oil. The correlation analysis showed that the thermal oxidation degree of hazelnut oil depended directly on the heating temperature, and linoleic acid content and GCAs (9-oxo) could be used as one of the indexes to evaluate the overall degree of oxidation of hazelnut oil. In addition, the polar component determination results show that hazelnut is unsuitable for high-temperature, long-term heat treatment. This study is of great significance for promoting the application of hazelnut oil in daily cooking. It plays a theoretical role in hazelnut oil’s fine processing and oxidation metamorphosis. We hope this study can expand the research scope of hazelnut oil in the field of food processing and increase the richness of edible methods of hazelnut oil.

Acknowledgements

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Table 6  Pearson correlation analysis of fatty acid with POV, p-AnV, TOTOX and TPC in heated oil samples.

<table>
<thead>
<tr>
<th></th>
<th>GCAs (9-oxo)</th>
<th>GCAs (10-oxo-8)</th>
<th>GCAs (sum)</th>
<th>POV</th>
<th>p-AnV</th>
<th>TOTOX</th>
<th>TPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCAs (9-oxo)</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GCAs (10-oxo-8)</td>
<td>0.944**</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GCAs (sum)</td>
<td>0.982**</td>
<td>0.002</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>POV</td>
<td>0.625*</td>
<td>0.288</td>
<td>0.530*</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-AnV</td>
<td>0.954**</td>
<td>0.023</td>
<td>0.956**</td>
<td>0.566*</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOTOX</td>
<td>0.867**</td>
<td>0.002</td>
<td>0.879**</td>
<td>0.275</td>
<td>0.913**</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>TPC</td>
<td>0.933**</td>
<td>0.010</td>
<td>0.935**</td>
<td>0.435*</td>
<td>0.959*</td>
<td>0.941**</td>
<td>1</td>
</tr>
</tbody>
</table>

**p ≤ 0.01, *p ≤ 0.05

Fig. 9  Formation mechanism of GCAs.
References

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