Effect of Storage Condition on Oil Oxidation of Flat-European Hybrid Hazelnut

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Abstract: In order to study the oxidative stability of hazelnut oil stored at room temperature, hazelnut oil accelerated oxidized at 62°C was used to determine peroxide value (POV), p-anisidine value (p-AV), total oxidation value (TOTOX), the content of fatty acids and volatile oxidative products. The correlation between the content of fatty acids or volatile oxidative products and three peroxidation indexes was analyzed. The results showed that the relative content of linoleic acid in hazelnut oil decreased significantly at the duration of accelerated oxidation (p < 0.05), which was in line with the zero-order oxidation kinetics model. The absolute content of four fatty acids all accorded with the zero-order oxidation kinetics model. Both relative and absolute content of linoleic acid can set up a slightly negative linear correlation with POV, p-AV and TOTOX, respectively (p < 0.05). The oxidation of unsaturated fatty acids in hazelnut oil produced a variety of volatile oxidation products, among which hexanal, 2-octenal, 2-decenal and 3-octene-2-one could establish a significantly positive correlation with POV, p-AV and TOTOX at a certain period of time, which could be used as a new index to evaluate the oxidative decomposition of unsaturated fatty acids in hazelnut oil during storage.

Key words: hazelnut oil, volatile oxides, storage, linoleic acid

1 Introduction

Hazelnut is distributed in 20 regions in China, particularly prolific in Liaoning Province. Due to cold ambience, flat-European hybrid hazelnut, a kind of hybrid hazelnut with Corylus heterophylla as female hazel, Corylus avellana as male parent, was chosen to plant in Liaoning Province. One of its most popular products is hazelnut oil. Hazelnut oil is rich in unsaturated fatty acid, mineral, phytosterol, tocopherol, etc. It can lower blood lipids, soften blood vessels, and prevent or reduce the incidence of cardiovascular and cerebrovascular diseases. However, the researches on hazelnut oil mainly focus on the optimization of the extraction process of it, the influence of different processing technologies to variety of fatty acids and on identification of adulteration, which hazelnut oil was added into olive oil because of lower price and wide planting areas in some countries like American and Turkey, etc.

Lipid oxidation has been known as a reaction, which is caused by the action of light, air and lipoxygenase, leading to unpleasant smell and bitter taste. It has been recognized as the major problem affecting edible oils, as it is the cause of important deteriorative changes in their chemical, sensory, and nutritional properties. As lipids oxidize, they may form hydroperoxides, which are susceptible to further oxidation or decomposition into secondary reaction products such as aldehydes, ketones, acids, and alcohols. All these products directly affect the quality of oils, and many of them are the major cause of off-flavor formation and changes in taste. These products are particularly relevant in oxidative-stress related diseases such as liver damage, intestinal tumors, atherosclerosis and cancers. Research into the problems of oxidative deterioration has been pursued for many years but it has been boosted by the recognition that such oxidations can cause damage to cell membranes and DNA, and may be involved in the aging process.

Abbreviations: POV or PV, peroxide value, p-AV, p-anisidine, TOTOX, total oxidation value, GC-MS, GasChromatography-MassSpectrometer, SFA, saturated fatty acids, MUFA, monounsaturated fatty acids, PUFA, polyunsaturated fatty acids.
process\textsuperscript{9}, hypertension\textsuperscript{10} and cancer growth\textsuperscript{11}.

The hazelnut oil composition is dominated by unsaturated fatty acids (oleic and linoleic), which amounts to >90\% of the total fatty acids present\textsuperscript{12, 13}, thus making hazelnut highly vulnerable to spoilage driven lipid oxidation\textsuperscript{14}. While the crude hazelnut oils are generally sold in the domestic vegetable oil industry, the price is quite higher compared to other ordinary edible oils such as soybean, canola, sunflower and corn oils\textsuperscript{15}. Therefore, it is necessary to study oxidation of hazelnut oil. At present, the oxidation of hazelnut oil is concentrated on the evaluation of the oxidative stability of hazelnut oil. The researchers used the rancimat test to evaluate the oxidative stability of hazelnut oil and compared the hazelnut oil with other oils\textsuperscript{16, 17}. For the first time, Zytkiewicz \textit{et al.} used PDSC (pressure differential scanning calorimetry) to evaluate the oxidative stability of hazelnut oil. Statistically significant linear correlations between PDSC and the rancimat values imply that PDSC can be recommended as an appropriate objective method for assessing the oxidative stability of hazelnut oil\textsuperscript{18}. The oxidation of hazelnut oil is actually the oxidation of fatty acids in hazelnut oil. Therefore, it is necessary to study the changes of fatty acids in the oxidation process of hazelnut oil and its products. There were studies about the changes of fatty acid content in extracted oil during storage of hazelnuts\textsuperscript{19}. However, the changes in fatty acids in the oxidation process of hazelnut oil and their products are rarely reported.

This paper covers determination of PV, p-AV, fatty acids and volatile oxidation products of hazelnut oil during the storage of 62\°C for 30 days to analyze the oxidation kinetics of lipid components in hazelnut oil simulating storage at room temperature. The correlation between the content of fatty acids or volatile oxidative products and three peroxide index values was analyzed to provide a novel method to evaluate the extent of hazelnut oil oxidation.

2 Materials and Methods

Liao Hazel NO.7 is a kind of hybrid hazelnut with \textit{Corylus heterophylla} as female hazel, \textit{Corylus avellana} as male parent. The hazelnuts were collected from trees cultivated in a single orchard, located in Huanren Manchu Autonomous County (40°94′34.52″N, 125°53′29.17″E, altitude 100 m) in Benxi, Liaoning province of China during the collection season in 2016. After harvesting by hand, the fresh hazelnuts were dried naturally under the sun on the ground and separated from hushes. Hazelnuts were kept in a dark refrigerator (−4\°C, 50-60\% RH) until extraction. Before extraction, the hazelnuts shells and skins were removed.

2.1 Raw material pretreatment

Hazel nut powder was obtained with a slight modification by Kim \textit{et al.}\textsuperscript{20}. In brief, the hazelnuts were removed the shells, blanched at 70\°C to remove the skins, and crushed with high-speed multifunctional crusher.

2.2 Extraction of hazelnut oil

Hazel nut oil was obtained by mixing hazelnut powder with N-hexane at a ratio of 1:6 g/mL (W/V), ultrasonic-assisted extraction at 35\°C for 40 min at a frequency ultrasonic power of 500W, and rotary evaporation at 40\°C to remove organic solvents\textsuperscript{21}.

2.3 Accelerated oxidation of oil sample

Hazel nut oil was placed in a colorless transparent glass bottle with a cap slightly capped. It was heated and oxidized for 30 days in a high-temperature test chamber at 62\°C. The hazelnut oil was shaken every 12 hours and its position in the incubator was changed randomly. The oxidized oil sample was taken out every 5 days partly\textsuperscript{22}.

2.4 Determination of peroxide value

2 g hazelnut oil sample was weighed (accurately to 0.001 g) and placed in a 250 mL iodine flask. 30 mL chloroform-glacial acetic acid mixed solution (2:3) was added into the iodine flask and dissolved the sample completely by shaking gently. 1.00 mL saturated potassium iodide solution was accurately added and the cover of iodine flask was fasten. The flask was shaken gently for 0.5 min, placed in a dark place for 3 min, taken out and added 100 mL water, then shook well. 0.01 mol/L sodium thiosulfate standard solution was used immediately to titrate the iodine precipitated. When titrated to light yellow, add 1 mL starch indicator, continue titrating and shake strongly until blue in the solution disappeared. At the same time, blank test was carried out. The volume of 0.01 mol·L\textsuperscript{-1} sodium thiosulfate solution consumed in blank test should not exceed 0.1 mL. The peroxide value is expressed by the mass fraction of peroxide equivalent to iodine. By formula:

\[
X = \frac{(V - V_0) \times c \times 0.1269}{m} \times 100
\]

Where X is peroxide value (g/100 g), V is volume of sodium thiosulfate standard solution consumed (mL), V\textsubscript{0} is volume of sodium thiosulfate standard solution consumed in blank test (mL); C is the concentration of sodium thiosulfate standard solution (mol·L\textsuperscript{-1}), M is sample mass (g), 0.1269 is the quality of iodine equivalent to the standard titration solution of 1.00 mL sodium thiosulfate, 100 is conversion coefficient.

2.5 Determination of p-anisidine value

The appropriate amount of oil sample was accurately weighed and placed in a capacity bottle of 25 mL. Hazel nut oil was dissolved with isoctane and the volume was fixed
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2.8 Establishment of a kinetic model for the oxidation of fatty acids in Hazelnut Oil

If the oxidation of fatty acids with time follows the zero-order kinetics, the change of fatty acid content is independent of its initial concentration, and the reaction rate equation is as follow:

\[- \frac{dF}{dt} = k_0\]

The result of its integration is \( F_t - F_0 = K_0t \). Taking the content of fatty acid as ordinate and time as abscissa, if the figure is a straight line, it can be proved that the automatic oxidation reaction of fatty acid meets zero order reaction, and the reaction rate constant is the absolute value of the slope of the straight line.

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

\[- \frac{dF}{dt} = kF\]

The result of its integration is \( \ln(F_t) = -kt + \ln(F_0) \). Taking the logarithm based on the change of fatty acid content is taken as the ordinate and the time as the abscissa, if the figure is a straight line, it can be proved that the automatic oxidation reaction of fatty acid is first order reaction, and the reaction rate constant is the absolute value of the slope of the straight line.

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

\[- \frac{dF}{dt} = kF^2\]

The result of its integration is \( 1/F_t - 1/F_0 = kt \). Taking the reciprocal of fatty acid as ordinate and time as abscissa, if the figure is a straight line, it can be proved that the automatic oxidation reaction of fatty acid is second order reaction, and the reaction rate constant is the absolute value of the slope of the straight line.

2.9 Determination of volatile oxidation products

5 mL hazelnut oil was separately extracted and put into a 20 mL headspace bottle. Under the condition of water
bath temperature of 55°C, the oil was balanced for 10 minutes, extracted for 35 minutes, and analyzed for 4 minutes by GC-MS.

**Statistical analysis of data**

Excel 2010 software and SPSS 19.0 software were used to analyze the data, and the results were expressed as x ± s (n=3), evaluated using analysis of variance (ANOVA), differences between means from triplicate analysis (p<0.05) were determined by Duncan’s multiple range test.

### 3 Results and Discussion

#### 3.1 Changes of oxidation index of hazelnut oil during storage

The peroxide value determined by iodometric titration is usually an indicator of the content of primary oxidation products. As shown in Fig. 1, the peroxide value increased slowly in 0~5 days, rapidly in 5~20 days and gently in 20 days. According to GB2716-2018, the peroxide value of qualified vegetable oil should be less than 0.25 g/100 g. The peroxide value of hazelnut oil on the 5th day of accelerated oxidation was 0.23 g/100 g, which proved that hazelnut oil still met the peroxide value requirement of vegetable oil at this time. Researchers found that the oil is stored at 62°C for one day, which is equivalent to one month at room temperature. Therefore, converted to storage at room temperature, hazelnut oil added without exogenous antioxidants would be edible in the first five months. After five months of storage at room temperature, its peroxide value will exceed the Chinese standard GB 2716-2018 requirements, so it is not recommended to eat. Animal experiments have shown that peroxide can cause rats diarrhea, enteritis, hypertrophy of liver, heart and kidney, fatty liver, liver degeneration, liver necrosis and eventually death in rats\(^\text{26}\). It is generally believed that peroxide value below 100 mmol/kg will not cause adverse reactions in animals, but taking the intake and physical factors into account, the value should not exceed 30 mmol/kg\(^\text{27}\). From this point of view, the first five days during accelerated oxidation, it still met the requirements, but on the 10th day it exceeded the optimal value. Accordingly, it is concluded that hazelnut oil could be stored for five months without adding exogenous antioxidants by the change of peroxide value in the accelerated oxidation process of hazelnut oil.

P-anisidine value is usually used as an indicator of the content of secondary oxidation products. As shown in Fig. 2, the p-anisidine value was around 0.1 in 0~5 days, and gradually increased in 5~25 days. After the 25th day, the rising trend of p-anisidine value slowed down resulted from secondary oxidation product production rate slowing down. From the point of view of secondary oxidation products, hazelnut oil without exogenous antioxidants could still be eaten at room temperature for five months.

TOTOX is often used to assess the degree of oxidation of lipids, whose advantage is the combination of the first-order oxidation product (hydrogen peroxide) with the second-order oxidation product (aldehydes etc). As shown in Fig. 3, the TOTOX was no more than 1 in 0~5 days, and gradually increased in 5~25 days. After the 25th day, the rising trend of TOTOX slowed down resulted from oxidation process slowing down. Its trend was generally similar to PV and p-AV.

![Fig. 1 Changes of peroxide value of hazelnut oil during accelerated oxidation.](image-url)
Analysis of Lipid Components in Hazelnut Oil

3.2 Change of fatty acid content in hazelnut oil and establishment of its oxidation kinetics equation

Five fatty acids including palmitic acid (hexadecanoic acid), stearic acid (octadecanoic acid), oleic acid (9-octadecanoic acid), 11-octadecanoic acid and linoleic acid (9,12-octadecadienoic acid) have been detected within 30 days of accelerated oxidation of hazelnut oil. Among them, the saturated fatty acids were palmitic acid, stearic acid, and the unsaturated fatty acids included linoleic acid, oleic acid and 11-octadecanoic acid. During accelerated oxidation, oleic acid was always the highest content (more than 80%) of the hazelnut oil, followed by linoleic acid, palmitic acid, stearic acid, 11-octadecanoic acid (Table 1). It was also reported earlier that oleic acid is the most abundant in hazelnut oil\(^{20}\). The content of unsaturated fatty acids was over 80%. This finding was close to the previous findings where the content of unsaturated fatty acids had been founded in 8 vegetable oils\(^{20}\). It was found that the ratio of oleic acid to linoleic acid could be used as one of the important criteria to measure the quality of nuts\(^{20}\). In this study, the contents of oleic acid and linoleic acid accounted for more than 90%. It's to be emphasized that the results were broadly similar to previous research\(^{31}\). Oleic acid could promote the decrease of low density lipoprotein and cholesterol in blood, which had good health effects. Linoleic acid, known as “scavenger of blood vessel”, could help to reduce blood lipids, soften blood vessels, and avoid the deposition of serum cholesterol on the blood vessel wall\(^{32}\).

It was showed that the relative content of palmitic acid increased significantly in 10-30 days of accelerated oxidation compared to previous day. While, the relative content of 11-octadecanoic acid and stearic acid did not show a drastic increase or decrease in the whole accelerated oxidation process. The relative content of oleic acid increased significantly during the accelerated oxidation \((p<0.05)\), and the content of linoleic acid exhibited a slightly decrease at the duration of accelerated oxidation process \((p<0.05)\) (Table 1). Similar to our results, it was reported that the content of PUFA decreased, while SFA and MUFA increased\(^{29}\). Based on the experimental evidence observed, it was reasonable to conclude that only the content of linoleic acid showed a drastic reduction during the whole accelerated oxidation process. Its kinetics equations have been shown in Table 2. Compared with the \(R^2\) of oxidation kinetics mentioned above, the oxidation kinetics of linoleic acid in hazelnut oil tended to meet the zero-order oxidation kinetics equation, and the regression model had statistical significance by ANOVA variance analysis. It’s to be emphasized that the results were broadly similar to the study, which exhibited that linoleic acid in sunflower oil, etc.

![Fig. 2](image-url) Changes of p-AV of hazelnut oil during accelerated oxidation.

![Fig. 3](image-url) Changes of TOTOX of hazelnut oil during accelerated oxidation.

### Table 1 Fatty acid composition (%) of hazelnut oil samples during accelerate oxidation.

| Fatty acid            | Accelerate time (days) |
|-----------------------|------------------------|
|                       | 0          | 5           | 10          | 15          | 20          | 25          | 30          |
| Palmitic acid         | 5.64±0.26  | 5.82±0.04ab | 5.65±0.04b  | 5.83±0.09ab | 5.85±0.05ab | 5.99±0.08a  | 5.94±0.06a  |
| Stearic acid          | 1.72±0.03b | 1.74±0.01a  | 1.77±0.03ab | 1.75±0.01ab | 1.74±0.01ab | 1.78±0.01ab | 1.70±0.07ab |
| Oleic acid            | 83.05±0.19c| 83.11±0.03e | 83.31±0.00d | 83.91±0.07c | 84.03±0.01c | 84.69±0.02b | 84.92±0.04a |
| 11-octadecanoic acid  | 1.15±0.02b | 1.18±0.02ab | 1.18±0.01ab | 1.21±0.01a  | 1.19±0.03ab | 1.21±0.01a  | 1.19±0.02ab |
| Linoleic acid         | 8.44±0.06a | 8.14±0.02b  | 8.09±0.01b  | 7.30±0.03c  | 7.18±0.02d  | 6.33±0.06c  | 6.24±0.07e  |

Values are expressed as mean±standart deviation. Different letters in columns for each fatty acid mean significantly different values among accelerate oxidation time, \(p < 0.05\).
soybean oil, corn oil, peanut oil, palm oil or camellia oil were all accorded with the zero-order oxidation kinetics model. The oxidation of polyunsaturated fatty acids produces aldehydes, which are in relation to pathophysiology, some of which are cytotoxic and genotoxic and are closely related to many diseases such as atherosclerosis, Alzheimer’s disease, cancer, inflammation and autoimmune diseases. PUFA mainly includes linolenic acid and linoleic acid. No linolenic acid was found in experimental hazelnut oil at detectable level. Depending on the geographical origin, climatic conditions and cultivar, there is the difference in the fatty acid of hazelnut oils. It was also reported that hazelnut oil contained linolenic acid (0–0.2%) in.

Therefore, it is significant to establish the oxidation kinetics model of linoleic acid in hazelnut oil at the duration of storage.

The result showed that the absolute contents of stearic acid, palmitic acid, oleic acid and linoleic acid were all decrease (Table 3). Their kinetics equations have been shown in Table 4. Based on absolute content, the oxidation kinetics of stearic acid, palmitic acid, oleic acid and linoleic acid were all fit in zero-order oxidation kinetics equation. Oxidation kinetics of main fatty acids of hazelnut oil based on absolute content could evaluate its rule of oxidation more correctly.

### Table 2

| Fatty acid | Equation | R²  | Rate constant |
|------------|----------|-----|---------------|
| Zero-order | $F(t) = -0.3964t + 8.9745$ | 0.951 | 0.3964 |
| First-order | $\ln[F(t)] = -0.0544t + 2.2115$ | 0.9434 | 0.0544 |
| Second-order | $1/F(t) = 0.0075t + 0.107$ | 0.9333 | 0.0075 |

### Table 3

| Fatty acid | Accelerate time (days) | 0 | 5 | 10 | 15 | 20 | 25 | 30 |
|------------|------------------------|---|---|----|----|----|----|----|
| Palmitic acid | 2.73±0.16a | 2.72±0.25a | 2.47±0.14b | 2.46±0.21b | 2.36±0.01c | 2.34±0.04c | 1.95±0.16d |
| Stearic acid | 2.16±0.13a | 2.06±0.16b | 1.98±0.07bc | 1.92±0.10c | 1.84±0.03d | 1.86±0.04d | 1.60±0.01e |
| Oleic acid | 36.44±0.80a | 33.13±1.42b | 31.03±1.53c | 30.19±1.12d | 28.51±0.18e | 28.32±0.70e | 23.42±0.76f |
| Linoleic acid | 6.54±0.06a | 5.63±0.06b | 5.10±0.03c | 4.35±0.04d | 3.92±0.01e | 3.31±0.01f | 2.55±0.01g |

Values are expressed as mean±standart deviation. Different letters in columns for each fatty acid mean significantly different values among accelerate oxidation time, $p < 0.05$.

### Table 4

| Fatty acid | Equation | R²  | Rate constant |
|------------|----------|-----|---------------|
| Zero-order | Palmitic acid | $F(t) = -0.0228t + 2.7718$ | 0.8659 | 0.0228 |
| First-order | Palmitic acid | $\ln[F(t)] = -0.0096t + 1.0272$ | 0.8389 | 0.0096 |
| Second-order | Palmitic acid | $1/F(t) = 0.0041t + 0.3543$ | 0.8063 | 0.0041 |
| Zero-order | Stearic acid | $F(t) = -0.0159t - 2.1541$ | 0.9071 | 0.0159 |
| First-order | Stearic acid | $\ln[F(t)] = -0.0084t + 0.7728$ | 0.8856 | 0.0084 |
| Second-order | Stearic acid | $1/F(t) = 0.0045t - 0.4585$ | 0.8594 | 0.0045 |
| Zero-order | Oleic acid | $F(t) = -0.3656t - 35.629$ | 0.9311 | 0.3656 |
| First-order | Oleic acid | $\ln[F(t)] = -0.0123t + 3.5826$ | 0.9158 | 0.0123 |
| Second-order | Oleic acid | $1/F(t) = 0.0004t - 0.0274$ | 0.8874 | 0.0004 |
| Zero-order | Linoleic acid | $F(t) = -0.1271t + 6.4132$ | 0.9956 | 0.1271 |
| First-order | Linoleic acid | $\ln[F(t)] = -0.0297t + 1.9074$ | 0.9775 | 0.0297 |
| Second-order | Linoleic acid | $1/F(t) = 0.0073t + 0.1327$ | 0.9185 | 0.0073 |

3.3 Evaluation of oxidation degree of hazelnut oil by changes of fatty acid content

The linear relationship between linoleic acid content (relative or absolute) and POV, p-AV as well as TOTOX was established by excel and SPSS. The experimental evidence obtained showed that the change of linoleic acid content...
could be negatively correlated with three oxidation indices and the oxidation degree of hazelnut oil could be judged by the decrease of linoleic acid content. As shown in Figs. 4 (a) and (b), the linear relationship equation between linoleic acid content and POV, p-AV as well as TOTOX could establish a significant negative correlation, which could be used to evaluate the oxidation degree of hazelnut oil. It could be concluded that linoleic acid could evaluate the oxidation degree of hazelnut oil in both absolute and relative content.

However, the changes of other fatty acids relative content were irregular, which couldn’t be established right linear correlation with peroxidation indexes. As shown in Figs. 5 and 6, the linear correlation between palmitic acid or stearic acid or oleic acid and peroxidation indexes could be established. Their Pearson correlation coefficient were all worse than that of linoleic acid. Accordingly, regardless of in terms of the relative content or the absolute content, linoleic acid in hazelnut oil could be used as an indicator to evaluate the degree of oxidation of hazelnut oil.

3.4 Changes of volatile oxidation products in hazelnut oil during storage

In the process of vegetable oil oxidation, hydrogen peroxide, the primary oxidation product, is firstly generated, and then regenerated into secondary oxidation products, mainly including volatile oxidation products such as aldehydes etc. Volatile oxidation products were determined.

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Fig. 4 Correlation between the content of the linoleic acid and peroxidation indexes during the accelerated oxidation of hazelnut oil.

Fig. 5 Correlation between the content of the palmitic acid or stearic acid and peroxidation indexes during the accelerated oxidation of hazelnut oil.
by headspace solid phase microextraction (HSSPME) combined with GC-MS at 5th, 10th, 15th, 20th, 25th and 30th days during the process of hazelnut oil accelerated oxidation. Alkanes, alcohols and aldehydes were detected, including three alkanes, two alcohols, one furan, eleven aldehydes and three ketones.

3.4.1 Aldehyde

Aldehydes as the predominant compound were produced during the oxidation of hazelnut oil, including saturated aldehydes, monounsaturated aldehydes and polyunsaturated aldehydes.

Saturated aldehydes, including hexanal, octanal and nonanal. As shown in Fig. 7, hexanal was generated on the 15th, 20th and 25th day, which showed an upward trend. On the 30th day, the content of hexanal decreased, probably due to its polymerization reaction, which resulted in the formation of a cyclic trimer, tripentyltrioxane. Octanal was generated on the 25th and 30th days, and its relative content was less than hexanal and gradually decreased. Octanal has a pleasant sweet orange aroma when it was extremely rare, which was a temporary permissible edible fragrance now. Nonanal existed for 10–30 days, and its relative content showed a downward trend. These saturated aldehydes were the main aldehydes in the oxidation process. They are fruity and aldehyde aromas at low concentrations, and pungent at high concentrations. Accordingly, saturated aldehydes might be the main source of hazelnut rancidity. As shown in Figs. 8-10, a significant
positive linear relationship could be established between the change of hexanal content in hazelnut oil and peroxide value during 15~25 days, as well as p-AV and TOTOX. Pearson correlation coefficients were 0.979*, 0.987*, 0.987*, respectively by SPSS analysis.

Monounsaturated aldehyde included 2-heptenal, 2-octenal, E-2-nonenal, 2-hexenal, 2-decenal, 2-undecenal and 2-methyl-2-butenal. As shown in Fig. 7, 2-heptenal existed for 10~30 days, and its relative content first increased and then decreased. 2-octenal existed for 10-30 days, and increased gradually in the 10~25 days, and decreased in the 30th days. As shown in Fig. 8-10, the change of 2-octenal content in 10~25 days could establish a significant positive correlation with POV, p-AV and TOTOX, the Pearson correlation coefficients were 0.995**, 0.970*, 0.973*, respectively. It could be used as an index within two years of storage at room temperature to evaluate the oxidation degree of hazelnut oil. E-2-nonenal was in existence for 15-30 days, but its relative content changed irregularly. 2-hexenal only existed on the 30th days, and its content was less than 1%. 2-decenal, which was in existence for 10~30 days, showed a gradual upward trend. As shown in Figs. 8-10, 2-decenal could also establish a significant positive correlation with POV, p-AV and TOTOX, the Pearson correlation coefficients of SPSS analysis were 0.899*, 0.959*, 0.958*, respectively. However, the correlation coefficients were lower than hexanal and 2-octenal. Therefore, it can be used to evaluate the oxidation degree of hazelnut oil when the hazelnut oil stores at room temperature for about over two years, which is far inferior to other markers as a primary oxidation product. Although 2-undecenal, which existed for 10-30 days, showed a gradual upward trend, it could not establish a good linear relationship with POV, p-AV and TOTOX, so it couldn’t be used as an index to evaluate the oxidation degree of hazelnut oil.

Polyunsaturated aldehydes included 2,4-nonadienal and 2,4-decadienal. As shown in Fig. 7, 2,4-nonadienal existed during 20~30 days and showed a gradual upward trend. It could establish a linear relationship with POV, p-AV and TOTOX. However, the Pearson correlation coefficients of 2,4-nonadienal with three lipid peroxidation indexes were not significant by SPSS analysis. 2,4-decadienal was in existence for 15~30 days, and its content change was irregular.

Saturated aldehydes are easily oxidized to generate corresponding acids. Unsaturated aldehydes are easily oxidized to generate short-chain hydrocarbons, aldehydes and dialdehydes, which may be the reason for the decrease of some aldehydes content.

3.4.2 Ketone

Ketones were mainly ketenes, including 3-octene-2-one, 3-nonene-2-one and 5-ethyl-3-nonene-6-one. As shown in Fig. 7, 3-octene-2-one, which existed in 15~25 days of ac-
celerated oxidation. As shown in Fig. 8-10, 3-octene-2-one had a significant positive correlation with POV, p-AV and TOTOX, the Pearson correlation coefficients of SPSS analysis were 0.998*, 1.000*, 1.000*, respectively. Therefore 3-octene-2-one could be used as a ketone index to evaluate the oxidation degree of hazelnut oil. 3-nonene-2-one only existed on the 10th day, while 5-ethyl-3-nonene-6-one only existed on the 30th day. Ketenes have a strong rose-like fragrance, a lower relative threshold and a greater contribution to the overall odor37.

3.4.3 Alcohol
As shown in Fig. 7, alcohols included saturated alcohol (1-octanol) and unsaturated alcohol (1-octene-3-alcohol), which existed during the 15~25 days and 15~30 days, respectively. But changes of their contents were not obvious. It could not establish a good linear relationship with POV, p-AV and TOTOX, so it could not be used as a marker. It is generally believed that they are degraded by secondary hydroperoxide of fatty acids or reduced by oxo-compound. The odor threshold of saturated alcohols is relatively high, and their contribution to the odor is small. The odor threshold of unsaturated alcohols is low, which has a great influence on the flavor of fatty acids38.

3.4.4 Furan
As shown in Fig. 7, 2-amyl furan could not establish a good linear relationship with the three peroxide indexes. It is generally considered to be the main and particular alkyl furan in the oxidation process of linoleic acid. The conjugated diene free radical, which produced by hydroxyl radical pyrolysis of linoleic acid, reacts with oxygen to form ethylene hydroperoxide, which is then cyclized by alkoxyl radical to form 2-amyl furan. Its threshold value is relatively low with aroma of soil and vegetables39.

3.4.5 Alkane
Alkanes were mainly undecane, dodecane and tridecane. As shown in Fig. 7, undecane always existed during the whole accelerated oxidation process, and the content of undecane decreased gradually. The other two alkanes, which decreased gradually, existed on the 15th and 10th day of accelerated oxidation, respectively.

4 Conclusions
This study confirmed that the oxidation of unsaturated fatty acids in hazelnut oil, especially of the linoleic, eventually generated volatile oxidation products such as aldehyde and ketones. Results suggested that linoleic, followed zero-order, could be used to evaluate the oxidation degree of hazelnut oil because a significant negative correlation could be established between linoleic acid content and the three oxidation indices. Hazelnut oil oxidation could produce secondary volatile oxidation products, which comprised aldehyde and ketones predominantly. Therefore, hexanal, 2-octanal, 2-decenal and 3-octene-2-one, which could be establish a acceptable linearity with three traditional oxidation indicators, could be used as indexes to assess the extent of hazelnut oil oxidation. The study provided new possibilities for the assessment of the oxidation degree of hazelnut oil, by using the content of linoleic acid and volatile oxides, such as hexanal, 2-octenal, 2-decenal and 3-octene-2-one.

Practical applications
The study provides new possibilities for the assessment of oxidation degree of hazelnut oil, by using the content of linoleic acid and volatile oxides, such as hexanal, 2-octenal, 2-decenal and 3-octene-2-one.

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Conflict of Interest
The authors declare that they have no conflicts of interest.

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