メタボロミクス手法を用いたフライ油の劣化特性のモデリング解析

Modeling Analysis on Deterioration Characteristics of Frying Oil Using Metabolomics Approach

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Modeling Analysis on Deterioration Characteristics of Frying Oil Using Metabolomics Approach

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Abstract

Deep frying is an old and most popular method of food processing, because it is not only easy and fast to operate, but also can give food crisp taste and attractive aroma, which is attributed to the chemical reactions in the process of frying. However, with the repeated frying for a long time, these chemical reactions will also produce undesirable products, leading to the deterioration of oil, and even with the intake of fried foods into the human body, which will have adverse effects on human health. Therefore, quality monitoring of frying oil is very important to ensure the safety of fried foods. At present, the quality evaluation indicators commonly used for frying oil are mainly divided into physical indicators and chemical indicators. However, the comparability and reproducibility of the results are not ideal for different frying oils and frying systems. With the increasing consumption of fried foods, it is urgent to develop new, fast, and widely applicable quality evaluation methods for frying oil.

In this research, frying oils were prepared from common edible oils and used as the research object. The composition, quality and flavor characteristics of frying oil were systematically studied by means of instrument analysis methods such as gas chromatography, liquid chromatography, gas chromatography-mass spectrometry and data processing methods such as regression analysis, correlation analysis and principal component analysis. After thoroughly understanding the deterioration characteristics of frying oil, three prediction models for the deterioration of frying oils were established. These models can be used to achieve the purpose of predicting the deterioration characteristics of edible oil during the frying process from the initial characteristics of the edible oil without going through complicated and time-consuming frying operations. The thesis consists of six chapters and is organized as follows:

In Chapter 1, the research background about deterioration mechanism of edible oil during frying and evaluation indicators of frying oil was described in detail. The chemical reactions that

occur in edible oil during the frying process are mainly hydrolysis, oxidation and polymerization. Due to the occurrence of these reactions during frying, edible oil is gradually deteriorated. The indicators for evaluating the deterioration of edible oil are mainly physical and chemical indicators. Finally, the content, purpose and significance of this research were briefly introduced.

In Chapter 2, the initial composition characteristics, quality and flavor characteristics of 10 commercially available oils, namely olive, safflower, rapeseed, rice bran, natural sesame, sesame, corn, soybean, natural perilla, and perilla oils were analyzed. The results showed that initial total unsaturated fatty acid (TUFA) and total tocopherol (TToc) were in the range of 83.49%–95.28% and 16.40–236.05 mg/100 g by using gas chromatography and liquid chromatography, respectively. Olive, safflower, rapeseed, and rice bran oils contained much oleic acid and α-tocopherol contents; Natural sesame, sesame, corn, and soybean oils contained much linoleic acid and γ-tocopherol contents; Natural perilla and perilla oils contained much linolenic acid and δ-tocopherol contents. The initial carbonyl value (CV) and total polar compounds (TPC) in 10 oils were in the range of 2.36–6.30 μmol/g and 0.0–6.0%, respectively. The initial CV and TPC of roasted oils (sesame and perilla oils) were higher than natural pressed oils (natural sesame and natural perilla oils), and those of polyunsaturated fatty acids (PUFA)-rich oils (such as corn and soybean oils) were higher than monounsaturated fatty acids (MUFA)-rich oils (such as olive and safflower oils). A total of 63 volatile compounds were detected by gas chromatography-mass spectrometry in the headspace of 10 oils, including 27 compounds produced during the roasting process that was only detected in roasted oils. It was their presence that caused the highest levels of volatile compounds to be detected in roasted oils. Except for roasted oils, olive oil was detected the highest content of volatile compounds. In addition to the special volatile compounds detected only in roasted oils, the proportion of alcohol detected was the largest among the volatile compounds detected, and the type of aldehydes was the most detected.

In Chapter 3, the changes in the essential composition of edible oils, namely fatty acids and tocopherols, were discussed during frying. Ten edible oils were intermittently fried with French fries

at 180 °C and the frying oil sample was collected every 2.5 hours, a frying cycle. The results suggested that the content of TUFA and TToc decreased almost linearly with heating time. Using the ratio of palmitic acid to oleic acid in the oils before deep frying (C16:0/C18:1), a model, $Y_{\mathrm{TUFA}} = \left[0.189\left(\frac{\mathrm{C16:0}}{\mathrm{C18:1}}\right)^2 + 0.054\left(\frac{\mathrm{C16:0}}{\mathrm{C18:1}}\right) + 0.185\right]t$, was built that can be used to predict the decomposition rate of TUFA (Y_{TUFA}) during frying in a variety of unsaturated fatty acid-based oils. By establishing a dynamic decomposition index, TUFA and TToc in oils showed alternating dynamic decomposition in multiple frying cycles. With the decomposition of TUFA, the order of the decomposition rates of tocopherol homologs in 10 oils was γ-tocopherol > α-tocopherol > δ-tocopherol. Through multiple linear regression analysis, the order of the effects of the decomposition of the tocopherol homologs on the decomposition of TUFA in 10 oils during frying was also as follows: γ-tocopherol > α-tocopherol > δ-tocopherol.

In Chapter 4, the quality changes of 10 frying oils were measured by using the deterioration evaluation indices, CV and TPC. Results showed that the CV and TPC of 10 oils increased linearly with heating time. The effects of the changes in the composition (unsaturated fatty acids and tocopherols) of oils on the increase in CV and TPC with heating time were revealed by using multiple linear regression analysis. The results showed that among the changes of oil composition, the decrease of PUFA and γ-tocopherol had the greatest influence on the increase of CV and TPC. By correlating changes in degradation indicators with the initial composition of the oil, the prediction models for CV ($CV_t = \left[4.37\left(\frac{PUFA}{TToc}\right)^2 - 5.64\left(\frac{PUFA}{TToc}\right) + 3.36\right]t + CV_0$) and for TPC ($TPC_t = \left[0.024\left(\frac{\mathrm{C18:2}}{\mathrm{C16:0}}\right)^2 - 0.065\left(\frac{\mathrm{C18:2}}{\mathrm{C16:0}}\right) + 0.819\right]t + TPC_0$) were established, respectively. Using these models, the CV and TPC of edible oil during frying at 180 °C can be predicted from the initial composition of the oil. At the same time, the frying life of edible oil can be inferred by using two models simultaneously according to the maximum allowable CV (50 μmol/g) and TPC (24%) stipulated by regulations.

In Chapter 5, the flavor changes in 10 oils during frying were evaluated. The change in volatile compounds level during frying was mainly related to the unsaturated fatty acid composition of the oil. The increase in the total peak area of volatile compounds was highest in oils with high oleic acid content, followed by linoleic acid rich oils. The aldehydes and alcohols detected in the oil accounted for a large proportion before and after heating. The effects of aldehydes, alcohols, and other volatile compounds detected on the flavor characteristics of oils during frying were explored by principal component analysis. The distribution of each oil on the score plot was mainly related to the fatty acid composition. The key volatile compounds affecting the changes during frying in oils with much MUFA were hexanal, (E)-2-hexenal, heptanal, (E)-2-heptenal, octanal, 2-octenal, nonanal, (E)-2-decenal, (E)-2-undecenal, 2-methyl-1-propanol, 1-pentanol, methylpyrazine, and butyl-cyclopentane. For oils rich in PUFA, the key volatile compounds were (Z)-2-penten-1-ol, acetic acid, and hexane. The correlation between the changes of volatile compounds detected and the decrease in TUFA and TToc, the increase in CV and TPC was analyzed, respectively. With the decrease of TUFA and TToc and increase of CV and TPC, most of the volatile compounds showed an increasing trend. The increase of pentanal showed a good correlation with the decrease of TUFA and TToc and increase of CV and TPC in most oils.

In Chapter 6, the main conclusions and limitations of this study and prospects for future work were presented. In general, this study can provide a deep understanding of the changes in composition, quality and flavor characteristics of edible oils during frying, accumulate scientific data for the research on the quality evaluation of frying oil. The establishment of three predictive models provides a reference and scientific basis for the establishment of a sound quality evaluation system for frying oil in the future.

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>	Greater than
<	Less than
=	Equal
±	Plus or minus
+	Addition
/	Per
–	Minus / Not detected
×	Multiply
∑	Total
Δ	Change
&	and
°C	Degree Centigrade
1-BuOH	1-Butanol
2,4-DNPH	2,4-Dinitrophenylhydrazine
AH	Inhibitor (antioxidant) molecule
AV	Acid value
$A^{\bullet}$	Inhibitor radical
C	Carbon
C16:0	Palmitic acid
C18:0	Stearic acid
C18:1	Oleic acid
C18:2	Linoleic acid
C18:3	Linolenic acid
C20:0	Arachidic acid
CO	Corn oil
CV	Carbonyl value
CV_0	Initial carbonyl value
CV_{25}	Carbonyl value after heating for 25 hours
DI	Dynamic index
FAME	Fatty acid methyl ester (s)
FOM	Food oil monitor
GC	Gas chromatography
GCMS	Gas chromatograph-mass spectrometer

$H^{\bullet}$	Hydrogen radical
JOCS	Japan Oil Chemists' Society
L	Liter
LH	Oxidizing lipid substrate
LOOH	Hydroperoxide
$LOO^{\bullet}$	Peroxyl radical
$LO^{\bullet}$	Alkoxy radical
$L^{\bullet}$	Alkyl radical
MUFA(s)	Monounsaturated fatty acid(s)
NP	Natural perilla oil
NS	Natural sesame oil
No.	Number
O/O_2	Oxygen
$OH^{\bullet}$	Hydroxyl radical
OL	Olive oil
P	Probability
PC1	First principal component
PC2	Second principal component
PCA	Principle component analysis
PL	Perilla oil
POV	Peroxide value
PUFA(s)	Polyunsaturated fatty acid (s)
R^2	Coefficient of Determination
RB	Rice bran oil
RI	Retention index
RS	Rapeseed oil
SB	Soybean oil
SF	Safflower oil
SFA	Saturated fatty acid (s)
SPSS	Statistical Package for the Social Sciences
SS	Sesame oil
TPC	Total polar compounds
TPC_0	Initial total polar compounds
TPC_{25}	Total polar compounds after heating for 25 hours
TToc	Total tocopherol
TUFA(s)	Total unsaturated fatty acid (s)

U.S.	United States
Y	Decomposition rate
d	Decomposition ratio
et al.	Et allii (and others)
etc.	et cetera
g	Gram
h	Hour
i.d.	Internal diameter
i.e	id est
k	Speed of change
kg	Kilogram
m	Meters
m/z	Mass-to-charge ratio
mL	Milliliter
meq	Milliequivalent
mg	Milligram
min	Minutes
mm	Millimeters
n	Frying cycle
nm	Nano meter
r	Correlation coefficient
rpm	Revolutions per minute
s	Second
t	Heating time
t_{CV}	Maximum frying time allowed according to carbonyl value standards
t_{TPC}	Maximum frying time allowed according to total polar compounds standards
µL	Microliter
µg	Microgram
µm	Micrometer
µmol	Micromole

Chapter 1 Introduction

1.1 Background

Edible oil is one of the indispensable ingredients in the diet. Its main functions are to provide energy, provide essential unsaturated fatty acids that cannot be synthesized by the human body and must be obtained from vegetable oils, as well as various fat-soluble vitamins (Piras et al., 2009). Common edible oils include soybean, rapeseed (canola), palm, corn, rice bran, olive, sunflower oils, and so on. The selection of edible oil depends mainly on its fragrance characteristics and composition, which can reflect the characteristics and advantages of edible oil. Triglycerides are the main components of commercially available oils, along with small amounts of sterols, tocopherols, and synthetic antioxidants. Triglyceride is formed by the combination of one molecule of glycerol and three molecules of fatty acids through an esterification reaction. Each oil has its own specific triglyceride composition, which is related to the type of fatty acids it contains and the specificity of the way in which fatty acids bind to glycerol. The chemical properties of triglycerides are mainly determined by fatty acids. In other words, the structure and composition of fatty acids, the basic building blocks of edible oil, affect the ultimate properties of oils. The fatty acid composition of some common edible oils is shown in Table 1-1.

Table 1-1 Fatty acid composition in 11 edible oils (Kamal-Eldin and Andersson, 1997)

Oil type	Fatty acids (% of total fatty acids)					
	Palmitic acid	Palmitoleic acid	Stearic acid	Oleic acid	Linoleic acid	Linolenic acid
Sunflower	5.2	0.1	3.7	33.7	56.5	0.0
Groundnut	11.2	0.0	3.6	41.1	35.5	0.1
Soybean	10.1	0.0	4.3	22.3	53.7	8.1
Cottonseed	23.0	0.0	2.3	15.6	55.6	0.3
Maize	11.6	0.0	2.5	38.7	44.7	1.4
Olive	13.8	1.4	2.8	71.6	9.0	1.0
Palm	44.8	0.0	4.6	38.9	9.5	0.4
Rapeseed	4.6	0.3	1.7	60.1	21.4	11.4
Linseed	5.6	0.0	3.2	17.7	15.7	57.8
Sesame	9.6	0.2	6.7	41.1	41.2	0.7
Perilla seed	6.4	0.0	1.6	13.8	15.5	62.6

Worldwide, the production and consumption of edible oil are growing steadily (Majchrzak et al., 2018). Edible oil is consumed in large quantities in daily life mainly through three ways, including being consumed directly for diet, being indirectly used for diet as an ingredient, and being consumed for commercial processing. Among them, commercial processing is the main way to consume edible oil. Deep frying is the most commonly used in commercialize food processing because it is simple and fast. It also generates very palatable foods through improving the flavor, color, and texture of food (Fillion and Henry, 1998). Large quantities of such fried foods are consumed each day all over the world. Examples include the fast food in US (e.g., French fries and doughnuts) (Paeratakul et al., 2003; Stevenson et al., 1984), Chinese traditional foods (e.g., fried dough sticks and fried spring rolls) (Li et al., 2016a), Japanese tempura, and even snacks such as potato chips, and fried biscuits. The attractive flavor and texture of these fried foods are mainly due to a lot of chemical reactions between the edible oil and the ingredients during the frying process. These chemical reactions are constantly occurring as fried foods are produced in large quantities. Besides, some harmful products will accumulate in the frying oil, deteriorating the quality of the frying oil, and ultimately affecting the quality of the fried food,

because the quality of the fried food is closely related to the quality of the oil used (Rossi et al., 2007). The oil absorption of fried foods, such as potato crisps, can be as high as 40% (Dobarganes et al., 2000). As people pay more attention to diet health, it is crucial to control the quality and safety of fried foods, and the root of which is to master the deterioration mechanism of frying oil.

1.1.1 Deterioration mechanism of edible oil during frying

Deep frying is the process of immersing food in a large amount of heated oil at 150 °C to 190 °C, and one of the most dynamic processes in food processing under the contact among food, oil, and air (Aladedunye and Przybylski, 2009). The heat transfer and mass transfer of food, oil, and air during the frying process are carried out simultaneously, resulting in a series of chemical reactions including hydrolysis, oxidation, and polymerization.

1.1.1.1 Hydrolysis of frying oil

The moisture carried in the food is heated to form steam during frying and evaporates by bubbling, which gradually decreases during frying. The moisture and heat cause hydrolysis of the oil. Hydrolysis is the most fundamental chemical reaction that occurs in oil. The ester bonds of triacylglycerols, the major component of oil, are broken by reacting with moisture to form diacylglycerols, monoacylglycerols, glycerols, and free fatty acids. The more moisture the food carries, the faster hydrolysis occurs (Dana et al., 2003). At the same time, diacylglycerols, monoacylglycerols, glycerols, and free fatty acids formed can accelerate the hydrolysis reaction of oil (Frega et al., 1999).

1.1.1.2 Thermal oxidation of frying oil

The lipid thermal oxidation reaction is one of the most basic and principal reaction, which involving the initiation, propagation, and termination of lipid radicals chain reaction. In the initiation of chain reaction, which is catalyzed by various factors such as light, heat and metal

ions, the hydrogen on the carbon-hydrogen bond of the fatty acid molecule with the weakest bond energy, is first removed and becomes a free radical ($H^{\bullet}$). The remaining part after the removal of $H^{\bullet}$ is called alkyl radical ($L^{\bullet}$).

$$LH \rightarrow L^{\bullet} + H^{\bullet}$$

Alkyl radicals react rapidly with molecular oxygen to form peroxyl radicals ($LOO^{\bullet}$) (Porter et al., 1995). Peroxyl radical extracts a hydrogen radical from another fatty acid molecule to form another alkyl radical and a hydroperoxide (LOOH). As the reactions progresses during the frying process, alkyl radical is continuously consumed and produced, causing a cyclical chain reaction. This is the propagation step of the chain reaction, which accelerates the thermal oxidation of oil.

$$L^{\bullet} + O_2 \rightarrow LOO^{\bullet}$$

$$LOO^{\bullet} + LH \rightarrow LOOH + L^{\bullet}$$

In addition, there are a variety of minor components with antioxidant properties in oil, such as tocopherol, which is rich in soybean oil, γ-oryzanol, which is rich in rice bran oil, and sesamolin, which is rich in sesame oil (Aladedunye, 2015). The presence of antioxidants can slow or inhibit the oxidation of fatty acids. It (AH) reacts with peroxyl radicals to form stable non-radical products and prevents the propagation of the chain reaction (Yanishlieva et al., 2002).

$$LOO^{\bullet} + AH \rightarrow LOOH + A^{\bullet}$$

$$LOO^{\bullet} + A^{\bullet} \rightarrow \text{non-radical products}$$

$$A^{\bullet} + A^{\bullet} \rightarrow \text{non-radical products}$$

Hydroperoxides generated during the propagation step can be decomposed into alkoxy radicals ($LO^{\bullet}$) and hydroxyl radicals ($OH^{\bullet}$). The reactions between alkoxy radicals, peroxyl radicals, and alkyl radicals form stable non-radical products to end the chain reaction. This step

is called chain termination. The rate of thermal oxidation of the oil increases with increasing oxygen and free radical concentrations (Paul et al., 1997).

$$LOOH \rightarrow LO^{\bullet} + OH^{\bullet}$$

$$LOO^{\bullet} + LOO^{\bullet} \rightarrow \text{non-radical products}$$

$$LO^{\bullet} + L^{\bullet} \rightarrow \text{non-radical products}$$

$$LO^{\bullet} + LO^{\bullet} \rightarrow \text{non-radical products}$$

$$LOO^{\bullet} + L^{\bullet} \rightarrow \text{non-radical products}$$

$$L^{\bullet} + L^{\bullet} \rightarrow \text{non-radical products}$$

1.1.1.3 Polymerization of frying oil

The polymerization of the frying oil is also a free radical reaction, the main products of which are triacylglycerol polymers, like dimers, trimers, and oligomers (Steel et al., 2006; Choe and Min, 2007). The oil is heated in the presence of oxygen, and thermal polymerization and oxidative polymerization occur in the oil to form complex large molecules polymers connected by –C–C–, –C–O–C–, and –C–O–O–C– bonds among triacylglycerols (Stevenson et al., 1984). According to the frying conditions and the unsaturated fatty acid composition of the oil, the formed polymers are divided into acyclic and cyclic polymers (Takeoka et al., 1997; Tompkins and Perkins, 2000). As shown in Figure 1-1, two allyl radicals that lose hydrogen can bond through a carbon-carbon bond to form a dimer. Alternatively, an allyl radical is bond to one or more unsaturated fatty chain via carbon-carbon bonds and then combine with a hydrogen radical to form malposed dimer, trimer or polymer (Zhang et al., 2012). The formation mechanism of a polymer containing –C–O–C– or –C–O–O–C– bonds is similar to that of –C–C– (Figure 1-2).

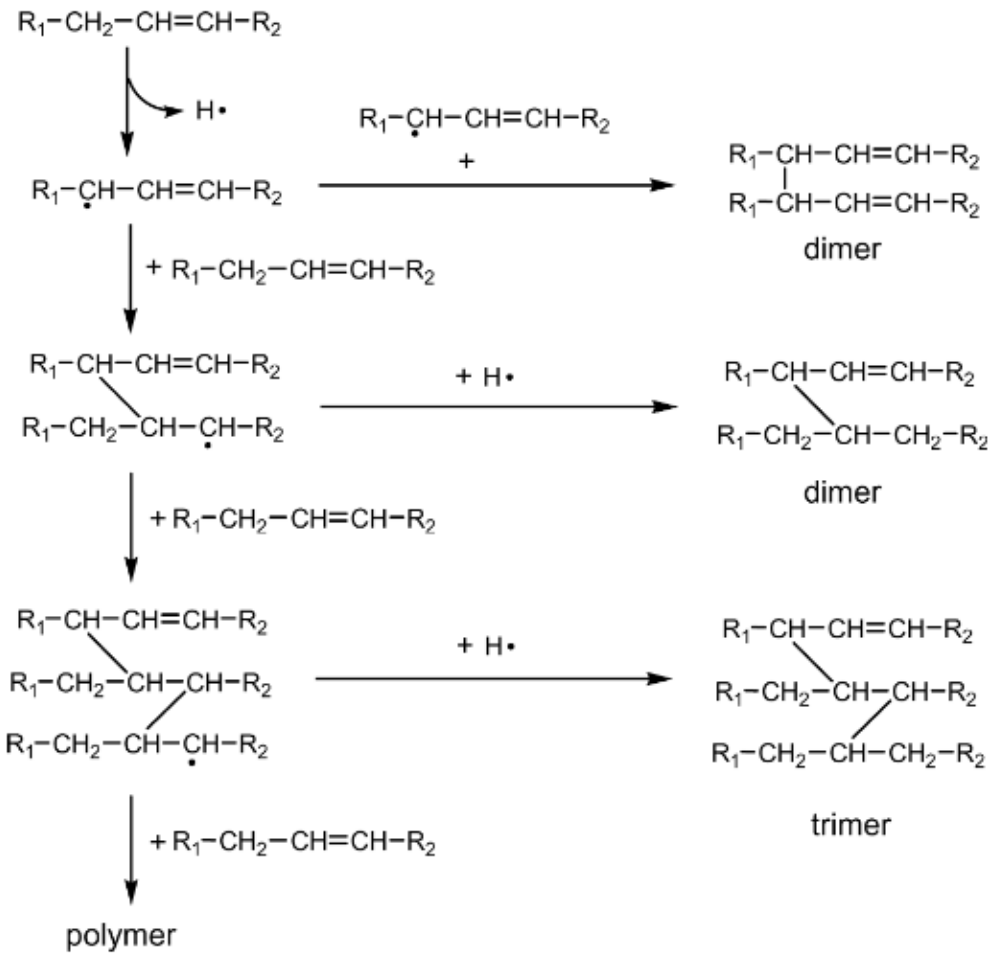

Figure 1-1 The formation mechanism of acyclic polymer containing –C–C– bond during deep frying (Choe and Min, 2007)

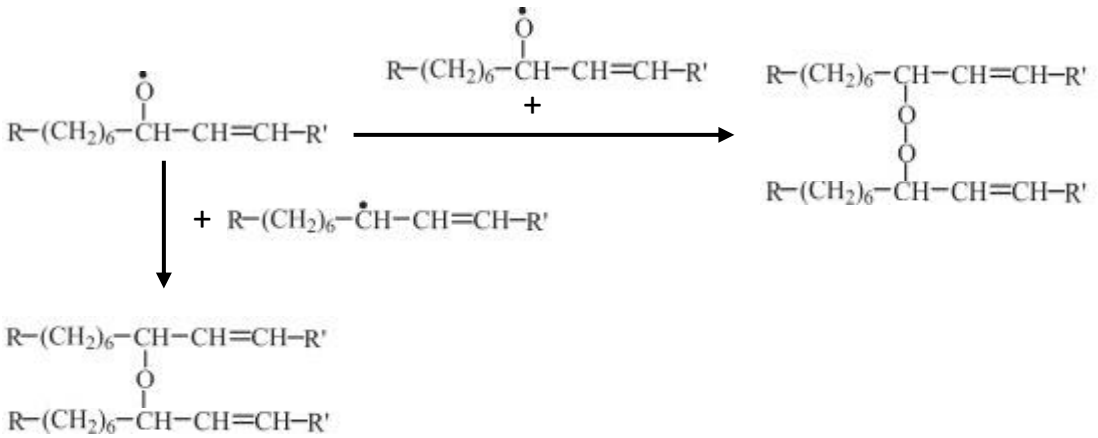

Figure 1-2 The formation mechanism of polymers containing –C–O–C– and –C–O–O–C– bonds during deep frying (Zhang et al., 2012)

The formation mechanism of cyclic polymer is shown in Figure 1-3. A triacylglycerol with polyunsaturated fatty chain loses a hydrogen radical and forms a radical with conjugated diene structure. This radical combines with another triacylglycerol, which has a polyunsaturated fatty chain, to form a dimeric radical intermediate, which was finally converted into a cyclic dimer due to intramolecular addition reaction. In addition to radical reaction, the cyclic polymers can also be generated by the Diels-Alder reaction (Figure 1-4). A triacylglycerol with polyunsaturated fatty chain loses a hydrogen radical firstly to form a conjugated diolefinic radical, and then obtains a hydrogen radical to form a triacylglycerol with a conjugated diene. It reacts with a compound containing an olefin to form a cyclic compound containing cyclohexene. The amount of cyclic compounds formed in the frying oil depends on the fatty acid composition of the oil and the frying temperature (Meltzer et al., 1981). The more linolenic acid content, the higher the frying temperature, the more cyclic compounds are formed (Rojo and Perkins, 1987).

The formation of polymers is related to the type of oil (unsaturated fatty acid composition), frying temperature and the number of frying times. With the increase in the number and temperatures of frying, the amount of polymer produced increases (Cuesta et al., 1993). Oils based on linoleic acid are more susceptible to polymerization than oils based on oleic acid (Takeoka et al., 1997; Bastida and Sánchez-Muniz, 2001). The production and accumulation of the polymer further accelerates the deterioration of the oil, increases the viscosity of the oil, and deepens the color of the oil (Tseng et al., 1996).

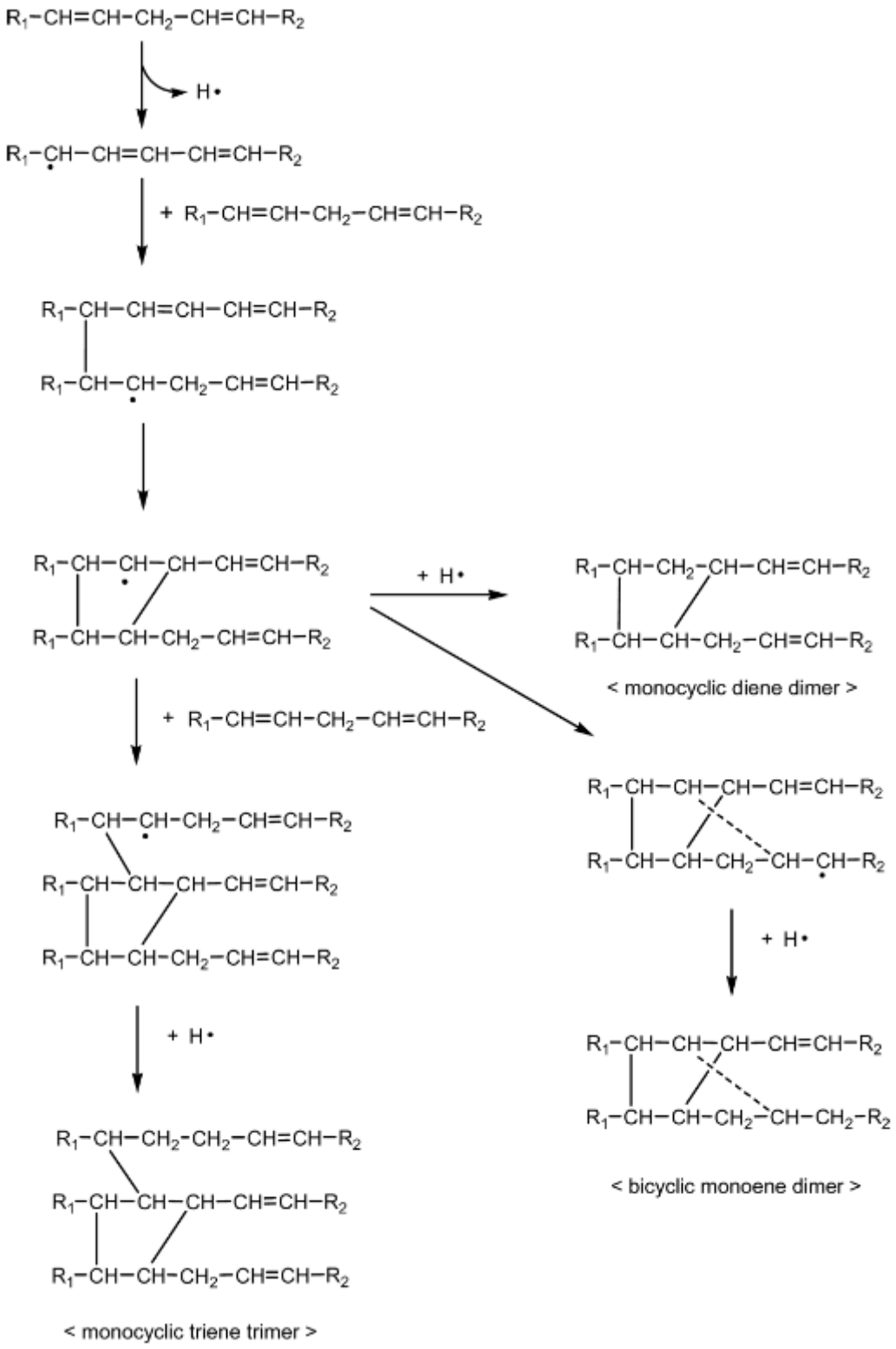

Figure 1-3 The formation mechanism of cyclic polymer by radical reaction during deep frying (Choe and Min, 2007)

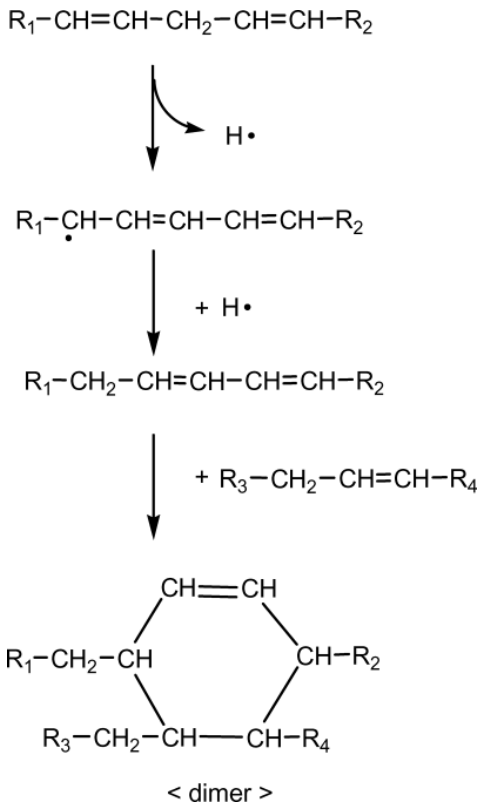

Figure 1-4 The formation mechanism of cyclic polymer by Diels-Alder reaction during deep frying (Choe and Min, 2007)

1.1.2 Evaluation indicators of frying oil

Along with the hydrolysis, oxidation and polymerization of the oil, a large amount of volatile and non-volatile compounds are produced in frying oil. Volatile compounds mostly volatilize with steam, while the remaining parts and non-volatile compounds accumulate in the oil or continue to participate in reactions, affecting the quality of oil and fried foods. Deep frying reduces the amount of unsaturated fatty acids and increases the foam, color, viscosity, free fatty acids, polar compounds, and polymers. The physical and chemical changes of the oil during frying are shown in Figure 1-5 (Choe and Min, 2007). In order to ensure the safety of fried foods, the evaluation of the quality of oil is particularly important. There are many indicators used to evaluate the quality of frying oil, which are divided into physical indicators and chemical indicators based on physical and chemical changes occurring in the oil.

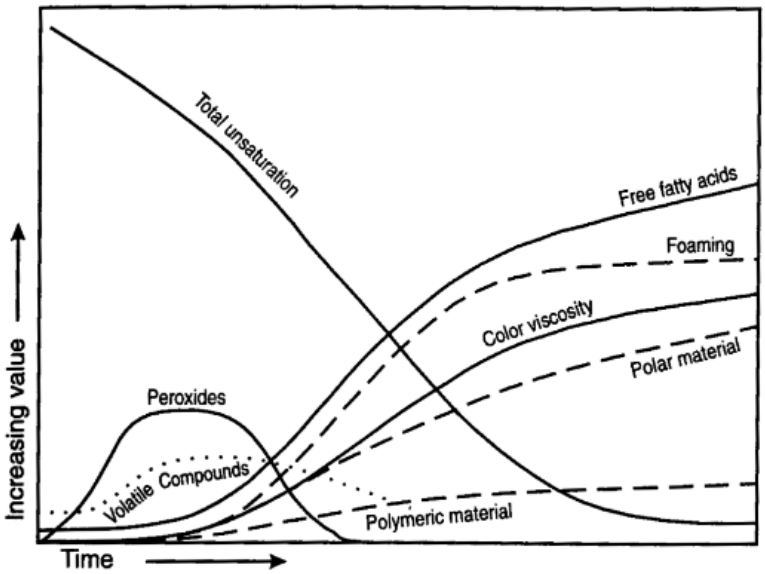

Figure 1-5 The physical and chemical changes of oil during frying (Choe and Min, 2007)

1.1.2.1 Physical indicators for deterioration evaluation of frying oil

Physical indicators for monitoring the deterioration of frying oil include density, viscosity, smoke point, color, refractive index, ultraviolet absorption, infrared spectrum, and dielectric constant (Gertz, 2000). Physical indicators are useful for evaluating the quality of frying oils. They tend to have characteristics of fast and simple that can intuitively reflect the quality of the frying oil.

1.1.2.1.1 Color

The change in color of frying oil is the most direct and most noticeable change, which is often used to quickly and intuitively evaluate the deterioration of frying oil. Each edible oil has a certain color before being used, which is related to the raw material of the oil and the refining degree of the oil. The higher the refining degree, the lighter the color of the oil. When used for frying, the color of the oil changes from a clear yellowish to a light brown, then to a dark brown (Xu et al., 1999). Due to the thermal oxidation, the formation of brown pigments, or the absorption of color from fried foods, during the frying process, the color of the oil gradually deepens during frying (Al-Kahtani, 1991; Man et al., 1996).

The frying time, frying temperature, and sample shape all have an effect on the color of the frying oil. Some scholars (Man et al., 1999; Xu et al., 1999) reported that the color of the oil deepened as the frying time increased when fried potato chips. Aladedunye and Przybylski (Aladedunye and Przybylski, 2009) studied the color change of canola oil after frying at 185 °C and 215 °C, and found that the higher the frying temperature, the faster the color of the oil deepens. Tyagi and Vasishtha (Tyagi and Vasishtha, 1996) used soybean oil and a mixture of partially hydrogenated vegetable oil for frying potatoes at 170, 180, and 190 °C, and found that the color change of the frying oil was affected by the frying temperature rather than the frying medium. Krokida et al. (Krokida et al., 2001) confirmed this conclusion and pointed out that the thinner the sample, the more obvious the color change of the oil. In addition to these external influences, there is a high correlation between the color and the deterioration of the oil during frying (Paul and Mittal, 1996a). Although the color change of oil is an intuitive indicator, it may not be a reliable indicator to evaluate the deterioration of frying oil (Urbančič et al., 2014). Therefore, it is necessary to evaluate the quality of oil together with other indicators.

1.1.2.1.2 Viscosity

The viscosity change of oil is also a relatively straightforward evaluation indicator for evaluating the deterioration of frying oil, which increases as the oil deteriorates (Silva and Singh, 1995). The oil is a mixture of triglycerides whose viscosity depends on the properties of the triglycerides present in the oil. Although viscosity is a physical indicator, it is related to the chemical properties such as chain length and unsaturation of the oil.

The viscosity of edible oil before frying is mainly related to oil unsaturation, the higher the unsaturation, the lower the viscosity of oil (Kim et al., 2010). This is because each double bond having a cis configuration causes a kink in the linear chain (Abramovič and Klofutar, 1998), the fatty acid molecules are dispersed rather than closely packed together, making the oil more fluid. As the frying progresses, the unsaturation of the oil decreases, so the viscosity of the oil increases. The change in viscosity caused by the change in the molecular size of the product

produced during frying is much greater than the change caused by the decrease in double bonds (Kalogianni et al., 2011). The increase in viscosity of frying oil is due to the occurrence of polymerization and the formation of polymer compounds (Stevenson et al., 1984; Besbes et al., 2005). Sánchez-Gimeno et al. (Sánchez-Gimeno et al., 2008) found that during the frying process, the viscosity of the extra virgin olive oil has a high correlation with the amount of polar compounds produced. Therefore, viscosity is considered to be a good indicator for evaluating oil deterioration (Benedito et al., 2002). By studying the relationship between viscosity and heating time, Bracco et al. (Bracco et al., 1981) found that the viscosity increases exponentially with heating time. This indicates that the increase in viscosity is controlled by at least two or more different kinetic processes, each showing a separate increase in viscosity.

1.1.2.1.3 Dielectric constant

Dielectric constant is an important physical property of an object, which measures the ability of an object to store charge (Paul and Mittal, 1996b). The content of polar substances in the medium directly affects the dielectric constant. The determination of dielectric properties has been increasingly seen as a non-destructive, simple, fast, real-time, and continuous method for assessing food changes (Fritsch, 1981).

Dielectric constant is one of the most important monitoring indicator for the quality control of frying oils. In the commercial frying operation process, it is instructive for the quality evaluation of frying oil together with the content of polymer (El-Shami et al., 1992; Paul and Mittal, 1996b; Inoue et al., 2002). The dielectric constant of the oil increases with frying time due to the polar groups are continuously generated during frying (White, 1991; Gertz, 2000). Since the measurement of dielectric constant can realize non-destructive, fast, and real-time evaluation of the quality of frying oil, the company, Northern instrument Corporation, based on this advantage developed a device called the Food Oil Sensor, which is widely used (Fritsch et al., 1979; Paradis and Nawar, 1981; Hein et al., 1998; Innawong et al., 2004).

Although the measurement of physical indicators is simple and fast, its measurement accuracy is not high. The change of these physical indicators is rooted in the occurrence of chemical reactions in the frying oil, and the chemical indicators can more clearly and accurately reflect the degree of chemical reactions than physical indicators, therefore they are widely used to evaluate the degree of oil deterioration.

1.1.2.2 Chemical indicators for deterioration evaluation of frying oil

To evaluate the degree of deterioration of frying oil, the most commonly used chemical indicators are peroxide value, carbonyl value, acid value, total polar compounds, etc., which are respectively evaluated for the reaction products with different properties generated at various stages in the oil deterioration process.

1.1.2.2.1 Peroxide value

Peroxide value (POV) is the total amount of hydroperoxides, the primary oxidation product of frying oil, which can be used to monitor the initial stages of oil oxidation (Saad et al., 2006; Park and Kim, 2016). POV is one of the most frequently determined quality parameters for edible oils during production, storage and sale (Li et al., 2016b). Various countries have established corresponding POV usage limits to ensure the safety of frying oil and fried foods (Firestone, 2007). According to the Japanese food hygiene regulations, when oil is used as a raw material to process food, POV must be less than 30 meq/kg (Hara et al., 2006).

As primary oxidation product of frying oil, the hydroperoxides are very unstable and easily decomposed by heat to form secondary oxidation products. Therefore, the POV of frying oil shows a trend of increasing first and then decreasing with the heating time (Man et al., 1999; Farhoosh and Moosavi, 2009; Li et al., 2016b). Some scholars (Augustin and Berry, 1983) pointed out that the use of POV in the frying process to indicate the degree of oxidative deterioration of frying oil is inaccurate because the peroxide formed is destroyed by high temperatures during the frying process and new peroxides are formed during the cooling of frying

oil. Therefore, POV is considered to be suitable for judging the degree of auto-oxidation of oil at normal temperature, but not suitable for evaluating the thermal oxidation process of oil during frying (Fritsh, 1981; Farhoosh and Moosavi, 2009).

1.1.2.2.2 Carbonyl value

Carbonyl value (CV) is the determination of the total content of the compounds containing carbonyl in frying oil. As mentioned above, the primary oxidation products are unstable and will be decomposed into secondary oxidation products, include a homologous series of small molecular ketones, aldehydes, alcohols, acids, lactones, and so on (Zhang et al., 2012). CV mainly monitors the content of carbonyl-containing compounds in these secondary oxidation products, which is therefore considered to be an effective monitoring indicator for secondary oxidation products. The determination of the CV is very important for evaluating the quality of frying oils and fried foods, because carbonyl compounds can cause rancidity, produce unpleasant odors, and reduce the nutritional value of the fried foods (Endo et al., 2001).

According to Japanese food hygiene regulations, the maximum CV allowable in frying oil is 50 μmol/g (Hara et al., 2006; Firestone, 2007). If the CV exceeds 50 μmol/g, the frying oil must be replaced with new oil. The increase of CV in the frying process is closely related to the change of POV. CV first increased slowly with the increase of POV, and then had a sharp increase with the decrease of POV at the end of induction period (Farhoosh and Moosavi, 2006; Li et al., 2016b). This is because when the peroxides accumulate to the maximum amount, they will degrade to a large amount to produce secondary oxidation products, resulting in a rapid increase in the CV. However, Farhoosh and Moosavi (Farhoosh and Moosavi, 2008) found that CV decreased after prolonged heating. This may be due to the decomposition of the carbonyl compounds caused by prolonged heating, forming new compounds, which are not in the category of carbonyl compounds, and thus a decrease in CV was detected. From this point of view, when the CV of the frying oil reaches 50 μmol/g for the first time, instead of the final value of CV reaching 50 μmol/g at the end of frying, it is necessary to exchange new oil.

1.1.2.2.3 Acid value

Acid value (AV) represents the total content of free fatty acids in oil. Free fatty acids are produced by the breakdown of triglycerides during hydrolysis, oxidation, and pyrolysis (Li et al., 2016b). AV is one of the main parameters reflecting the deterioration of frying oil. Many countries have set limits on the use of AV to ensure the safety of frying oils and fried foods (Firestone, 2007). According to the Japanese food hygiene regulations, when the AV of frying oil is more than 2.5 mg/g, it must be replaced with new oil (Hara et al., 2006).

During the frying process, AV gradually increases with heating time and the oxygen concentration (Fujisaki et al., 2001; Park and Kim, 2016). The hydrolysis reaction of frying oil increased the content of free fatty acids, and the free fatty acids generated with small molecule were easy to volatilize or degrade at high temperature, which reduced the content of free fatty acids. Under the combined effect of the two, AV slowly increases (Li et al., 2016b). On the other hand, some scholars believe that there is no direct relationship between the quality of frying oil and AV (Pazola et al., 1985; Gertz, 2000). Therefore, it is not recommended to use AV alone as an evaluation indicator (Xu et al., 1999; Sanibal and Mancini-Filho, 2004).

1.1.2.2.4 Total polar compounds

The total polar compound (TPC) is a generic term for all polar compounds other than triglycerides in oil and contains all breakdown products during the deterioration process (Melton et al., 1994). The determination of TPC in frying oil is considered to be the most accurate evaluation method for the degree of oxidative deterioration of the frying oil (Blumenthal, 1991; Houhoula et al., 2002; Sanibal and Mancini-Filho, 2004). As a result, it is used in many countries to test the deterioration degree of frying oil, and it is stipulated that oil should be discarded when TPC reaches 24-27%, depending on the regulations of each country (Firestone, 2007; Karakaya and Şimşek, 2011; Hosseini et al., 2016).

The composition and level of TPC are related to the use history of frying oil and the unsaturation degree of oil (Bender et al., 1988). The higher the oil's unsaturation, the faster the TPC increases. During the frying process, TPC increases significantly with the increase of frying time, which may be due to the continuous heating to promote chemical reactions such as polymerization, pyrolysis, hydrolysis, oxidation, etc., resulting in a large amount of reaction product formed and accumulated (Li et al., 2016b). At any frying temperature, TPC increases linearly with frying time, frying days, and frying times (Arroyo et al., 1992; Houhoula et al., 2002; Melton et al., 1994; Sánchez-Muniz et al., 1993).

The reactions occurred in the frying process are complicated. Whether using physical or chemical indicators to evaluate the quality of frying oil, using only one indicator often does not accurately reflect the deterioration degree of frying oil. It is usually necessary to use several indicators to obtain accurate evaluation results.

1.2 Research purpose and significance

1.2.1 Deficiencies in existing research

After a long time of high temperature repeated frying and expose to oxygen in the air, the oil will produce a series of complex chemical reactions such as thermal oxidation, thermal cracking, thermal polymerization, etc., generating a large number of lipid peroxidation products and oxidation products, which accompanied by color deepening, viscosity increase and astringent, bitter, sour and other peculiar odors produced. Many oxides produced during the frying process are carcinogenic and mutagenic, which has been confirmed by many studies (Hageman et al., 1988; Esterbauer, 1993; Kubow, 1992; Yang et al., 2000; Saguy and Dana, 2003). The safety of edible oils has become a common concern for consumers, the scientific community, as well as oil producers and the fried food manufacturing industry. The root of all these lies in accurately grasping the quality change of the oil in the frying process, studying the

use limit of the oil, in order to avoid the long time frying at high temperature produces harmful substances to human body.

As for the evaluation of the quality of frying oil, as described above, a number of physical and chemical indicators are used. However, the comparability and reproducibility of the results are not ideal for different frying oils and different frying systems. Because the harmful substances produced by the use of frying oil will vary significantly according to the composition of unsaturated fatty acids and antioxidants in edible oil, frying time, frying temperature, and so on. These indicators cannot accurately evaluate the quality of all edible oils. Therefore, a more comprehensive exploration and development of a faster and simpler evaluation method is needed for the deterioration research and quality control of frying oil.

1.2.2 Research content

Ten kinds of common edible oil on the market, namely olive oil, safflower oil, rapeseed oil, rice bran oil, natural sesame oil, sesame oil, corn oil, soybean oil, natural perilla oil, and perilla oil, were selected for research. The initial composition characteristics, i.e. the content and composition of fatty acid and tocopherol, initial quality characteristics, i.e. initial CV and TPC, and initial flavor characteristics of the 10 oils were studied. The effects of initial composition characteristics on initial quality characteristics and initial flavor characteristics were also investigated.

Simulating the frying conditions in life, taking 10 oils at 180 °C, the most commonly used frying temperature, intermittently frying French fries at the different heating times to prepare frying oil samples. French fries produced by the same manufacturer are always selected for the experiment, in order to ensure the consistency of frying conditions among the 10 oils. Meanwhile, the composition of French fries is simple, so as to minimize the impact of fried foods on the change of frying oil, and to ensure that the results obtained are caused by the difference between the oil varieties. The composition changes, quality changes, and flavor changes of 10

frying oils with heating time and the relationship between them were studied. The internal influence factors, namely composition characteristics, on these changes was also discussed. The prediction models of decomposition rate of total unsaturated fatty acid, CV, and TPC of frying oil were established based on the initial composition.

1.2.3 Research purpose and significance

By analyzing the initial composition, initial quality and initial flavor characteristics of each edible oil, the initial characteristics of 10 edible oils were fully and comprehensively grasped. Through the study of the changes in fatty acids and tocopherols during frying, the essential changes of frying oil were explored. These essential changes lead to changes in evaluation indicators, CV and TPC. These essential changes are perceived by people in the form of flavor changes, and flavor analysis explains the products produced by the essential changes and the compounds that lead to changes in evaluation indicators. The predictive models based on the initial composition of oil can be used to predict the deterioration of oil in the frying process without complicated frying operation. On the other hand, according to the national discarding point, the frying life of the oil can be predicted. In the future, the initial composition of the edible oil can be adjusted according to the expected usage, and finally the purpose of controlling the quality of the edible oil during the frying process can be achieved.

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Chapter 2 Initial characteristics of edible oils

2.1 Abstract

Ten commercially available oils, namely olive, safflower, rapeseed, rice bran, natural sesame, sesame, corn, soybean, natural perilla, perilla oils, were analyzed for initial compositional characteristics, quality and flavor characteristics. Results showed that the initial contents of total unsaturated fatty acid, total tocopherol, carbonyl value (CV_0), and total polar compounds (TPC_0) in the 10 oils were distributed in the range of 83.49%–95.28%, 16.40–236.05 mg/100 g, 2.36–6.30 μmol/g, and 0.0–6.0%, respectively. The dominant tocopherol in oils rich in polyunsaturated fatty acids (PUFA) was γ-tocopherol, except for natural perilla oil (δ-tocopherol dominant), and the main tocopherol in oils rich in monounsaturated fatty acids (MUFA) was α-tocopherol. The PUFA-rich oils had higher tocopherol contents than the MUFA-rich oils. The CV_0 and TPC_0 results of roasted oils were higher than natural pressed oils, and those of PUFA-rich oils were higher than MUFA-rich oils. A total of 63 volatile compounds were detected by gas chromatography-mass spectrometry in the headspace of the 10 oils, including 27 compounds produced during the roasting process that was only detected in roasted oils. It was their presence that caused the highest levels of volatile compounds to be detected in roasted oils. Except for roasted oils, olive oil was detected the highest content of volatile compounds. In addition to the special volatile compounds detected only in roasted oils, the proportion of alcohol detected was the largest among the volatile compounds detected, and the type of aldehydes was the most detected.

2.2 Introduction

Edible vegetable oil is an integral part of the dietary structure, not only because of its sensory contribution, but also because it provides human with essential unsaturated fatty acids, as well as various fat-soluble vitamins (Piras et al., 2009; Dorni et al., 2018). The production and consumption of edible oil is growing steadily worldwide (Majchrzak et al., 2018). With the improvement of living standards and the enhancement of people's awareness of pursuing nutrition and health, people gradually begin to pay attention to the quality of edible oil, the root of which is to understand the composition characteristics of edible oil. All edible oils are a mixture of more than 96% triacylglycerols and minor components (mainly tocopherols) (Tan and Che Man, 2000). Triacylglycerol is a combination of glycerol and three fatty acids in the form of esters. Due to the diversity of fatty acids and the manner in which they are combined, the types of triacylglycerols are also diverse, resulting in the diversity of oil composition. The difference in composition of oil is characterized by stability, sensory, and quality (Kamal-Eldin, 2006).

Fatty acid composition is an important index to evaluate the nutritional quality of vegetable oil. The chemical properties of triacylglycerol are mainly determined by fatty acids. In other words, the structure and composition of fatty acids, as the basic unit of oil, affect the properties of oil. Common fatty acids are mainly oleic acid, linoleic acid, linolenic acid, stearic acid, palmitic acid and so on. They almost exist in all vegetable oils. The higher the content of unsaturated fatty acids in vegetable oil, the higher the nutritional value and the more significant the physiological effect. The unsaturated fatty acids in vegetable oil mainly include oleic acid, linoleic acid, and linolenic acid, among which linoleic acid and linolenic acid are important sources of essential fatty acids for human (Dorni et al., 2018).

Tocopherol is a fat-soluble vitamin, which is the most widely present and abundant minor components in vegetable edible oil. It is known for its antioxidant properties in oils. It can only

be synthesized by plants and is an important dietary nutrient for humans (Kamal-Eldin and Appelqvist, 1996). Tocopherol exerts antioxidant properties by contributing the hydrogen from the phenolic hydroxyl to prevent the propagation of free radical chain reactions that occurs in the oxidation of oils. Besides tocopherol, there are other minor components with antioxidant properties in edible oil (Shyu and Hwang, 2002; Boskou et al., 2005; Besbes et al., 2004; Dimitrios, 2006), but tocopherol is considered a major antioxidant for stability of edible oil due to its relatively high lipid solubility (Burton et al., 1985).

The popularity of edible oil is inseparable from its flavor. Each edible oil has its own unique flavor, making it different from other edible oils. Flavor is also a major consideration when people choose the type of edible oil in life. The flavor of edible oils is mainly produced by a large number of volatile substances at low concentrations, including saturated and unsaturated aromatic hydrocarbons, aldehydes, alcohols, ketones, esters and other substances. Due to the special flavor of olive oil, there have been many studies on the flavor composition characteristics of olive oil (Flath et al., 1973; Kiritsakis, 1998; Temime et al., 2006; Luna et al., 2006). Another edible oil with a characteristic flavor is roasted edible oil. Many studies have reported the flavor components of sesame oil at different roasting times and roasting temperatures (Schieberle, 1996; Kim et al., 2000; Park et al., 2011). In addition to these two typical edible oils, little research has been done on the flavor components of other edible oils. Since the flavor is the most intuitive sensory perception of the quality of edible oil for humans, it is necessary to comprehensively study the flavor characteristics of various edible oils.

In this study, 10 edible oils were studied in detail for their compositional characteristics, including fatty acid composition and tocopherol composition. Their quality was evaluated using evaluation indicators, carbonyl compounds value and total polar compounds. Finally, their flavor characteristics were determined. The relationship among composition, quality and flavor was studied.

2.3 Materials and methods

2.3.1 Materials and reagents

2.3.1.1 Materials

Ten commercially available edible oils, namely, olive oil (OL), safflower oil (SF), rapeseed oil (RS), rice bran oil (RB), natural sesame oil (NS), natural perilla oil (NP), corn oil (CO), soybean oil (SB), sesame oil (SS), and perilla oil (PL) were purchased from local food stores (Akita, Japan). The NS and NP are not roasted before refining whereas SS and PL are. These oils were stored at – 18 °C until they were analyzed.

2.3.1.2 Reagents and standards

Hexane, methanol, acetic acid, isopropanol, butylated hydroxytoluene, potassium hydroxide, 2,4-dinitrophenylhydrazine (2,4-DNPH), and 1-butanol (1-BuOH) were purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). Standard reagents, fatty acid methyl standards, Vitamin E reference standards (d-α-, β-, γ-, and δ-tocopherol), 2,2,5,7,8-pentamethyl-6-hydroxychroman, and *trans*-2-decenal standard were also purchased from FUJIFILM Wako Pure Chemical Corporation. Standard mixture of *n*-alkanes (C6-C16) was bought from Restek Corporation (U.S.). Hydrochloric acid was purchased from Kanto Chemical Company Limited (Tokyo, Japan). Hexane and isopropanol were of high-performance liquid chromatography grade and all other chemicals and reagents were of analytical grade.

2.3.2 Analytical methods

2.3.2.1 Determination of fatty acid composition

Capillary gas chromatography (GC-2010, Shimadzu Company, Japan) was used to qualitatively and quantitatively investigate the fatty acid of the oil samples. Fatty acid methyl esters (FAME) were prepared in accordance with the method described in the literature (David

et al., 2005; Ichihara et al., 1996). Briefly, fatty acids were transesterified into the corresponding FAME by vortexing the oil sample (approximately 0.1 g) in hexane (10 mL) with a solution of methanolic potassium hydroxide (0.1 mL, 11.2 g/100 mL). A HP-88 capillary column (100 m × 0.25 mm, 0.20 μm film thickness; Agilent Technologies International Japan, Limited, Tokyo, Japan) was used to detect the FAME. The column temperature was first increased from 120 to 170 °C at 10 °C per min, then increased to 250 °C at 4 °C per min, and finally maintained at 250 °C for 5 min. The temperature of the flame ionization detector was set at 260 °C. The sample (1 μL) was injected using an AOC-20i auto injector with a split ratio of 1:30. The FAME samples were identified by comparing their retention times with those of known fatty acid standards. The results are reported in relative area percentages (Liu et al., 2018).

2.3.2.2 Determination of tocopherol contents

The contents of different tocopherols were determined using normal phase high-performance liquid chromatography (Shimadzu Company, Kyoto, Japan) equipped with a SCL-10Avp system controller, a CTO-10ACvp column oven, and a RF-10AXL fluorescence detector. The column oven was set at 40 °C. A normal-phase Shodex silica 5SIL 4D analytical column (150 mm × 4.6 mm i.d., Showa Denko K.K., Tokyo, Japan) was used for separation, and detection was performed with a fluorescence detector with an excitation wavelength of 298 nm and emission wavelength of 325 nm. We weighed each oil sample (about 100 mg depending on the tocopherol content) and dissolved into 10 mL hexane. The internal standard 2,2,5,7,8-pentamethyl-6-hydroxychroman was added, and the sample was filtered through a 0.20-μm membrane filter (Toyo Roshi Kaisha, Limited, Tokyo, Japan). An aliquot (10 μL) of each filtered sample was injected using a SIL-10ADvp auto injector. The mobile phase was composed of hexane, isopropanol, and acetic acid with a volume ratio of 1000:6:5, and contained 5 μg/mL of butylated hydroxytoluene. The mobile phase flow rate was 0.8 mL/min. The concentration of each tocopherol was quantified using separate calibration curves prepared for α-, β-, γ-, and δ-tocopherol (Liu et al., 2019).

2.3.2.3 Determination of carbonyl value

The carbonyl value (CV) of the oils were determined according to the Japan Oil Chemists' Society Official Method Tentative 13-2013 Carbonyl Value (Butanol Method) (JOCS, 2013). Specifically, a 2,4-DNPH solution was prepared by dissolving 50 mg of 2,4-DNPH in 100 mL of 1-BuOH containing 3.5 mL of concentrated hydrochloric acid. An oil sample (50–500 mg) was put into a 10 mL volumetric flask, which was then filled to the mark with 1-BuOH. 2-Decenal was dissolved in 1-BuOH and diluted to concentrations of 100, 200, and 400 μmol/L to prepare standard solutions. An aliquot (1 mL) of a standard solution or oil sample was placed in a 15 mL test tube and mixed with 1 mL of the 2,4-DNPH solution. The test tube was heated in a 40 °C water bath for 20 min and then cooled to room temperature in tap water. Potassium hydroxide (8 g) was dissolved in 100mL 1-BuOH, and 8 mL of this solution was added to the tube. The tube was shaken vigorously and then centrifuged at 3000 rpm for 5 min at room temperature. The absorption spectrum (420 nm) of the supernatant was measured with a spectrophotometer (Benchmark Plus Microplate Reader, Bio-Rad, Tokyo, Japan) (Liu et al., 2020).

2.3.2.4 Determination of total polar compounds

A Food Oil Monitor (FOM 320, Ebro Electronics, Ingolstadt, Germany) was used to rapidly measure the total polar compounds (TPC) level in the hot oil, according to the manufacturer's instructions. The sensor of the monitor was first immersed in a hot oil sample at its optimal operating temperature (150 to 180 °C), then the oil was gently stirred for 20 s to ensure an even temperature distribution. The sensor was kept in the hot oil until the TPC value and the temperature on the monitor screen were stable and displayed continuously. This operation was repeated at least three times to ensure that the temperature displayed each time was within a range of ± 2 °C, then the most frequent stable value of TPC was recorded.

2.3.2.5 Determination of volatile compounds

The analysis for volatile compounds of oils was performed using a gas chromatograph-mass spectrometer (Shimadzu Company) with a GCMS-QP2020 system, which equipped with a SH-Rxi-5Sil MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness, Shimadzu Company). About 1 g of oil sample was placed in a 20 mL vial that was closed with magnetic caps. After 30 min of incubation at 80°C, 1 μL sample was injected with a split ratio of 1:10 and the injection time was 0.5 min. The analyses were made using helium as the carrier gas with a total flow of 11.0 mL/min and a column flow of 1.00 mL/min. The column temperature was held at 40 °C for 5 min isothermally, increased at 4 °C/min to 250 °C, then held for 3 min. The ion source and interface temperatures were maintained at 200 and 230 °C, respectively. The mass spectrometer was operated in full scan mode and mass spectra in the 35-350 m/z range were recorded. The standard alkane mixture (C6-C16) was also injected and analyzed in the same way to calculate the retention indices of the volatile compounds tested. The identification of volatile compounds was mainly based on mass spectrum and retention index to reference the NIST 17 Mass Spectral Library and literatures about oils.

2.3.3 Statistical analysis

Each oil sample was analyzed in triplicate. Data are presented as means ± standard deviations. Data processing was carried out using Microsoft Excel 2016. Principal component analysis (PCA) was conducted using SPSS 17.0.

2.4 Results and discussion

2.4.1 Initial composition characteristics of oils

2.4.1.1 Initial fatty acid composition

The detailed fatty acid composition of 10 commercial edible oils were measured (Liu et al., 2018) and presented in Table 2-1. The 10 oils showed different characteristics for the

compositions and contents of fatty acids. The major fatty acids in the oil samples were palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), and linolenic acid (C18:3). C18:1, C18:2, and C18:3 are the most common and abundant unsaturated fatty acid in oils, and the sum of them is called total unsaturated fatty acids (TUFA). C18:1 is an unsaturated fatty acid containing a double bond and belongs to monounsaturated fatty acid (MUFA). C18:2 and C18:3 are unsaturated fatty acids containing two and three double bonds, respectively, belonging to polyunsaturated fatty acids (PUFA). In addition to unsaturated fatty acids containing double bonds, the remaining fatty acids that do not contain double bonds are collectively referred to as saturated fatty acids (SFA).

Among all the oils, the highest contents of C18:1 were observed in OL (81.51%), in agreement with the data reported in the literature (Boskou, 2015). SF also contained high levels of C18:1 (79.69%). They contained the lowest C18:2 content (6.27% for OL and 13.58% for SF) and a small amount of C18:3 (about 0.3%), so that they had the lowest contents of PUFA (6.62% and 13.91% for OL and SF, respectively).

The composition of RS was dominated by C18:1 (67.71%), and it was also rich in C18:3 (9.26%). RS had the highest content of TUFA (95.28%) among the oils, in accordance with the data obtained by Matthäus (Matthäus, 2006) and Mittelbach (Mittelbach and Gangl, 2001). It contained the lowest content of SFA (4.72%) among 10 oils, in accordance with that RS had the lowest content of SFA of all the commodity oils (Przybylski, 2005).

RB had the lowest TUFA content (83.49%) among these oils. It was dominated by C18:1 (46.68%) and C18:2 (35.34%). NS and SS had similar compositions and contents of fatty acids, probably because they are made from the same raw material. The contents of C18:1 (41.25% for NS and 38.88% for SS) and C18:2 (45.67% for NS and 47.74% for SS) were almost equal. Only about 0.2% of C18:3 was detected in SS and NS.

CO had the highest C18:2 content (58.35%), which was in agreement with previous results (Farhoosh et al., 2009), and C18:3 was not detected. C18:2 was the main fatty acid in SB (57.83%), and the content of C18:3 was also high (9.63%).

Like NS and SS, NP and PL are also made from the same raw material and they had similar compositions and contents of fatty acids in this study. Therefore, it seems that the pressing method had no obvious effect on the fatty acid compositions of the oils, in agreement with previous studies (Wroniak et al., 2008). Among the oils, they had the highest PUFA contents (76.85% for NP and 78.17% for PL), with C18:3 predominant (64.26% for NP and 65.83% for PL), and the lowest C18:1 contents (16.68% for NP and 15.18% for PL), which was in accordance with the data obtained by Przybylski (Przybylski, 2005).

In conclusion, all the oils contained large amounts of TUFA (83.49%–95.28%). C18:1 was the main fatty acid in OL, SF, RS, and RB. C18:2 was predominant in NS, SS, CO, and SB. In addition, C18:1 and C18:2 had almost equal proportions of RB, NS, and SS. C18:3 was the main fatty acid component of NP and PL.

Table 2-1 Fatty acid profiles (%) of oil samples

Oil name	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	PUFA	TUFA	SFA
Olive oil	8.58±0.14	2.44±0.03	81.51±0.15	6.27±0.13	0.35±0.02	0.86±0.03	6.62	88.12	11.88
Safflower oil	4.31±0.13	1.71±0.17	79.69±0.80	13.58±0.60	0.33±0.23	0.39±0.18	13.91	93.60	6.40
Rapeseed oil	3.22±0.08	1.28±0.02	67.71±0.77	18.31±0.30	9.26±0.58	0.21±0.03	27.57	95.28	4.72
Rice bran oil	14.98±0.10	1.53±0.14	46.68±0.14	35.34±0.55	1.47±0.31	-	36.81	83.49	16.51
Natural sesame oil	8.12±0.08	4.71±0.02	41.25±0.14	45.67±0.25	0.25±0.07	-	45.92	87.17	12.83
Sesame oil	8.20±0.16	4.57±0.06	38.88±0.20	47.74±0.37	0.21±0.02	0.39±0.01	47.95	86.83	13.17
Corn oil	10.67±0.21	1.47±0.01	28.49±0.22	58.35±0.56	-	1.02±0.45	58.35	86.83	13.17
Soybean oil	10.09±0.11	3.24±0.15	19.21±0.32	57.83±0.35	9.63±0.21	-	67.46	86.67	13.33
Natural perilla oil	5.16±0.01	1.31±0.03	16.68±0.07	12.59±0.04	64.26±0.04	-	76.85	93.53	6.47
Perilla oil	5.10±0.02	1.54±0.03	15.18±0.03	12.34±0.03	65.83±0.03	-	78.17	93.35	6.65

A “-” indicates not detected. Other trace elements in the results can be ignored.

2.4.1.2 Initial tocopherol composition

The initial tocopherol compositions and contents of 10 commercial edible oils were measured (Liu et al., 2019), as shown in Table 2-2. Four tocopherol homologs were detected in these oils, and their sum was expressed as total tocopherol (TToc).

α-Tocopherol had the highest proportion at 88.04% in OL and 96.01% in SF among 10 oils. However, the actual content of α-tocopherol detected in these two oils was small (14.44 mg/100 g for OL and 38.67 mg/100 g for SF), mainly due to the lowest content of TToc at 16.40 mg/100 g for OL and 40.27 mg/100 g for SF. No δ-tocopherol was found in OL or SF.

The TToc content in RS was very high (126.92 mg/100 g), and the main tocopherols were γ-tocopherol (58.83%) and α-tocopherol (36.48%). The content of δ-tocopherol detected in RS was 5.46 mg/100 g. For the tocopherols detected in RB, α-tocopherol had the highest content and proportion (38.37 mg/100 g and 81.73%), followed by γ-tocopherol (6.13 mg/100 g and 13.06%), and the content of TToc was low (46.95 mg/100 g). A small amount of δ-tocopherol was detected (0.35 mg/100 g).

Among the tocopherols, only γ-tocopherol was detected in NS and SS. The content of TToc in NS (47.32 mg/100 g) was less than that in SS (64.55 mg/100 g). The main tocopherol detected in CO was γ-tocopherol (44.17 mg/100 g, 70.32%), followed by α-tocopherol (17.00 mg/100 g, 27.07%). There was 1.18 mg/100 g of δ-tocopherol was detected. The TToc content in SB was very high (171.37 mg/100 g), with γ-tocopherol having the highest content (123.31 mg/100 g, 71.95%), followed by α- (27.20 mg/100 g, 15.87%) and δ-tocopherol (18.89 mg/100 g, 11.02%).

Different from the results of similar fatty acid composition in NP and PL, there were some large differences in their contents and compositions of tocopherols. NP had the largest TToc content (236.05 mg/100 g), which was mainly δ-tocopherol (67.55%) and γ-tocopherol (31.67%). β-Tocopherol was not detected in NP. While PL had a much lower TToc content (78.51 mg/100 g) than NP, and it had a high proportion of γ-tocopherol (93.97%). The contents of α- and γ-

tocopherol were very similar in NP and PL (α-tocopherol: 1.86 mg/100 g for NP and 2.37 mg/100 g for PL, γ-tocopherol: 74.75 mg/100 g for NP and 73.78 mg/100 g for PL), but the content of δ-tocopherol was very different (159.44 mg/100 g in NP and 1.04 mg/100 g in PL).

In brief, α-tocopherol was the main tocopherol detected in OL, SF and RB, with the lowest TToc content. NP had the highest percentage of δ-tocopherol and the highest TToc content. γ-Tocopherol was only detected in NS and SS and was mainly in the other four oils, namely RS, CO, SB, and PL.

Table 2-2 Tocopherol compositions and contents of oil samples

Oil name	Tocopherol (mg/100 g of oil)				
	α	β	γ	δ	TToc
Olive oil	14.44±0.94 (88.04)*	0.57±0.03 (3.46)	1.40±0.04 (8.50)	- -	16.40 (100.00)
Safflower oil	38.67±0.63 (96.01)	0.70±0.01 (1.74)	0.90±0.01 (2.24)	- -	40.27 (100.00)
Rapeseed oil	46.30±0.39 (36.48)	0.50±0.03 (0.39)	74.66±1.56 (58.83)	5.46±0.08 (4.30)	126.92 (100.00)
Rice bran oil	38.37±1.08 (81.73)	2.10±0.15 (4.47)	6.13±0.16 (13.06)	0.35±0.02 (0.74)	46.95 (100.00)
Natural sesame oil	- -	- -	47.32±0.92 (100.00)	- -	47.32 (100.00)
Sesame oil	- -	- -	64.55±4.15 (100.00)	- -	64.55 (100.00)
Corn oil	17.00±0.24 (27.07)	0.47±0.00 (0.74)	44.17±1.06 (70.32)	1.18±0.01 (1.87)	62.81 (100.00)
Soybean oil	27.20±0.56 (15.87)	1.97±0.27 (1.15)	123.31±4.25 (71.95)	18.89±0.51 (11.02)	171.37 (100.00)
Natural perilla oil	1.86±0.11 (0.79)	- -	74.75±0.84 (31.67)	159.44±0.80 (67.55)	236.05 (100.00)
Perilla oil	2.37±0.13 (3.02)	1.32±0.04 (1.68)	73.78±1.15 (93.97)	1.04±0.07 (1.33)	78.51 (100.00)

*The data in parentheses are the percentages of tocopherol (%).

A "-" indicates not detected. Other trace elements in the results were ignored.

2.4.1.3 Initial fatty acid and tocopherol composition characteristics of oils

The PCA was performed on the unsaturated fatty acids (C18:1, C18:2, C18:3, PUFA, and TUFA) and tocopherols (α-, β-, γ-, and δ-tocopherol, and TToc) in the 10 different oils (Figure 2-1). The first two principal components were selected, accounting for 68.51% of the total variance. With respect to these principal components, the 10 edible oils were separated into three groups (Figure 2-1*a*). SF, OL, RS, and RB, which were rich in C18:1, were distributed in the left region of Figure 2-1*a*. OL and SF were close, because they had similar unsaturated fatty acid and tocopherol composition characteristics, containing a large proportion of C18:1 and α-tocopherol. While RS was a little far from them. This was because RS contained more TUFA, C18:3, and TToc than OL and SF, and it was also affected by δ-tocopherol, which was not detected in OL and SF. Although RB was also based on C18:1, it contained a lot of C18:2 compared with SF, OL, and RS, causing its distribution to be far away from them.

NS, SS, CO, and SB, which had high C18:2, were located in the lower region. They all were dominated by γ-tocopherol. SB deviated because it contained more C18:3 and δ-tocopherol than the other three oils.

NP and PL, which were rich in C18:3 and had high contents of TUFA, were located in the upper right region of the figure. NP was different from the other oils because it contained a large amount of δ-tocopherol, which caused its position to be farther away from the other oils.

From the Figure 2-1*b*, the first principal component (PC1) explained 44.03% of the total variance and was mainly affected by C18:1, C18:3, PUFA, TToc, γ-tocopherol, and δ-tocopherol. Therefore, PC1 reflected both the unsaturated fatty acid and tocopherol characteristics of the oils. The second principal component (PC2) explained 24.48% of the total variance and was dominated by C18:2 and TUFA. Consequently, PC2 mainly reflected the unsaturated fatty acid characteristics of the oils.

Therefore, in the PCA results of depending on the composition characteristics of unsaturated fatty acids and tocopherols, the distribution of oils was affected by the composition characteristics of unsaturated fatty acids more than the composition characteristics of tocopherols.

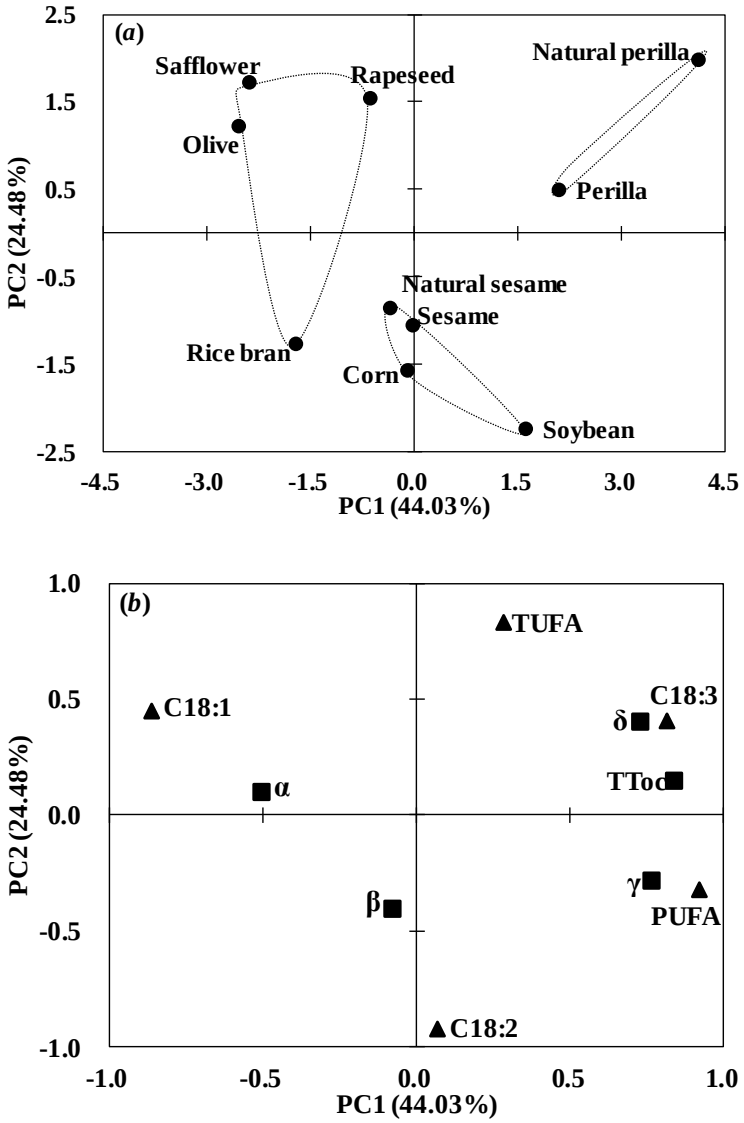


Figure 2-1 Principal component analysis of tocopherols and unsaturated fatty acids in 10 oils: (*a*) principal component scores and (*b*) factor loadings

2.4.2 Initial quality of oils

2.4.2.1 Initial carbonyl value of oils

The oils had different CV (Table 2-3). The initial CV (CV_0) for the oil samples covered a wide range from 2.36 to 6.30 μmol/g, indicating that there obvious initial quality differences among the oil samples. The order of the CV_0 results for the different types of oils from smallest to largest was natural pressed oils, roasted oils, oils rich in MUFA, and oils rich in PUFA. The CV_0 results of roasted oils were higher than those of natural pressed oils, indicating that roasting increases the CV_0 of roasted edible oil compared with that of the corresponding natural pressed oil. Meanwhile, the CV_0 results of PUFA-rich oils were higher than those of MUFA-rich oils. These results are consistent with an earlier study, which showed that the CV of edible oils mainly depended on the pretreatment methods used in oil production and the types of oil containing diverse fatty acid compositions (Berry and McKerrigan, 1958).

Table 2-3 The initial carbonyl value (CV_0) of oils

Oil name	CV_0 (μmol/g)
Natural sesame oil	2.36±0.11
Natural perilla oil	2.46±0.17
Sesame oil	3.02±0.24
Perilla oil	3.12±0.11
Olive oil	3.41±0.21
Rapeseed oil	4.32±0.29
Corn oil	4.48±0.40
Safflower oil	4.67±0.32
Rice bran oil	5.92±0.38
Soybean oil	6.30±0.13

2.4.2.2 Initial total polar compounds of oils

The initial TPC level before frying (TPC_0) of the 10 oils was determined (Table 2-4). The TPC_0 of the 10 oils ranged from 0.0% to 6.0%, showing that the initial quality of the 10 oils varied widely. The TPC level of unused oils usually ranges between 0.4% and 6.4% (Farhoosh and Tavassoli-

Kafrani, 2011; Lumley, 1988), so the initial quality of these oils in terms of TPC level was normal. The differences in the values of TPC_0 of the oils may have be caused by the refining process (Ruiz-Méndez et al., 1997) or by auto-oxidation during storage before purchase. No polar compounds were detected in the natural pressed oils, NS and NP, possibly because no polar compounds had been formed during the pressing process which did not use any heat treatment. No polar compounds were detected in PL, probably because it was a roasted oil with high stability and containing a relatively high tocopherol content. The TPC_0 values of the oils in ascending order were: natural pressed oils, oils rich in MUFA, and oils rich in PUFA.

Table 2-4 The initial total polar compounds (TPC_0) of oils

Oil name	TPC_0 (%)
Natural sesame oil	0.0
Natural perilla oil	0.0
Perilla oil	0.0
Olive oil	0.5
Safflower oil	0.5
Corn oil	0.5
Rice bran oil	1.0
Rapeseed oil	3.0
Sesame oil	6.0
Soybean oil	6.0

From the above results, the order of CV_0 and TPC_0 in 10 oils from small to large was natural pressed oils, roasted oils, oils rich in MUFA, and oils rich in PUFA. This showed that the initial quality of 10 oils, natural pressed oils were better than roasted oils, oils rich in MUFA were better than oils rich in PUFA.

2.4.3 Initial flavor characteristics of oils

The initial flavor characteristics of these 10 oils were determined by measuring the volatile components. A total of 63 ingredients were detected in 10 oils (Table 2-5), including 6 alcohols, 14

aldehydes, 5 alkanes, 2 ketone, 3 pyridines, 1 furan, 1 alkene, 1 benzene, 1 acid, 2 esters, and 27 substances detected only in SS and PL.

As can be seen from the table, the alcohols detected, although only six, were dominant in these oils, except for SS and PL. Alcohol was detected in large quantities. Especially in OL, the total area of alcohols detected was the largest. Conversely, the total area of alcohols detected in CO was least. Aldehydes were the most widely detected substance in 10 oils, which were also account for a large proportion of the total area of all substances detected. The total area of aldehydes detected was the largest in SS, whereas the smallest in NP. There were five alkanes detected, and the total area was also a large percentage of the total area of all substances. The proportion of the total area of alkanes detected in NS to its total area of all substances detected was the largest among these oils, and the proportion of NP and PL was the smallest. Other compounds including ketones, pyridines, furan, alkene, benzene, acid, and esters, were rarely detected in oils except pyrazines detected in PL was 11.40%, acetic acid detected was 21.60% in SS and 17.91% in PL, and esters detected in CO was 15.44%. The remaining 27 substances detected only in SS and PL, mainly ketones, nitrogen-containing compounds, and sulfur-containing compounds, were produced during the roasting process, accounting for 24.68% of the total area in SS and 26.84% of the total area in PL.

The total area of all substances detected was largest in SS and PL, which were roasted oils. Followed by OL, NS, NP, SB, RS, these oils pressed from the seeds or fruits of plants. The least content was detected in RB and CO, which derived from plant peel and germ. SF had the smallest amount of volatile substances detected, although it was also made by pressing seeds. In addition to being related to the source from where the oil was pressed, the volatile component content was also related to the composition of unsaturated fatty acid. Oils with a large amount of PUFA, especially those with a high content of C18:3, had higher levels of volatile substances than those with less C18:3.

Table 2-5 The peak area of volatile compounds identified in the headspace of oils

Volatile compound	RI	Olive oil	Safflower oil	Rapeseed oil	Rice bran oil	Natural sesame oil
Ethanol	<600	838801±13014	-	-	-	-
2-methylPropanol	<600	31167±1592	56782±444	53358±1082	83284±3432	161408±6689
1-Penten-3-ol	714	-	-	23117±219	1738±51	-
(Z)-2-Penten-1-ol	716	-	-	-	-	-
1-Pentanol	795	-	-	1276±118	1922±92	3294±261
1-Octanol	1097	-	-	-	-	-
Total alcohols		869968	56782	77751	86944	164702
Total alcohols (%)		62.43	61.21	43.79	74.37	51.27
Butanal	619	269969±3757	-	1193±2	1007±176	-
2-Butenal	692	-	-	5375±189	-	-
2-methyl-Butanal	704	-	4898±4	-	989±8	-
Pentanal	724	10314±177	8163±805	8360±286	7661±174	10715±714
(E)-2-Pentenal	779	-	-	2846±47	-	-
Hexanal	824	4439±63	7521±251	24279±1361	10964±529	27409±175
Furfural	854	-	-	-	-	-
(E)-2-Hexenal	877	-	-	-	-	618±29
Heptanal	927	-	-	-	-	1382±92
(E)-2-Heptenal	981	-	-	2144±22	2157±153	6470±175
(E,E)-2,4-Heptadienal	1036	-	-	7527±50	-	-
2-Octenal	1083	303±1	-	-	-	414±4

Nonanal	1132	-	-	2294±94	913±54	2781±97
(E,E)-2,4-Decadienal	1350	-	-	-	-	674±16
Total aldehydes		285025	20582	54018	23691	50463
Total aldehydes (%)		20.46	22.19	30.42	20.27	15.71
Hexane	641	197619±5467	-	34489±1138	-	99079±1697
methyl-Cyclopentane	667	2592±30	-	-	-	4141±163
Heptane	709	-	8243±413	-	-	-
Decane	1027	-	-	-	-	897±54
Decamethylcyclopentasiloxane	1170	-	5716±729	-	5651±688	-
Total alkanes		200211	13959	34489	5651	104117
Total alkanes (%)		14.37	15.05	19.43	4.83	32.41
2-Hexanone	815	-	-	-	-	-
2-Octanone	914	-	-	582±7	-	-
Total ketones		-	-	582	-	-
Total ketones (%)		-	-	0.33	-	-
methylPyrazine	844	1383±96	-	-	-	-
2-Ethyl-6-methylpyrazine	1021	-	-	2969±75	-	-
2,3,5-Trimethylpyrazine	1025	-	-	-	-	-
Total pyrazines		1383	-	2969	-	-
Total pyrazines (%)		0.10	-	1.67	-	-
2-pentylFuran	1015	-	-	1241±29	616±87	1959±68
Total furans		-	-	1241	616	1959
Total furans (%)		-	-	0.70	0.53	0.61

1-Heptene	719	-	1437±29	-	-	-
Total alkenes		-	1437	-	-	-
Total alkenes (%)		-	1.55	-	-	-
Toluene	792	28309±208	-	656±29	-	-
Total benzenes		28309	-	656	-	-
Total benzenes (%)		2.03	-	0.37	-	-
Acetic acid	628	-	-	5841±107	-	-
Total acids		-	-	5841	-	-
Total acids (%)		-	-	3.29	-	-
Acetic acid methyl ester	604	-	-	-	-	-
Ethyl Acetate	653	8507±441	-	-	-	-
Total esters		8507	-	-	-	-
Total esters (%)		0.61	-	-	-	-
2-Butanone	637	-	-	-	-	-
1,4-Pentadien-3-ol	681	-	-	-	-	-
2-Pentanone	699	-	-	-	-	-
3-Methylpyridazine	743	-	-	-	-	-
Pyrazine	753	-	-	-	-	-
Dimethyl disulfide	764	-	-	-	-	-
Pyrrole	772	-	-	-	-	-
3-Butenenitrile, 3-methyl-	787	-	-	-	-	-
3-methyl-Thiophene	805	-	-	-	-	-
1-Octene	829	-	-	-	-	-

4-Methylthiazole	837	-	-	-	-	-
1-Hexanol	896	-	-	-	-	-
2,4-Dimethylthiazole	907	-	-	-	-	-
1-(2-furanyl)-Ethanone	931	-	-	-	-	-
2,5-Dimethylpyrazine	934	-	-	-	-	-
Ethylpyrazine	937	-	-	-	-	-
2,3-Dimethylpyrazine	939	-	-	-	-	-
3,10-Dioxatricyclo[4.3.1.0(2,4)]dec-7-ene, (1.alpha.,2.alpha.,4.alpha.,6.alpha.)-	969	-	-	-	-	-
5-methyl-2-Furancarboxaldehyde	984	-	-	-	-	-
3-Octanone	1011	-	-	-	-	-
1-(1H-pyrrol-2-yl)-Ethanone	1034	-	-	-	-	-
Acetylpyrazine	1046	-	-	-	-	-
2-Acetyl-3,4,5,6-tetrahydropyridine	1062	-	-	-	-	-
3-ethyl-2,5-dimethyl-Pyrazine	1101	-	-	-	-	-
2-methoxy-Phenol	1110	-	-	-	-	-
Furan, 3-(4-methyl-3-pentenyl)-	1126	-	-	-	-	-
Perilla ketone	1279	-	-	-	-	-
Total special compounds		-	-	-	-	-
Total special compounds (%)		-	-	-	-	-
Total volatile compounds		1393403	92760	177547	116902	321241

Table 2-5 The peak area of volatile compounds identified in the headspace of oils (continued)

Volatile compound	RI	Sesame oil	Corn oil	Soybean oil	Natural perilla oil	Perilla oil
Ethanol	<600	284867±15056	-	-	31464±939	50818±2235
2-methylPropanol	<600	317401±13460	46971±867	74989±1101	174722±2699	473731±16168
1-Penten-3-ol	714	-	-	-	5494±405	-
(Z)-2-Penten-1-ol	716	25124±1309	-	4273±193	-	68265±1541
1-Pentanol	795	14102±397	843±66	1833±52	-	6628±16
1-Octanol	1097	-	-	-	-	2631±91
Total alcohols		641494	47814	81095	211680	602073
Total alcohols (%)		23.02	45.50	38.59	91.70	28.90
Butanal	619	211564±8981	-	14137±482	-	72698±4024
2-Butenal	692	-	-	-	1865±85	352±5
2-methyl-Butanal	704	10152±348	1453±72	23199±462	-	-
Pentanal	724	21923±887	4889±118	17011±585	1367±13	-
(E)-2-Pentenal	779	-	-	-	1078±8	5477±48
Hexanal	824	37699±789	24841±661	18009±768	11172±834	24073±844
Furfural	854	28038±1715	-	-	-	-
(E)-2-Hexenal	877	7577±33	-	426±0	-	12028±461
Heptanal	927	2810±227	-	529±3	-	5955±293
(E)-2-Heptenal	981	1337±11	-	2827±29	-	-
(E,E)-2,4-Heptadienal	1036	-	-	1392±193	-	6105±157
2-Octenal	1083	-	-	-	-	-

Nonanal	1132	1659±34	-	627±18	-	481±3
(E,E)-2,4-Decadienal	1350	-	-	-	-	-
Total aldehydes		322759	31183	78157	15482	127169
Total aldehydes (%)		11.58	29.67	37.19	6.71	6.11
Hexane	641	351446±5917	4587±268	14759±929	2192±55	-
methyl-Cyclopentane	667	2822±21	-	-	-	3271±150
Heptane	709	-	-	16462±315	-	-
Decane	1027	1731±229	-	1999±78	-	465±64
Decamethylcyclopentasiloxane	1170	-	3506±225	-	-	1858±311
Total alkanes		355999	8093	33220	2192	5594
Total alkanes (%)		12.77	7.70	15.81	0.95	0.27
2-Hexanone	815	1063±31	-	-	-	-
2-Octanone	914	3647±248	-	366±21	-	-
Total ketones		4710	-	366	-	-
Total ketones (%)		0.17	-	0.17	-	-
methylPyrazine	844	10594±332	-	-	-	224872±4220
2-Ethyl-6-methylpyrazine	1021	6454±118	-	760±14	-	1244±47
2,3,5-Trimethylpyrazine	1025	24793±82	-	-	-	11300±183
Total pyrazines		41841	-	760	-	237416
Total pyrazines (%)		1.50	-	0.36	-	11.40
2-pentylFuran	1015	7755±393	-	881±39	-	-
Total furans		7755	-	881	-	-
Total furans (%)		0.28	-	0.42	-	-

1-Heptene	719	-	-	-	-	-
Total alkenes		-	-	-	-	-
Total alkenes (%)		-	-	-	-	-
Toluene	792	-	-	2588±96	-	-
Total benzenes		-	-	2588	-	-
Total benzenes (%)		-	-	1.23	-	-
Acetic acid	628	601924±21389	1783±26	1893±153	1485±1	373152±13546
Total acids		601924	1783	1893	1485	373152
Total acids (%)		21.60	1.70	0.90	0.64	17.91
Acetic acid methyl ester	604	122676±3601	16223±264	-	-	178565±6434
Ethyl Acetate	653	-	-	11196±273	-	-
Total esters		122676	16223	11196	-	178565
Total esters (%)		4.40	15.44	5.33	-	8.57
2-Butanone	637	-	-	-	-	172286±3742
1,4-Pentadien-3-ol	681	9498±111	-	-	-	-
2-Pentanone	699	7161±46	-	-	-	97480±738
3-Methylpyridazine	743	5560±305	-	-	-	6980±303
Pyrazine	753	123291±4536	-	-	-	45134±944
Dimethyl disulfide	764	84144±2125	-	-	-	20544±656
Pyrrole	772	32209±1011	-	-	-	-
3-Butenenitrile, 3-methyl-	787	-	-	-	-	12940±207
3-methyl-Thiophene	805	8426±146	-	-	-	-
1-Octene	829	3583±76	-	-	-	10202±252

4-Methylthiazole	837	27591±1475	-	-	-	7648±165
1-Hexanol	896	51549±1675	-	-	-	40770±504
2,4-Dimethylthiazole	907	28629±1176	-	-	-	2356±128
1-(2-furanyl)-Ethanone	931	14361±444	-	-	-	7157±295
2,5-Dimethylpyrazine	934	181627±3930	-	-	-	54673±1528
Ethylpyrazine	937	25245±470	-	-	-	6998±15
2,3-Dimethylpyrazine	939	36574±2848	-	-	-	17436±337
3,10-Dioxatricyclo[4.3.1.0(2,4)]dec-7-ene, (1.alpha.,2.alpha.,4.alpha.,6.alpha.)-	969	-	-	-	-	1259±65
5-methyl-2-Furancarboxaldehyde	984	13403±618	-	-	-	8475±48
3-Octanone	1011	-	-	-	-	5272±82
1-(1H-pyrrol-2-yl)-Ethanone	1034	7355±130	-	-	-	-
Acetylpyrazine	1046	2483±67	-	-	-	-
2-Acetyl-3,4,5,6-tetrahydropyridine	1062	3770±106	-	-	-	-
3-ethyl-2,5-dimethyl-Pyrazine	1101	8146±172	-	-	-	-
2-methoxy-Phenol	1110	13290±619	-	-	-	-
Furan, 3-(4-methyl-3-pentenyl)-	1126	-	-	-	-	2289±123
Perilla ketone	1279	-	-	-	-	39098±1310
Total special compounds		687898	-	-	-	558997
Total special compounds (%)		24.68	-	-	-	26.84
Total volatile compounds		2787056	105096	210156	230839	2082965

RI means retention index, which was calculated for the SH-RxiTM-5SilMS capillary column.

The identification of volatile compounds was mainly based on mass spectrum and retention indices to reference the NIST 17 Mass Spectral Library and literatures about oils.

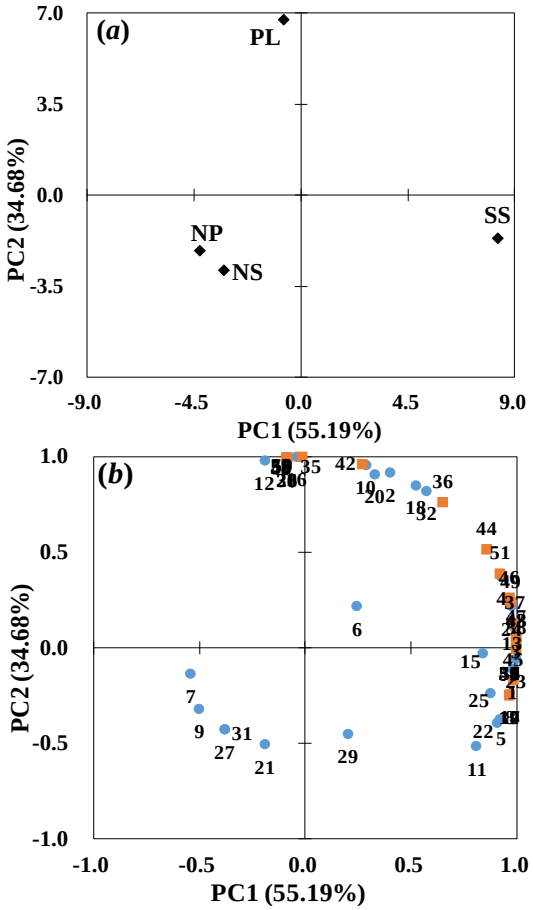
The total of a kind of substances is the sum of the peak areas, and the total (%) refers to the percentage of the total area of a kind of substances detected in an oil to the total area of all substances detected in this oil.

A “-” indicates not detected.

SS and NS came from the same raw materials, as were PL and NP. However, their flavor components detected varied considerably. SS and PL are traditionally tailor-made by roasting, mechanical pressing, and simple refining from the raw seeds. The roasting process is the main cause of their difference from other oils because many aromatic compounds are produced by the roasting process that affects on the flavor quality of roasted oils (Kim et al., 2000). As a result, SS and PL have roasted, nutty, and distinctive flavors.

Except for the 27 special components detected only in SS and PL, the types and peak areas of the common components detected in SS and PL were much larger than those detected in NS and NP (Table 2-5). In order to explore the contribution of the volatile components of roasted oils and natural pressed oils to the flavor characteristics of these four oils, a PCA was carried out using all the volatile components detected from these four oils (SS, NS, PL, and NP). As shown in Figure 2-2, the first two principal components, PC1 and PC2, accounted for 89.87% of the total variance (55.19% for PC1 and 34.68% for PC2), thus explaining significant information within these volatile compounds and flavor characteristics of these four oils.

The specific substances were concentrated in the position closest to 1 in the positive direction of the PC1 and PC2 axes (Figure 2-2*b*), indicating that they have a considerable contribution to the flavor characteristics of the roasted oils. It was their presence that brought roasted oils a unique flavor different from other oils. Combined with the Figure 2-2*a*, the components affecting the flavor of SS were mainly concentrated in the positive direction of PC1, while the components affecting the flavor of PL were mainly concentrated in the positive direction of PC2. This was the reason for the difference between SS and PL, that is, they were all roasted oils, but the flavor characteristics were different. In addition to those specific substances, SS and PL also contained a large number of common substances compared to NS and NP. These substances were also distributed in the positive direction of PC1 and PC2 close to 1, making roasted oils and natural pressed oils significantly separated.



No.	Volatile compound (●)	No.	Volatile compound (■)
1	Ethanol	33	2-Butanone
2	2-methylPropanol	34	1,4-Pentadien-3-ol
3	Butanal	35	2-Pentanone
4	Acetic acid	36	3-Methylpyridazine
5	Hexane	37	Pyrazine
6	methyl-Cyclopentane	38	Dimethyl disulfide
7	2-Butenal	39	Pyrrole
8	2-methyl-Butanal	40	3-methyl-3-Butenenitrile
9	1-Penten-3-ol	41	3-methyl-Thiophene
10	(Z)-2-Penten-1-ol	42	1-Octene
11	Pentanal	43	4-Methylthiazole
12	(E)-2-Pentenal	44	1-Hexanol
13	1-Pentanol	45	2,4-Dimethylthiazole
14	2-Hexanone	46	1-(2-furanyl)-Ethanone
15	Hexanal	47	2,5-Dimethylpyrazine
16	methylPyrazine	48	Ethylpyrazine
17	Furfural	49	2,3-Dimethylpyrazine
18	(E)-2-Hexenal	50	3,10-Dioxatricyclo[4.3.1.0(2,4)]dec-7-ene, (1.alpha.,2.alpha.,4.alpha.,6.alpha.)-
19	2-Octanone		
20	Heptanal		
21	(E)-2-Heptenal	51	5-methyl-2-Furancarboxaldehyde
22	2-Pentylfuran	52	3-Octanone
23	2-Ethyl-6-methylpyrazine	53	1-(1H-pyrrol-2-yl)-Ethanone
24	2,3,5-Trimethylpyrazine	54	Acetylpyrazine
25	Decane	55	2-Acetyl-3,4,5,6-tetrahydropyridine
26	(E,E)-2,4-Heptadienal	56	3-ethyl-2,5-dimethyl-Pyrazine
27	2-Octenal	57	2-methoxy-Phenol
28	1-Octanol	58	3-(4-methyl-3-pentenyl)-Furan
29	Nonanal	59	Perilla ketone
30	Decamethylcyclopentasiloxane		
31	(E,E)-2,4-Decadienal		
32	Acetic acid methyl ester		

Figure 2-2 Principal component analysis of flavor characteristics of SS, NS, PL, and NP: (*a*) principal component scores and (*b*) factor loadings

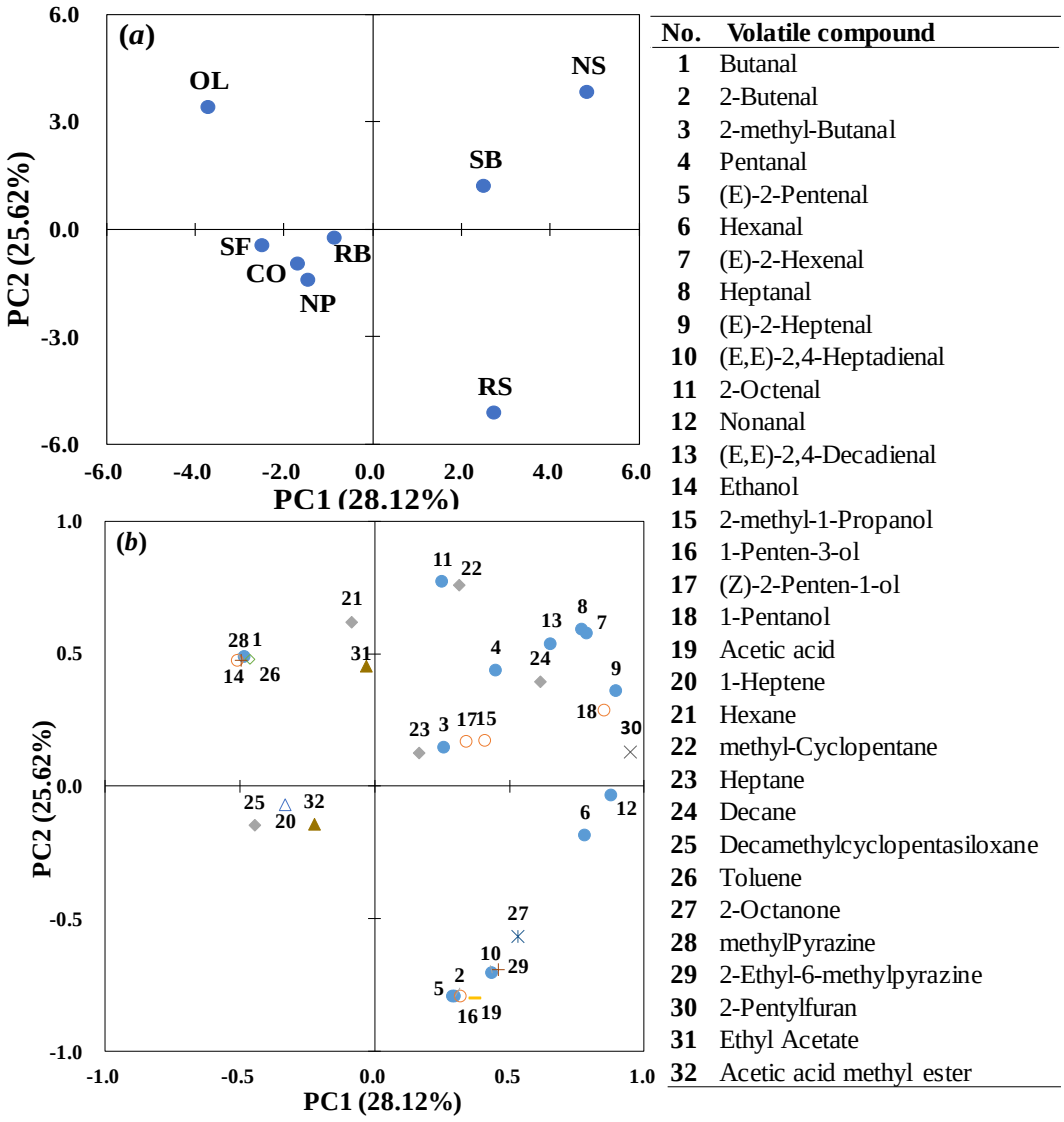
The numbers in Figure 2-2(*b*) represent compounds: 1—32 was common volatile substances that also can be detected in other oils, ●. 33—59 was specific substances that can only be detected in SS and PL, ■.

In addition, (E)-2-heptenal and 2-pentylfuran were distributed below the PC1 axis, and only detected in SS and NS, which were the main factors that caused SS and NS to be distributed below PC1. 2-Octenal and (E,E)-2,4-decadienal were only detected by a small amount in NS, distributed in the lower left of the figure, which were the main substances affecting the position of NS.

(E)-2-Pentenal was located on the left side of the figure, which was only detected in PL and NP, making the distribution of PL and NP different from SS and NS. 2-Butenal was only detected in NP and PL, and the amount detected by PL is very small. Together with 1-penten-3-ol, which was

only detected in NP, their contribution to the flavor characteristics of NP determined the location of the NP distribution.

Both the Table 2-5 and the Figure 2-2 clearly showed that the flavor properties of roasted oils were quite different from those of unroasted oils, thus it was only when roasted oils were excluded that the flavor properties of unroasted oils can be studied clearly. Therefore, PCA was subjected to analyze the effects of these common volatile components detected on the initial flavor of the eight unroasted oils. Score and loading plots of PCA for common volatile components detected in eight edible oils are shown in Figure 2-3. PC1 and PC2 expressed 28.12% and 25.62% of the total variability, respectively. According to the scoring plot (Figure 2-3*a*), PC1 and PC2 clearly distinguished these oils with different flavor composition characteristics. Affected by 1-pentanol, 2-pentylfuran, hexane, decane, and aldehydes, including (E)-2-hexenal, heptanal, (E)-2-heptenal, nonanal, NS and SB were distributed in the upper right of the figure. NS was also affected by (E,E)-2,4-decadienal, 2-octenal, and methyl-cyclopentane, which caused it to be distributed above. SB was distributed below because it was also affected by ethyl acetate, acetic acid, (E,E)-2,4-heptadienal, 2-octanone, 2-ethyl-6-methylpyrazine, 2-methyl-butanal, (Z)-2-penten-1-ol, and heptane. The categories of volatile compounds affected SB were the most.



No.	Volatile compound
1	Butanal
2	2-Butenal
3	2-methyl-Butanal
4	Pentanal
5	(E)-2-Pentenal
6	Hexanal
7	(E)-2-Hexenal
8	Heptanal
9	(E)-2-Heptenal
10	(E,E)-2,4-Heptadienal
11	2-Octenal
12	Nonanal
13	(E,E)-2,4-Decadienal
14	Ethanol
15	2-methyl-1-Propanol
16	1-Penten-3-ol
17	(Z)-2-Penten-1-ol
18	1-Pentanol
19	Acetic acid
20	1-Heptene
21	Hexane
22	methyl-Cyclopentane
23	Heptane
24	Decane
25	Decamethylcyclopentasiloxane
26	Toluene
27	2-Octanone
28	methylPyrazine
29	2-Ethyl-6-methylpyrazine
30	2-Pentylfuran
31	Ethyl Acetate
32	Acetic acid methyl ester

Figure 2-3 Principal component analysis of initial flavor characteristics of eight oils: (*a*) principal component scores and (*b*) factor loadings

RS was distributed at the bottom right of the figure, mainly affected by 1-penten-3-ol, acetic acid, 2-octanone, 2-ethyl-6-methylpyrazine, and aldehydes including 2-butenal, (E)-2-pentenal, (E,E)-2,4-heptadienal, and nonanal. NS, SB, and RS had many volatile components detected, which may be related to the high content of linoleic acid contained.

OL was located in the upper left of the figure, mainly affected by ethanol, butanal, toluene, methylpyrazine, ethyl acetate, and hexane. There were few volatile components detected in SF, CO, NP, and RB, which located at the bottom left of the figure. SF was affected by 1-heptene,

decamethylcyclopentasiloxane, heptane, and 2-methyl-butanal. CO was affected by decamethylcyclopentasiloxane, acetic acid methyl ester, 2-methyl-butanal, acetic acid, and hexane. NP was affected by ethanol, 2-butenal, (E)-2-pentenal, 1-penten-3-ol, acetic acid, and hexane. RB was affected by decamethylcyclopentasiloxane, butanal, 1-penten-3-ol, 2-methyl-butanal, and nananal. Few ingredients can be detected in these four oils simultaneously. Although these four oils were distributed in the same area, they were mainly affected by their characteristic volatiles, not their common components.

As shown in loading plot of PCA (Figure 2-3*b*), a total of 32 ingredients were detected in eight oils, including 13 aldehydes, 5 alcohols, 5 alkanes, 2 pyridines, 2 esters, 1 acid, 1 alkene, 1 benzene, 1 ketone, and 1 furan. In the positive direction, PC1 was strongly related to 1-pentanol, 2-pentylfuran, and aldehydes, including hexanal, (E)-2-hexenal, heptanal, (E)-2-heptenal, nonanal. Main volatile compounds positively correlated to PC2 were 2-octenal and methyl-cyclopentane, whereas the main substances negatively correlated to PC2 were 1-penten-3-ol, acetic acid, and aldehydes including 2-butenal, (E)-2-pentenal, (E,E)-2,4-heptadienal. Among the first two PC selected, aldehydes contributed a lot, followed by alcohols. Generally, aldehydes have a low odor threshold, and there are 13 aldehydes detected in fresh edible oils, so that they have a relatively large contribution to the overall odor of edible oils.

Pentanal, hexanal, and 2-methylpropanol were common components detected in all eight oils. Pentanal had the flavor of almond, malt, and pungent. The flavor of hexanal is described as green, apple, and sweet, while 2-methylpropanol is described as ethyl acetate-like and green (Morales et al., 1997; Kiritsakis, 1998). Only these three substances are detected in all oils, indicating the diversity and complexity of the flavor characteristics of the oil.

2.5 Conclusions

Ten commercially available oils were bought and analyzed for fatty acid and tocopherol composition, CV and TPC, and flavor characteristics. These oils had a high level of TUFA contents. The composition and content of tocopherols varied widely. Oils with high contents of α-tocopherol were oleic acid-rich, while PUFA-rich oils had a high content of γ- or δ-tocopherol. By measuring CV and TPC, the quality of the oils was determined, in order of natural pressed oils, roasted oils, MUFA-rich oils, PUFA-rich oils from good to poor. There were 63 volatile components were detected in 10 oils, resulting in the diversity of flavor characteristics in the 10 oils. The level of flavor components was related to the composition of unsaturated fatty acids, and oils with a high content of PUFA had high levels of volatile substances. SS and PL had distinct flavor from other oils, mainly contributed by ketones, nitrogen-containing compounds, and sulfur-containing compounds. As common substances, only pentanal, hexanal, and 2-methylpropanol were detected, indicating that each oil had its own flavor characteristics. In summary, unsaturated fatty acids are closely related to the composition, quality and flavor characteristics of the oils.

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Chapter 3 Change in composition characteristics of oils during frying

3.1 Abstract

The changes in the fatty acid and tocopherol composition characteristics of the 10 edible oils were investigated during deep frying. French fries were intermittently fried for 5 h each day for five consecutive days at 180 °C in these oils. The results suggested that both the decomposition of total unsaturated fatty acid (TUFA) and total tocopherol (TToc) were linear with heating time (*t*). The decomposition of TToc is faster than that of TUFA since the slope values obtained from fitting equations ($Y = k\,t$) k_{TToc} (1.520–14.483) were obviously larger than k_{TUFA} (0.155–0.270). The ratio of palmitic acid to oleic acid in the oils before deep frying (C16:0 / C18:1) had an important impact on the decomposition of a variety of unsaturated fatty acid-based oils, and can be used as an evaluation index for predicting the decomposition of such oils before deep frying. Further, the equation ($Y_{\mathrm{TUFA}} = \left[0.189\left(\frac{\mathrm{C16:0}}{\mathrm{C18:1}}\right)^2 + 0.054\left(\frac{\mathrm{C16:0}}{\mathrm{C18:1}}\right) + 0.185\right]t$) can be used to determine the decomposition rate of TUFA in a variety of unsaturated fatty acid-based oils. By establishing a dynamic decomposition index, TUFA and TToc in oils showed dynamic decomposition over multiple frying cycles. With the decomposition of TUFA, the decomposition rates of tocopherol homologs were in the order γ-tocopherol > α-tocopherol > δ-tocopherol in the 10 oils, regardless of the initial content and composition of tocopherol and fatty acids. It was also found that higher oil unsaturation led to slower tocopherol decomposition during frying, with more tocopherol remaining after frying. By multiple regression analysis, a model ($\Delta\mathrm{TUFA}_t = 0.049\,\Delta\alpha_t + 0.044\,\Delta\gamma_t + 0.052\,\Delta\delta_t + 0.733$) was obtained, which revealed that the effects of tocopherol homologs on decomposition of unsaturated fatty acid in 10 oils during frying were in the same order, that is, γ-tocopherol > α-tocopherol > δ-tocopherol. The obtained results showed that decomposition characteristics of oils are related to their fatty acid compositions.

3.2 Introduction

Deep frying is commonly used in the food industry because it is simple and enables the processing of bulk food (Saguy and Dana, 2003); it improves the flavor, color, and texture of food. Large quantities of such fried foods are consumed each day all over the world. Examples include the fast food of Europe (e.g., French fries and fried chicken), Chinese traditional foods (e.g., fried dough sticks and fried spring rolls), Japanese tempura, and even snacks such as potato chips, and fried biscuits. However, with the increasing consumption of fried foods, people are paying more attention to their safety (Stier, 2013).

The safety of deep-fried foods largely depends on the quality of the frying oil (Innawong et al., 2004). Because during deep frying, food is immersed in the oil, and heat and fat exchange occur rapidly (Dobarganes et al., 2000; Vitrac et al., 2000). Although deep frying makes food taste good, many chemical reactions—including oxidation, hydrolysis, fission, and polymerization—also occur during deep frying (Choe and Min, 2007; Li et al., 2008; Karimi et al., 2017), because the oil is exposed to oxygen and moisture from the food at high temperatures. These reactions continue to occur as the oils are used repeatedly. They reduce the proportion of unsaturated fatty acids, which are beneficial to the human body, impair the flavor of the food, increase the proportion of unwanted polar substances and polymers, and adversely affect the foaming properties, color, and viscosity of the oil (Choe and Min, 2007; Nayak et al., 2016). These changes have led to the deterioration of edible oil, and will eventually lead to deterioration of fried foods (Nayak et al., 2016), which can affect the safety of the food for humans.

Fortunately, edible oils contain some antioxidants that can maintain their stability (Yanishlieva and Marinova, 2001). Because of relatively high liposolubility, tocopherol is regarded as a safe and effective antioxidant as an additive or an endogenous substance in edible oils (Warner and Moser, 2009). Each edible oil has a specific fatty acid composition and

tocopherol content, which not only makes it unique but also contributes to its oxidation stability (Yuki and Ishikawa, 1976).

Tocopherol occurs as four homologs, namely, α-, β-, γ-, and δ-tocopherols, as determined by the number and position of methyl groups on the chromanol ring. These four tocopherol homologs have been widely reported to have different activities with different decomposition rates (Player et al., 2006; Ko et al., 2010; Lampi and Kamal-Eldin, 1998), which are closely related to temperature (Réblová, 2006; Seppanen et al., 2010). Some researchers have investigated the different decomposition rates of tocopherol homologs artificially added in antioxidant-stripped oils (Warner and Moser, 2009; Barrera-Arellano et al., 2002). However, the conclusions obtained from research using edible oils with natural tocopherol are different with that using antioxidant-stripped oils with adding purified tocopherols, because the tocopherol decomposition is influenced by many uncontrollable factors, including other antioxidants and trace metals in oils that can be removed by stripping antioxidant for purification (Kamal-Eldin and Appelqvist, 1996; Mba et al., 2017).

The decomposition rates of tocopherols under frying conditions in commercial oils has also been studied. Gordon and Kourimská (Gordon and Kourimská, 1995) researched the changes in tocopherol content of commercial low erucic natural rapeseed oil during frying and found that α-tocopherol was lost much faster than γ- or δ-tocopherol. Normand et al. (Normand et al., 2001) studied tocopherols decomposition rates of commercial four regular and modified canola oils. The results showed that γ-tocopherol decomposed faster than α-tocopherol in regular oil, high oleic oil, and low linolenic oil, while the opposite trend was found in high-oleic and low-linolenic oil. Aladedunye and Przybylski (Aladedunye and Przybylski, 2013) researched the frying stability of commercial three high oleic sunflower oils differing in linoleic acid contents and composition of tocopherols, who found that decomposition of γ-tocopherol was faster than α-tocopherol. However, it was found that the varieties of commercial edible oils used in these studies were not sufficient and the conclusion for decomposition rates of tocopherol homologs in frying

oils was still not very clear. Accordingly, there is a great need to continue to comprehensively study the decomposition rates of fatty acids and tocopherols in various commercially available oils during the actual frying process.

The purpose of this study was to investigate the decomposition characteristics of unsaturated fatty acids and tocopherols in 10 edible oils during frying, to explore the main internal factors that affect their decomposition characteristics, and to reveal the relationship between the decomposition of unsaturated fatty acids and the decomposition of tocopherols. Ten commercial edible oils were used for deep frying experiments. Changes in the composition of fatty acids and tocopherols in oils were investigated, and the main internal factor that affecting decomposition of unsaturated fatty acids and tocopherols was explored during deep frying. Starting from the fatty acid composition of each edible oil before deep frying, a way of predicting decomposition of TUFA during frying was found. The relationship between the decomposition of unsaturated fatty acids and the decomposition of tocopherols was revealed during deep frying. Further, the decomposition rates of different tocopherol homologs were determined in these 10 oils during deep frying. Meanwhile, the effects of tocopherol homologs on decomposition of unsaturated fatty acids were investigated by using multiple linear regression analysis.

3.3 Materials and methods

3.3.1 Materials and reagents

3.3.1.1 Preparation of deep-frying oil samples

Frozen par-fried French fries were obtained from a local food store and used for deep frying. The edible oils used for the frying experiment were the same as that in 2.3.1.1 Materials in Chapter 2. Each type of oil (4 L) was used for deep frying in a TF-40A restaurant-style stainless steel electric fryer (Taiji & Company, Limited, Kanagawa, Japan) at 180 °C. When the temperature of the oil reached 180 °C, frozen French fries (100-g batches) were fried for 3 min at 27-min intervals. This deep-frying procedure was carried out for 5 h each day for five

consecutive days. The fresh oil hasn't been added over the entire deep frying process. During deep frying, 200 mL of frying oil was drawn off every 2.5 h and stored at −18 °C until required for analysis.

3.3.1.2 Reagents and standards

Fatty acid methyl standards, hexane, methanol, acetic acid, isopropanol, and butylated hydroxytoluene were purchased from Wako Pure Chemical Industries, Limited (Osaka, Japan). Vitamin E reference standards (d-α-, β-, γ-, δ-tocopherol) and 2,2,5,7,8-pentamethyl-6-hydroxychroman were also purchased from Wako Pure Chemical Industries, Limited. Potassium hydroxide was purchased from Kanto Chemical Company, Incorporated (Tokyo, Japan). Hexane and isopropanol were of high performance liquid chromatography grade and all other chemicals and reagents were of analytical grade.

3.3.2 Analytical methods

3.3.2.1 Determination of fatty acid composition

The method for fatty acid analysis of frying oil was the same as that mentioned in 2.3.2.1 Determination of fatty acid composition in Chapter 2.

3.3.2.2 Determination of tocopherol contents

The analysis for tocopherol contents of frying oils was the same as that mentioned in 2.3.2.2 Determination of tocopherol contents in Chapter 2.

3.3.3 Statistical analysis

Each oil sample was analyzed in triplicate. Data are presented as means ± standard deviations. Linear regression analysis was carried out using Microsoft Excel 2016. PCA and multiple linear regression analysis were conducted using SPSS 17.0.

3.4 Results and discussion

3.4.1 Trends, influencing factors and prediction model for decomposition of unsaturated fatty acids

3.4.1.1 Changes in the fatty acid compositions of the oils during frying

The decomposition of the TUFA content with heating time was plotted (Figure 3-1). All oils showed a similar decreasing trend for the TUFA content. The decomposition of the TUFA content showed a good linear relationship with the heating time, and the decomposition rate gradually increased as the heating time increased.

The decomposition rate of the TUFA content (Y_{TUFA}) was correlated with the heating time (t) in each oil after fitting using the equation,

$$Y_{TUFA} = k_{TUFA}\, t \tag{3-1}$$

as shown in Table 3-1. The k_{TUFA} is the slope of the fitting equation for the TUFA content decomposition rate over time with frying. A larger k_{TUFA} indicates that the TUFA content decreases faster. The k_{TUFA} was great in SB, PL, and CO, in which the content of PUFA was great. The k_{TUFA} in OL, SF, and RS, in which C18:1 was the dominant fatty acid, was relatively slow. Typically, the degradation of C18:1 is slower than that of PUFA (Aladedunye and Przybylski, 2013). Although the fatty acid compositions of NS and SS were similar, the k_{TUFA} in NS was much greater than that in SS. This may be because the total amount of phenolic compounds increases significantly following roasting in the refining process, resulting in the higher oxidation stability of SS (Borjian Borojeni et al., 2016). Consequently, SS had a greater oxidative stability with a smaller k_{TUFA} (0.170). Similar to NS and SS, the k_{TUFA} in NP was also greater than that in PL. SB had the largest k_{TUFA} (0.270). Therefore, the TUFA content of SB was decreased most rapidly, i.e., SB had the greatest decomposition speed of the frying oils tested. The same trend has been reported by Tyagi and Vasishtha (Tyagi and Vasishtha, 1996), wherein vanaspati (a partially hydrogenated vegetable oil blend comprising peanut, cottonseed, nigerseed, palm, rapeseed, mustard, rice bran, soybean,

sunflower, corn, safflower, and sesame oils in varying proportions) was more stable than soybean oil during deep frying. As a result, the TUFA content decreased slowly in oleic acid-rich oils. By contrast, PUFA-rich oils showed a rapid decrease in the TUFA content. It shows that the decomposition rate of TUFA was related to the unsaturated fatty acid composition.

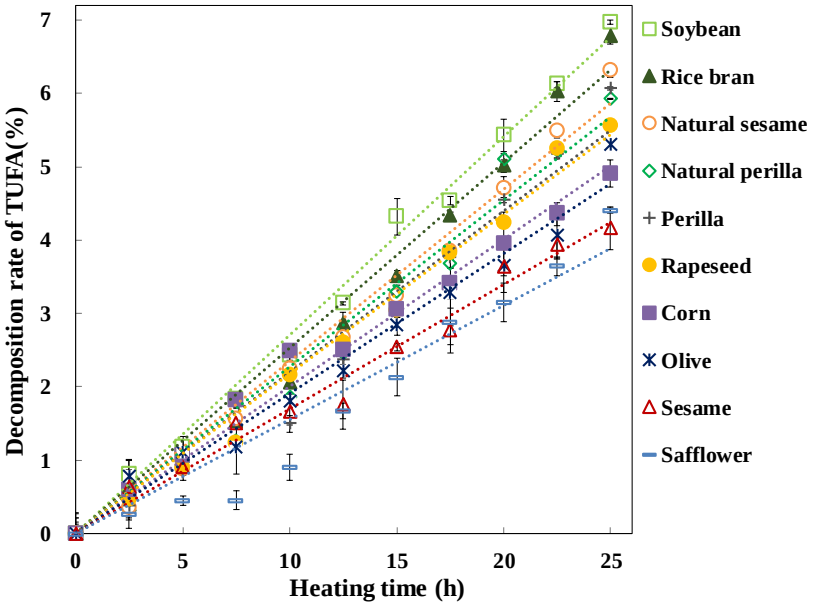

Figure 3-1 The decomposition rates of total unsaturated fatty acid (TUFA) with heating time (t) during deep frying

Table 3-1 Fitting results of the decomposition rates of total unsaturated fatty acid (TUFA) with frying time (t) according to equation $Y_{TUFA} = k_{TUFA}\, t$

Oil name	k_{TUFA}	Determination coefficient (R^2)
Soybean oil	0.270	0.993
Rice bran oil	0.253	0.982
Natural sesame oil	0.234	0.985
Natural perilla oil	0.227	0.975
Perilla oil	0.220	0.967
Rapeseed oil	0.218	0.989
Corn oil	0.200	0.985
Olive oil	0.191	0.978
Sesame oil	0.170	0.982
Safflower oil	0.155	0.937

3.4.1.2 Main internal factor affecting decomposition of total unsaturated fatty acids

The main factor that affected deterioration during deep frying was different for each oil. However, in the present work, the effect of unsaturated fatty acids was staple in the process of oil degradation. Therefore, multiple linear regression was used to analyze the main internal factor affecting TUFA decomposition between the changes in TUFA and changes in MUFA and PUFA. The results of multiple linear regression was shown in Table 3-2, indicated that both MUFA and PUFA had significant effects on the TUFA decomposition ($P < 0.001$). The determination coefficient (R^2) indicated that 99.9% of the variance of the TUFA decomposition was explained by simultaneous changes in MUFA and PUFA contents throughout the heating process. To compare the effects of these different independent variables (i.e., $\Delta MUFA_t$ and $\Delta PUFA_t$) on the dependent variable ($\Delta TUFA_t$), the standardized coefficients were compared. It was found that PUFA had a large effect on the TUFA decomposition as it had a large coefficient of 1.890. By comparison, the effect of MUFA was relatively small as it had a small coefficient (1.090). Therefore, in terms of the effect on the TUFA decomposition during frying, the effect of PUFA was greater than that of MUFA in the 10 oils.

Table 3-2 Multiple linear regression analysis results between the change in TUFA and the changes in MUFA and PUFA contents with heating time

Multiple linear regression equation	Variable	Unstandardized coefficient	Standard error	Standardized coefficient	*P*
$\Delta TUFA_t = b_0 + b_1 \Delta MUFA_t + b_2 \Delta PUFA_t$	Constant	0.008	0.007		0.253
	$\Delta MUFA_t$	1.005	0.005	1.090	< 0.001
	$\Delta PUFA_t$	1.003	0.003	1.890	< 0.001

$R^2 = 0.999$, adjust $R^2 = 0.999$, $P < 0.001$

b_0–b_2 are coefficient constants; $\Delta TUFA_t$, $\Delta MUFA_t$, and $\Delta PUFA_t$ are independent variables that show the changes in total unsaturated fatty acid, monounsaturated fatty acid, and polyunsaturated fatty acid contents with heating time, respectively (%); and t is the heating time (0–25 h).

3.4.1.3 Establishment of prediction index for decomposition of total unsaturated fatty acids

The relationship between the unsaturated fatty acid decomposition of each frying oil during deep frying and the fatty acid composition of the oil before frying was elucidated to devise a means of predicting the unsaturated fatty acid decomposition of the frying oil. Because unsaturated fatty acid played a major role in the decomposition of the oils, the relationship was determined between the decomposition of each oil and unsaturated fatty acid composition before frying. Correlation analysis of the k_{TUFA} and the parameters related to unsaturated fatty acid before deep frying was carried out (Table 3-3). The k_{TUFA} is the slope of the equation that describes a plot of the decomposition rate of TUFA versus heating time, and represents the decomposition speed of TUFA in the oils during deep frying.

The correlation was poor between the k_{TUFA} and the content of C18:1, C18:2, and C18:3 (correlation coefficients were -0.533, 0.314, and 0.218, respectively). The same was true for PUFA and TUFA (correlation coefficients were 0.488 and -0.306, respectively). As an indicator of the oxidative deterioration, the content ratio of linoleic acid to palmitic acid (C18:2 / C16:0) has been proposed in refined, bleached and deodorized palm olein (Augustin et al., 1987), sesame, canola oil, and their blends (Alireza et al., 2010). The C18:2 is comparatively susceptible to oxidation whereas C16:0 is more stable to oxidation. Therefore, the C18:2 / C16:0 is usually used to indicate the extent of oil deterioration (Gan et al., 2005). The correlation between the C18:2 / C16:0 and the decomposition of these oils has also been analyzed. It was found that the C18:2 / C16:0 was inadequate for the full range of oils due to the relatively weak correlation (the coefficient of 0.110) in the present study. However, the C16:0 / C18:1 was found closely correlated with the k_{TUFA} (the coefficient of 0.661). This means that the C16:0 / C18:1 has an important impact on the decomposition speed of TUFA in these tested oils. Moreover, it suggested that the C16:0 / C18:1 could be used as a predictive index to predict the TUFA

decomposition rate of a variety of unsaturated fatty acid-based frying oils due to the diversity of edible oils chosen in the present work.

Table 3-3 Correlation analysis of the relationship between the decomposition speed of the TUFA (k_{TUFA}) during frying and the parameters related to initial unsaturated fatty acid

Parameters	Correlation coefficient (r)
C18:1	-0.533
C18:2	0.314
C18:3	0.218
PUFA	0.488
TUFA	-0.306
C18:1 / C16:0	-0.480
C18:2 / C16:0	0.110
(C18:1+ C18:2) / C16:0	-0.432
PUFA / C16:0	0.240
TUFA / C16:0	-0.288
C16:0 / C18:1	0.661
C16:0 / C18:2	-0.184
C16:0 / (C18:1+ C18:2)	0.541
C16:0 / PUFA	-0.240
C16:0 / TUFA	0.418

Values represent the Pearson correlation coefficient for the linear analysis ($P < 0.01$).

The equation

$$k_{TUFA} = 0.189 \left(\frac{C16:0}{C18:1}\right)^2 + 0.054\left(\frac{C16:0}{C18:1}\right) + 0.185 \quad (3\text{-}2)$$

($r = 0.673$) was derived to describe the relationship between the decomposition speed of TUFA (k_{TUFA}) and the predictive index (C16:0 / C18:1), as shown in Figure 3-2.

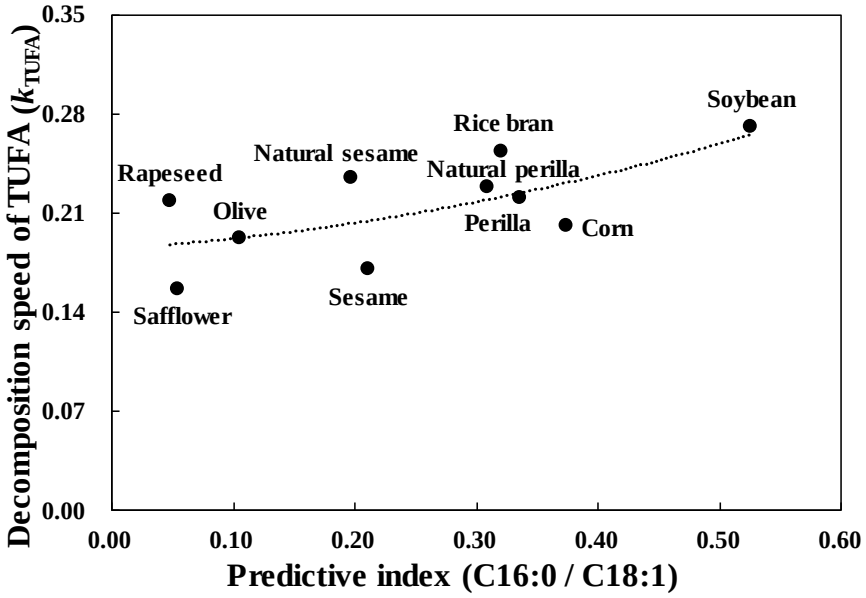

Figure 3-2 The relationship between the predictive index (C16:0 / C18:1) and the decomposition speed of TUFA (k_{TUFA})

The C16:0 / C18:1 of any edible oils can be determined from an analysis of their fatty acid composition before deep frying. Once C16:0 / C18:1 has been determined, the k_{TUFA} can be calculated according to the Equation (3-2). The decomposition rate of TUFA in the oil versus the heating time can then be obtained according to the Equation (3-1). Combining Equations (3-1) and (3-2), the Equation (3-3) can be obtained.

$$Y_{TUFA} = \left[0.189 \left(\frac{C16:0}{C18:1}\right)^2 + 0.054\left(\frac{C16:0}{C18:1}\right) + 0.185\right] t \quad (3\text{-}3)$$

As expected, the above results suggested that the decomposition trend of TUFA in the oil during deep frying could be determined by using Equation (3-3).

3.4.2 Trends and influencing factors for decomposition of total tocopherol contents and its relationship with the decomposition of unsaturated fatty acid

3.4.2.1 Decomposition of total tocopherol contents during deep frying

The decomposition rate of TToc content with heating time was plotted (Figure 3-3). The TToc content decreased obviously during deep frying, and obvious differences were observed among the oils. The TToc content decomposition rates in OL and SF were clearly different to those in other oils. In these two oils, the TToc content rapidly decreased to a very low level within 7.5 h, at which time it had almost completely decomposed. By contrast, the TToc content of other oils decreased steadily over heating time, except for NS and CO. The TToc content in NS quickly dropped to zero between 5 and 12.5 h. The TToc content in CO decreased steadily with heating time until 15 h, and then the TToc decomposition speed became slower. The decomposition rate in NP was the lowest up to 25 h. The TToc decomposition speed of oils may be related to their TToc content. The TToc contents were the least in OL and SF, thus their TToc content decomposition speeds were the fastest. In contrast, NP had the most TToc content, so the TToc content decomposition was slowest among the 10 oils.

The TToc content decomposition rate increased gradually with the heating time and showed a good linear relationship with the heating time (t). Fitting using the equation

$$Y_{\mathrm{TToc}} = k_{\mathrm{TToc}}\, t \tag{3-4}$$

where k_{TToc} is the slope, showed that a bigger the k_{TToc} was related to a faster decrease in the TToc content (Table 3-4). Among the oils, SF had the fastest TToc content decomposition, whereas NP had the slowest TToc content decomposition. Overall, the TToc content decomposition speeds in oleic acid-rich oils were faster than those PUFA-rich oils, which is agree with that a higher degree of oil unsaturation results in a slower decrease in tocopherol levels (Yuki and Ishikawa 1976). Consequently, the TToc content decomposition in an oil during deep frying is closely related to the TToc content and the unsaturated fatty acid composition of the oil.

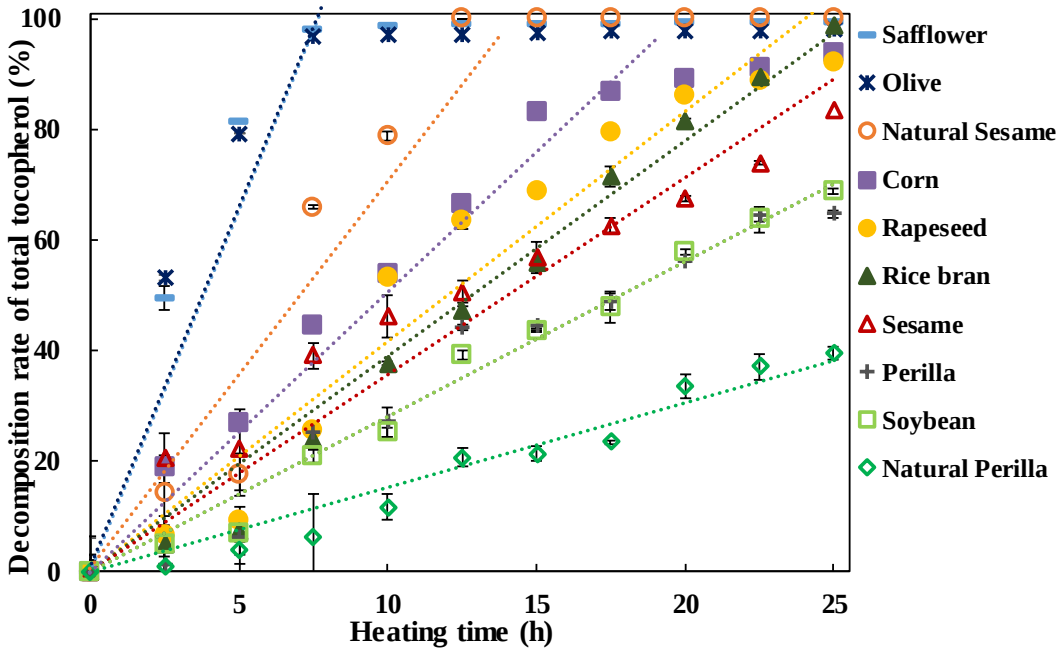

Figure 3-3 The decomposition rates of total tocopherol (TToc) with heating time (t) during frying

Table 3-4 Fitting result of the decomposition rates of total tocopherol (TToc) with heating time (t) according to equation $Y_{TToc} = k_{TToc}\, t$

Oil name	k_{TToc}	Determination coefficient (R^2)
Safflower oil *	14.483	0.934
Olive oil *	14.316	0.912
Natural sesame oil *	7.721	0.934
Corn oil *	5.498	0.991
Rapeseed oil	4.164	0.945
Rice bran oil	3.898	0.980
Sesame oil	3.568	0.915
Perilla oil	2.806	0.961
Soybean oil	2.797	0.984
Natural perilla oil	1.520	0.954

*For fitting of the decomposition rate to the frying time we only used data for regions of obvious decompositions in the tocopherol content, and ignored the period when the final tocopherol content reached a very low level or remained stable. The tocopherol contents of OL and SF only reduced rapidly in the first three frying cycles and then reached very low levels and tended to be stable. Consequently, only the first three frying cycles were used for their TToc decomposition rates. Data up to 7.5 h were used for OL and SF, up to 12.5 h for NS, and up to 15 h for CO.

3.4.2.2 Factors influencing the decomposition speed of total tocopherol and total unsaturated fatty acid

To evaluate the contributions of the decomposition rates of the C18:1, C18:2, and C18:3 contents to TUFA, a fitting analysis of the decomposition rate of each unsaturated fatty acid with heating time was performed using the equation $Y = k\ t$, then $k_{18:1}$, $k_{18:2}$, and $k_{18:3}$ were obtained. The k_α, k_β, k_γ, and k_δ were obtained by the similar method. PCA was carried out using the data of each unsaturated fatty acid decomposition speeds (k_{TUFA}, $k_{18:1}$, $k_{18:2}$, and $k_{18:3}$) and the data of tocopherol decomposition speeds (k_{TToc}, k_α, k_β, k_γ, and k_δ) of all oils (Figure 3-4). The scores plot of the first two principal components (PC1 and PC2) was shown in Figure 3-4*a*, which described 78.46% of the total variance with 61.76% by PC1 and 16.70% by PC2. As shown in Figure 3-4*a*, all oils were respectively located in the positive and negative axis of PC1 according to *k*-values of unsaturated fatty acids and tocopherols, indicating that all oils had obvious difference of the decomposition characteristics. The factor loadings of PC1 was shown in Figure 3-4*b*. In the positive direction, PC1 was strongly related to k_{TToc}, k_α, k_γ, and $k_{18:1}$, whereas in the negative direction, $k_{18:3}$ and k_{TUFA} were dominant. The k_α and k_γ showed the same trend as k_{TToc}, and it was especially apparent for k_γ. It was thought that the decomposition speed of TToc content was mainly related to that of γ- and α-tocopherol. On the contrary, the decomposition speed of δ-tocopherol was opposite to that of TToc, that is, the TToc in the oil with a fast decomposition of δ-tocopherol showed the slow decomposition speed. In addition, $k_{18:3}$ and k_{TUFA} showed the same trend, indicating that the C18:3 content decomposition speed contributed greatly to the TUFA decomposition speed. While $k_{18:1}$ and k_{TUFA} showed opposite trend, it indicated that the TUFA decomposition speed in the oil with a fast decomposition of C18:1 was slow. In conclusion, the C18:3 content decomposition speed has a large contribution to decomposition of the TUFA content, and decomposition speed of the TToc content is mainly related to that of γ- and α-tocopherol contents.

As shown in Figure 3-4, OL and SF, which had the fastest TToc content decomposition speeds (Table 3-4) and the slowest TUFA decomposition speeds (Table 3-1), showed similar decomposition characteristics. It was strongly related to k_{α} and $k_{18:1}$. The decomposition characteristics of RS, RB, SB, and CO, namely, relatively fast TUFA content decomposition speeds and moderate TToc content decomposition speeds, were related to k_{α}, k_{γ}, $k_{18:1}$ and $k_{18:2}$. The SS and NS with very similar decomposition characteristics were negatively located along PC2. The decomposition characteristics were related to k_{γ}, $k_{18:1}$ and $k_{18:2}$. PL and NP had moderate TUFA content decomposition speeds and the slowest TToc content decomposition speeds, and were closely related to k_{δ} and $k_{18:3}$. Although PL and NP have quite different tocopherol compositions and contents, they had similar decomposition characteristics due to distribute in the same region of the figure, indicating that the unsaturated fatty acid and tocopherol content decompositions was more dependent on the fatty acid composition of the oil. In summary, the composition differences among the oils lead to different decomposition characteristics of unsaturated fatty acid and tocopherol.

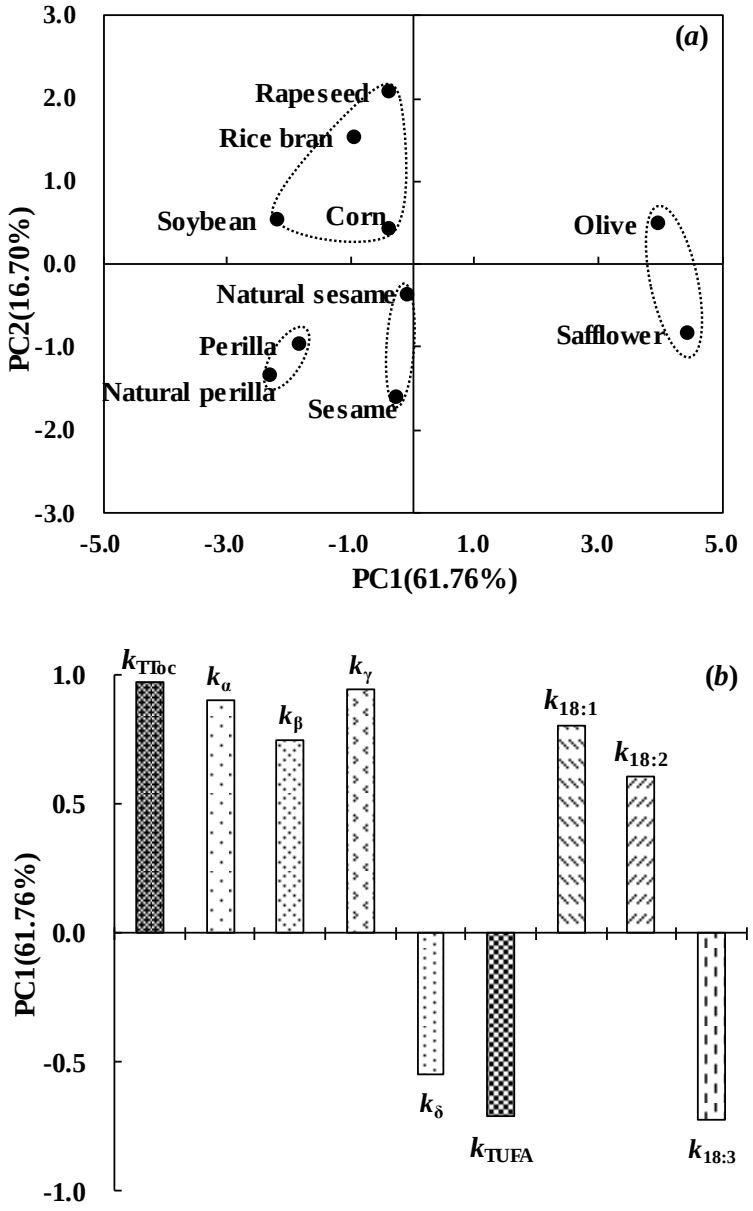

Figure 3-4 Principal component analysis of the slopes of unsaturated fatty acid and tocopherol decomposition rates during deep frying: (*a*) principal component scores; (*b*) factor loadings of PC1

The $k_{TToc,}$ k_{α}, k_{β}, k_{γ}, k_{δ}, k_{TUFA}, $k_{18:1}$, $k_{18:2}$, and $k_{18:3}$ indicate the slopes of fitting equations ($Y = k\ t$) of the decomposition rates of total tocopherol (TToc), α-, β-, γ-, δ-, total unsaturated fatty acid (TUFA), oleic acid, linoleic acid, and linolenic acid respectively, with heating time.

3.4.2.3 Dynamic decomposition characteristics of total unsaturated fatty acid and total tocopherol during deep frying

To investigate the specific decomposition characteristics of unsaturated fatty acids and tocopherols with different decomposition rates in frying cycles, a dynamic index (DI) was established as a ratio of the decomposition ratio of TUFA to that of TToc in each frying cycle using the following equations:

$$d(\mathrm{TUFA})_n = \frac{\mathrm{TUFA}_{n-1} - \mathrm{TUFA}_n}{\sum_{n=1}^{10}(\mathrm{TUFA}_{n-1} - \mathrm{TUFA}_n)} \times 100 \quad (3\text{-}5)$$

$$d(\mathrm{TToc})_n = \frac{\mathrm{TToc}_{n-1} - \mathrm{TToc}_n}{\sum_{n=1}^{10}(\mathrm{TToc}_{n-1} - \mathrm{TToc}_n)} \times 100 \quad (3\text{-}6)$$

$$\mathrm{DI}_n = \frac{d(\mathrm{TUFA})_n}{d(\mathrm{TToc})_n} \quad (3\text{-}7)$$

where *d*(TUFA) is the decomposition ratio of TUFA (%); *d*(TToc) is the decomposition ratio of TToc (%); and *n* is the number of frying cycles (*n* = 1 to 10, each cycle = 2.5 h). Therefore, results are classed as follows: DI_n < 1, the TToc decomposition ratio is larger than that of TUFA in the selected frying cycle, and tocopherol has strong antioxidant effect; DI_n = 1, the decomposition ratio of TToc is equal to that of TUFA in the frying cycle, and the antioxidant effect of tocopherol is equal to the decomposition of TUFA; and DI_n > 1, the decomposition ratio of TUFA is larger than that of TToc in the frying cycle, and tocopherol has weak antioxidant effect. The dynamic interaction between tocopherol and unsaturated fatty acids is finished when tocopherol is completely decomposed, and there is no need to further study the DI.

The oleic acid-rich OL and SF had very similar decomposition characteristics (Figure 3-5*a*). In the first three frying cycles, DI was less than 1 and the tocopherols (α-tocopherol dominant) had strong antioxidant effect at this stage. According to the TToc decomposition rate plot (Figure 3-3), the TToc content decreased rapidly from the beginning of deep frying up to 7.5 h, when it was almost completely decomposed. After the rapid decomposition of tocopherol, DI was greater

than one from the fourth frying cycle to the last frying cycle. It indicates that tocopherol has weak antioxidant effect that is not sufficient to compensate for the decomposition of TUFA at this stage.

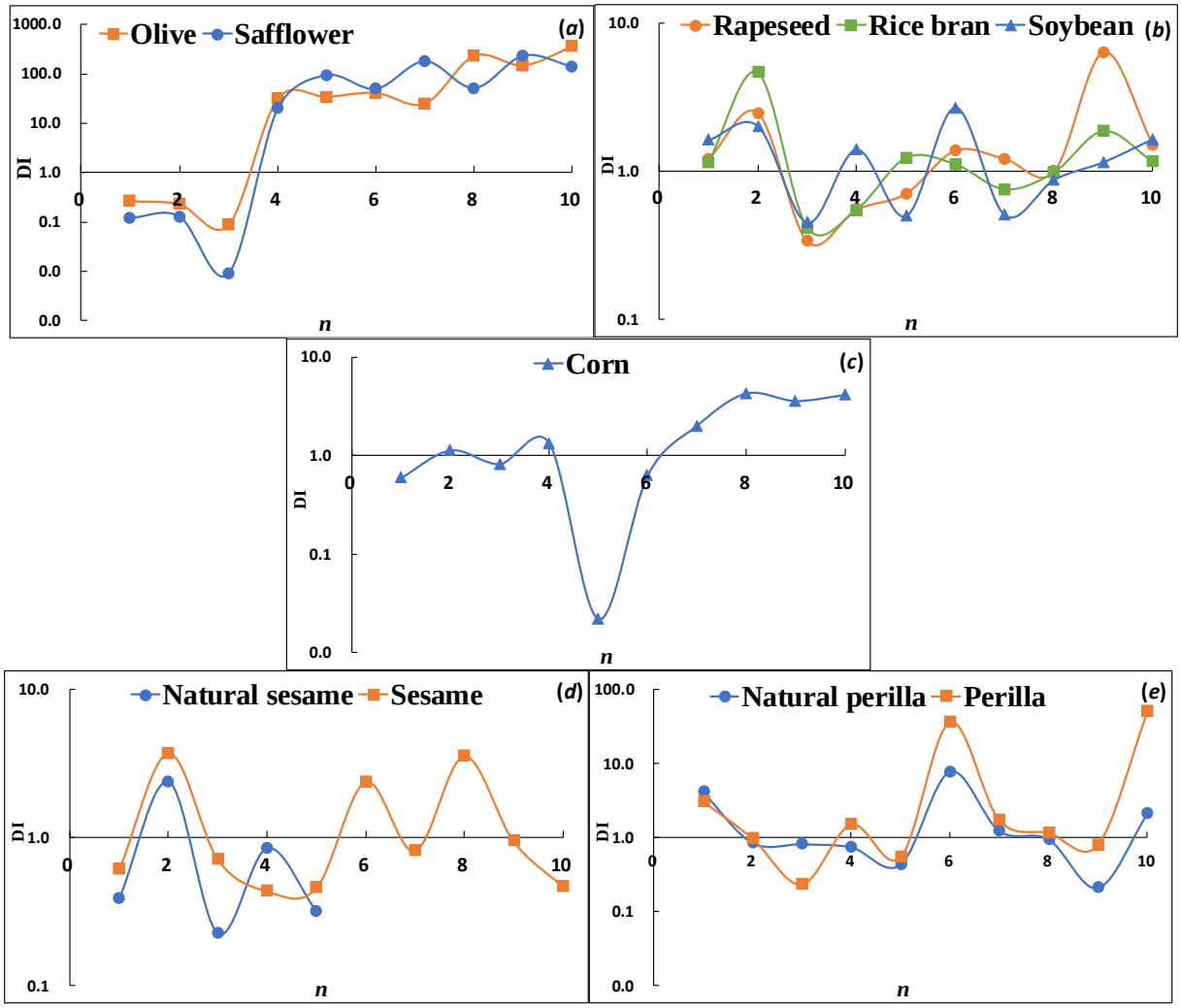

Figure 3-5 The dynamic index (DI) of oils during deep frying

n is the number of frying cycles. Each cycle is 2.5 hour, and *n* is from 1 to 10.

The oleic and linoleic acid-rich RS, RB, and SB contain all types of tocopherols and showed similar decomposition trends during the deep frying process, especially for the first cycle up to the fourth (Figure 3-5*b*). In the first two frying cycles, DI was greater than one, the antioxidant effect of tocopherol was weak, and TUFA decomposed rapidly. In the third frying cycle, tocopherol had strong antioxidant effect with DI less than one, which slowed the decomposition

of TUFA. In the fourth cycle, we observed differences in the decomposition trends of these three oils. In the fourth frying cycle, tocopherol had strong antioxidant effect in RS and RB but not in SB. The changes in the antioxidant effect of tocopherol in SB were very regular, with an alternating pattern of strong and weak antioxidant effect up to the final stage of frying. In subsequent frying cycles, tocopherol had weak antioxidant effect in RS and RB. Slightly stronger antioxidant effect was observed in the fifth and eighth cycles in RS and in the seventh and eighth cycles in RB, and TUFA continuously decomposed throughout the cycles.

Although CO, RB, RS, SB had the similar decomposition properties for unsaturated fatty acids and tocopherol (Figure 3-4*a*), the specific decomposition trend of corn oil was slightly different from that of the other oils (Figure 3-5*c*). In the first, third, fifth, and sixth frying cycles, DI < 1 indicated that tocopherol in CO had strong antioxidant effect. From the seventh cycle until the end of frying, DI > 1 indicated that tocopherol had weak antioxidant effect and TUFA continuously decomposed. The unique decomposition characteristics of corn oil may be related to its fatty acid composition. Among these oils, CO had the highest levels of linoleic acid (58.35%) and contained no C18:3.

A similar decomposition trend was observed for SS and NS (Figure 3-5*d*). In the first frying cycle, the antioxidant effect of tocopherol (γ-tocopherol) was strong with DI less than one. In the early stages of frying, the decomposition trend of NS was similar to that of SS. For NS, the tocopherol decomposed extremely rapidly from 5 h to 12.5 h (Figure 3-3), and tocopherol had strong antioxidant effect between the third and fifth frying cycles. By the sixth frying cycle, tocopherol was completely decomposed and the dynamic interaction between tocopherol and unsaturated fatty acids was finished. This makes the decomposition characteristics of NS unique. Tocopherol in SS had weak antioxidant effect (DI > 1) only in the second, sixth, and eighth cycles. In the other cycles, tocopherol had strong antioxidant effect and TUFA decomposed slowly. For the PUFA-rich oils, SS with the slowest decomposition speed of TUFA (Table 3-1) could be explained by the strong antioxidant effect of tocopherol in the deep frying process and

sesamol produced during refining process. Some researchers have found that sesame oil has high oxidative stability because of the production of large quantities of sesamol rather than the initial γ-tocopherol content (Fukuda et al. 1986; Lee et al. 2010).

The PL and NP, which were linolenic acid-rich, showed similar decomposition trends (Figure 3-5*e*), which again indicated that the decomposition characteristics of commercial edible oils are mainly determined by their fatty acid compositions. Tocopherol in NP showed strong antioxidant effect (DI < 1) in the second, third, fourth, fifth, eighth, and ninth frying cycles because of its high initial TToc content and high content of δ-tocopherol. The decomposition speed of TUFA in NP was faster than that of PL as the k_{TUFA} of NP was larger than that of PL (Table 3-1), even if the initial tocopherol content of NP was three times that of PL. It indicates that PL, which had undergone high temperature processing, has greatly improved thermal oxidation stability compared with NP. Other studies have shown that the oxidation stability of perilla oil extracted from roasted seeds is better than that of natural perilla oil during storage at 50 °C (Kim et al. 1996) and 60 °C (Zhao et al. 2012).

3.4.3 Decomposition of tocopherol homologs and their effects on the decomposition of unsaturated fatty acid

3.4.3.1 Relationship between total tocopherol and total unsaturated fatty acid decomposition during deep frying

The relationship between the decomposition rate of the TToc contents and that of the TUFA contents during frying is shown in Figure 3-6. At the beginning of frying protocol, the TToc content in SF, OL, and NS, which contained a lot of oleic acid, decomposed rapidly, while the TUFA content decomposed very slowly compared with the TToc content. At the end of the frying, TToc was completely decomposed in these three oils. For CO, SS, RS, and RB, mainly comprising oleic acid and linoleic acid, TToc and TUFA were decomposed steadily during

frying. At the end of frying, TToc was almost completely decomposed in these four oils. TToc in PL, SB, and NP, in which PUFAs were dominant, decomposed slowly compared with other oils during frying, while TUFA decomposed faster than other oils. At the end of frying, TToc was present in surplus.

At the end of frying (25 h), in terms of TUFA, it was the most decomposed in SB, with a decomposition value of 6.97%. However, TToc was almost completely decomposed in many oils, and even the least decomposed oil, NP, had a value of 39.34%. Accordingly, the TToc decomposition was more rapid than TUFA decomposition in every oil characterized by frying, indicating that the tocopherols played a role in slowing the decomposition of unsaturated fatty acids.

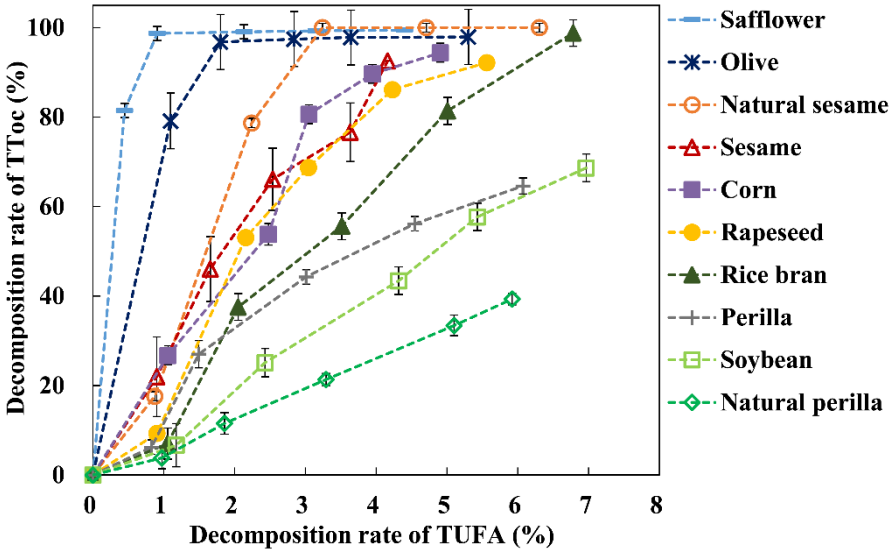

Figure 3-6 Relationship between the decomposition rate of the total tocopherol (TToc) contents and that of the total unsaturated fatty acid (TUFA) contents during deep frying

3.4.3.2 Decomposition rate of the tocopherol homologs

Based on the results above, the decomposition speed of TToc and TUFA during frying was linked to the initial unsaturated fatty acids composition in the oils. Therefore, the oils were grouped according to the initial fatty acid composition to obtain plots and determine the decomposition rate of every tocopherol homolog. Three tocopherol homologs that are major

tocopherols in oils, namely, α-, γ-, and δ-tocopherol, were investigated. The decomposition rate of tocopherol homologs contents of the 10 oils differed greatly during frying process depending on the type of tocopherol and oil.

Figure 3-7*A* shows the relationship between decomposition rate of three tocopherol homologs contents and that of TUFA in oleic-acid-rich oils (OL, SF, and RS) during frying. In SF and OL, γ-tocopherol and α-tocopherol had almost the same decomposition rate during frying. In RS, γ-tocopherol had a greater decomposition rate compared with that of α-tocopherol. As δ-tocopherol was also detected in RS, the decomposition rate of tocopherol homologues in RS was γ > α > δ. The same result was observed in high oleic sunflower oil with a linoleic acid content of 9.5% (Aladedunye and Przybylski, 2013).

For the RB, the relationship between decomposition rate of tocopherols contents and that of TUFA is shown in Figure 3-7*B*. The decomposition rate of tocopherol homologs in RB was γ > α > δ. In SS and NS (Figure 3-7*C*), only γ-tocopherol was detected and was shown to rapidly decompose. The relationship between the decomposition rate of tocopherol homologs contents and that of TUFA in CO and SB is shown in Figure 3-7*D*. At the end of the frying process, the tocopherol decomposition rate remained in the order of γ > α > δ. Unlike CO or other oils, which had similar decomposition rates between α and γ, SB showed similar decomposition rates between α and δ. For NP (Figure 3-7*E*) and PL (Figure 3-7*F*), the same order of tocopherol decomposition rate was observed. It indicated that the decomposition of tocopherol homologs during frying was consistent with this order, γ > α > δ, for all edible oils here, regardless of the initial tocopherol and fatty acid contents and compositions.

Furthermore, the residual TUFA contents were not very different after 25 h of heating, but the remaining tocopherol contents varied greatly among the oils. For oils with a high oleic acid content (Figure 3-7*A*), such as SF and OL, the tocopherols had almost completely decomposed. For RS, in which the TUFA content was the highest, the residual tocopherol content was less

than 40% relative to the initial content. For RB, SS, and NS (Figure 3-7*B*, *C*), with similar oleic acid and linoleic acid contents, the remaining tocopherol content was less than 20% of the initial content. In linoleic-acid-rich oils (Figure 3-7*D*), the residual tocopherol content was below 60%, which was more than those of oils containing high oleic acid contents. Oils with large linolenic acid contents (Figure 3-7*E*, *F*) had significantly higher residual tocopherol contents than other oils. After 25 h of heating, a large amount of tocopherol remained, especially δ-tocopherol in NP, with a relative content of 69.30%. Therefore, a higher degree of oil unsaturation resulted in a higher relative residual tocopherol content, with less tocopherol decomposed during frying. This result agreed with previous reports (Barrera-Arellano et al., 2002; Normand et al., 2001; Kajimoto et al., 1991; Yuki and Ishikawa, 1976), which showed that the TToc residue content in oils with high unsaturation was more than that in oils with low unsaturation.

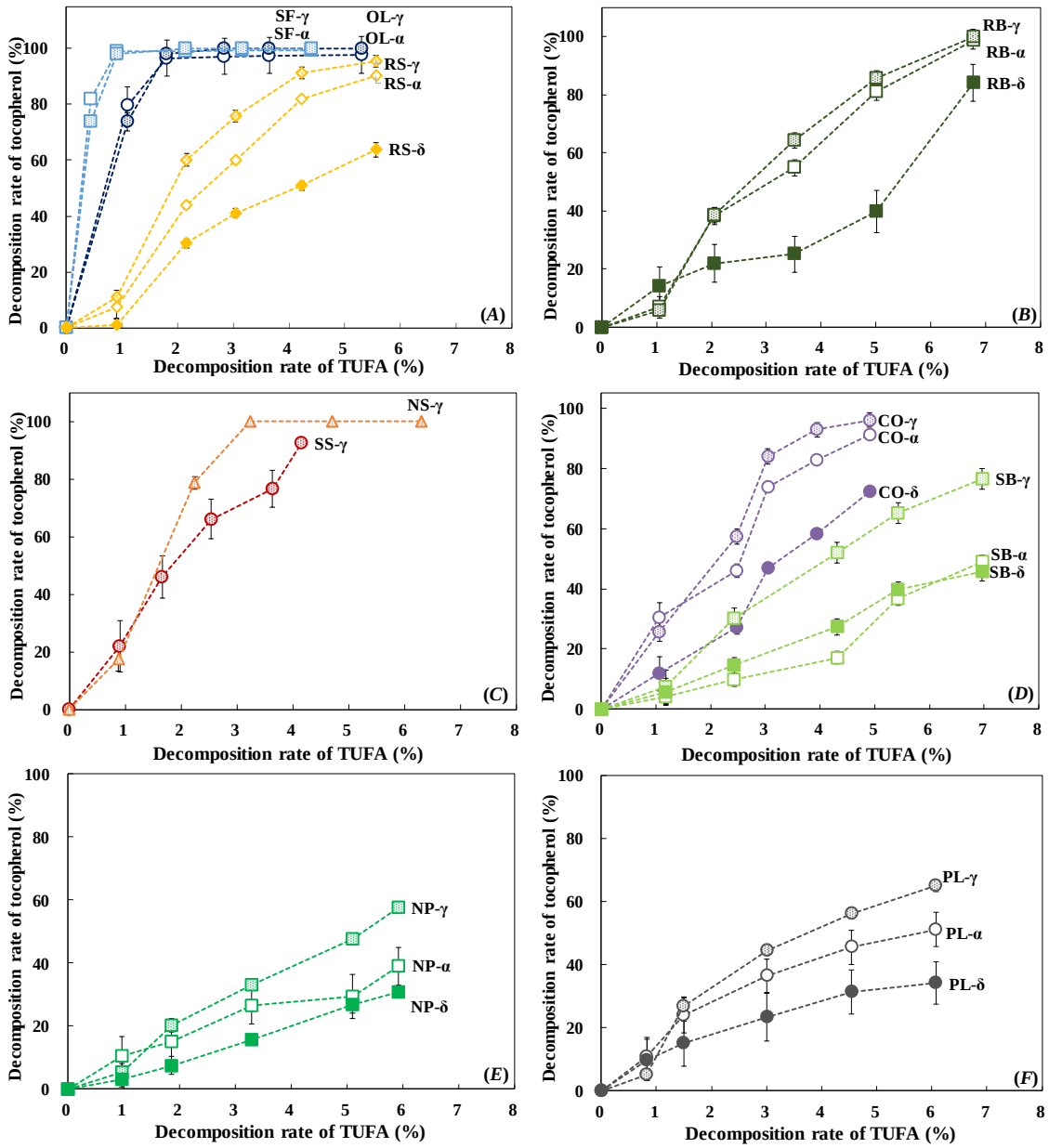

Figure 3-7 Relationship between decomposition rate of tocopherol homologs contents and that of total unsaturated fatty acid (TUFA) contents during frying: (*A*) OL: olive, SF: safflower, RS: rapeseed oils; (*B*) RB: rice bran oil; (*C*) SS: sesame, NS: natural sesame oils; (*D*) CO: corn, SB: soybean oils; (*E*) NP: natural perilla oil; and (*F*) PL: perilla oil

3.4.3.3 Effect of tocopherol homologs on decomposition of unsaturated fatty acid

Multiple regression analysis is usually used to relate the value of a continuous dependent variable to the values of several independent variables (Andreu-Sevilla et al., 2008). Here it was carried out to explore the effects of three tocopherol homologs on decomposition of TUFA. As

shown in Table 3-5, this regression analysis had statistical significance ($P < 0.001$). All independent variables, $\Delta\alpha_t$, $\Delta\gamma_t$, and $\Delta\delta_t$, had significant effects on the decomposition of TUFA ($P < 0.05$). The determination coefficient of the regression analysis was 0.620, which means that 62.0% of the variance of $\Delta TUFA_t$ was explained by these three tocopherol homologs. The adjusted determination coefficient was 0.599. By comparing the standardized regression coefficients, it can be seen that the coefficient of $\Delta\gamma_t$ (0.611) was much larger than coefficients of $\Delta\alpha_t$ (0.359) and $\Delta\delta_t$ (0.257), which means the decomposition of γ-tocopherol had the greatest influence on the decomposition of TUFA for all oils during frying. The coefficient of $\Delta\alpha_t$ was close to that of $\Delta\delta_t$ but greater than the latter, which indicated that the effect of α-tocopherol was slightly larger than δ-tocopherol on the decomposition of TUFA. As a result, γ-tocopherol had the greatest impact, followed by α-tocopherol, and δ-tocopherol had the smallest impact on the decomposition of TUFA for all oils during frying.

The multiple linear regression model, $\Delta TUFA_t = 0.049\ \Delta\alpha_t + 0.044\ \Delta\gamma_t + 0.052\ \Delta\delta_t + 0.733$, was generated from the coefficients in Table 3-5. This model may be used to predict the value of one of the variables when other variables are known, that is, to roughly predict the decomposition of TUFA or tocopherol homologs in any oil during frying. From this model, if α-tocopherol decomposes 1 mg/100 g, TUFA will decompose 0.049% accordingly. Similarly, if γ- and δ-tocopherol decompose 1 mg/100 g respectively, TUFA will decompose 0.044% and 0.052% respectively.

The decomposition of TUFA during frying may indirectly reflect the antioxidant capacity of tocopherols. TUFA decreases slowly during frying, indicating that the stability of the oil is good, namely, the antioxidant capacity of tocopherol contained in the oil is strong. From this point, γ-tocopherol had the strongest antioxidant capacity, followed by α-tocopherol, and δ-tocopherol had the weakest antioxidant capacity among them.

The effect of tocopherol homologs on decomposition of TUFA from large to small was γ > α > δ for all oils here, which was completely consistent with the order of decomposition rate of tocopherol homologs. Among three tocopherol homologs, γ-tocopherol had the largest decomposition rate relative to its initial content and played the greatest role in the decomposition of TUFA. Therefore, γ-tocopherol probably had the strongest antioxidant capacity, which needs further verification.

Table 3-5 Multiple linear regression analysis of the effects of tocopherol homologs on the decomposition of total unsaturated fatty acid (TUFA)

Multiple linear regression equation	Variable	Unstandardized coefficient	Standard error	Standardized coefficient	*P*
	Constant	0.733	0.231		0.002
$\Delta TUFA_t = B_1 \Delta\alpha_t + B_2 \Delta\gamma_t + B_3$	$\Delta\alpha_t$	0.049	0.011	0.359	<0.001
$\Delta\delta_t + B_0$	$\Delta\gamma_t$	0.044	0.006	0.611	<0.001
	$\Delta\delta_t$	0.052	0.017	0.257	0.004

F (3, 56) = 30.392, P < 0.001, R^2=0.620, adjusted R^2=0.599.

In the multiple linear regression equation, $\Delta TUFA_t$ is the dependent variable showing the decomposition of TUFA of all oils with heating time (%); B_1, B_2, B_3, and B_0 are coefficient constants; $\Delta\alpha_t$, $\Delta\gamma_t$, and $\Delta\delta_t$ are independent variables showing the decomposition of α-, γ-, and δ-tocopherol of all oils with heating time, respectively (mg/100 g); and t refers to the heating time (0, 5, 10, 15, 20, 25 h).

3.5 Conclusions

In this work, 10 commercial edible oils were investigated the changes in composition characteristics of unsaturated fatty acids and tocopherols during frying. TUFA and TToc showed a linear decrease during the frying process. The influence of PUFA on the decomposition of TUFA was most noticeable in the oils during frying. The ratio of palmitic acid to oleic acid before deep frying can be used as a predictive index for predicting the decomposition rate of TUFA. The Equation (3-3) can be used to determine the decomposition rate of TUFA in a variety of unsaturated fatty acid-based oils. The result provides a very convenient and quick evaluation index for predicting the decomposition rate of unsaturated fatty acid-based oils. However, only studying changes in fatty acid composition is limited, the thermal degradation of oil is a complex process accompanying with changes of many indicators. Future work is to combine with other evaluation indicators to comprehensively predict thermal degradation of frying oils.

During the deep frying process, decomposition of tocopherols and unsaturated fatty acids exhibited a dynamic trend with alternating fast and slow decomposition. This resulted in different commercial edible oils having different decomposition characteristics. The tocopherol composition affected this process, but it was mainly affected by the fatty acid composition.

The decomposition rates of tocopherol homologs in oils with different composition characteristics were in agreement with the conclusion that γ-tocopherol had the largest decomposition rate, followed by α-tocopherol, while δ-tocopherol was the lowest. Furthermore, after 25 h of heating, TToc almost completely decomposed due to its fast decomposition in oils dominated by oleic acid, while it decomposed slowly in oils rich in PUFA, and still had a large surplus. The effect of γ-tocopherol on decomposition of TUFA was the greatest, followed by α-tocopherol, and that of δ-tocopherol was the smallest for all oils during frying. Tocopherol homologs exhibited a completely consistent mechanism during frying among the ten oils with very different composition, which could provide theoretical support for a better understanding the mechanism of tocopherol homologs acting in different oils under real frying conditions.

3.6 Reference

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Chapter 4 The quality change of oils during frying

4.1 Abstract

To determine the quality changes of oil during frying and construct predictive models for the deterioration indices of oil, the changes in the carbonyl value (CV) and total polar compounds (TPC) of 10 commercial edible oils during frying at 180 °C were investigated. During frying, the CV and TPC of 10 oils increased linearly with heating time at different speeds. The effects of intrinsic factors (unsaturated fatty acids and tocopherols) on the CV and TPC increase were revealed by using multiple regression analysis. The results indicated that polyunsaturated fatty acid (PUFA) and γ-tocopherol had the greatest effects on the CV and TPC increases. Based on these results, the ratio of the initial content of PUFA to that of total tocopherol (TToc) was selected as a predictive index and a prediction model, $CV_t = \left[4.37\left(\frac{PUFA}{TToc}\right)^2 - 5.64\left(\frac{PUFA}{TToc}\right) + 3.36\right]t + CV_0$, was established. Similarly, the initial content ratio of linoleic acid to palmitic acid was selected as a predictive index, and then a predictive model, $TPC_t = \left[0.024\left(\frac{\mathrm{C18:2}}{\mathrm{C16:0}}\right)^2 - 0.065\left(\frac{\mathrm{C18:2}}{\mathrm{C16:0}}\right) + 0.819\right]t + TPC_0$, was established. Using these models, the CV and TPC of edible oil during frying at 180 °C can be predicted from the initial composition of the oil. On the other hand, the frying life of edible oil can be inferred by using two models simultaneously according to the maximum allowable CV (50 μmol/g) and TPC (24%) stipulated by regulations.

4.2 Introduction

Deep frying is a common and popular food processing method. With the popularity of fried foods around the world, the quality and safety of fried food has received widespread attention (Gadiraju et al., 2015; Nguyen et al., 2017). The quality of fried food depends heavily on the quality of the frying oil because the original fats in the food are almost completely replaced by frying oil (Gertz et al., 2017). Accordingly, the quality of fried food can be controlled and optimized by controlling the quality of frying oil.

During repeated high-temperature frying, oil is in contact with oxygen in the air and water from the food, and chemical reactions such as oxidation, hydrolysis, and polymerization occur continuously (Karimi et al., 2017; Nayak et al., 2016). With the continuous occurrence of complex chemical reactions, oil is constantly deteriorated, and some harmful substances in oil are constantly generated and accumulated (Vorria et al., 2004). These substances can be absorbed by the fried food and could endanger human health (Aladedunye and Przybylski, 2009). Therefore, it is particularly important to evaluate the deterioration of frying oil in detail to ensure the safety of fried food.

The carbonyl value (CV) reflects the total amount of carbonyl compounds in the secondary oxidation products produced during oil deterioration, which seems to be a good chemical index for evaluating deterioration of frying oil (Farhoosh and Tavassoli-Kafrani, 2011). The determination of the CV is very important because carbonyl compounds lead to rancidity, produce unpleasant odors, and reduce the nutritional value of the fried food (Endo et al., 2001). In previous studies on the CV (Farhoosh and Moosavi, 2007; Farhoosh and Moosavi, 2008; Totani et al., 2006; Farhoosh et al., 2012), it was used as an index to monitor the deterioration of frying oil in time-consuming frying experiments, which use large quantities of ingredients and are costly. Moreover, the CV analysis of the sample during frying also requires a lot of manpower and time.

Total polar compounds (TPC) are all polar compounds other than oils (triacylglycerols), which indicate all degradation products during oil oxidation such as peroxides, their decomposition

products, polymers, and free fatty acids. In most cases, the determination of TPC is the most credible indicator of deterioration of frying oil (Houhoula et al., 2002; Li et al., 2017). Therefore, TPC is widely used as an indicator for evaluating the deterioration of frying oil in various countries. Regarding the usage limit of TPC, many countries have also made corresponding regulations (Firestone, 2007; Hosseini et al., 2016). Following these regulations, many scholars have done a lot of research using a complex standard measurement method to determine TPC to evaluate the degradation degree of the frying oil (Houhoula et al., 2003; Takeoka et al., 1997; Houhoula et al., 2002; Warner and Gupta, 2005). Recently, there have also been rapid assay instruments and methods developed to quickly and easily determine the degradation degree of oil in the frying process (Karakaya and Şimşek, 2011; Chen et al., 2013; Gil et al., 2004; Li et al., 2016). Even so, the conclusions obtained only explain the deterioration degree of the frying oil, and the time-consuming frying operation must be carried out.

The objective of this study was to determine the quality changes of oil during frying and establish models for predicting changes in the CV and TPC during frying without the requirement for deep frying experiments. Ten commercial edible oils were used to fry French fries at 180 °C. Changes in the CV and TPC of the 10 oils with heating time were monitored during frying. Multiple regression analysis was used to reveal the effects of main intrinsic factors of the oils on CV and TPC changes during frying. By analyzing the relationship between the initial compositions of the edible oils and the CV and TPC changes, two prediction models were established that could be used to infer the CV and TPC during frying at 180 °C from the initial composition of any edible oil, respectively. In this way, the deterioration of edible oil during frying can be evaluated simply and quickly without frying operation. Simultaneously, the frying life of edible oil can be inferred according to the maximum allowable CV and TPC stipulated by regulations.

4.3 Materials and methods

4.3.1 Materials and reagents

4.3.1.1 Preparation of deep-frying oil samples

Frying oil samples used were the same as that samples in 3.3.1.1 in Chapter 3.

4.3.1.2 Reagents and standards

Potassium hydroxide, 2,4-DNPH, 1-BuOH, and *trans*-2-decenal standard were purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). Hydrochloric acid was purchased from Kanto Chemical Company Limited (Tokyo, Japan).

4.3.2 Analytical methods

4.3.2.1 Determination of carbonyl value

The method for determination of carbonyl value of frying oil was the same as that mentioned in 2.3.2.3 Determination of carbonyl value in Chapter 2.

4.3.2.2 Determination of total polar compounds

A fast measuring instrument was used to analyze the total polar compounds content in frying oil in real time. The analysis for total polar compounds of frying oils was the same as that mentioned in 2.3.2.4 Determination of total polar compounds in Chapter 2.

4.3.3 Statistical analysis

Each oil sample was analyzed in triplicate. Data are presented as means ± standard deviations. Linear regression analysis was carried out using Microsoft Excel 2016. Multiple linear regression analysis was conducted using SPSS 17.0.

4.4 Results and discussion

4.4.1 Changes trend, influencing factors, and establishment of the predictive model for carbonyl value during frying

4.4.1.1 Changes in carbonyl value during deep frying

The CV of the 10 oils after heating for 25 h (CV_{25}) was shown in Table 4-1. The CV_{25} range was 43.99–59.28 μmol/g, and compared with the CV_0 results, this range indicated that the content of carbonyl compounds increased dramatically during frying. According to food safety requirements stipulated by the Japanese Agricultural Standard, the maximum CV allowable in frying oil is 50 μmol/g (Hara et al., 2006). The CV_{25} results of NS, NP, RS, CO, and SB exceeded this limit. Conversely, the CV_{25} results of SS, PL, OL, SF, and RB did not reach this limit. This was considered to be related to the CV_0 as well as the initial fatty acid and tocopherol compositions. The CV_{25} results of natural pressed oils exceeded those of roasted oils, which was the opposite trend to that observed for the oils in their initial state (i.e., the CV_0).

Table 4-1 Changes in the carbonyl value (CV) during deep frying

Oil name	CV_0 (μmol/g)	CV_{25} (μmol/g)	ΔCV_{25} (μmol/g)
Natural sesame	2.36±0.11	57.46±0.72	55.10
Natural perilla	2.46±0.17	52.67±3.47	50.21
Sesame	3.02±0.24	45.39±3.88	42.37
Perilla	3.12±0.11	46.68±0.94	43.56
Olive	3.41±0.21	48.72±1.62	45.31
Rapeseed	4.32±0.29	59.28±1.47	54.96
Corn	4.48±0.40	52.34±1.72	47.86
Safflower	4.67±0.32	43.99±3.76	39.32
Rice bran	5.92±0.38	45.77±3.13	39.85
Soybean	6.30±0.13	54.67±2.82	48.37

CV_0, initial CV before heating; CV_{25}, CV after heating for 25 h; and ΔCV_{25}, the change in CV during 25 h of heating

The frying process caused substantial increases in the CV (ΔCV_{25}) for these oils (Table 4-1). NS had the largest ΔCV_{25} and NP also had a high ΔCV_{25}. These results indicate that natural pressed oils have low carbonyl compound contents before frying, and are easily oxidized to produce carbonyl compounds once heated. By contrast, SF and RB had the lowest ΔCV_{25} results among the oils, although they had high CV_0 results. The CV of all oils increased almost linearly with the heating time during frying (Figure 4-1).

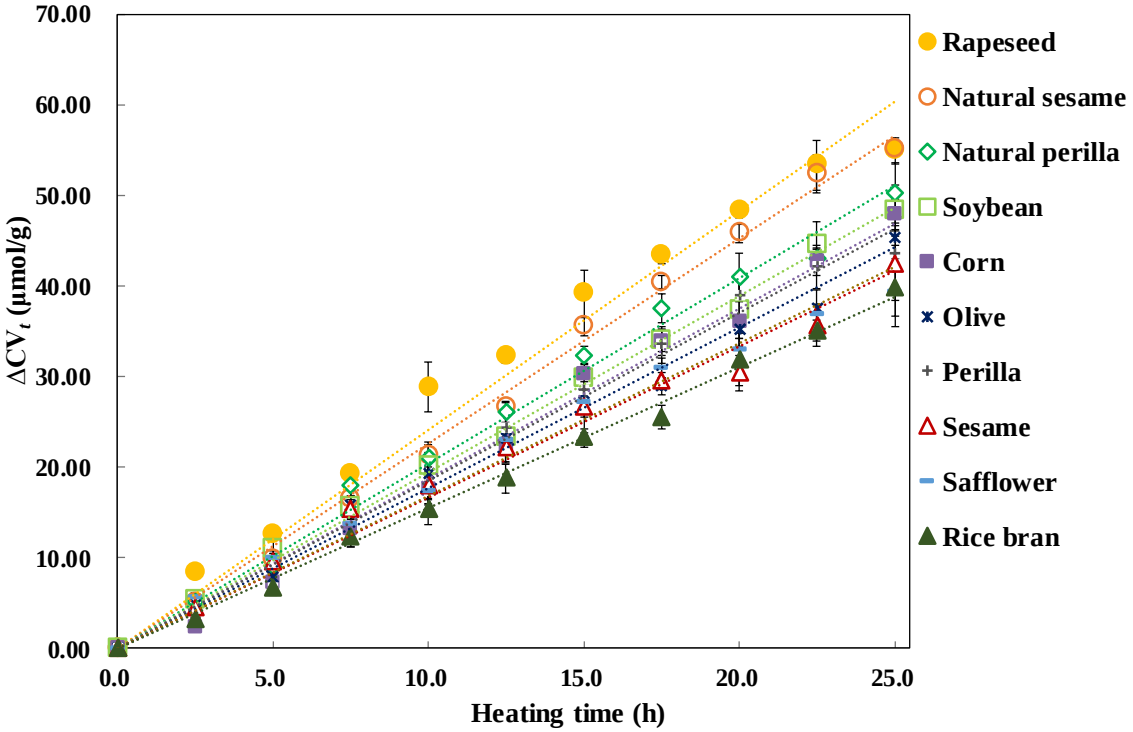

Figure 4-1 Increases in the carbonyl value with heating time (ΔCV_t)

The increases in CV with the heating time (ΔCV_t) could be fitted using the follow equation:

$$\Delta CV_t = CV_t - CV_0 = k_{CV}t \quad (4\text{-}1)$$

where k_{CV} is the slope of the fitting equation for the increase in CV over heating time, and indicates the increasing speed of the CV. A large k_{CV} means that the CV increases at a fast speed. The CV of the 10 oils increased at considerably different speeds during frying (Table 4-2). Among the oils, the CV of RS increased at the fastest speed (k_{CV} = 2.415). This was followed by the natural pressed oils. In terms of the CV, RS reached the maximum allowable limit for frying oil (50 μmol/g)

sooner than the other oils under the present experimental conditions. Therefore, among these oils, RS is the least suitable for frying. RB had the slowest increase in the CV and the smallest k_{CV} (1.554). The k_{CV} of RS was 1.55 times that of RB. This showed an obvious difference among the oils in the increase speeds of the CV. It was also found from Table 4-2 that the increases in the CVs in PUFA-rich oils were higher than those in MUFA-rich oils, except for RS, which had the highest TUFA content. These results are consistent with earlier studies that found the CV increased rapidly in highly unsaturated oils during frying (Shyu et al., 1998; Aladedunye and Przybylski, 2013). This may be because of the large number of double bonds in unsaturated fatty acids, which could increase the formation rates and amounts of the degradation products at the end of the induction period (Martín-Polvillo et al., 2004; Choe and Min, 2006).

Table 4-2 Fitting results for the change in the carbonyl value (ΔCV) with heating time (t) according to the equation $\Delta CV_t = k_{CV}\, t$

Oil name	The slope of fitting equation (k_{CV})	Determination coefficient (R^2)
Rapeseed oil	2.415	0.979
Natural sesame oil	2.263	0.996
Natural perilla oil	2.041	0.991
Soybean oil	1.944	0.997
Corn oil	1.877	0.991
Perilla oil	1.854	0.990
Olive oil	1.770	0.989
Safflower oil	1.683	0.986
Sesame oil	1.669	0.984
Rice bran oil	1.554	0.996

4.4.1.2 The main intrinsic factors affecting the carbonyl value during frying

The unsaturated fatty acid composition greatly affects oil quality (Zambiazi et al., 2007), which is the source of oil deterioration during frying. The CV is a measure of secondary oxidation products of oil deterioration. Therefore, it is necessary to explore the relationship between increases in the

CV and decreases in the content of unsaturated fatty acids during frying. Tocopherols, which have antioxidant effects, can affect the formation rate of secondary oxidation products (i.e., carbonyl compounds) to a certain extent. Moreover, unsaturated fatty acids and tocopherol showed simultaneous dynamic decomposition in the frying process (Liu et al., 2019). Therefore, the effect of the changes in tocopherol on the increase in the CV was also explored.

Table 4-3 Multiple linear regression analysis results between the change in the CV and the decrease in unsaturated fatty acid and tocopherol contents with heating time

Multiple linear regression equation	Variable	Unstandardized coefficient	Standard error	Standardized coefficient	*P*	
(i) $\Delta CV_t = b_0 + b_1 \Delta TUFA_t + b_2 \Delta TToc_t$	Constant	2.868	0.757		<0.001	R^2 =0.915
	$\Delta TUFA_t$	-7.550	0.414	-0.811	<0.001	adjust R^2 = 0.914
	$\Delta TToc_t$	-0.095	0.024	-0.179	<0.001	$P < 0.001$
(ii) $\Delta CV_t = b_3 + b_4 \Delta MUFA_t + b_5 \Delta PUFA_t + b_6 \Delta\alpha_t + b_7 \Delta\gamma_t + b_8 \Delta\delta_t$	Constant	2.424	0.756		0.002	
	$\Delta MUFA_t$	-8.601	0.647	-1.003	<0.001	R^2 =0.922
	$\Delta PUFA_t$	-7.726	0.411	-1.564	<0.001	adjust R^2 = 0.918
	$\Delta\alpha_t$	-0.124	0.038	-0.105	0.001	
	$\Delta\gamma_t$	-0.145	0.032	-0.223	<0.001	$P < 0.001$
	$\Delta\delta_t$	-0.043	0.058	-0.024	0.46	

ΔCV_t is a dependent variable that shows the increase in the CV of all oils with heating time (μmol/g); b_0–b_8 are coefficient constants; $\Delta TUFA_t$, $\Delta MUFA_t$, and $\Delta PUFA_t$ are independent variables that show the changes in TUFA, MUFA, and PUFA contents with heating time, respectively (%); $\Delta TToc_t$, $\Delta\alpha_t$, $\Delta\gamma_t$, and $\Delta\delta_t$ are independent variables that show the decreases in TToc, α-, γ-, and δ-tocopherol contents with heating time, respectively (mg/100 g); and t is the heating time (0–25 h).

Multiple linear regression analysis was carried out between the increase in the CV and the decrease in TUFA and TToc contents with heating time to simultaneously evaluate the effects of TUFA and TToc on the increase in the CV. The results of multiple linear regression with equation (i), as shown in Table 4-3, indicated that both TUFA and TToc had significant effects on the CV increase ($P < 0.001$). The coefficient of determination indicated that 91.5% of the variance of the

CV increase was explained by simultaneous decreases in TUFA and TToc contents throughout the heating process. To compare the effects of these different independent variables (i.e., $\Delta TUFA_t$ and $\Delta TToc_t$) on the dependent variable (ΔCV_t), the standardized coefficients were compared. It was found that TUFA had a large effect on the CV increase as it had a large coefficient of −0.811. By comparison, the effect of TToc was relatively small as it had a small coefficient (−0.179). Accordingly, the following multiple linear regression model was obtained:

$$\Delta CV_t = 2.868 - 7.550\Delta TUFA_t - 0.095\Delta TToc_t \quad (4\text{-}2)$$

where ΔCV_t (μmol/g) is the increase in the CV of the oil with heating time during frying; $\Delta TUFA_t$ (%) and $\Delta TToc_t$ (mg/100 g) are the decreases in the TUFA and TToc contents of the oils with heating time, respectively; and t is heating time (h). From this model, if the TUFA content decreases by 1% during frying, the CV will increase by 7.550 μmol/g. Similarly, if the TToc content decreases by 1 mg/100 g during frying, the CV will increase by 0.095 μmol/g.

The TUFA content in an oil is composed of MUFA and PUFA, and the TToc content consists of different tocopherol homologs. Taking the decrease in unsaturated fatty acids and tocopherol homologs contents as independent variables and the increase in the CV as the dependent variable, multiple regression analysis was conducted to explore the effects of specific oil compositions on the increase in the CV. Fitting results (Table 4-3) were obtained by multiple linear regression with equation (ii). The following model was obtained:

$$\Delta CV_t = 2.424 - 8.601\Delta MUFA_t - 7.726\Delta PUFA_t - 0.124\Delta\alpha_t - 0.145\Delta\gamma_t - 0.043\Delta\delta_t \quad (4\text{-}3)$$

where ΔCV_t is the increase in the CV of the oil with heating time (μmol/g); $\Delta MUFA_t$ and $\Delta PUFA_t$ are changes in the MUFA and PUFA contents with heating time, respectively (%); $\Delta\alpha_t$, $\Delta\gamma_t$, and $\Delta\delta_t$ are decreases in the α-, γ-, and δ-tocopherol contents of the oils with heating time, respectively (mg/100 g); and t is the heating time (h). The determination coefficient of the regression analysis was 0.922, which means that 92.2% of the variance of ΔCV_t was explained by the model, and the adjusted determination coefficient was 0.918, indicating that there was a linear correlation between

the increase in the CV and the change in oil composition during frying. A comparison of the standardized coefficients showed that the effect of PUFA on the increase of CV with heating time (−1.564) was greater than that of MUFA (−1.003). Meanwhile, the impact of γ-tocopherol (−0.223) on the increase of CV was greater than that α-tocopherol (−0.105), and both of these compounds had a greater impact than δ-tocopherol (−0.024). Excluding δ-tocopherol, the independent variables (i.e., MUFA, PUFA, α-, and γ-tocopherol) had significant effects on the CV increase during frying. Therefore, in terms of the effect on the CV increase during frying, the effects of unsaturated fatty acids were greater than those of tocopherols. Among these compounds, PUFA had a greater influence than MUFA. The order of influence of tocopherol homologs on the increase in the CV in the oil during frying from largest to smallest was γ-, α-, and δ-tocopherol.

4.4.1.3 Establishment of a prediction model for the carbonyl value

The CV is an important index to characterize the deterioration of frying oil and to judge whether frying oil can be reused or should be replaced. It would be very useful if increases in the CV during the frying process could be predicted and the deterioration of frying oil could be accurately judged according to the composition of the oil. Because both unsaturated fatty acids and tocopherols affect the formation of carbonyl compounds, a predictor that combines both unsaturated fatty acid and tocopherol should be accurate. Together with the major effects of PUFA and γ-tocopherol on CV changes during frying, combination of the initial PUFA and initial γ-tocopherol contents was considered to establish a predictive indicator. However, the initial contents of γ-tocopherol in olive oil and safflower oil were too low, which greatly affected the prediction results. Considering the large differences among the contents of tocopherol homologs in the initial oils, it was best to consider all tocopherol homologs together and use TToc. After establishing and comparing various predictive indices, the initial content ratio of PUFA/TToc was selected as the most appropriate index with the highest correlation coefficient (r = 0.817) with the speed of increase of the CV (k_{CV}). The relationship between PUFA/TToc and k_{CV} of each

oil was roughly quadratic, as shown in Figure 4-2, and the following equation was obtained after fitting:

$$k_{CV} = 4.37\left(\frac{PUFA}{TToc}\right)^2 - 5.64\left(\frac{PUFA}{TToc}\right) + 3.36 \quad (4\text{-}4)$$

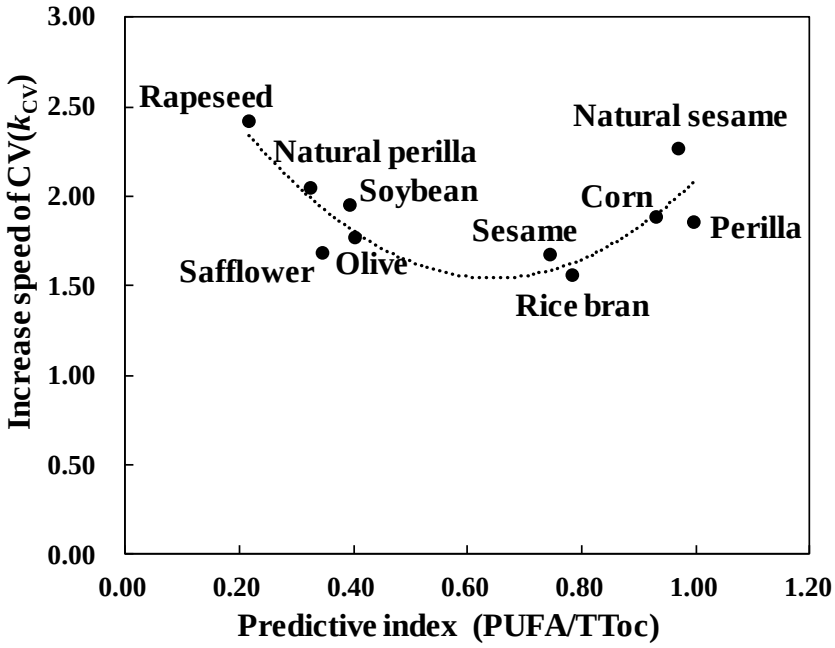

Figure 4-2 The relationship between the predictive index (PUFA/TToc) and the increase speed of the carbonyl value (k_{CV})

PUFA/TToc is the initial content ratio of polyunsaturated fatty acid to total tocopherol of the oil.

According to Equation (4-4), k_{CV} can be approximated from the initial composition of the oil. Combined with k_{CV} and the CV_0 in Equation (4-1), the following equation was obtained:

$$CV_t = \left[4.37\left(\frac{PUFA}{TToc}\right)^2 - 5.64\left(\frac{PUFA}{TToc}\right) + 3.36\right]t + CV_0 \quad (4\text{-}5)$$

Equation (4-5) can be used to predict the CV_t during frying at 180 °C from the initial composition of edible oil. Considering the oils used in this study is universal and the frying temperature of 180 °C is most common, the obtained model showed the practical importance for the fried food industry. Importantly, the CV of any oil during frying at 180 °C can be predicted,

and deterioration of frying oil can be accurately predicted without complicated frying experiments. Equation (4-5) can also be expressed as follows:

$$t_{CV} = \frac{CV_t - CV_0}{4.37\left(\frac{PUFA}{TTOC}\right)^2 - 5.64\left(\frac{PUFA}{TTOC}\right) + 3.36} \quad (4\text{-}6)$$

Using Equation (4-6) and the allowable CV limit stipulated by the national standard (50 μmol/g), the frying life of edible oil at 180 °C can be predicted. In this way, suitable oils can be chosen for frying.

4.4.2 Changes trend, influencing factors, and establishment of the predictive model for total polar compounds during frying

4.4.2.1 Changes in total polar compounds during deep frying

The TPC levels after heating for 25 h (TPC_{25}) were measured and are shown in Table 4-4. The TPC_{25} values of the RS, CO, SS, NS, and SB exceeded the upper limit (≤ 24%), while those for the OL, SF, NP, PL, and RB did not. The lower TPC_{25} values for the OL, SF, and RB may be related to their higher oleic acid content. The TPC_{25} values of the NP and PL were low, probably because of their low TPC_0 value and high tocopherol content. The TPC_{25} value was significantly higher than TPC_0, the difference being represented by ΔTPC_{25} (Table 4-4). Of these oils, NS had the largest ΔTPC_{25} value. This was a natural pressed oil, with no polar compounds detected before frying which could be easily oxidized to produce polar compounds once heated, resulting in a rapid increase in TPC level. Although NP was also a natural pressed oil, with no polar compounds detected before frying, the ΔTPC_{25} value was still not high, probably because of its high tocopherol content, which acted as an antioxidant to slow down the formation of polar compounds. The SB, SS, and CO, with their high linoleic acid contents, exhibited large ΔTPC_{25} values, whereas the OL, SF, and RB, which were rich in oleic acid content, exhibited smaller ΔTPC_{25} values.

Table 4-4 Changes in the total polar compounds (TPC) level of 10 edible oils during deep frying at 180 °C

Oil name	TPC_0 (%)	TPC_{25} (%)	ΔTPC_{25} (%)
Olive oil	0.5	20.9	20.4
Safflower oil	0.5	21.3	20.8
Natural perilla oil	0.0	21.5	21.5
Perilla oil	0.0	21.5	21.5
Rice bran oil	1.0	23.5	22.5
Rapeseed oil	3.0	27.5	24.5
Corn oil	0.5	28.4	27.9
Sesame oil	6.0	33.5	27.5
Natural sesame oil	0.0	35.5	35.5
Soybean oil	6.0	39.0	33.0

TPC_0, initial TPC level before frying; TPC_{25}, TPC level after heating for 25 h; and ΔTPC_{25}, the increase in TPC level after 25 h of heating at 180 °C.

The increase in TPC level during heating is shown in Figure 4-3. As the heating time increased, the TPC level increased almost linearly, with this increase (ΔTPC_t) being fitted using the follow equation:

$$\Delta TPC_t = TPC_t - TPC_0 = k_{TPC}t \quad (4\text{-}7)$$

where k_{TPC} is the slope of the line of best fit between TPC level and heating time, and represents the rate of increase in the TPC level, a large k_{TPC} meaning that the TPC level was increasing rapidly.

The 10 oils had different k_{TPC} values (Table 4-5). Of these oils, the TPC level of SB increased most rapidly (k_{TPC} = 1.451), followed by NS (k_{TPC} = 1.370). In contrast, OL had the smallest k_{TPC} value (0.771), the slowest rate of increase in TPC level. The k_{TPC} of SB was about 1.88 times that of OL. This result showed that there was a significant difference in the rate of increase in TPC level. Overall, the rate of increase in TPC levels in PUFA-rich oils was greater than those in

MUFA-rich oils, except for rapeseed oil. RS had a relatively high k_{TPC} value (1.053), indicating that its TPC level increased relatively quickly, possibly related to its high content of TUFA.

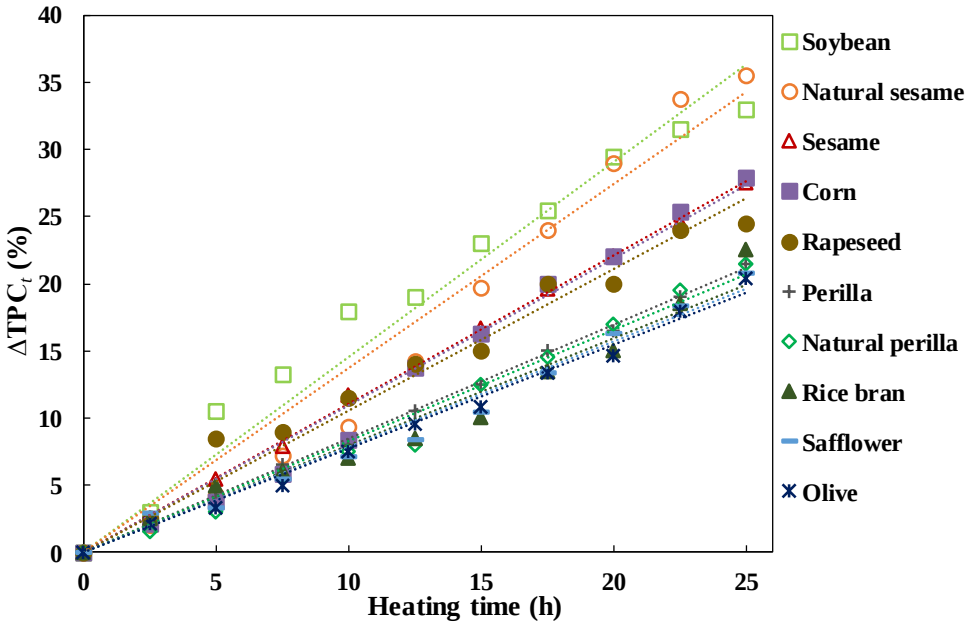

Figure 4-3 Increase in TPC level (%) of 10 edible oils with heating time (h) at 180 °C

Table 4-5 Slope of the linear equation, $\Delta TPC_t = k_{TPC}\ t$, and its coefficient showing the increase in TPC level of 10 edible oils with heating time and its coefficient of determination

Oil name	k_{TPC}	R^2
Soybean oil	1.451	0.965
Natural sesame oil	1.370	0.965
Sesame oil	1.104	0.999
Corn oil	1.092	0.982
Rapeseed oil	1.053	0.969
Perilla oil	0.845	0.998
Natural perilla oil	0.828	0.982
Rice bran oil	0.797	0.966
Safflower oil	0.784	0.982
Olive oil	0.771	0.991

4.4.2.2 The main intrinsic factors affecting the change of total polar compounds during frying

In general, the oxidative stability of edible oil is determined by its unsaturated fatty acid composition and antioxidants content, mainly tocopherols (Kamal-Eldin, 2006). Multiple linear regression analysis was performed to evaluate the influence of unsaturated fatty acids on the increase in TPC level, based on the decrease in the contents of oleic, linoleic, and linolenic acids with heating time (equation (iii), Table 4-6). The results indicated that unsaturated fatty acids had a significant effect on the increase in TPC level ($P < 0.001$). The coefficient of determination (R^2) indicated that 89.6% of the variance of the TPC increase was explained by the decrease in unsaturated fatty acids during frying. The effect of oleic, linoleic, and linolenic acids on the increase in TPC level can be compared using the standardized coefficients. Linoleic acid had the largest effect on the increase in TPC level with a large standardized coefficient of −1.388, followed by linolenic acid, with a standardized coefficient of −1.061. The effect of oleic acid was the smallest as shown by its small standardized coefficient (−0.730). The multiple linear regression procedure established the following equation:

$$\Delta\mathrm{TPC}_t = 0.885 - 3.630\ \Delta\mathrm{C18{:}1}_t - 4.903\ \Delta\mathrm{C18{:}2}_t - 3.737\ \Delta\mathrm{C18{:}3}_t \qquad (4\text{-}8)$$

where $\Delta\mathrm{TPC}_t$ is the increase in the TPC level of the oil with heating time during frying (%); $\Delta\mathrm{C18{:}1}_t$, $\Delta\mathrm{C18{:}2}_t$, and $\Delta\mathrm{C18{:}3}_t$ are the decreases in the contents of oleic acid, linoleic acid and linolenic acid of the oils with heating time, respectively (%); and *t* refers to the heating time (h).

Equation (4-8) shows that if the C18:2 content decreases by 1% during frying, the TPC level will increase by 4.903%. Similarly, if the contents of C18:1 and C18:3 decreases by 1% during frying, the TPC level will increase by 3.630% and 3.737%, respectively. Therefore, in terms of the effect on increasing the TPC level during frying, the effect of C18:2 was greatest, followed by that of C18:3, and C18:1.

Table 4-6 Multiple linear regression analysis showing the effect of the decrease in unsaturated fatty acids and tocopherols contents with heating time on the increase in TPC level in edible oils

Multiple linear regression equation	Variable	Unstandardized coefficient	Standard error	Standardized coefficient	*P*	
(iii) $\Delta TPC_t = b_0 + b_1 \Delta C18{:}1_t + b_2 \Delta C18{:}2_t + b_3 \Delta C18{:}3_t$	Constant	0.885	0.487		0.072	R^2 =0.896
	$\Delta C18{:}1_t$	-3.630	0.389	-0.730	<0.001	adjust R^2 =0.893
	$\Delta C18{:}2_t$	-4.903	0.222	-1.388	<0.001	*P*<0.001
	$\Delta C18{:}3_t$	-3.737	0.246	-1.061	<0.001	
(iv) $\Delta TPC_t = b_4 + b_5 \Delta\alpha_t + b_6 \Delta\gamma_t + b_7 \Delta\delta_t$	Constant	4.018	0.843		<0.001	R^2 =0.647
	$\Delta\alpha_t$	-0.166	0.040	-0.243	<0.001	adjust R^2 = 0.637
	$\Delta\gamma_t$	-0.289	0.022	-0.769	<0.001	*P*<0.001
	$\Delta\delta_t$	-0.040	0.064	-0.037	0.535	

ΔTPC_t is the dependent variable showing the increase in TPC level of all oils with heating time (%); b_0–b_7 are coefficient constants; Δ $C18{:}1_t$, $\Delta C18{:}2_t$, and $\Delta C18{:}3_t$ are independent variables showing the changes in oleic acid, linoleic acid and linolenic acid contents with heating time, respectively (%); $\Delta\alpha_t$, $\Delta\gamma_t$, and $\Delta\delta_t$ are independent variables showing the decreases in α-, γ-, and δ-tocopherol contents with heating time, respectively (mg/100 g); and *t* refers to the heating time (0–25 h).

Similarly, the influence of tocopherols on increasing the TPC level was also revealed using multiple linear regression analysis between the increase in TPC level and the decrease in the contents of α-, γ-, and δ-tocopherol with heating time (equation (iv), Table 4-6). This indicated that tocopherols had a significant effect on the increase in TPC level ($P < 0.001$) with multiple linear regression establishing the following equation:

$$\Delta TPC_t = 4.018 - 0.166\Delta\alpha_t - 0.289\Delta\gamma_t - 0.040\Delta\delta_t \quad (4\text{-}9)$$

where ΔTPC_t is the increase in the TPC level of the oils with heating time (%); $\Delta\alpha_t$, $\Delta\gamma_t$, and $\Delta\delta_t$ are decreases in the contents of α-, γ-, and δ-tocopherol contents of the oils with heating time, respectively (mg/100 g); and *t* refers to the heating time (h).

The determination coefficient of the multiple linear regression analysis was 0.647, which means that only 64.7% of the variance of ΔTPC_t was explained by Equation (4-9). α-Tocopherol and γ-tocopherol had significant effects on the increase in the TPC level ($P < 0.001$). γ-Tocopherol had the greatest effect on the increase in TPC level with a large standardized coefficient of −0.769, followed by α-tocopherol (−0.243) with that of δ-tocopherol being much smaller (−0.037).

4.4.2.3 Establishment of a prediction model for the total polar compounds

The TPC level is an important indicator for evaluating the deterioration of frying oils. It would be convenient to accurately predict the TPC level of frying oils based on its initial composition before the frying operation. Therefore, the increase in TPC level during frying was related to the initial composition of the oil. The results of multiple linear regression showed that unsaturated fatty acids, especially linoleic acid, had a more significant effect on increasing the TPC level than tocopherols. By combining the initial contents of the unsaturated fatty acids and tocopherol, indices based on unsaturated fatty acid content, or on tocopherol content, or on unsaturated fatty acid and tocopherol contents, were established then correlated with k_{TPC} (data not shown in detail). In comparison with these indices, the correlation between the ratio of linoleic acid to palmitic acid (C18:2/C16:0) and k_{TPC} was the highest ($r = 0.866$). Therefore, the ratio of linoleic acid to palmitic acid was selected as a predictive index. The relationship between the predictive index and k_{TPC}, shown in Figure 4-4, is expressed by Equation (4-10):

$$k_{\mathrm{TPC}} = 0.024\left(\frac{\mathrm{C18:2}}{\mathrm{C16:0}}\right)^2 - 0.065\left(\frac{\mathrm{C18:2}}{\mathrm{C16:0}}\right) + 0.819 \tag{4-10}$$

Equation (4-10) can be used to estimate k_{TPC} from the initial content ratio of linoleic acid to palmitic acid of an oil. By combining Equation (4-10) with k_{TPC} and TPC_0 in Equation (4-7), the following equation was obtained:

$$TPC_t = \left[0.024\left(\frac{\mathrm{C18:2}}{\mathrm{C16:0}}\right)^2 - 0.065\left(\frac{\mathrm{C18:2}}{\mathrm{C16:0}}\right) + 0.819\right]t + TPC_0 \tag{4-11}$$

Equation (4-11) can be used to predict TPC_t during frying just from a knowledge of the initial composition of an edible oil. Therefore, the TPC level of any oil during frying at 180 °C can be predicted without undertaking complex frying experiments to quickly predict the degree of deterioration of the oil. Equation (4-11) can also be expressed as follows:

$$t_{TPC} = \frac{TPC_t - TPC_0}{0.024\left(\frac{C18:2}{C16:0}\right)^2 - 0.065\left(\frac{C18:2}{C16:0}\right) + 0.819} \quad (4\text{-}12)$$

By using Equation (4-12) and the maximum allowable level of TPC (≤ 24%), the frying life of edible oil at 180 °C (t_{TPC}) can be predicted based on the initial fatty acid composition and the TPC_0 of an edible oil. The oils used in the present study are universal and a frying temperature of 180 °C is also very commonly used, so the models established for predicting the TPC level of a frying oil and the frying life of an edible oil have practical significance for use in food manufacturing as well as in the restaurant and fast food sectors of the foodservice industry.

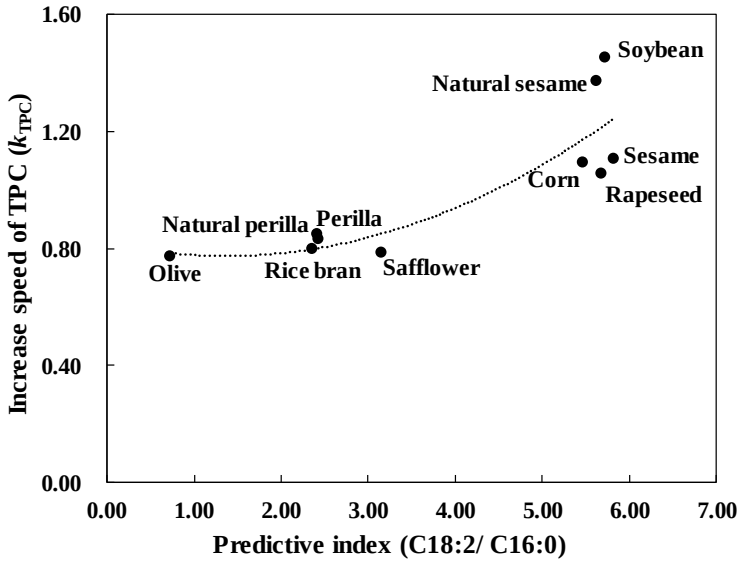

Figure 4-4 The relationship between the predictive index (C18:2/C16:0) and the rate of increase in the total polar compounds (k_{TPC}) of the 10 edible oils

C18:2 / C16:0 is the initial ratio of the contents of linoleic acid to palmitic acid.

4.4.3 Calculation of frying life for oils using the established prediction models

CV and TPC level are important indicators of deterioration evaluation of frying oil, and both gradually increased during the frying process. The correlation between the change of CV and TPC with heating time was shown in Table 4-7. The changes of CV and TPC have a good correlation in 10 oils during frying (0.978-0.995). In combination with the above results, it was known that CV and TPC increased linearly with time during heating. By comparing the increase speed of CV (k_{CV} in Table 4-2) with that of TPC (k_{TPC} in Table 4-5), it can be obtained that all k_{CV} were greater than k_{TPC}, which indicated the increase speed of CV was faster than the increase speed of TPC in the 10 oils during the frying process.

Table 4-7 Correlation between the ΔCV_t and ΔTPC_t with heating time

Oil name	Correlation coefficient (r)
Olive oil	0.990
Safflower oil	0.978
Rapeseed oil	0.986
Rice bran oil	0.983
Natural sesame oil	0.993
Sesame oil	0.994
Corn oil	0.995
Soybean oil	0.989
Natural perilla oil	0.988
Perilla oil	0.992

With CV as the evaluation indicator of frying oil, using the prediction model for the frying life of edible oil (Equation (4-6)) and the maximum allowable CV (≤ 50 μmol/g), the frying life of 10 oils (t_{CV}) can be derived from the initial content of PUFA/TToc and the initial CV before frying. Using the prediction model for the frying life of edible oil in Equation (4-12) when the TPC level reaches 24%, the t_{TPC} of the 10 edible oils can be calculated from information on the initial ratio of linoleic acid to palmitic acid contents and their TPC_0 value. The frying life, t_{TPC} and t_{CV} of the 10 oils are shown in Table 4-8.

Table 4-8 The predicted frying life of 10 edible oils according to the prediction models

Oil name	t_{CV} (h)	t_{TPC} (h)
Rice bran oil	27.1	28.8
Olive oil	26.0	30.0
Natural perilla oil	23.9	29.9
Safflower oil	23.4	27.6
Perilla oil	22.6	29.9
Corn oil	24.1	19.9
Natural sesame oil	23.8	19.8
Rapeseed oil	19.5	17.1
Soybean oil	24.1	14.6
Sesame oil	29.7	14.4

t_{TPC} was calculated from the prediction model $t_{TPC} = \frac{TPC_t - TPC_0}{0.024\left(\frac{C18:2}{C16:0}\right)^2 - 0.065\left(\frac{C18:2}{C16:0}\right) + 0.819}$ with a maximum allowable value of total polar compounds of 24%; t_{CV} was calculated from the prediction model $t_{CV} = \frac{CV_t - CV_0}{4.37\left(\frac{PUFA}{TToc}\right)^2 - 5.64\left(\frac{PUFA}{TToc}\right) + 3.36}$ with a maximum allowable carbonyl value of 50 μmol/g.

The t_{CV} varied from 19.5 to 29.7 h, while t_{TPC} of the 10 oils varied from 14.4 to 30.0 h. The estimates of the frying life of the 10 oils was not consistent using the two prediction models established with CV and TPC level as the evaluation indicators. The TPC levels of the RB, OL, NP, SF, and PL reached the limiting value of 24% later than the CV, meaning that estimates of their frying life were longer. In contrast, in the CO, NS, RS, SB, and SS, the TPC levels reached the maximum limit of 24% before the CV, so estimates of their frying life were shorter.

To ensure the safety of fried foods and minimize the risks human health, the frying life of an edible oil meeting the limiting values of both CV and TPC is considered to be the safest where the shorter of t_{CV} and t_{TPC} is deemed the safest frying life of an oil. Therefore, from the perspective of safety, SS had the shortest frying life of the 10 oils studied here (14.4 h) so could be considered the oil most unsuitable for frying. In contrast, RB exhibited the longest frying life

(27.1 h) so RB could be considered the oil most suitable for deep frying at 180 °C. It should be emphasized that for predicting the frying life of an edible vegetable oil at 180 °C, Equations (4-6) and (4-12) should be used simultaneously. The results should be compared, then the shorter one can be taken as the safest frying life of an edible oil that meets the limits of CV and TPC at the same time.

4.5 Conclusions

In this work, the quality change characteristics, namely CV and TPC, of the 10 oils during frying were explored. CV and TPC increased linearly with heating time during frying. The TPC and CV of PUFA-rich oils increased faster than those of MUFA-rich oils. At the same time, the increasing speed was also related to the tocopherol content of the oils. The multiple regression analysis revealed the effect of PUFA on the increase in the CV and TPC was greater than that of MUFA. For effects from tocopherols, the effect of γ-tocopherol was greater than that of α-tocopherol, and δ-tocopherol had the smallest effect. The predictive indices, PUFA/TToc and C18:2/C16:0, which are the ratio of initial contents, can be used to predict increases in the CV and TPC during frying at 180 °C from the initial composition of edible oil, respectively. Using these indices, the prediction models, $CV_t = \left[4.37\left(\frac{PUFA}{TToc}\right)^2 - 5.64\left(\frac{PUFA}{TToc}\right) + 3.36\right]t + CV_0$ and $TPC_t = \left[0.024\left(\frac{\text{C18:2}}{\text{C16:0}}\right)^2 - 0.065\left(\frac{\text{C18:2}}{\text{C16:0}}\right) + 0.819\right]t + TPC_0$, were established. These models can be used to predict the CV and TPC of any oil during frying at 180 °C and evaluate oil deterioration without complicated frying experiments. At the same time, the safest frying life of the oil can also be predicted by using these two predictive models simultaneously.

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Chapter 5 The flavor change of oils during frying

5.1 Abstract

The flavor changes of the 10 oils during frying were evaluated by gas chromatography-mass spectrometry. The changes in volatile compounds in oils during frying was mainly related to the composition of unsaturated fatty acids. The total area of volatile substances increased significantly in oleic acid rich oils, followed by linoleic acid rich oils, while decreased slightly in linolenic acid rich perilla oils. Both alcohols and aldehydes detected in oils account for a large proportion before and after frying. By using principal component analysis, the effects of aldehydes, alcohols and other substances detected on the flavor characteristics of oils during frying were explored respectively. The key volatile compounds affecting the changes during frying in oils with much monounsaturated fatty acid were hexanal, (E)-2-hexenal, heptanal, (E)-2-heptenal, octanal, 2-octenal, nonanal, (E)-2-decenal, (E)-2-undecenal, 2-methyl-1-propanol, 1-pentanol, methylpyrazine, and butyl-cyclopentane. For oils rich in polyunsaturated fatty acid, the key volatile compounds were (Z)-2-penten-1-ol, acetic acid, and hexane. The relationship between the changes of volatile components detected and the changes of total unsaturated fatty acid (TUFA), total tocopherol (TToc), carbonyl value (CV), and total polar compounds (TPC) were analyzed respectively by correlation analysis. With the decrease of TUFA and TToc and increase of CV and TPC, most of the volatile substances showed an increasing trend. The increase of pentanal showed good correlation with them in most oils.

5.2 Introduction

Deep frying is a popular method of food preparation in the world, not only because of its simple and fast operation, but also because it can bring unique flavor to fried foods. The popularity of fried foods is inseparable from its palatable taste and pleasant flavor. Many chemical reactions occur during the frying process, producing a series of volatile substances (Choe and Min, 2007; Zhang et al., 2012). The volatile substances formed are easily volatilized during high temperature and long-term frying and are also absorbed by the oil (Zhang et al., 2018). When oil absorbs these substances, it will produce a unique flavor, which will directly affect the flavor of fried foods through mass transfer (Pokorny, 1989). The flavors developed during the frying process were evaluated as fruity, grassy, buttery, burnt, nutty, and fishy (Choe and Min, 2007). During the frying process, the oil produces not only an attractive aroma but also an unpleasant one. The concentration and intensity of these flavors vary widely between different frying systems or different stages of the same frying system. Therefore, studying the formation and change characteristics of volatile substances in frying oil is of great significance for understanding the flavor characteristics of fried foods, which can help to enhance the attractive aroma and avoid unpleasant odors.

The aroma components of edible oils are very complex and involve the characterization of a large number of volatile compounds, which has become a difficult and hot topic in current research. A large number of studies on the aroma components of edible oils have been reported (Zhu et al., 2001; Ivanova-Petropulos et al., 2015; Ahro et al., 2002; Yang et al., 2013; Sano et al., 2014). They have some guiding significance for the characterization of compounds in subsequent studies, but these are not for the study on frying oils. Because the moisture carried by the food during the frying process will cause intense boiling and produce a large amount of steam, which will cause the volatiles that have been generated to volatilize a lot. Romano et al. (Romano et al., 2013) found that the heated oil showed significant amounts of aldehydes

compared to the frying oil. Therefore, the research on the frying oil is different from the heated oil or the oil at normal temperature. Research on the changes in the aroma components of frying oils has recently been paid attention to, and some scholars have done corresponding research (Takeoka et al., 1996; Zhang et al., 2015; Zhang et al., 2018; Romano et al., 2013). Zhang et al. (Zhang et al., 2015; Zhang et al., 2018) studied the changes in aldehydes and other volatile substances formed by soybean oil over time during frying wheat dough and frying chicken breast meat. Because only soybean oil has been studied, the results are very limited. Research on volatile substances in frying oil is necessary to be carried out more comprehensively.

The purpose of this study is to study the changes of volatile substances produced from 10 oils during frying with different frying time. Ten commercial edible oils were used to fry French fries at 180 °C. The volatile substances produced before and after frying were detected by gas chromatography mass spectrometry. The effect of changes in volatile substances detected during frying on the flavor characteristics of oil was analyzed. The relationship between changes in volatile substances and changes in unsaturated fatty acids, tocopherols, carbonyl value, and total polar compounds during frying was discussed, respectively. The key volatile compounds affecting the changes of oils during frying were found.

5.3 Materials and methods

5.3.1 Materials and reagents

Frying oil samples used were the same as that samples in 3.3.1.1 in Chapter 3. Standard mixture of *n*-alkanes (C6-C16) was bought from Restek Corporation (U.S.).

5.3.2 Analytical methods

The method for determination of volatile compounds of frying oil was the same as that mentioned in 2.3.2.5 Determination of volatile compounds in Chapter 2.

5.3.3 Statistical analysis

Each oil sample was analyzed in triplicate. Data are presented as means ± standard deviations. Correlation analysis was carried out using Microsoft Excel 2016. PCA was conducted using SPSS 17.0.

5.4 Results and discussion

5.4.1 Changes in volatile compounds before and after frying

The initial and final peak areas of the volatile compounds detected in the 10 oils during 25h of heating are shown in Table 5-1. Before frying (0 h), the largest peak area of volatile substances were detected in SS and PL, followed by OL, NS, NP, SB, and RS. The smallest peak area of volatile substances was detected in RB, CO, and SF. At the end of heating (25 h), SS still contained the largest peak area of volatile substances, followed by OL and PL. Then followed by RB, RS, and SF, which contained high oleic acid content. Oils with high PUFA, namely NS, CO, SB, and NP, had the smaller peak area of volatile substances detected. NP, in particular, which had the highest content of PUFA, mainly linolenic acid, had the smallest peak area of volatile substances detected. The results showed that the content of volatile compounds in frying oils was closely related to the composition of unsaturated fatty acids. The oils with more MUFA had more volatile substances detected, on the contrary, the oils with more PUFA had less volatile substances detected.

Table 5-1 The peak areas of the volatile compounds detected in the 10 oils at 0 h and 25 h during frying

Volatile compound	RI	Olive		Safflower		Rapeseed		Rice bran		Natural sesame	
		0h	25h	0h	25h	0h	25h	0h	25h	0h	25h
Ethanol	<600	838801±13014	584580±12701	-	-	-	-	-	-	-	-
2-methyl-1-Propanol	<600	31167±1592	433081±6650	56782±444	165337±3870	53358±1082	280047±10661	83284±3432	432472±2164	161408±6689	94633±4578
1-Penten-3-ol	714	0±0	16755±476	-	-	23117±219	22985±497	1738±51	6439±298	-	-
(Z)-2-Penten-1-ol	716	-	-	-	-	-	-	-	-	0±0	8426±497
1-Pentanol	795	0±0	22788±692	0±0	11577±147	1276±118	8053±352	1922±92	20074±552	3294±261	9005±344
1-Heptanol	997	0±0	4177±102	0±0	1507±6	-	-	-	-	-	-
1-Octanol	1097	0±0	2204±52	-	-	-	-	-	-	-	-
Total alcohols		869968	1063585	56782	178421	77751	311085	86944	458985	164702	112064
Total alcohols (%)		62.43	37.48	61.21	30.88	43.79	46.66	74.37	36.14	51.27	24.84
Butanal	619	269969±3757	489382±5640	-	-	1193±2	1787±45	1007±176	426182±2079	0±0	2530±128
2-Butenal	692	0±0	8654±378	-	-	5375±189	12929±704	-	-	-	-
2-methyl-Butanal	704	-	-	4898±4	9084±215	-	-	989±8	7826±256	0±0	10025±416
Pentanal	724	10314±177	285509±4182	8163±805	93839±852	8360±286	72091±1274	7661±174	92316±1549	10715±714	78745±1954
(E)-2-Methyl-2-butenal	766	-	-	-	-	-	-	-	-	-	-
2-Pentenal, (E)-	779	0±0	7185±206	-	-	2846±47	6790±381	-	-	-	-
Hexanal	824	4439±63	758292±11535	7521±251	190716±1422	24279±1361	119751±954	10964±529	181929±4756	27409±175	165954±6174
Furfural	854	-	-	-	-	-	-	-	-	-	-
2-Hexenal, (E)-	877	0±0	2312±89	0±0	2259±18	-	-	0±0	2943±41	618±29	1325±38
Heptanal	927	0±0	27140±1018	0±0	7713±50	0±0	6855±464	0±0	5824±280	1382±92	3857±463
2-Heptenal, (E)-	981	0±0	16290±183	0±0	10696±441	2144±22	6722±111	2157±153	22484±120	6470±175	12686±311

Octanal	1029	0±0	24151±916	0±0	6792±78	0±0	3183±4	0±0	2662±116	0±0	1589±102
2,4-Heptadienal, (E,E)-	1036	0±0	2032±80	-	-	7527±50	13166±423	0±0	3203±163	-	-
2-Octenal	1083	303±1	5219±109	0±0	1394±27	0±0	1126±103	0±0	3467±22	414±4	1033±23
Nonanal	1132	0±0	16848±392	0±0	18732±147	2294±94	11518±858	913±54	12601±260	2781±97	3314±244
(E)-2-Nonenal	1187	0±0	1489±54	0±0	796±21	-	-	-	-	-	-
2-Decenal, (E)-	1294	0±0	3547±189	0±0	3455±262	0±0	1385±52	0±0	2163±92	0±0	918±26
2,4-Undecadienal	1327	-	-	-	-	-	-	0±0	2625±41	-	-
2,4-Decadienal, (E,E)-	1350	-	-	0±0	3201±18	0±0	2338±146	0±0	11868±500	674±16	5248±290
(E)-2-Undecenal	1396	0±0	1716±116	0±0	1854±43	-	-	0±0	1115±4	-	-
Total aldehydes		285025	1649766	20582	350531	54018	259641	23691	779208	50463	287224
Total aldehydes (%)		20.46	58.13	22.19	60.66	30.42	38.94	20.27	61.35	15.71	63.67
Hexane	641	197619±5467	86339±1720	0±0	17290±1081	34489±1138	63855±1392	0±0	16426±65	99079±1697	19467±617
methyl-Cyclopentane	667	2592±30	2359±169	-	-	-	-	-	-	4141±163	1105±79
Heptane	709	-	-	8243±413	9508±355	-	-	-	-	0±0	12137±57
Cyclopentane, butyl-	957	0±0	1580±74	0±0	1260±85	0±0	1230±9	0±0	1386±166	-	-
Decane	1027	-	-	-	-	-	-	-	-	897±54	1678±120
Decamethylcyclopentasiloxane	1170	-	-	5716±729	8325±837	-	-	5651±688	3538±45	-	-
Total alkanes		200211	90278	13959	36383	34489	65085	5651	21350	104117	34387
Total alkanes (%)		14.37	3.18	15.05	6.30	19.43	9.76	4.83	1.68	32.41	7.62
2-Hexanone	815	-	-	-	-	-	-	-	-	-	-
2-Octanone	914	0±0	1471±107	-	-	582±7	3783±298	-	-	-	-
Total ketones		0	1471	0	0	582	3783	0	0	0	0
Total ketones (%)		0.00	0.05	0.00	0.00	0.33	0.57	0.00	0.00	0.00	0.00

methylPyrazine	844	1383±96	2039±72	-	-	-	-	-	-	-	-
2-Ethyl-6-methylpyrazine	1021	-	-	-	-	2969±75	3639±83	-	-	-	-
2,3,5-Trimethylpyrazine	1025	-	-	-	-	-	-	-	-	-	-
Total pyrazines		1383	2039	0	0	2969	3639	0	0	0	0
Total pyrazines (%)		0.10	0.07	0.00	0.00	1.67	0.55	0.00	0.00	0.00	0.00
Acetic acid methyl ester	604	-	-	-	-	-	-	-	-	-	-
Ethyl Acetate	653	8507±441	19820±202	-	-	-	-	-	-	0±0	8271±226
Total esters		8507	19820	0	0	0	0	0	0	0	8271
Total esters (%)		0.61	0.70	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.83
2-pentylfuran	1015	0±0	6117±214	0±0	5027±95	1241±29	2701±109	616±87	10514±365	1959±68	4251±53
Total furans		0	6117	0	5027	1241	2701	616	10514	1959	4251
Total furans (%)		0.00	0.22	0.00	0.87	0.70	0.41	0.53	0.83	0.61	0.94
Toluene	792	28309±208	4769±313	-	-	656±29	1348±118	-	-	-	-
Total benzenes		28309	4769	0	0	656	1348	0	0	0	0
Total benzenes (%)		2.03	0.17	0.00	0.00	0.37	0.20	0.00	0.00	0.00	0.00
1-Heptene	719	-	-	1437±29	2610±11	-	-	-	-	-	-
Total alkenes		0	0	1437	2610	0	0	0	0	0	0
Total alkenes (%)		0.00	0.00	1.55	0.45	0.00	0.00	0.00	0.00	0.00	0.00
Acetic acid	628	-	-	0±0	4850±119	5841±107	19429±117	-	-	0±0	4911±179
Total acids		0	0	0	4850	5841	19429	0	0	0	4911
Total acids (%)		0.00	0.00	0.00	0.84	3.29	2.91	0.00	0.00	0.00	1.09
Total compounds		1393403	2837845	92760	577822	177547	666711	116902	1270057	321241	451108

Table 5-1 The peak areas of the volatile compounds detected in the 10 oils at 0 h and 25 h during frying (continued)

Volatile compound	RI	Sesame		Corn		Soybean		Natural perilla		Perilla	
		0h	25h	0h	25h	0h	25h	0h	25h	0h	25h
Ethanol	<600	284867±15056	2243036±77985	-	-	-	-	31464±939	18285±584	50818±2235	87212±2584
2-methyl-1-Propanol	<600	317401±13460	73387±4165	46971±867	206947±5854	74989±1101	166928±1418	174722±2699	168050±1589	473731±16168	779409±12250
1-Penten-3-ol	714	-	-	0±0	4904±106	-	-	5494±405	27242±413	-	-
(Z)-2-Penten-1-ol	716	25124±1309	10013±73	-	-	4273±193	10458±455	-	-	68265±1541	83604±654
1-Pentanol	795	14102±397	18350±1013	843±66	14040±730	1833±52	7567±208	0±0	1128±79	6628±16	1733±108
1-Heptanol	997	-	-	-	-	-	-	-	-	-	-
1-Octanol	1097	-	-	-	-	-	-	-	-	2631±91	0±0
Total alcohols		641494	2344786	47814	225891	81095	184953	211680	214705	602073	951958
Total alcohols (%)		30.56	58.43	45.50	45.94	38.59	34.19	91.70	62.52	39.51	69.43
Butanal	619	211564±8981	678541±21442	-	-	14137±482	1056±13	-	-	72698±4024	0±0
2-Butenal	692	-	-	-	-	-	-	1865±85	13331±702	352±5	52354±951
2-methyl-Butanal	704	10152±348	18299±350	1453±72	0±0	23199±462	14325±204	-	-	0±0	6286±301
Pentanal	724	21923±887	225832±6298	4889±118	36021±894	17011±585	89394±4512	1367±13	16116±1831	0±0	126905±5454
(E)-2-Methyl-2-butenal	766	-	-	-	-	-	-	-	-	0±0	4509±38
2-Pentenal, (E)-	779	-	-	-	-	-	-	1078±8	7051±60	5477±48	20664±688
Hexanal	824	37699±789	173849±1695	24841±661	141083±2855	18009±768	108026±3329	11172±834	7678±315	24073±844	18808±641
Furfural	854	28038±1715	6769±116	-	-	-	-	-	-	-	-
2-Hexenal, (E)-	877	7577±33	1535±115	0±0	3756±246	426±0	1276±34	-	-	12028±461	1310±45
Heptanal	927	2810±227	7845±374	0±0	3407±71	529±3	2549±172	-	-	5955±293	0±0
2-Heptenal, (E)-	981	1337±11	8264±97	0±0	22861±726	2827±29	10484±235	0±0	1267±72	0±0	1819±46

Octanal	1029	0±0	3948±93	0±0	1115±15	-	-	-	-	-	-
2,4-Heptadienal, (E,E)-	1036	-	-	-	-	1392±193	10184±271	0±0	34620±848	6105±157	40573±233
2-Octenal	1083	0±0	2122±160	0±0	2293±89	0±0	1677±63	-	-	-	-
Nonanal	1132	1659±34	8458±280	0±0	4556±303	627±18	2204±171	0±0	1284±90	481±3	1323±102
(E)-2-Nonenal	1187	0±0	2342±116	-	-	-	-	-	-	-	-
2-Decenal, (E)-	1294	-	-	-	-	-	-	-	-	-	-
2,4-Undecadienal	1327	-	-	0±0	3446±11	0±0	1661±43	-	-	-	-
2,4-Decadienal, (E,E)-	1350	-	-	0±0	15124±1453	0±0	6846±262	-	-	-	-
(E)-2-Undecenal	1396	-	-	-	-	-	-	-	-	-	-
Total aldehydes		322759	1137804	31183	233662	78157	249682	15482	81347	127169	274551
Total aldehydes (%)		15.38	28.35	29.67	47.52	37.19	46.16	6.71	23.69	8.34	20.02
Hexane	641	351446±5917	418268±22277	4587±268	0±0	14759±929	38857±1048	2192±55	24481±1037	0±0	48514±2143
methyl-Cyclopentane	667	2822±21	6809±112	-	-	-	-	-	-	3271±150	0±0
Heptane	709	-	-	-	-	16462±315	16968±538	-	-	-	-
Cyclopentane, butyl-	957	-	-	-	-	-	-	-	-	-	-
Decane	1027	1731±229	308±28	-	-	1999±78	1768±103	-	-	465±64	252±6
Decamethylcyclopentasiloxane	1170	-	-	3506±225	7066±270	-	-	-	-	1858±311	1577±107
Total alkanes		355999	425385	8093	7066	33220	57593	2192	24481	5594	50343
Total alkanes (%)		16.96	10.60	7.70	1.44	15.81	10.65	0.95	7.13	0.37	3.67
2-Hexanone	815	1063±31	6263±236	-	-	-	-	-	-	-	-
2-Octanone	914	3647±248	15583±87	-	-	366±21	5066±17	-	-	-	-
Total ketones		4710	21846	0	0	366	5066	0	0	0	0
Total ketones (%)		0.22	0.54	0.00	0.00	0.17	0.94	0.00	0.00	0.00	0.00

methylPyrazine	844	10594±332	3896±185	-	-	-	-	-	-	224872±4220	0±0
2-Ethyl-6-methylpyrazine	1021	6454±118	0±0	-	-	760±14	2963±210	0±0	8990±175	1244±47	13143±48
2,3,5-Trimethylpyrazine	1025	24793±82	0±0	-	-	-	-	-	-	11300±183	1208±115
Total pyrazines		41841	3896	0	0	760	2963	0	8990	237416	14351
Total pyrazines (%)		1.99	0.10	0.00	0.00	0.36	0.55	0.00	2.62	15.58	1.05
Acetic acid methyl ester	604	122676±3601	0±0	16223±264	0±0	-	-	-	-	178565±6434	0±0
Ethyl Acetate	653	0±0	17546±392	-	-	11196±273	17746±147	-	-	-	-
Total esters		122676	17546	16223	0	11196	17746	0	0	178565	0
Total esters (%)		5.84	0.44	15.44	0.00	5.33	3.28	0.00	0.00	11.72	0.00
2-pentylfuran	1015	7755±393	17258±784	0±0	14558±501	881±39	5803±426	-	-	-	-
Total furans		7755	17258	0	14558	881	5803	0	0	0	0
Total furans (%)		0.37	0.43	0.00	2.96	0.42	1.07	0.00	0.00	0.00	0.00
Toluene	792	-	-	-	-	2588±96	2676±87	0±0	1115±40	-	-
Total benzenes		0	0	0	0	2588	2676	0	1115	0	0
Total benzenes (%)		0.00	0.00	0.00	0.00	1.23	0.49	0.00	0.32	0.00	0.00
1-Heptene	719	-	-	-	-	-	-	-	-	-	-
Total alkenes		0	0	0	0	0	0	0	0	0	0
Total alkenes (%)		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetic acid	628	601924±21389	44560±1641	1783±26	10503±524	1893±153	14429±175	1485±1	12755±341	373152±13546	79920±2261
Total acids		601924	44560	1783	10503	1893	14429	1485	12755	373152	79920
Total acids (%)		28.67	1.11	1.70	2.14	0.90	2.67	0.64	3.71	24.49	5.83
Total compounds		2099158	4013081	105096	491680	210156	540911	230839	343393	1523969	1371123

RI means retention index, which was calculated for the SH-RxiTM-5SilMS capillary column. The identification of volatile compounds was mainly based on mass spectrum and retention indices to reference the NIST 17 Mass Spectral Library and literatures about oils.

The total of a kind of substances is the sum of the peak areas, and the total (%) refers to the percentage of the total area of a kind of substances detected in an oil to the total area of all substances detected in this oil.

The special substances detected only in the roasted oils (SS and PL) are not shown in the table because they are all evaporated after heating.

A “-” indicates not detected.

By comparing the total area of volatile compounds before and after heating, it was found that the total area of volatile compounds detected in these oils increased, except for PL. It was also found that in the oils based on oleic acid, the total area of volatile substances was greatly increased compared with that before heating, especially in RB, in which the total area was about ten times that before heating. They were followed by oils with a high linoleic acid content. In NP with more linolenic acid, the total area after heating was 0.5 times that before heating, while in PL, the total area after heating was slightly reduced. The change in the area of volatiles in oil before and after heating was mainly related to the composition of the unsaturated fatty acids. Oils containing much oleic acid were more stable during heating because the double bond cleavage of oleic acid was much slower than that of linoleic acid and linolenic acid. Among the decomposition products formed after the breaking of each unsaturated fatty acid, the volatile compounds generated by the cleavage of oleic acid had a relatively large molecular weight and were easily accumulated in the frying oil, so that they can be detected in a large amount. On the contrary, the products produced by the thermal decomposition of linolenic acid had a small molecular weight, which was easy to volatilize instead of accumulating in the subsequent frying process. As a result, the amount of volatile compounds detected was low.

In this study, in addition to the unique aroma of roasted oils, a total of 43 individual volatile compounds were identified, including aldehydes, alcohols, alkanes, ketones, pyrazines, esters, furan, benzene, alkene, and acid. They determined the flavor characteristics of the oil during its use in frying.

Alcohols are produced by the oxidative decomposition of unsaturated fatty acids (Zhang et al., 2018). Seven alcohols were detected in these oils. The percentage of the total area of alcohols detected in OL, SF, RB, NS, and NP before heating was greater than after heating. While in SS and PL, the percentage of the total area of alcohols before heating was smaller than after heating. The percentage of the total area of alcohols before and after heating was almost constant in RS, CO, and SB. The total area of alcohols actually detected increased in all oils after heating, except for NS.

Twenty aldehydes were detected, and they were also the most volatile species detected. The percentage of total area detected in 10 oils was smaller before heating than after heating, as was the actual total area. It showed that a large amount of aldehydes were formed and accumulated during the heating process. This conclusion was also confirmed by observing the area changes of various aldehydes detected in oils. Many aldehydes were not detected before heating, but were detected at the end of frying, all of which were produced by thermal deterioration of oils.

There were six alkanes were detected in these oils. The formation of alkanes is due to the free radical reaction of unsaturated and saturated fatty acyl chains in oil (Zhang et al., 2018). The percentage of the total area of alkanes detected in oils before heating was greater than after heating, except for NP and PL. However, as for the total area of alkanes actually detected, only CO, NS, and OL were reduced after heating, while other oils were increased.

Some people think that the ketones detected during the frying process were related to the flavor of the fried food (Zhang et al., 2018). Some people think that they may have potential harm to human health (Qu et al., 1992). Only two ketones were detected, 2-hexanone and 2-octanone. 2-Hexanone was only detected in SS. In OL, RS, SS, and SB in which ketones were detected, the total area of the ketones and their proportion increased after heating.

Pyrazine is a heterocyclic compound with roasted and nutty flavor, produced during the roasting of seeds (Ivanova-Petropulos et al., 2015). In addition to being detected in roasted oils, pyrazines were also detected in OL, RS, SB, and NP, which were all pressed from seeds. As the heating progressed, the total area and proportion of pyrazines detected in SS and PL were decreased. This was due to the fact that the pyrazine produced during the roasted process volatilized during up to 25 hours of heating and frying.

Two esters were detected in these oils. Acetic acid methyl ester was widely detected in SS, CO, and PL before heating, but it was not detected after heating. It showed that acetic acid methyl ester,

produced by auto-oxidation, was highly volatile, as soon as heating it completely volatilized. Ethyl acetate, detected in OL, NS, SS, and SB, was increased after heating.

In addition, 2-pentyfuran, toluene, 1-heptene, and acetic acid were also detected. 2-Pentyfuran was detected in oils except for NP and PL and its area was increased after heating. It is one of the causes of the off-flavor of frying oil (Prevot et al., 1988). Toluene was detected in small amounts in RS, SB, and NP and increased in area after heating. Conversely, it was large in area and reduced after heating in OL. Toluene is a toxic substance that does not contribute to the desirable flavor of frying foods (Choe and Min, 2007). 1-Heptene was only detected by a small amount in SF and the area was almost unchanged when heated to 25 hours. Acetic acid was detected in large quantities in these oils, and the areas after heating were greater than before heating, except for roasted oils. A large amount of acetic acid was detected before heating in SS and PL, accounting for 28.67% and 24.49% of the total area of all volatile compounds, respectively. The area of acetic acid after heating was greatly reduced, accounting for 1.11% and 5.83% of the total area, respectively. The results once again showed that the compounds produced during the roasting process of oil were unstable during prolonged heating and easily volatilized.

The total area of alcohols detected in OL, SF, RB, NS, SB, and CO accounted for the largest proportion of the total area of all compounds before heating, while the total area of aldehydes was the largest after heating. In RS, SS, PL, and NP, the total area of alcohols was the largest before and after heating. No matter before and after frying, alcohol and aldehyde in each oil account for a large proportion, which is related to their low odor threshold.

5.4.2 The effect of changes in the volatile compounds with the heating time on the flavor of oils

5.4.2.1 The effect of changes in aldehydes with heating time on the flavor of oils

Figure 5-1 shows the total area of aldehydes detected in 10 frying oils during frying. The total area of aldehydes increased regularly with heating time in RS, NS, SB, and PL. While it increased irregularly in OL, SF, RB, SS, and CO. Unlike other oils, the total area of aldehydes in NP hardly increased with heating time. This is related to its composition and processing method. NP contains a large amount of linolenic acid and tocopherols and has not been roasted at high temperature. The double bonds in linolenic acid are easy to break once heated, resulting in low-molecular-weight volatile substances. These substances are easy to volatilize with fume in the subsequent heating process. On the other hand, a large amount of tocopherols in NP, especially δ-tocopherol, play a protective role. Consequently, there are few volatile substances that can be detected in the frying oil, and the content is almost unchanged. On the contrary, OL contains a large amount of oleic acid which is not easy to break and a small amount of tocopherols. As a result, the total area of aldehydes detected in OL was obviously the largest of these oils, and it increased significantly as the heating time increased. Similarly, the total area of aldehydes was the largest in oleic acid-based oils, followed by linoleic acid-based oils, and the smallest in linolenic acid-based oils.

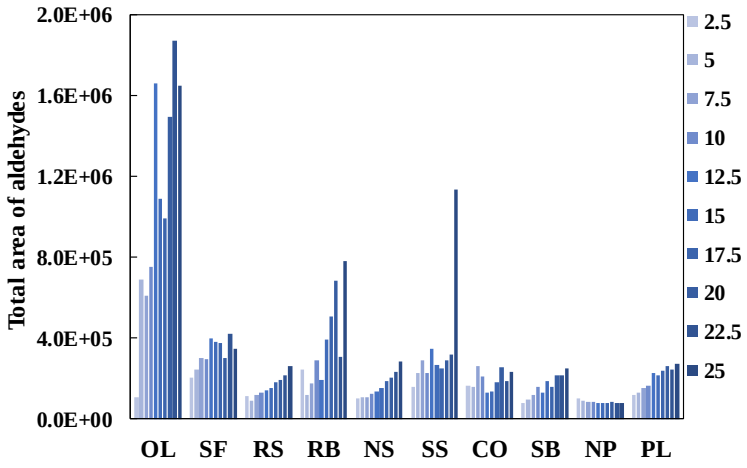


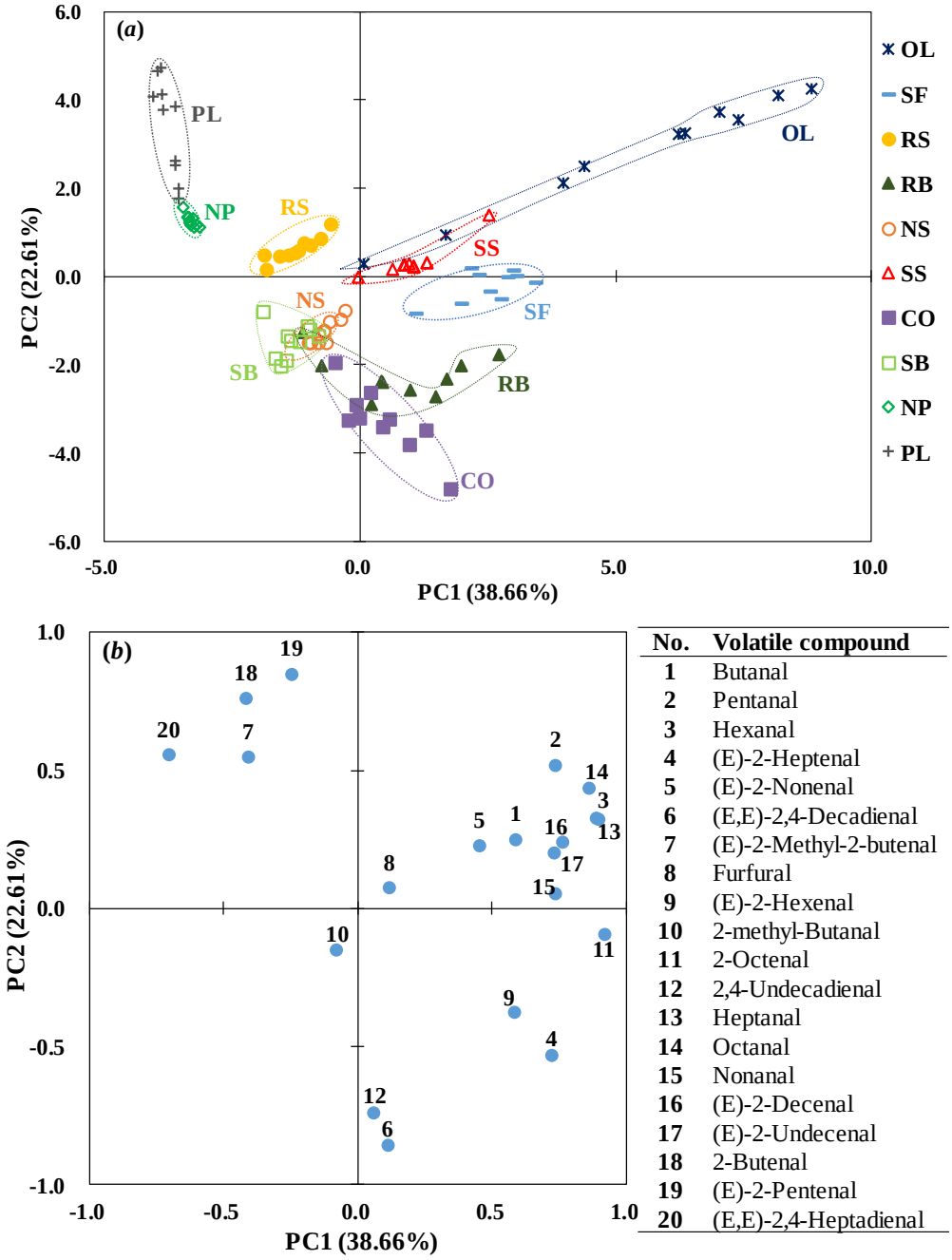
Figure 5-1 The total area of aldehydes detected in the 10 frying oils during frying

Twenty aldehydes were identified in these oils. PCA was used to explore the contribution of different aldehydes on the flavor changes of the 10 frying oils. Score and loading plots of PCA for changes of all aldehydes detected in 10 frying oils are shown in Figure 5-2. The PC1 and PC2 expressed 38.66% and 22.61% of the variability of all aldehydes changes, respectively.

Projection of the oils on the first two principal components (explained variability: 61.27%) showed a clear separation of the 10 oils (Figure 5-2*a*). The distribution of all aldehydes detected in OL over heating time was very scattered on the score plots, indicating that the aldehydes detected in OL varied greatly with heating time. Conversely, the distribution of all aldehydes detected in NP over heating time was the most concentrated, indicating that the aldehydes detected in the NP changed little with heating time. This was consistent with Figure 5-1. According to the distribution of these oils, it can be found that it was related to the composition of unsaturated fatty acids, that is, the distribution of aldehydes detected in each oil was related to the unsaturated fatty acid composition of the oil.

In the frying process, the aldehydes detected in OL were the most and the area was the largest. OL, the oil with the highest oleic acid content, was located in the positive direction of PC1 and PC2, mainly affected by butanal, pentanal, hexanal, heptanal, octanal, nonanal, (E)-2-nonenal, (E)-2-decenal, and (E)-2-undecenal. Heptanal, octanal, nonanal, (E)-2-decenal, and (E)-2-undecenal were thermal decomposition products derived from oleic acid (Snyder et al., 1985; Zhang et al., 2015), while butanal, pentanal, hexanal, and (E)-2-nonenal were thermal decomposition products derived from linoleic acid (Morales et al., 1997). Previous studies have also found that saturated aldehydes, such as pentanal, hexanal, octanal, and nonanal, are the main products of oxidized olive oil (Snyder et al., 1985). SF, another oleic acid-based oil, lied on the axis of PC1, mainly affected by pentanal, hexanal, and nonanal. (E)-2-undecenal was only detected in RB, OL, and SF, but the content is very small.

Oils containing a large amount of linoleic acid, namely NS, SB, CO, and RB, were located in the lower part of PC1 and were all affected by (E)-2-hexenal, (E)-2-heptenal, and (E,E)-2,4-decadienal. (E)-2-Heptenal and (E,E)-2,4-decadienal were products of linoleic acid oxidation, which were considered to be the source of attractive aromas produced during frying (RG, 1989). In addition, SB, CO, and RB were also affected by 2,4-undecadienal, which were not detected in NS.



No.	Volatile compound
1	Butanal
2	Pentanal
3	Hexanal
4	(E)-2-Heptenal
5	(E)-2-Nonenal
6	(E,E)-2,4-Decadienal
7	(E)-2-Methyl-2-butenal
8	Furfural
9	(E)-2-Hexenal
10	2-methyl-Butanal
11	2-Octenal
12	2,4-Undecadienal
13	Heptanal
14	Octanal
15	Nonanal
16	(E)-2-Decenal
17	(E)-2-Undecenal
18	2-Butenal
19	(E)-2-Pentenal
20	(E,E)-2,4-Heptadienal

Figure 5-2 Score (*a*) and loading plots (*b*) of principal component analysis for changes of all aldehydes detected in the 10 frying oils

The distribution of SS almost coincided with OL. In addition to being affected by butanal, pentanal, and hexanal, like OL, it was also affected by 2-methyl-butanal, like the linoleic acid-rich oils. Furthermore, SS was also affected by furfural, which was only detected in SS. Furfural can easily turn brown or dark red when exposed to light or air, which is the reason why the color of roasted sesame oil was obviously deepened (Yang et al., 2013).

NP and PL, mainly composed of linolenic acid, distributed in the upper left of Figure 5-2*a*. The aldehydes, 2-butenal, (E)-2-pentenal, and (E,E)-2,4-heptadienal, were the major contributors to their distribution. These three aldehydes were all oxidation product produced from linolenic acid (Sano et al., 2014; Zhang et al., 2015). Among them, 2-butenal was only detected in PL, NP, RS, and OL and the amount in PL was the most. (E)-2-Methyl-2-butenal was only detected in PL.

RS was mainly affected by 2-butenal, pentanal, hexanal, (E,E)-2,4-heptadienal, and nonanal. The distribution of RS was close to that of oils with much oleic acid and oils with much linoleic acid, and also close to linolenic acid-based oils, indicating that it was simultaneously affected by the aldehydes produced by these three unsaturated fatty acids. Therefore, as the TUFA content decreased linearly with heating time (Liu et al., 2019), the total content of aldehydes detected in RS increased linearly with heating time (Figure 5-1).

From loading plots (Figure 5-2*b*), PC1 was strongly related to pentanal, hexanal, heptanal, (E)-2-heptenal, octanal, 2-octenal, nonanal, (E)-2-decenal, and (E)-2-undecenal in the positive direction, whereas in the negative direction, (E,E)-2,4-heptadienal was dominant. Main aldehydes positively correlated to PC2 were 2-butenal and (E)-2-pentenal, whereas the main substances negatively correlated to PC2 were 2,4-undecadienal and (E,E)-2,4-decadienal.

Pentanal, hexanal, (E)-2-heptenal, and nonanal were aldehydes detected in all 10 oils. They may be the source of the unpleasant odor (Prevot et al., 1988; Matthaus and Bruhl, 2004; Raghavan et al., 1994). However, (E)-2-heptenal is also considered to be related to the attractive aroma produced during the frying process (Prevot et al., 1988), which may be related to its concentration.

Because they can be detected in all oils, they can be used as flavor evaluation indicator for frying oils. At present, they have been widely used as quality monitoring indicators of oil for automatic oxidation processes (Warner et al., 1978; Abdalla and Roozen, 1999; Kanavouras et al., 2004).

5.4.2.2 The effect of changes in alcohols with heating time on the flavor of oils

Figure 5-3 shows the total area of alcohols detected in 10 frying oils during frying. Except for RS, the total area of alcohols detected in other oils did not gradually increase with increasing heating time. It indicates that as the heating time increasing, the unsaturated fatty acid would be thermally oxidized to form alcohols, but the alcohols formed were not stable and would be lost in the subsequent frying operation. Zhang et al. (Zhang et al., 2018) also found in the process of frying, the strong boiling caused by the addition of food could lead to a large loss of alcohols formed. The total area of alcohols detected in OL was obviously the largest of these oils, followed by PL, and they increased significantly as the heating time increased.

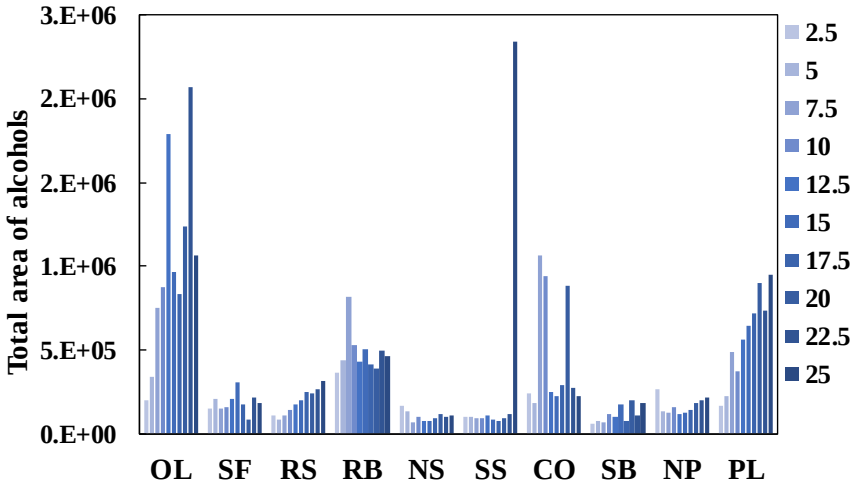


Figure 5-3 The total area of alcohols detected in the 10 frying oils during frying

PCA was performed on the changes of all alcohols detected in the 10 oils during frying. The result was shown in Figure 5-4, which described 61.56% of the total variance with 42.15% by PC1 and 19.41% by PC2. Affected by various alcohols detected, the score plots of the flavor characteristics of each oil during frying with the extension of heating time were clearly separated

according to the type of oil (Figure 5-4*a*). Since OL had the most kinds of alcohols detected and the highest total area of alcohols, and its total area changed the most with the extension of heating time, its score plots presented the most scattered, followed by PL. Conversely, alcohols detected in NS had the smallest total area and the smallest change with heating time, therefore its score plots was the most concentrated.

OL was distributed along the positive direction of the PC1 axis and affected by ethanol, 2-methylpropanol, 1-pentanol, 1-heptanol, and 1-octanol simultaneously. 1-Heptanol and 1-octanol were decomposition products of oleic acid, while ethanol and 1-pentanol were thermal decomposition products derived from linoleic acid. 1-Octanol was only detected in OL. Although it had a small amount, it had the greatest contribution to PC1, which was the main reason affecting the distribution of OL and the unique aroma source from alcohol that distinguished OL from other oils. SF was adjacent to the distribution of OL and affected by 2-methylpropanol, 1-pentanol, and 1-heptanol. 1-Heptanol was only detected in OL and SF, which may be related to the fact that OL and SF contained the most oleic acid content.

RB, CO, RS, and NP were all affected by 2-methylpropanol, 1-penten-3-ol, and 1-pentanol. Therefore, their distribution was close, but the difference in the content of these three alcohols leaded to a slight difference in their distribution. SB, NS, and SS were affected by 2-methylpropanol, (Z)-2-penten-1-ol, and 1-pentanol, and mainly distributed to the left of the PC2 axis. The 25-hour sample of SS was strongly influenced by ethanol, making it distributed away from other points of SS in score plots. Ethanol, 2-methylpropanol, and (Z)-2-penten-1-ol mainly affected PL, so that it was distributed in the upper left of the Figure 5-4*a*.

2-Methylpropanol and 1-pentanol were detected in all oils. They are considered to be involved in the off-flavor in the frying oils (Matthaus and Bruhl, 2004; Lee and Choe, 2012). In addition, (Z)-2-penten-1-ol was not detected in the oil in which 1-penten-3-ol was detected, and 1-penten-3-ol was not detected in the oil in which (Z)-2-penten-1-ol was detected. This may be due to the positional

isomerization of hydroxyl and double bond in 1-penten-3-ol to form 2-penten-1-ol under the reaction conditions of frying.

From the factor loadings (Figure 5-4*b*), ethanol, 1-pentanol, 1-heptanol, and 1-octanol were mainly contributed to PC1. 2-Methylpropanol and (Z)-2-penten-1-ol were contributed to positive direction of PC2, while 1-penten-3-ol was contributed to negative direction of PC2.

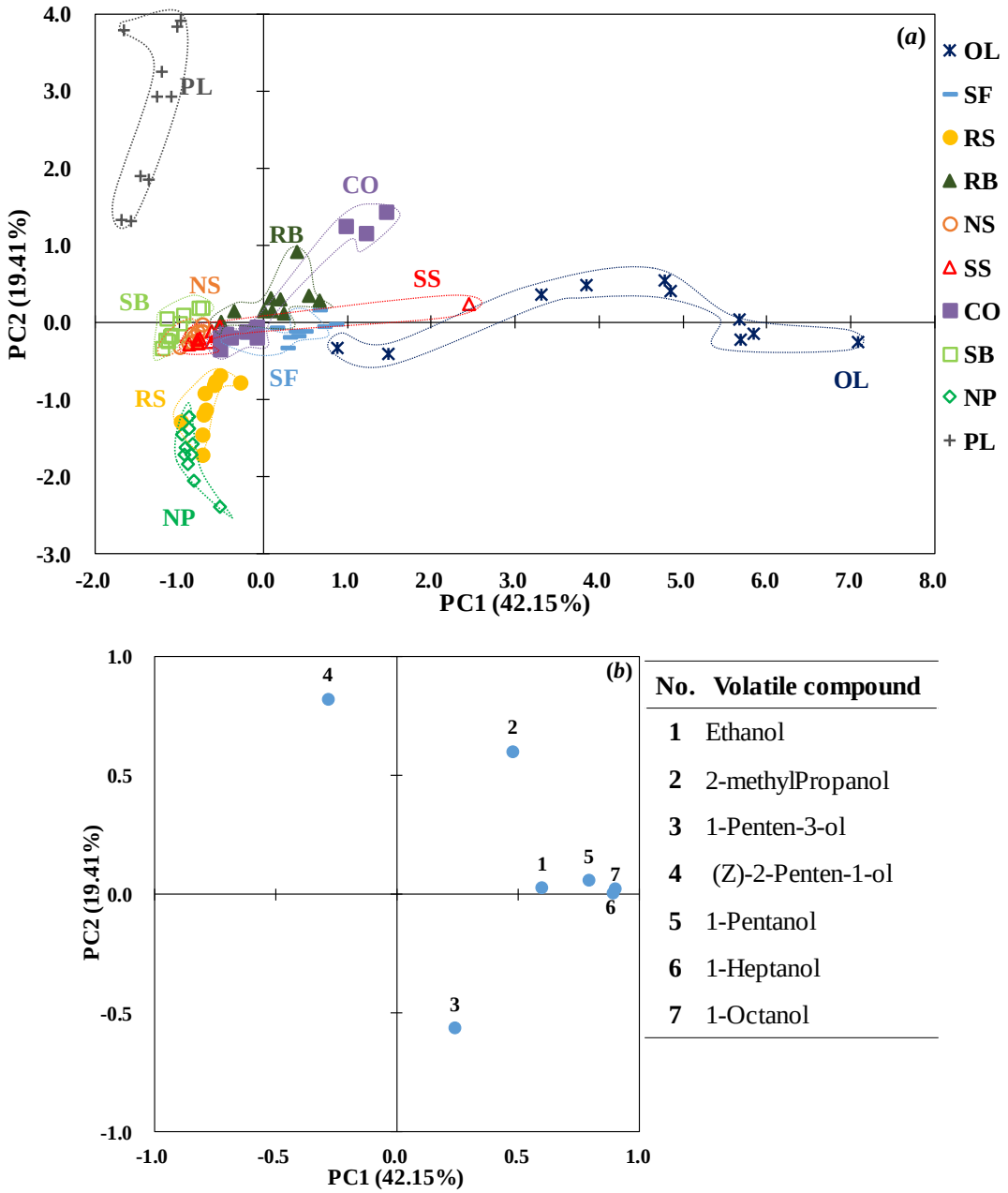


Figure 5-4 Principal component analysis of changes in all alcohols detected in the 10 frying oils: (*a*) score and (*b*) loading plots

5.4.2.3 The effect of changes in other volatile compounds except aldehydes and alcohols with heating time on the flavor of oils

In addition to aldehydes and alcohols, alkanes, ketones, pyridines, esters, furans, benzene, alkenes, and acids have also been detected in frying oils. Aldehydes and alcohols account for a large proportion of all volatile compounds detected, while only a small amount and type of the other volatile compounds are detected. Therefore, they are considered as one category. Figure 5-5 shows the total area of these compounds detected in the 10 frying oils during frying. Among these oils, the total area of these substances detected in SS and PL was the largest.

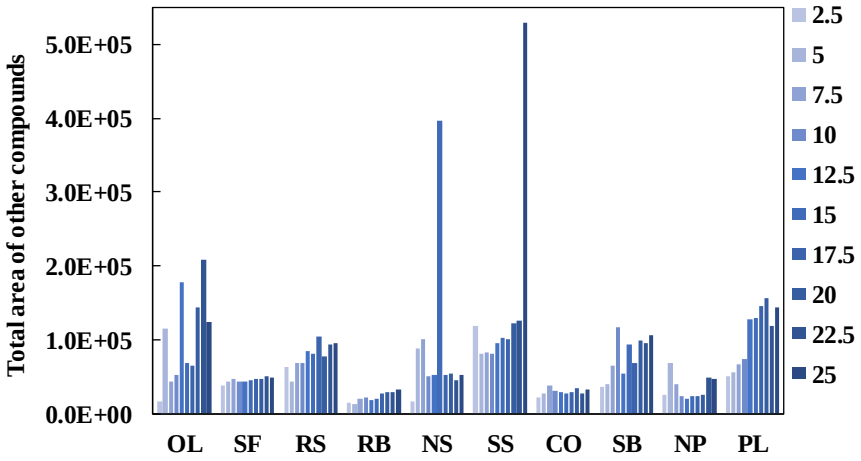


Figure 5-5 The total area of other compounds except aldehydes and alcohols detected in the 10 frying oils during frying

PCA was also performed on the changes of all volatile compounds except aldehydes and alcohols detected in 10 oils during frying (Figure 5-6). The first two principal components account for only 48.45% of the total variance, due to the variety of these substances and the lack of similarity. PC1 expressed 28.89% of the variability of all other compounds changes while PC2 expressed 19.56% of the variability.

2-Hexanone, 2-octanone, methyl pyrazine, ethyl acetate, 2-pentylfuran, hexane, methyl-cyclopentane, and decane mainly affected the distribution of SS, which was distributed in the upper right part of the Figure 5-6*a*. 2-Hexanone was only detected in SS among them.

Although 2-octanone, methylpyrazine, methyl-cyclopentane, and butyl-cyclopentane were little in content, they together with ethyl acetate, 2-pentylfuran, toluene, and hexane played a major role in the distribution of OL. OL was mainly distributed in the lower right part of the figure. The cyclic alkanes, methyl-cyclopentane and butyl-cyclopentane, were mainly detected in oils containing a large amount of oleic acid. Methyl-cyclopentane was only detected in OL, SS, and NS. While butyl-cyclopentane was only detected in OL, SF, RS, and RB. Long-term frying at high temperature caused the formation of cyclic hydrocarbons such as methyl-cyclopentane, butyl-cyclopentane, etc., but the content detected was small due to their relatively low volatility. This result was consistent with the conclusion of previous study (Alencar et al., 1983), which found that small amounts of cyclic hydrocarbons as pyrolysis products were detected in the oleic acid-based triglycerides. Toluene was only detected in OL, RS, SB, and NP, which may be related to their relatively high linolenic acid content (Zhang et al., 2018). Methylpyrazine was only detected in small amounts in OL and SS.

CO, RB, and SF were located at the bottom left of the figure, which were mainly affected by 2-pentylfuran and decamethylcyclopentasiloxane. The distribution of RS, NS, and SB was at the center and affected by 2-pentylfuran, acetic acid, and hexane simultaneously. In addition, RS and SB were also affected by 2-octanone and 2-ethyl-6-methylpyrazine, causing them to be mainly located above the PC1 axis. Similarly, NS and SB were also affected by ethyl acetate, heptane, and decane, causing them to be distributed on the right side of the PC2 axis. Except PL and NP, 2-pentylfuran was detected in all other oils, which was the oxidative decomposition product of linoleic acid. It was often considered to be the cause of offensive odor of SB, which was initially bean flavor and grass flavor, and after further development, was fishy flavor and painty flavor (Min et al., 2003).

NP and PL were distributed on the upper left of the figure, mainly affected by acetic acid and 2-ethyl-6-methylpyrazine. 2-Ethyl-6-methylpyrazine was only detected in RS, SB, PL, and NP, which gave these oils nutty, roasting, and sweet aroma. In addition, PL was also affected by 2,3,5-trimethylpyrazine, which was only detected in small amounts in PL. It was abundant in SS and PL before heating and volatized immediately upon heating.

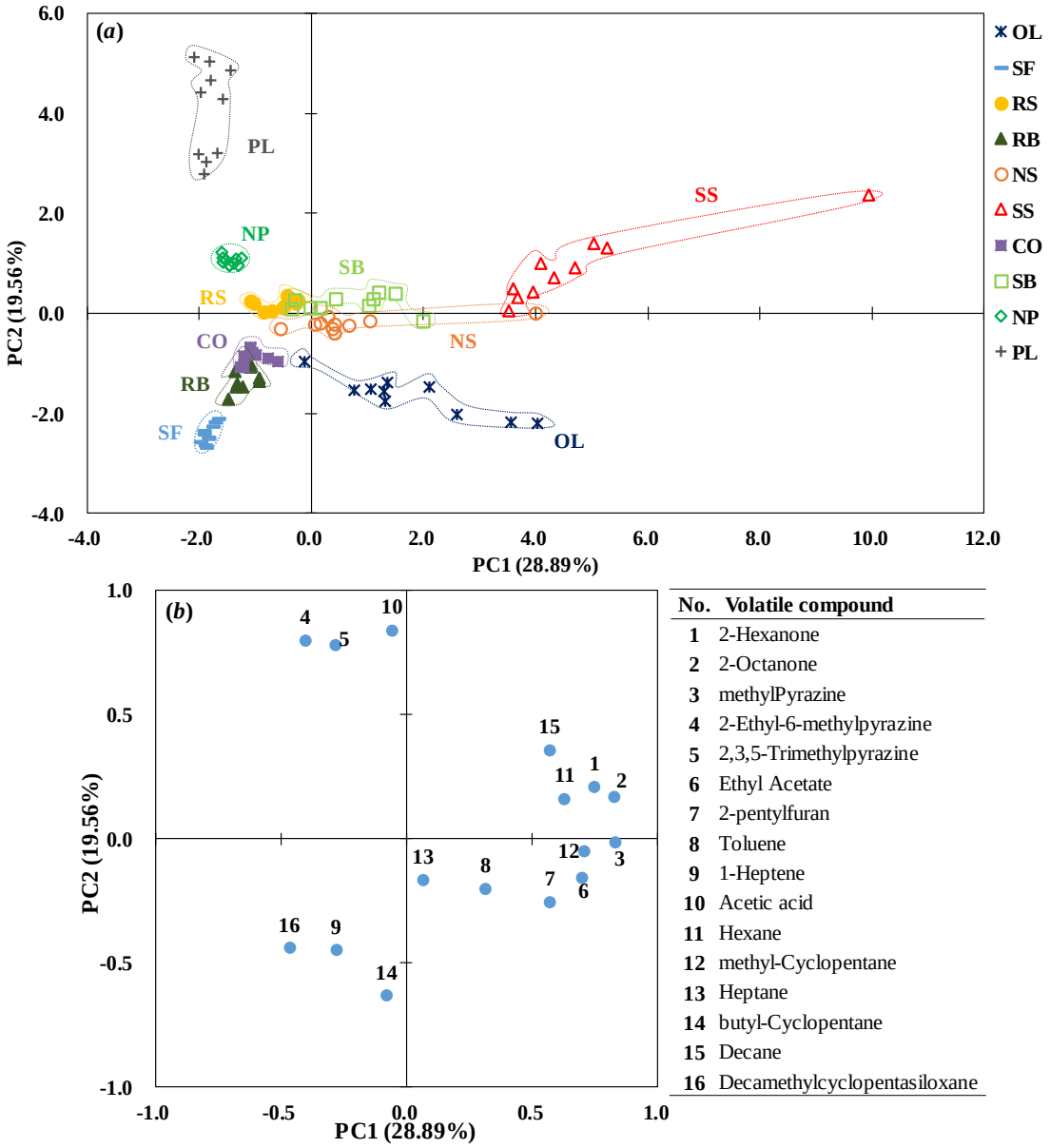


Figure 5-6 Principal component analysis of changes in all compounds except aldehydes and alcohols detected in the 10 frying oils: (*a*) score and (*b*) loading plots

From the factor loadings (Figure 5-6*b*), PC1 was mainly contributed by ketones including 2-hexanone and 2-octanone, methylpyrazine, ethyl acetate, and methyl-cyclopentane. PC2 was mainly contributed by acetic acid and pyrazines including 2-ethyl-6-methylpyrazine and 2,3,5-trimethylpyrazine in the positive direction, whereas the main substances negatively correlated to PC2 was butylcyclopentane. Volatile substances in addition to aldehydes and alcohols detected in oils have little in common and are more complex, but they are also an important part affecting the flavor quality of frying oil, which needs to be further explored.

5.4.3 The relationship between the changes of volatile components detected and the changes of total unsaturated fatty acid, total tocopherol, carbonyl value, and total polar compounds

5.4.3.1 The relationship between the changes of volatile components detected and the changes of total unsaturated fatty acid

To explore the relationship between the changes of volatile compounds with heating time and the changes of TUFA in oils, the correlation analysis between them has been carried out (Table 5-2). Because TUFA linearly decreased with heating time, the negative correlation coefficient in the table indicated that the volatile compound increased with the decrease of TUFA, while the positive correlation coefficient indicated that the volatile compound decreased with the decrease of TUFA. Moreover, the large coefficient indicated that the change of volatile compound was closely related to the decrease of TUFA. The correlation coefficients were mostly negative, indicating that as the TUFA content decreased, the content of most of volatile compounds was gradually increasing.

Pentanal was detected in all oils, and its correlation coefficients were negative in all oils. Except for the relatively small coefficient in SF (-0.579), CO (-0.582), and NP (-0.478), the correlation coefficients in other oils were large, indicating that it gradually increased with the decrease of TUFA in these oils. Although correlation coefficients of (E)-2-heptenal and nonanal, which were also detected in all oils, were negative, they were small, that is, the increase of (E)-2-heptenal and nonanal were not closely related to the decrease of TUFA in each oil. Hexanal, 2-methylpropanol, 1-pentanol, and hexane were detected in all oils, but their changes were inconsistent among 10 oils. Octanal and 2-octanone had a high negative correlation in the oils that can be detected, indicating that their increase and the decrease of TUFA were closely related as long as they can be detected in the oil.

In addition, hexanal, heptanal, and octanal had high correlation coefficients with the decreases of TUFA in oils rich in oleic acid. They may be used for quality evaluation of oils with high oleic

acid content. There were high correlation coefficients between the changes of most volatile compounds detected in RB and the changes in TUFA, indicating that most volatile compounds detected in RB increased regularly, especially aldehydes. The increase of many volatile compounds with small molecular weights detected in PL (2-butenal, 2-methyl-butanal, pentanal, (E)-2-methyl-2-butenal, and (E)-2-pentenal) was highly correlated with the decrease of TUFA. In addition, other volatile compounds detected in PL changed almost irregularly. There is not a good correlation between the changes in volatile compounds detected in CO and NP and the changes in TUFA, indicating that the changes in volatile compounds detected in CO and NP were irregular.

Table 5-2 The correlation between the area changes of volatile compounds and the changes of total unsaturated fatty acid in the 10 oils with heating time

Correlation coefficient		Total unsaturated fatty acid									
		OL	SF	RS	RB	NS	SS	CO	SB	NP	PL
Aldehyde	Butanal	-0.416	-	0.118	-0.604	-0.404	-	-	0.574	-	0.425
	2-Butenal	-0.562	-	-0.810	-	-	-0.745	-	-	-0.391	-0.807
	2-methyl-Butanal	-	-0.774	-	-0.898	-0.775	-0.810	0.538	0.186	-	-0.817
	Pentanal	-0.908	-0.579	-0.986	-0.986	-0.977	-0.979	-0.582	-0.986	-0.478	-0.977
	(E)-2-Methyl-2-butenal	-	-	-	-	-	-0.886	-	-	-	-0.925
	(E)-2-Pentenal	-0.614	-	-0.790	-	-	-0.885	-	-	-0.232	-0.922
	Hexanal	-0.896	-0.771	-0.975	-0.982	-0.967	-0.970	-0.544	-0.973	0.260	-0.397
	(E)-2-Hexenal	-0.784	-0.386	-	-0.858	-0.279	-0.743	-0.462	-0.742	-	0.380
	Heptanal	-0.971	-0.894	-0.917	-0.922	-0.889	-	-0.616	-0.916	-	0.425
	(E)-2-Heptenal	-0.723	-0.377	-0.753	-0.934	-0.359	-0.776	-0.627	-0.656	-0.578	-0.702
	Octanal	-0.971	-0.864	-0.906	-0.985	-0.820	-	-0.770	-	-	-
	(E,E)-2,4-Heptadienal	0.176	-	0.511	-0.216	-	0.862	-	0.010	-0.166	-0.060
	2-Octenal	-0.853	-0.557	-0.736	-0.922	-0.378	-	-0.549	-0.693	-	-
	Nonanal	-0.731	-0.035	-0.656	-0.849	-0.056	-0.599	-0.359	-0.708	-0.814	-0.747
	(E)-2-Nonenal	-0.715	-0.519	-	-	-	-	-	-	-	-
	(E)-2-Decenal	-0.424	-0.297	-0.736	-0.938	-0.354	-	-	-	-	-
	2,4-Undecadienal	-	-	-	-0.402	-	-	-0.383	-0.220	-	-
	(E,E)-2,4-Decadienal	-	0.455	0.302	-0.515	0.121	-	-0.388	-0.224	-	-
	(E)-2-Undecenal	-0.358	-0.253	-	-0.928	-	-	-	-	-	-

	Ethanol	-0.327	-	-	-	-	-0.422	-	-	0.085	-0.039
	2-methylPropanol	-0.334	-0.220	-0.983	-0.165	0.533	0.535	-0.145	-0.695	-0.067	-0.855
	1-Penten-3-ol	-0.572	-	0.623	-0.220	-	-	-0.226	-	0.143	-
Alcohol	(Z)-2-Penten-1-ol	-	-	-	-	-0.957	0.157	-	-0.728	-	-0.519
	1-Pentanol	-0.904	-0.603	-0.904	-0.962	-0.842	-0.408	-0.555	-0.907	-0.538	0.259
	1-Heptanol	-0.928	-0.554	-	-	-	-	-	-	-	-
	1-Octanol	-0.820	-	-	-	-	-	-	-	-	0.425
	2-Hexanone	-	-	-	-	-	-0.918	-	-	-	-
	2-Octanone	-0.806	-	-0.977	-	-	-0.881	-	-0.975	-	-
	methylPyrazine	-0.639	-	-	-	-	0.492	-	-	-	0.425
	2-Ethyl-6-methylpyrazine	-	-	0.605	-	-	0.510	-	-0.098	-0.191	-0.461
	2,3,5-Trimethylpyrazine	-	-	-	-	-	0.510	-	-	-	0.394
	Ethyl Acetate	-0.698	-	-	-	-0.512	-0.794	-	-0.451	-	-
Substance	2-Pentylfuran	-0.608	-0.211	-0.950	-0.895	-0.901	0.167	-0.330	-0.959	-	-
other than	Toluene	0.235	-	-0.347	-	-	-	-	-0.033	-0.147	-
aldehyde and	1-Heptene	-	-0.945	-	-	-	-	-	-	-	-
alcohol	Acetic acid	-	0.046	-0.936	-	-0.939	0.465	-0.866	-0.971	-0.759	0.228
	Hexane	-0.020	-0.885	-0.770	-0.976	0.115	-0.070	0.538	-0.971	-0.069	-0.760
	methyl-Cyclopentane	-0.326	-	-	-	0.207	-0.271	-	-	-	0.425
	Heptane	-	-0.286	-	-	-0.743	-	-	0.012	-	-
	butyl-Cyclopentane	-0.536	-0.130	-0.301	-0.754	-	-	-	-	-	-
	Decane	-	-	-	-	-0.692	0.410	-	0.082	-	0.059
	Decamethylcyclopentasiloxane	-	0.277	-	0.159	-	-	-0.582	-	-	0.374

“-”, indicates that the compound has not been detected, or that the correlation coefficient is less than 0.001.

5.4.3.2 The relationship between the changes of volatile components detected and the changes of total tocopherol

Because tocopherol exerts its antioxidative effect and gradually decreases during the frying process, in order to explore the inhibitory effect of tocopherol on the volatile components produced, the correlation between the changes of volatile compounds with heating time and the reduction in TToc in oils has been analyzed (Table 5-3). Because TToc gradually decreased with heating time, the negative correlation coefficient in the table indicated that the volatile compound increased with the decrease of TToc, while the positive correlation coefficient indicated that the volatile compound decreased with the decrease of TToc. Moreover, the greater the correlation coefficient, the closer the relationship between the change of volatile compound and the decrease of TToc.

The correlation coefficients were mostly negative, indicating that as the weakening of antioxidant effect of TToc, most volatile compounds were gradually formed and accumulated. The correlation coefficients of pentanal and (E)-2-heptenal, detected in all oils, were all negative and most of them were large, indicating that pentanal and (E)-2-heptenal gradually increased with the decrease of TToc in these oils. Hexanal, 2-methylpropanol, 1-pentanol, and hexane were detected in all oils, but their changes were inconsistent among 10 oils. Octanal, (E)-2-decenal, and 2-octanone had a high negative correlation in the oils that can be detected, indicating that their increase and the decrease of TToc were closely related as long as they can be detected in the oil.

The increase of pentanal, hexanal, heptanal, (E)-2-heptenal, octanal, 2-octenal, (E)-2-decenal, 1-pentanol, and 2-pentylfuran had a high correlation with the decrease of TToc in oils rich in oleic acid. The increase in volatile components, (E)-2-hexenal and (E)-2-undecenal, detected in OL, SF, and RB showed a good correlation with the reduction of TToc. (E)-2-Nonenal and 1-heptanol, only detected in OL and SF, had a regular increase with the decrease in TToc. Compared with other oils, the increase in volatile compounds detected in oils with a high oleic acid content had the greatest correlation with the decrease in tocopherol content.

For NS, only the increase of 2-methylbutanal, octanal, 2-pentylfuran, and heptane had a good correlation with the decrease of TToc (correlation coefficient was greater than 0.8). The increase in volatile components with smaller molecular weights detected in SS correlated well with the decrease in TToc. For CO, only the increase of 2-ethyl-6-methylpyrazine and hexane had a good correlation with the decrease of TToc.

The changes of volatile components, 2-butenal, 2-methyl-butanal, pentanal, (E)-2-methyl-2-butenal, (E)-2-pentenal, 2-methylpropanol, and hexane, detected in PL showed a good negative correlation with the reduction of TToc. In contrast, all changes in volatile components detected in NP did not correlate well with the reduction in tocopherol.

In summary, with the decrease of TUFA and TToc, most of the volatile components showed an increasing trend. Pentanal was detected in all oils, and its increase was closely related to the reduction of TUFA and TToc. Therefore, pentanal may be used as a flavor evaluation index for frying oil. Among the oils that 2-octanone can be detected, its increase was closely related to the decrease of TUFA and TToc. In addition, hexanal, heptanal, and octanal can be used as flavor evaluation indicators for oils with high oleic acid content.

Table 5-3 The correlation between the area changes of volatile compounds and the content changes of total tocopherol in the 10 oils with heating time

Correlation coefficient		Total tocopherol									
		OL	SF	RS	RB	NS	SS	CO	SB	NP	PL
Aldehyde	Butanal	-0.170	-	-	-0.622	-0.650	-	-	0.571	-	0.474
	2-Butenal	-0.819	-	-0.788	-	-	-0.841	-	-	-0.334	-0.881
	2-methyl-Butanal	-	-0.519	-	-0.902	-0.854	-0.924	0.597	0.173	-	-0.894
	Pentanal	-0.776	-0.841	-0.938	-0.978	-0.738	-0.973	-0.545	-0.986	-0.413	-0.981
	(E)-2-Methyl-2-butenal	-	-	-	-	-	-0.911	-	-	-	-0.948
	(E)-2-Pentenal	-0.805	-	-0.736	-	-	-0.942	-	-	-0.181	-0.967
	Hexanal	-0.769	-0.890	-0.916	-0.967	-0.703	-0.953	-0.462	-0.950	0.283	-0.337
	(E)-2-Hexenal	-0.906	-0.852	-	-0.874	-0.431	-0.896	-0.471	-0.731	-	0.424
	Heptanal	-0.743	-0.846	-0.891	-0.901	-0.625	-	-0.621	-0.887	-	0.474
	(E)-2-Heptenal	-0.909	-0.932	-0.721	-0.929	-0.491	-0.844	-0.646	-0.629	-0.556	-0.757
	Octanal	-0.748	-0.900	-0.876	-0.983	-0.897	-	-0.792	-	-	-
	(E,E)-2,4-Heptadienal	-0.500	-	0.533	-0.240	-	0.800	-	0.045	-0.129	-0.129
	2-Octenal	-0.855	-0.932	-0.735	-0.943	-0.344	-	-0.569	-0.689	-	-
	Nonanal	-0.895	-0.585	-0.703	-0.871	-	-0.612	-0.376	-0.692	-0.781	-0.778
	(E)-2-Nonenal	-0.947	-0.940	-	-	-	-	-	-	-	-
	(E)-2-Decenal	-0.946	-0.935	-0.728	-0.940	-0.548	-	-	-	-	-
	2,4-Undecadienal	-	-	-	-0.428	-	-	-0.432	-0.202	-	-
	(E,E)-2,4-Decadienal	-	-0.299	0.295	-0.551	-0.147	-	-0.434	-0.232	-	-
	(E)-2-Undecenal	-0.894	-0.896	-	-0.939	-	-	-	-	-	-

	Ethanol	0.034	-	-	-	-	-0.395	-	-	0.082	-0.091
	2-methylPropanol	-0.697	-0.524	-0.954	-0.166	0.835	0.650	-0.139	-0.674	-0.049	-0.820
	1-Penten-3-ol	-0.839	-	0.650	-0.243	-	-	-0.228	-	0.197	-
Alcohol	(Z)-2-Penten-1-ol	-	-	-	-	-0.797	0.295	-	-0.723	-	-0.617
	1-Pentanol	-0.852	-0.922	-0.876	-0.956	-0.719	-0.327	-0.549	-0.885	-0.489	0.316
	1-Heptanol	-0.866	-0.973	-	-	-	-	-	-	-	-
	1-Octanol	-0.938	-	-	-	-	-	-	-	-	0.474
	2-Hexanone	-	-	-	-	-	-0.870	-0.344	-	-	-
	2-Octanone	-0.799	-	-0.993	-	-	-0.858	-	-0.960	-	-
	methylPyrazine	-0.685	-	-	-	-	0.613	-	-	-	0.474
	2-Ethyl-6-methylpyrazine	-	-	0.624	-	-	0.622	-0.865	-0.067	-0.154	-0.538
	2,3,5-Trimethylpyrazine	-	-	-	-	-	0.622	0.597	-	-	0.447
	Ethyl Acetate	-0.644	-	-	-	-0.750	-0.836	-	-0.440	-	-
Substance	2-Pentylfuran	-0.953	-0.679	-0.969	-0.880	-0.806	0.073	-	-0.942	-	-
other than	Toluene	0.688	-	-0.299	-	-	-	-	-0.038	-0.097	-
aldehyde and	1-Heptene	-	-0.611	-	-	-	-	-	-	-	-
alcohol	Acetic acid	-	-0.737	-0.937	-	-0.700	0.582	-0.656	-0.956	-0.712	0.283
	Hexane	0.457	-0.859	-0.811	-0.967	-0.054	0.024	-0.967	-0.972	-0.029	-0.845
	methyl-Cyclopentane	-0.046	-	-	-	0.048	-0.240	1.000	-	-	0.474
	Heptane	-	0.067	-	-	-0.824	-	0.971	0.004	-	-
	butyl-Cyclopentane	-0.936	-0.819	-0.349	-0.773	-	-	-	-	-	-
	Decane	-	-	-	-	-0.619	0.323	-	0.089	-	-0.105
	Decamethylcyclopentasiloxane	-	-0.186	-	0.079	-	-	-	-	-	0.397

“-”, indicates that the compound has not been detected, or that the correlation coefficient is less than 0.001.

5.4.3.3 The relationship between the changes of volatile components containing carbonyl and the changes of carbonyl value

Most of the volatile compounds detected contain carbonyl, which make up the CV of the frying oil. To explore the relationship between the changes of volatile compounds containing carbonyl with heating time and the changes of CV in oils, the correlation analysis between them has been carried out (Table 5-4). Due to CV linearly increased with heating time during frying, the positive correlation coefficient indicated that the volatile compound increased with the increase of CV, whereas the negative correlation coefficient in the table indicated that the volatile compound decreased with the increase of CV. Moreover, the large coefficient indicated that the change of volatile compound was closely related to the increase of CV. Most of the correlation coefficients were positive, indicating that as the CV increased, the content of most of volatile compounds containing carbonyl was gradually increasing.

Pentanal was detected in all oils. The correlation coefficients between its changes and the increase of CV were positive in 10 oils. Except for the relatively small coefficient in CO (0.483), and NP (0.492), the correlation coefficients in other oils were large, indicating that it gradually increased with the increase of CV in these oils. Although correlation coefficients of (E)-2-heptenal and nonanal, which were also detected in all oils, were positive, they were small in some oils, like SS and NS. It indicated that the increase of (E)-2- heptenal and nonanal were not closely related to the increase of CV in each oil. Hexanal was also detected in all oils, but its changes were inconsistent in 10 oils. 2-Octanone had a high negative correlation in the oils that can be detected, indicating that its increase and the increase of CV were closely related as long as it can be detected in the oil.

The increase of hexanal, heptanal, and octanal had a high correlation with the increase of CV in oils rich in oleic acid. Compared with other oils, the volatile components containing carbonyl showing a good correlation between the increase in volatile substances and the increase in CV in oils containing much oleic acid were the most, especially in RB, followed by oils rich in linoleic

acid. The increase in volatile substances containing carbonyl with a small molecular weight detected in the PL correlated well with the increase in CV, while the increase in all volatile substances containing carbonyl detected in the NP did not correlate well with the increase in CV.

Table 5-4 The correlation between the area changes of volatile compounds containing carbonyl and the changes of carbonyl value with heating time

Correlation coefficient	Carbonyl value									
	OL	SF	RS	RB	NS	SS	CO	SB	NP	PL
Butanal	0.399	-	-0.032	0.610	0.476	0.363	-	-0.611	-	-0.486
2-Butenal	0.678	-	0.796	-	-	-	-	-	0.399	0.865
2-methyl-Butanal	-	0.762	-	0.901	0.823	0.530	-0.466	-0.184	-	0.889
Pentanal	0.958	0.718	0.959	0.991	0.954	0.943	0.483	0.979	0.492	0.995
(E)-2-Methyl-2-butenal	-	-	-	-	-	-	-	-	-	0.961
(E)-2-Pentenal	0.723	-	0.784	-	-	-	-	-	0.250	0.959
Hexanal	0.948	0.889	0.938	0.984	0.941	0.654	0.465	0.958	-0.389	0.339
Furfural	-	-	-	-	-	-0.396	-	-	-	-
(E)-2-Hexenal	0.860	0.561	-	0.891	0.316	-0.410	0.361	0.732	-	-0.438
Heptanal	0.987	0.957	0.921	0.933	0.882	0.899	0.524	0.908	-	-0.486
(E)-2-Heptenal	0.812	0.579	0.781	0.954	0.395	0.375	0.538	0.667	0.627	0.760
Octanal	0.989	0.954	0.923	0.992	0.840	0.483	0.721	-	-	-
(E,E)-2,4-Heptadienal	-0.137	-	-0.464	0.286	-	-	-	0.028	0.238	0.125
2-Octenal	0.921	0.725	0.793	0.949	0.378	0.542	0.451	0.730	-	-
Nonanal	0.738	0.152	0.737	0.890	0.034	0.129	0.257	0.741	0.833	0.779
(E)-2-Nonenal	0.782	0.672	-	-	-	0.022	-	-	-	-
(E)-2-Decenal	0.518	0.508	0.790	0.961	0.374	-	-	-	-	-
2,4-Undecadienal	-	-	-	0.458	-	-	0.296	0.285	-	-
(E,E)-2,4-Decadienal	-	-0.318	-0.227	0.571	-0.086	-	0.298	0.287	-	-
(E)-2-Undecenal	0.465	0.475	-	0.939	-	-	-	-	-	-
2-Hexanone	-	-	-	-	-	0.919	-	-	-	-
2-Octanone	0.879	-	0.989	-	-	0.899	-	0.972	-	-
Ethyl Acetate	0.783	-	-	-	0.576	0.849	-	0.455	-	-
Acetic acid	-	0.157	0.945	-	0.917	-0.489	0.837	0.962	0.723	-0.291

"-", indicates that the compound has not been detected, or that the correlation coefficient is less than 0.001.

5.4.3.4 The relationship between the changes of volatile components detected and the changes of total polar compounds

All volatile substances detected in the oil are polar compounds and their changes have an effect on the change of TPC. Correlation analysis between the changes of volatile compounds detected and the increase in TPC during frying was conducted (Table 5-5). Most of the correlation coefficients were positive, indicating that these volatile compounds increased as TPC increased during frying. Because ΔTPC_t had a good linear relationship with time, volatile substances with high correlation coefficient also increased with time during the frying process.

As common substances detected in all 10 oils, pentanal, (E)-2-heptenal, and nonanal increased with increasing TPC in all oils. Except that the correlation coefficients in SF, CO, and NP were small, the increase of pentanal detected in other oils had a good linear relationship with the increase of TPC. As to (E)-2-heptenal and nonanal, the correlation coefficients were only large in RB and small in other oils. Hexanal, 2-methylPropanol, 1-Pentanol, and hexane were also detected in all oils. However, there were positive and negative correlation coefficients between their changes and the increase of TPC, indicating that their change trend in all oils is inconsistent, either increasing or decreasing. In addition, 2-octanone was detected in OL, RS, SS, and SB, and its increase was highly correlated with the increase in TPC, indicating that it would accumulate over time as long as it was detected during frying.

The increase of hexanal, heptanal, and octanal had high correlation coefficients with the increase of TPC in oils rich in oleic acid. The volatile components showing a good correlation between the increase in volatile substances and the increase in TPC in oils rich in oleic acid were the most, especially in RB, followed by oils rich in linoleic acid. The increase in volatile components with a small molecular weight detected in PL correlated well with the increase in TPC. For NP, only the increase of nonanal had a good correlation with the increase in TPC, with the correlation coefficient was 0.817.

With the increase of oil deterioration indices, CV and TPC, most of the volatile substances showed an increasing trend, indicating that they contributed to the increase of CV and TPC. Pentanal was detected in all oils, and its increase showed good correlation with the increase of CV and TPC in most oils. Hexanal, heptanal, and octanal can be detected in oils with high oleic acid content and their increase showed good correlation with the increase of CV and TPC.

From the correlation results, the increase of pentanal was closely related to the reduction of TUFA and TToc and the increase of CV and TPC in all oils, and it can be used as a flavor evaluation index for frying oil. Hexanal, heptanal, and octanal can be used as flavor evaluation indicators for oils with high oleic acid content. In addition, it shows that the increase of CV and TPC is mainly due to the contribution of the specific components of each oil.

Table 5-5 The correlation between the area changes of volatile compounds and the changes of total polar compounds with heating time

Correlation coefficient		Total polar compounds									
		OL	SF	RS	RB	NS	SS	CO	SB	NP	PL
Aldehyde	Butanal	0.440	-	-0.012	0.613	0.405	0.340	-	-0.637	-	-0.504
	2-Butenal	0.600	-	0.759	-	-	-	-	-	0.363	0.855
	2-methyl-Butanal	-	0.802	-	0.896	0.785	0.530	-0.446	-0.150	-	0.871
	Pentanal	0.936	0.603	0.951	0.989	0.968	0.926	0.443	0.972	0.481	0.991
	(E)-2-Methyl-2-butenal	-	-	-	-	-	-	-	-	-	0.944
	(E)-2-Pentenal	0.662	-	0.764	-	-	-	-	-	0.208	0.944
	Hexanal	0.927	0.796	0.929	0.989	0.962	0.587	0.454	0.926	-0.293	0.317
	(E)-2-Hexenal	-	-	-	-	-	-0.366	-	-	-	-
	Heptanal	0.816	0.444	-	0.870	0.239	-0.372	0.317	0.747	-	-0.459
	(E)-2-Heptenal	0.987	0.915	0.921	0.935	0.904	0.881	0.483	0.903	-	-0.504
	Octanal	0.757	0.442	0.772	0.942	0.330	0.327	0.498	0.702	0.572	0.763
	(E,E)-2,4-Heptadienal	0.987	0.896	0.918	0.984	0.801	0.430	0.685	-	-	-
	2-Octenal	-0.195	-	-0.442	0.238	-	-	-	0.095	0.163	0.143
	Nonanal	0.884	0.607	0.790	0.906	0.342	0.509	0.396	0.788	-	-
	(E)-2-Nonenal	0.719	0.107	0.724	0.842	0.013	0.074	0.215	0.789	0.817	0.765
	(E)-2-Decenal	0.734	0.589	-	-	-	-0.045	-	-	-	-
	2,4-Undecadienal	0.444	0.376	0.794	0.936	0.295	-	-	-	-	-
	(E,E)-2,4-Decadienal	-	-	-	0.405	-	-	0.242	0.352	-	-
	(E)-2-Undecenal	-	-0.379	-0.195	0.500	-0.170	-	0.238	0.387	-	-

	Ethanol	0.397	-	-	-	-	0.436	-	-	-0.030	0.047
	2-methylPropanol	0.349	0.206	0.952	0.204	-0.495	-0.527	-0.017	0.662	0.034	0.815
	1-Penten-3-ol	0.613	-	-0.651	0.244	-	-	0.063	-	-0.173	-
Alcohol	(Z)-2-Penten-1-ol	-	-	-	-	0.949	-0.147	-	0.783	-	0.517
	1-Pentanol	0.929	0.651	0.890	0.966	0.827	0.419	0.418	0.894	0.532	-0.344
	1-Heptanol	0.941	0.630	-	-	-	-	-	-	-	-
	1-Octanol	0.836	-	-	-	-	-	-	-	-	-0.504
	2-Hexanone	-	-	-	-	-	0.924	-	-	-	-
	2-Octanone	0.846	-	0.965	-	-	0.889	-	0.964	-	-
	methylPyrazine	0.699	-	-	-	-	-0.501	-	-	-	-0.504
	2-Ethyl-6-methylpyrazine	-	-	-0.550	-	-	-0.498	-	0.198	0.182	0.540
	2,3,5-Trimethylpyrazine	-	-	-	-	-	-0.498	-	-	-	-0.475
	Ethyl Acetate	0.757	-	-	-	0.516	0.812	-	0.487	-	-
Substance	2-Pentylfuran	0.622	0.277	0.935	0.912	0.914	-0.188	0.162	0.936	-	-
other than	Toluene	-0.186	-	0.324	-	-	-	-	0.091	0.190	-
aldehyde and	1-Heptene	-	0.925	-	-	-	-	-	-	-	-
alcohol	Acetic acid	-	0.061	0.935	-	0.939	-0.454	0.811	0.959	0.763	-0.313
	Hexane	0.064	0.912	0.762	0.982	-0.092	0.082	-0.446	0.956	0.068	0.797
	methyl-Cyclopentane	0.374	-	-	-	-0.184	0.278	-	-	-	-0.504
	Heptane	-	0.285	-	-	0.757	-	-	0.072	-	-
	butyl-Cyclopentane	0.546	0.224	0.365	0.778	-	-	-	-	-	-
	Decane	-	-	-	-	0.669	-0.410	-	-0.042	-	0.009
	Decamethylcyclopentasiloxane	-	-0.230	-	-0.162	-	-	0.589	-	-	-0.365

“-”, indicates that the compound has not been detected, or that the correlation coefficient is less than 0.001.

5.4.4 The key volatile compounds affecting the changes of oils during frying

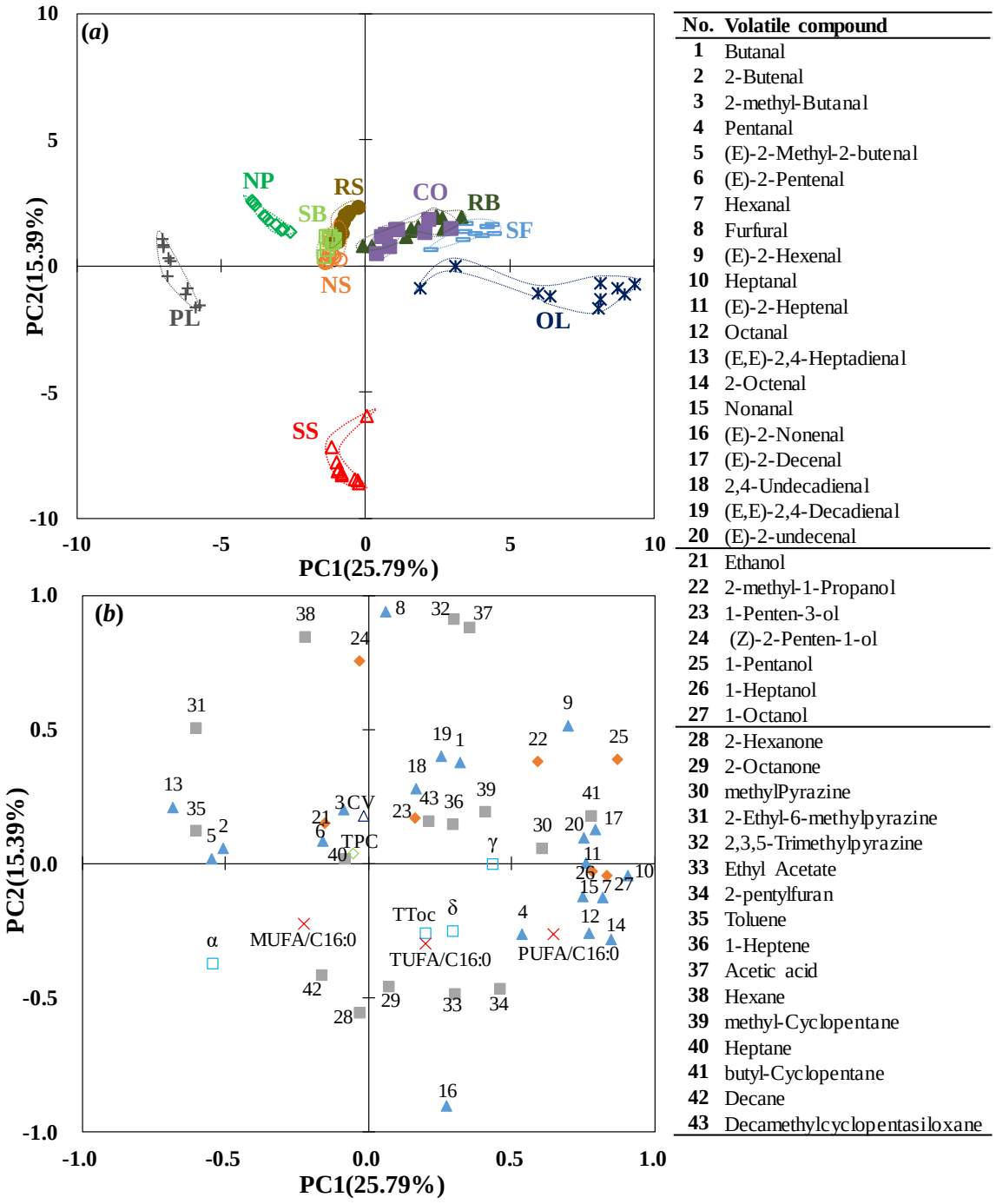
To reveal the relationship between various changes in oil during frying and find out the key volatile substances that affect the flavor change of oil, PCA was carried out among the changes in CV, TPC, tocopherols, unsaturated fatty acids, and all volatile compounds detected in the 10 oils during frying. The score and loading plots of the first two principal components are shown in Figure 5-7, which explained 41.18% of the variability with 25.79% by PC1 and 15.39% by PC2. Only 41.18% of the variability was explained, which was mainly related to the diversity and complexity of the changes of 10 oils during frying.

Oils with a lot of MUFA (OL, SF, and RB) were distributed near the positive direction of the PC1 axis. They were affected by large amounts of volatile compounds, including a lot of aldehydes, such as hexanal, (E)-2-hexenal, heptanal, (E)-2-heptenal, octanal, 2-octenal, nonanal, (E)-2-decenal, and (E)-2-undecenal, two alcohols (2-methyl-1-propanol and 1-pentanol), and other volatile compounds like methylpyrazine and butyl-cyclopentane. This is because they contain much MUFA, which were relatively stable compared with PUFA during frying, and the volatile compounds produced after the double bond breakage have a relatively large molecular weight, are not easy to volatilize, and easily accumulate in frying oils. Therefore, they were detected to contain a large number of volatile compounds.

For CO, RS, NS, SB, and NP, in which PUFA was dominated, they were densely distributed above the PC1 axis and mainly contributed by (Z)-2-penten-1-ol, acetic acid, and hexane. Unlike MUFA-rich oils, there were few volatile compounds detected in PUFA-rich oils, mainly because PUFA was easily decomposed during frying and the resulting products had a small molecular weight, which is not easy to accumulate and be detected in the frying oil.

For roasted oils, PL and SS, they were distributed away from other oils. A large number of volatile compounds detected before frying and heating were evaporated after heating. Although a large number of volatile compounds were also detected during subsequent frying, they did not

contribute significantly to the distribution of PL and SS. 2-Butenal, (E)-2-methyl-2-butenal, and (E,E)-2,4-heptadienal contributed a lot to the distribution of PL. SS was distributed along the negative direction of PC2 and was mainly affected by (E)-2-nonenal and 2-hexanone.



No.	Volatile compound
1	Butanal
2	2-Butenal
3	2-methyl-Butanal
4	Pentanal
5	(E)-2-Methyl-2-butenal
6	(E)-2-Pentenal
7	Hexanal
8	Furfural
9	(E)-2-Hexenal
10	Heptanal
11	(E)-2-Heptenal
12	Octanal
13	(E,E)-2,4-Heptadienal
14	2-Octenal
15	Nonanal
16	(E)-2-Nonenal
17	(E)-2-Decenal
18	2,4-Undecadienal
19	(E,E)-2,4-Decadienal
20	(E)-2-undecenal
21	Ethanol
22	2-methyl-1-Propanol
23	1-Penten-3-ol
24	(Z)-2-Penten-1-ol
25	1-Pentanol
26	1-Heptanol
27	1-Octanol
28	2-Hexanone
29	2-Octanone
30	methylPyrazine
31	2-Ethyl-6-methylpyrazine
32	2,3,5-Trimethylpyrazine
33	Ethyl Acetate
34	2-pentylfuran
35	Toluene
36	1-Heptene
37	Acetic acid
38	Hexane
39	methyl-Cyclopentane
40	Heptane
41	butyl-Cyclopentane
42	Decane
43	Decamethylcyclopentasiloxane

Figure 5-7 Principal component analysis of changes in CV, TPC, tocopherols (TOC), unsaturated fatty acids (UFA), and all volatile compounds during frying: (*a*) score and (*b*) loading

▲ Aldehyde:1-20 ◆ Alcohol:21-27 ■ Others:28-43 △ CV ◇ TPC □ TOC × UFA

According to the various changes of the 10 oils during the frying process, the volatile compounds that determine the distribution position of each oil on the PCA score plot are the key influencing factors that affect the changes of oils during frying. Accordingly, the key volatile compounds affecting the changes during frying in oils with much MUFA were hexanal, (E)-2-hexenal, heptanal, (E)-2-heptenal, octanal, 2-octenal, nonanal, (E)-2-decenal, (E)-2-undecenal, 2-methyl-1-propanol, 1-pentanol, methylpyrazine, and butyl-cyclopentane. For oils rich in PUFA, the key volatile compounds were (Z)-2-penten-1-ol, acetic acid, and hexane. 2-Butenal, (E)-2-methyl-2-butenal, (E,E)-2,4-heptadienal, (E)-2-nonenal, and 2-hexanone were the key volatile compounds for roasted oils, PL and SS.

5.5 Conclusions

In this work, the flavor changes of 10 oils during frying were analyzed. The changes in the area of volatile compounds in oils before and after heating was mainly affected by the composition of unsaturated fatty acids. The more oleic acid contained in the oil, the more the total area of volatile substances increases. Alcohols and aldehydes in oils always accounted for a large proportion. The effects of changes in aldehydes, alcohols and other volatile substances detected on the flavor characteristics of frying oils were explored respectively by PCA. The correlation between the changes of volatile components detected and the changes in TUFA, TToc, CV, and TPC were discussed, respectively. Most volatile substances showed an increasing trend with the decrease of TUFA and TToc and increase of CV and TPC. Pentanal, was detected in all oils, its increase had a good correlation with the reduction of TUFA and TToc and the increase of CV and TPC, thus it is recommended as a flavor evaluation index for frying oil. Hexanal, heptanal, and octanal can be used as flavor evaluation indicators for oils with high oleic acid content. Based on the results of PCA using the changes in CV, TPC, tocopherols, unsaturated fatty acids, and all volatile compounds detected in the 10 oils during frying, the key volatile compounds affecting the changes in oils during frying were found.

5.6 Reference

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Chapter 6 Overall conclusions, limitations and prospects for future work

6.1 Main conclusions

Based on this research content and results, the following main conclusions were obtained:

1. The dominant tocopherol in oils rich in PUFA was γ-tocopherol, except for natural perilla oil (δ-tocopherol dominant), and the main tocopherol in oils rich in MUFA was α-tocopherol (Chapter 2).
2. The initial CV and TPC of roasted oils were higher than natural pressed oils, and those of PUFA-rich oils were higher than MUFA-rich oils (Chapter 2).
3. The proportion of alcohol was the largest among the volatile compounds detected in the oils before frying, and the type of aldehydes was the most detected (Chapter 2).
4. TUFA and TToc in oils showed alternating dynamic decomposition in multiple frying cycles during frying (Chapter 3).
5. With the decomposition of TUFA, the decomposition rates of tocopherol homologs were in the order γ-tocopherol > α-tocopherol > δ-tocopherol in the 10 oils. The effects of tocopherol homologs on decomposition of TUFA in the 10 oils during frying were in the same order, that is, γ-tocopherol > α-tocopherol > δ-tocopherol (Chapter 3).
6. A model, $Y_{\mathrm{TUFA}} = \left[0.189\left(\frac{\mathrm{C16:0}}{\mathrm{C18:1}}\right)^2 + 0.054\left(\frac{\mathrm{C16:0}}{\mathrm{C18:1}}\right) + 0.185\right]t$, was built that can be used to predict the decomposition rate of TUFA during frying in a variety of unsaturated fatty acid-based oils (Chapter 3).
7. The decrease of PUFA and γ-tocopherol had the greatest influence on the linear increase of CV and TPC (Chapter 4).

8. Using the prediction model ($CV_t = \left[4.37\left(\frac{PUFA}{TToc}\right)^2 - 5.64\left(\frac{PUFA}{TToc}\right) + 3.36\right]t + CV_0$), the CV of edible oil during frying at 180 °C can be predicted from the initial composition of the oil (Chapter 4).
9. Using the prediction model ($TPC_t = \left[0.024\left(\frac{\text{C18:2}}{\text{C16:0}}\right)^2 - 0.065\left(\frac{\text{C18:2}}{\text{C16:0}}\right) + 0.819\right]t + TPC_0$), the TPC of edible oil during frying at 180 °C can be predicted from the initial composition of the oil (Chapter 4).
10. The frying life of edible oil can be inferred by using two models simultaneously according to the maximum allowable CV (≤ 50 μmol/g) and TPC (≤ 24%) (Chapter 4).
11. The change in level of volatile compounds during frying was mainly related to the unsaturated fatty acid composition of the oil (Chapter 5).
12. The key volatile compounds affecting the changes during frying in oils with much MUFA were hexanal, (E)-2-hexenal, heptanal, (E)-2-heptenal, octanal, 2-octenal, nonanal, (E)-2-decenal, (E)-2-undecenal, 2-methyl-1-propanol, 1-pentanol, methylpyrazine, and butyl-cyclopentane. For oils rich in PUFA, the key volatile compounds were (Z)-2-penten-1-ol, acetic acid, and hexane (Chapter 5).
13. The increase of pentanal showed a good correlation with the decrease of TUFA and TToc and increase of CV and TPC in most oils (Chapter 5).

6.2 Limitations and prospects for future work

In this research, the edible oil was intermittently fried and the fresh oil hasn't been added over the entire deep frying process. However, the frying methods frequently used in homes, restaurants, or large-scale frying industries usually add new oils regularly or irregularly. The results in the present study were obtained under laboratory frying conditions. Therefore, future research on frying should be based on more realistic frying conditions.

In the current study, only tocopherols were studied for antioxidants contained in edible oils. In fact, other components in the oil such as sterols, tocotrienols, and carotenes also have antioxidant properties and should also be investigated. In particular, sesamol contains in sesame oil and oryzanol contains in rice bran oil may have better antioxidant properties than tocopherol. The interaction between the different minor components may also contribute to the stability of the frying oil, which deserves further investigation.

This work comparative studied the frying degradation of 10 commercially available oils. Since these oils are purchased from the market, the consistency of the processing methods and whether or not tocopherol is added are suspected, that is, the initial different state of the oils may be caused by many factors. In general, an ideal frying study should be conducted on all oils with different properties but using the same production method. Besides, the same type of oil should be used more from different suppliers. Moreover, established predictive models require more edible oils to verify their accuracy and feasibility. Therefore, more edible oils are needed to perfect and improve the accuracy of the models.

As for the analysis of polar compounds, this study used a simple hand-held test instrument to measure the TPC in a fast and real-time manner, the accuracy of which remains to be discussed. In fact, the polar compounds in oil have a wide range of complex compositions. Because the determination of polar compounds is considered to be the most reliable indicator for evaluating oil degradation. In order to better grasp the deterioration mechanism of oil during frying and

understand the composition and content of polar compounds in the oil, further and more detailed work needs to be carried out.

The flavor composition characteristic of edible oils is very complicated, and it has diversity among different oils. The volatile substances are easy to volatilize during the frying process. The discussion in the current study is limited. The flavor characteristics, sources, concentration trends, and influencing factors of various volatile substances need to be further explored. On this basis, find out the key flavor components of each oil, and apply reasonable control, development, and utilization, and finally achieve the purpose of satisfying different sensory needs of consumers.