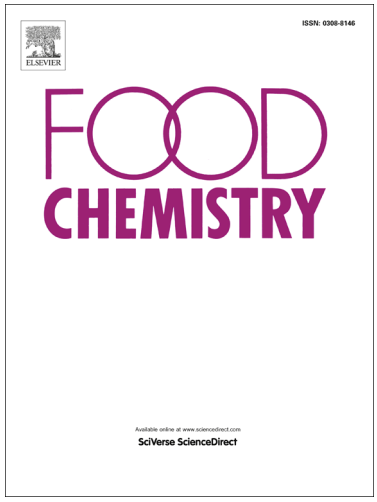


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# Evaluation of the non-aldehyde volatile compounds formed during deep-fat frying process

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Abstract: To investigate the non-aldehyde volatile profile resulting from deep-fat frying, volatile compounds formed during the processes of heating soybean oil (SO), frying wheat dough (WD), and frying chicken breast meat (CBM) were comparatively studied. By using gas chromatography-mass spectrometry and internal standard method, alkanes, alkenes, alkynes, alcohols, ketones, nitrogen-containing volatiles (NCVs), and other volatiles were qualitatively and relatively quantitatively detected. NCVs were detected only in CBM-fried oil samples. Some volatiles (e.g. 2-pentylfuran and 2-pentylpyridine) were observed to increase in concentration, whereas others (e.g. 4-methyl-1,4-heptadiene and 7-methyl-3,4-octadiene) were observed to first increase and then decrease in concentration as the heating or frying time increased. Reduced quantity and concentrations of volatiles were observed in the food-fried oil samples which might be related to the intensified reactions induced by food components. The detection of some harmful volatiles in considerable

concentrations indicated further attention might be paid to the safety of deep-fat frying.

Keywords: Soybean oil; Deep-fat frying; Volatile compounds; Nitrogen-containing volatiles

Chemical compounds studied in this article

Tetradecane (PubChem CID: 12389); 4-Methyl-1,4-heptadiene (PubChem CID: 5362810); 1-Octen-3-ol (PubChem CID: 18827); 3-Nonen-2-one (PubChem CID: 5317045); 2-Pentylpyridine (PubChem CID: 16800); Amantadine (PubChem CID: 2130); 2-Pentylfuran (PubChem CID: 19602); 1-Methyldecahydronaphthalene (PubChem CID: 34193); 1-Ethyl-2,4-dimethylbenzene (PubChem CID: 13403); Dibutyl phthalate (PubChem CID: 3026)

## 1. Introduction

As a type of thermally processed food, fried food is widely consumed in daily life because of its characteristic palatable taste and flavor. The flavor of fried food generally originates from the volatile compounds generated or absorbed by the fried food during the frying process. Some of these volatile compounds are also formed and dissolved in the frying oil. These compounds are well known to be easily volatilized under the conditions of high temperature and long frying time.

Three major chemical reactions, namely, thermal oxidation, hydrolysis, and polymerization, have been proposed to characterize the primary chemical alterations involving triacylglycerols (TAGs, major component of the frying medium) during deep-fat frying process (Zhang, Saleh, Chen, & Shen, 2012). Among the complex

products of these reactions, volatile compounds are the main product formed from the oxidative degradation of TAGs. However, the reaction substrates involved in the complex chemical reactions are not only from the constituents of frying oil but also from the components of fried food and the reaction intermediates. Thus, the formation mechanisms of volatile compounds are complicated, and the specific composition of the volatile compounds generated is also complex. Therefore, elucidating the composition of volatile compounds released during deep-fat frying process has instructive significance in explaining the mechanism of formation of this type of products. Finally, understanding the process is helpful for the practical operation of deep-fat frying and the production of fried food.

Moreover, volatiles generated during deep-fat frying process are usually harmful to the health of the cooks, who are regularly exposed to these volatiles over many years. For example, polycyclic aromatic hydrocarbons (PAHs) and heterocyclic amines can increase the risk of developing lung cancer (Lee & Gany, 2013) and respiratory tract cancer (Cao et al., 2013). Therefore, determining the potentially harmful products is necessary for providing guidance for the consumption of fried food.

Many papers have been published characterizing the types of volatile compounds formed during deep-fat frying process, which could be reflected in detail in previous review (Zhang, Qin, Li, Shen, & Saleh, 2015a). However, few studies have investigated the different volatile compounds of different food types fried in soybean oil (SO) (Hosseini, Ghorbani, Meshginfar, & Mahoonak, 2016). Furthermore,

systematic research on the mechanism of formation of the typical volatile compounds has seldom been reported (Abdulkarim, Long, Lai, Muhammad, & Ghazali, 2007; Bansal, Zhou, Barlow, Lo, & Neo, 2010). SO was selected for deep-fat frying because of its high yield and consumption, relatively low price, and high level of unsaturated fatty acids (UFAs, such as linoleic and linolenic acids). The changes in profiles of volatile aldehydes during the processes of SO heating, frying wheat dough (WD), and frying chicken breast meat (CBM) were reported in our previous study (Zhang, Qin, Lin, Shen, & Saleh, 2015b). Therefore, in this study, different profiles of non-aldehyde volatile compounds for different types of deep-fat frying are comparatively characterized, and the possible mechanisms of formation of typical volatiles are proposed.

## 2. Materials and Methods

### 2.1. Materials and Chemicals

Refined SO (first grade), wheat flour (high gluten), and chilled CBM were purchased from a local marketplace. The fatty acid composition of SO was previously reported as: 10.36% palmitic acid, 4.49% stearic acid, 22.49% oleic acid (O), 50.15% linoleic acid (L), and 10.54% linolenic acid (Ln) (Zhang, Saleh, & Shen, 2016).

Propyl propionate (99%, 100 mL) and paraffin (C5-C20) standard solvent were purchased from Sigma-Aldrich. Chromatographically pure hexane was acquired from MREDA (Beijing) Technology Limited Company. Propyl propionate dissolved in hexane (1:9, v/v) was used as an internal standard.

## 2.2. Sample preparation

### 2.2.1. Sample pretreatment

WD was prepared at the daily use level by mixing wheat flour and deionized water in a mass ratio of 2:1 in a mixer (CS-B5A, Hong Yang Casting Ltd., Guangzhou, China). The prepared WD was placed in a refrigerator at 4 °C overnight and was then kneaded into a disc with a diameter of 10 cm and a thickness of 0.6 cm just before the frying treatment. CBM was freshly purchased in the morning at the daily use level and manually cut into uniform strips with a sectional area of 0.6 cm × 0.6 cm and a length of approximate 8 cm.

### 2.2.2. Frying process

The frying procedure protocols were similar to those in a previous report (Zhang et al., 2015b). Briefly, a simulated deep-fat frying operation (180 ± 2 °C) was performed in a domestic scale electric fryer with double cylinders (HY-82EX, Guangzhou Huili Food Machinery Co., Ltd., China) using practical food frying process. Specifically, 5 L of SO was placed into one of the cylinders and heated to the set temperature (180 °C) to perform one frying treatment. The practical temperature was measured at various times to monitor the frying temperature and no fresh SO was added during the whole course. A batch of food material (approximate 100 g) was placed into a stainless steel screen frame and completely immersed into the heated SO. Frying times for WD and CBM were 10 min and 5 min, respectively, because of the different characteristics of these two food materials. Interval times among the batches

of food material were 5 min and 10 min for WD and CBM, respectively. Four batches of foods were sequentially fried in 1 h. The deep-fat frying process was carried out for 8 h/day over a period of 7 consecutive days. Approximately 60 mL of oil sample were collected every 2 h during deep-fat frying process. Chilled water bath was used to cool the oil sample to ambient temperature in a beaker with a sealing film made of polyethylene as quickly as possible for the following solid-phase microextraction (SPME) treatment.

As a control, SO was only heated under the same conditions used in the deep-fat frying treatments. The sampling method of heated oil samples was the same as the sampling of food-fried oil samples. Heating or frying processes were performed in triplicate and a total of 45 L of fresh soybean oil was used.

2.3. SPME treatment of volatile compounds

Extraction of volatile compounds was carried out using a 50/30 μm SPME fiber coated with polydimethylsiloxane/divinylbenzene/carboxen (PDMS/DVB/CAR) mounted to an SPME manual holder assembly (Supelco, Bellefonte, PA, USA) and a constant temperature magnetic stirrer (PC-420, Corning Inc. Life Science, Acton, MA, USA). The fiber was conditioned following the recommendations of the manufacturer prior to the first use.

The SPME conditions were modified from the previous study (Zhang et al., 2015b). Briefly, oil sample (5.0000 g) and internal standard solution (0.0060 g) were accurately weighed into a 15-mL SPME vial with a 1-cm rotor by difference method,

and were then sealed with a specialized cap. Thus, the final concentration of internal standard in oil sample was 120 mg/kg. The vial loaded with the oil sample was placed into a water bath maintained at 60 °C on a magnetic stirrer (PC-420D, Corning, NY, USA). The liquid level of the water bath was adjusted to the half-height of the vial. The manual holder assembly was then inserted into the vial to expose the SPME fiber at the position of 1 cm over the oil surface. The processes of sample loading and fiber insertion were also completed as quickly as possible. A total of 50 min was taken to perform the extraction of volatile compounds by stirring and agitation at gear 5. Each oil sample was SPME-treated under the same conditions.

2.4. GC-MS analysis of volatile compounds

Analyses of volatile compounds were carried out on an Agilent gas chromatograph (7890A) coupled with an Agilent mass spectrometer (5975C series), which was interfaced to a GC workstation for the data analysis. After the SPME extraction, the fiber was immediately inserted into the injection port and desorbed for 2 min at 250 °C. Helium (99.999%) was used as the carrier gas, and the flow rate was 1 mL/min. Separation of volatile compounds was performed on a DB-5MS column (30 m × 0.25 mm × 0.25 μm, J&W Scientific, Folsom, CA, USA) with weak polarity and in the splitless mode for the best separation efficiency. The temperature was isothermal for 2 min at 40 °C, was raised to 160 °C at a rate of 5 °C/min, isothermal for 2 min at 160 °C raised to 250 °C at 10 °C/min and then maintained at 250 °C for 10 min. The temperatures of the transfer line, the ion source, and the quadrupole mass

filter were set at 250, 230, and 150 °C, respectively. The mass spectrum was acquired over the m/z range 30-450 in the full-scan mode by electron ionization with an ionization energy of 70 eV.

Paraffin (C5-C20) standard solvent was separated and analyzed under the same GC and MS conditions in liquid injection mode with an injection volume of 1 μL. Volatile compounds were analyzed qualitatively using both the NIST08.L MS library on the basis of their mass spectra and the Flavornet and LRI&odour Database according to their calculated relative retention index (RI) (Bianchi, Careri, Mangia, & Musci, 2007). All volatile compounds were assumed to have the same response effect and were efficiently separated under the selected separation conditions. On this basis, internal standard method was used to analyze the volatile compounds quantitatively (Chyau & Mau, 2001; Vichi, Castellote, Pizzale, Conte, Buxaderas, & López-Tamames, 2003).

### 2.5. Statistical analysis

Analysis of variance (ANOVA) was used to study the concentration changes of the volatile compounds during deep-fat frying process. Data processing and analysis were performed using SPSS 17.0 for Windows (SPSS Corp., Chicago, USA) and Microsoft Excel 2007 software. All figures were drawn using Origin 7.5 software (OriginLab Corp., Northampton, England).

## 3. Results and discussion

Volatile compounds are difficult to be collected for analysis during a practical frying process. However, most of the volatiles formed during extended heating or frying processes are dissolved in frying oil and could be qualitatively and quantitatively analyzed using SPME technique (Zhang et al., 2015a). The application of SPME fiber coated with various materials on the trapping of the most volatiles in food matrix was based on the similar absorption and desorption properties of these compounds in the selected coatings (Xu, Chen, Xiong, Fan, Wang, & Liu, 2016). Meanwhile, the degree of the maximum absorption and desorption of the absorbed volatiles in sunflower oil was also repeatedly confirmed using different SPME fibers (Doleschall, Recseg, Kemény, & Kővári, 2003). Largest quantity and lowest amount of volatiles were observed using CAR and PDMS fiber, respectively. The volatiles trapped by DVB fiber showed more polar. Therefore, as a SPME fiber with all the advantages of individual material and wide applicability, PDMS/DVB/CAR fiber was used for effectively trapping both the polar and non-polar volatiles of vegetable oils (Petersen, Kleeberg, Jahreis, Busch-Stockfisch, & Fritsche, 2012) and was selected in this study.

As shown in Figure 1, total ion chromatograms of the collected oil samples for the three treatments showed certain variations as the processing time increased. When SO was heated or fried, thermal oxidation of unsaturated TAGs occurred to generate a series of oxidized TAGs, oxidative decomposition products, and polymerized products. Various types of products were closely related to the relatively high content of UFAs in SO. Among these products, volatile compounds are the main oxidative

decomposition products of unsaturated TAGs. Thus, many volatile compounds were detected at retention times from 10 to 20 min in the chromatograms of oil samples collected during the heating or frying processes. Moreover, along with the proceeding of heating or deep-fat frying, the profile of volatile compounds varied and included the generation of new products, increases in amounts, decreases in amounts, and disappearance of the formed products. The RI and MS analysis results showed, as shown in Table 1 (typical volatiles with regular change tendency in concentration), in addition to the aldehydes, seven types of volatile compounds (alkanes, alkenes, alkynes, alcohols, ketones, NCVs, and other volatiles) were observed during heating or deep-fat frying of SO based on the chemical structure of the detected volatiles. According to Table 1, the maximum concentrations of most volatiles were detected in the heated oil samples; however, the minimum concentrations of most volatiles were observed in the CBM-fried oil samples. For example, the concentrations of 2-methylbicyclo[2.2.2]octane and 2-pentylfuran were 2.913 and 11.243 mg/kg for the heated oil sample of 7-2h and were 0.206 and 5.064 mg/kg for the CBM-fried oil samples of 5-2h and 5-8h, respectively. These detected quantity and concentration distributions of the various types of volatiles, namely the largest concentration of aldehydes (Zhang et al., 2015b), followed the alkylbenzenes, furans, alcohols, alkenes, and others in the frying oil samples, was accordance with those in heated commercial or high oleic rapeseed oils reported by Petersen et al. (Petersen et al., 2012). In addition, it could also conclude that the possible formation mechanisms of the detected volatiles were various and they can be further interacted each other.

3.1. Alkanes

The appearance of hydrocarbons in frying oil is attributed to the free radical reaction of unsaturated and saturated fatty acyl chains. The results of qualitative and quantitative analyses of hydrocarbons of the three types of oil samples are listed in Supplement 1. A total of 47, 31, and 23 alkanes, including straight-chain alkanes, side-chain alkanes, and cycloalkanes, were measured in the oil samples collected during the processes of heating, frying WD, and frying CBM, respectively. According to the characteristics of chemical reactions during deep-fat frying process, straight-chain alkanes were likely formed via the oxidative decomposition of UFAs, the free radical reactions and the thermal decarboxylation of saturated fatty acids (SFAs) (Osmont, Catoire, Gökalp, & Swihart, 2007; van der Klis & van den Hoorn, 2011). Side-chain alkanes were produced from the free radical reaction of both UFAs and SFAs. The formation of cycloalkanes was related to the cyclization of alkane radicals generated by free radical reactions (Porter, Caldwell, & Mills, 1995).

Among these alkanes, the amounts of straight-chain alkanes, such as tetradecane and pentadecane, exhibited an increasing trend in concentration for the heated oil samples and tended to first increase and then decrease with increasing frying time in the food-fried oil samples (Figure 2). The maximum concentrations of tetradecane and pentadecane, 1.074 and 0.670 mg/kg, were observed in the oil sample of 7-8h and 7-2h for heating of SO. Comparatively, the concentrations of these two alkanes in the food-fried oil samples were lower than those in the heated oil samples due to the volatilization induced by the intense frying procedure. Straight-chain alkanes with a

carbon number less than 11 were not detected, which reflects the characteristics of the complex reactions occurring during deep-fat frying process. Moreover, the concentrations of alkanes detected in the heated oil samples were almost higher than those concentrations of alkanes detected in the WD-fried or CBM-fried oil samples. These phenomena might be related to the minor amounts of some alkanes formed and the addition of food components, such as water and proteins. The complex reactions induced by water or proteins might influence the formation of alkanes and the consequent reactions occurred among these alkane products. Furthermore, the addition of water and proteins caused intense boiling in the frying oil during the food frying process, resulting in the loss of alkane products. These descriptions were rightly reflected by the abundant emission of volatiles when WD or CBM was fried.

3.2. Alkenes

Alkene profiles of oil samples exhibited the most complex composition among all of the detected volatiles, shown in Supplement 2. A total of 93, 65, and 51 alkenes, including straight-chain monoenes, substituted monoenes, straight-chain dienes, substituted dienes, and cyclic monoenes or dienes, and their configurational isomers, were observed in the frying oil samples collected during the processes of heating, frying WD, and frying CBM, respectively. As the main oxidative decomposition products of UFAs, alkenes were formed from the combination reaction between unsaturated alkane radicals or between unsaturated alkane radical and hydrogen radical (Chung, Eiserich, & Shibamoto, 1993).

Complex properties of positional isomerism and *cis-trans* isomerism of carbon-carbon double bonds (C=C) were observed for the detected straight-chain monoenes. For example, (*Z*)-3-dodecene, (*E*)-3-dodecene, 4-dodecene, (*Z*)-5-dodecene, (*E*)-5-dodecene, (*Z*)-6-dodecene, and (*E*)-6-dodecene were detected at the same retention time. The same phenomenon was observed for the series of undecene, tridecene, tetradecene, and hexadecene. Cyclic monoenes or dienes were discontinuously detected in all the oil samples due to their thermal instability. The formation of these cyclic alkenes, such as substituted cyclohexenes and substituted cyclooctenes, might be related to the cyclization during the free radical reaction of unsaturated fatty acid. In addition, substituted cyclohexenes might be formed by Diels-Alder reaction between oleic acid and linoleic acid under frying condition (Nawar, 1998). The diversity of isomers reflects the complex isomerization occurring during deep-fat frying process.

Moreover, some of the detected alkenes, such as dienes, might participate in subsequent reactions to produce other alkenes or alkanes. Among the dienes detected, the concentrations of 1,7-octadiene, 1,3-nonadiene, 1,11-dodecadiene, 4-methyl-1,4-heptadiene, and 7-methyl-3,4-octadiene changed in a relatively regular trend. 1,7-Octadiene, 1,3-nonadiene, and 1,11-dodecadiene were generated by free radical reaction and double-bond positional isomerization of linoleic acid and linolenic acid. Therefore, their concentrations regularly increased with increasing frying time. As shown in Figure 3, with the similar formation paths, the concentrations of 4-methyl-1,4-heptadiene and 7-methyl-3,4-octadiene first increased

and then decreased as the frying time increased. For example, concentration of 4-methyl-1,4-heptadiene increased from 0 in fresh SO to 3.679 mg/kg in oil sample of 5-2h and then decreased to 2.304 mg/kg in oil sample of 7-8h for the SO heating treatment. Correspondingly, methyl ethyl cyclopentene and 2-methyl-bicyclo[2.2.2]octane were not detected when deep-fat frying began; however, their concentrations in the food-fried oil samples increased after certain time. These phenomena might be attributable to the concerted reaction or isomerization of 4-methyl-1,4-heptadiene and 7-methyl-3,4-octadiene to form these two cyclic compounds under high temperature conditions (Figure 3).

By comparing the profiles of the alkenes in the oil samples collected during the processes of heating, frying WD, and frying CBM, the quantity and concentrations of the alkenes detected was reduced when the SO was fried with food, especially the CBM. This phenomenon was also related to the more complex chemical components contained in CBM compared to the components in WD.

### 3.3. Alkynes

The quantity of the alkynes detected were lower than that of alkanes and alkenes for the oil samples collected during the processes of heating, frying WD, and frying CBM, as shown Supplement 3. The formation of alkynes in the oxidation of UFAs was just reported in small studies (Frankel, 1984). Combined with the proposed formation of alkynes from hydroperoxides of fatty acids and the free radical components of frying oil, the formation of alkynes might occur via combination of

two free radicals. For example, a pentyl radical might be combined with 1-decenyl radical to form 7-pentadecyne, which was present in all of the heated oil samples and in some food-fried oil samples.

The quantity and concentration of alkynes detected in the food-fried oil samples were also less than those of alkynes detected in the heated oil samples. The addition of food components might influence the combination reaction between the free radicals or promote the consequent reactions occurring in alkynes to reduce the formation of these carbon-carbon triple bonds-containing volatiles.

### 3.4. Alcohols

As shown in Supplement 4, we detected 31, 20, and 16 alcohols in the oil samples collected during the processes of heating, frying WD, and frying CBM, respectively. Among these alcohols, saturated, unsaturated, and cyclic alcohols were observed. Alcohol volatiles are also formed by the oxidative decomposition of UFAs. For example, 1-octanol might be the decomposition product of oleic acid-10-hydroperoxide (Selke, Rohwedder, & Dutton, 1977). Therefore, 1-octanol was observed to first increase from not detectable in fresh SO to 2.670 mg/kg in oil sample of 4-2h and then decrease from this maximum to 1.105 mg/kg oil sample of 7-8h during oil heating process. Another typical alcohol observed in higher concentration compared to the detected hydrocarbons was 1-octen-3-ol. As a secondary alcohol with a mushroom-like odor, 1-octen-3-ol was detected in greater amounts in thermally treated conventional rapeseed oil than in thermally treated

high-oleic rapeseed oil (Petersen et al., 2012). Therefore, 1-octen-3-ol was regarded as a decomposition product of linoleic acid-10-hydroperoxide (Asaaf, Hadar, & Dosoretz, 1997). On the basis of the reaction conditions involved in deep-fat frying, 1-octen-3-ol might be formed by the positional isomerization of hydroxyl and C=C in 2-octen-1-ol, which was formed from the decomposition of linoleic acid-10-hydroperoxide.

The largest concentrations of 1-octen-3-ol were 11.690 mg/kg in the oil sample of 5-8h (oil sample collected at the eighth hour in the fifth day), 5.333 mg/kg in the oil sample of 3-8h, and 4.434 mg/kg in the oil sample of 1-6h for the heating, frying of WD, and frying of CBM, respectively. Therefore, the addition of food components promoted the oxidation decomposition of UFAs or caused greater loss of the alcohols as result of the intense boiling during deep-fat frying process.

### 3.5. Ketones

The volatile ketone profiles of oil samples collected from SO heating, WD frying, and CBM frying are shown in Supplement 5. Volatile ketones are considered to be related to the flavor of fried food; for example, 6-dodecanone and 1-phenyl-1-propanone emit floral aromas (Petersen et al., 2012). However, the volatile ketones produced during deep-fat frying are regarded as substances potentially harmful to human health (Qu et al., 1992). On the one hand, volatile ketones such as methyl ketones could be the thermal peroxidation products of SFAs. On the other hand, alkenes, alcohols and aldehydes formed from the oxidative

decomposition of UFAs such as 6-dodecanone oxidized from 6-dodecene could be oxidized to generate ketones during deep-fat frying process.

The typical ketone continuously detected in all the oil samples was 3-nonen-2-one with a change tendency of first increase and then decrease in concentration, which was shown in Figure 4A. 3-Nonen-2-one was detected in oil samples collected during simulated food frying in corn oil and trilinolein, but not in oil samples collected during simulated food frying in hydrogenated cottonseed oil and triolein (Chang, Peterson, & Ho 1978). Therefore, linoleic acid might be the precursor of 3-nonen-2-one. Given that the amount of (*E*)-2-nonenal formed by oxidative decomposition of linoleic acid was observed to first increase and then decrease (Zhang et al., 2015b), 3-nonen-2-one might be formed by oxidation of the aldehyde group and positional isomerization of C=C in (*E*)-2-nonenal.

Cyclic ketones such as 4-ethenyl-cyclohexanone, 4-isopropenylcyclohexanone, and *cis*-5-methyl-spiro[3.4]octan-1-one were also detected discontinuously. Cyclohexanone and its derivatives were detected during the heating of corn oil at 200 °C. Therefore, this type of cyclic ketone was formed under high temperatures or long frying time. Combining the changes in the types and concentrations of the detected substituted cyclohexenes, cyclohexanol, spirocyclic hydrocarbons, 4-isopropenylcyclohexanone, and *cis*-5-methyl-spiro[3.4]octan-1-one might be the oxidation products of D-limonene and *cis*,*trans*-1,6-dimethylspiro[4.5]decane, respectively. As shown in Figure 4B, the amount of 1(3*H*)-isobenzofuranone was observed to have a tendency of first increase and then decrease. On the basis of the

molecular structural characteristics, 1(3*H*)-isobenzofuranone might be formed by the decomposition and intramolecular electron rearrangement of the cyclic peroxides of PUFAs (Yin, Xu, & Porter, 2011).

The addition of food components also influenced the profiles of volatile ketones in oil samples by reducing the quantity and concentration of the detected ketones. These influences were more significant when CBM was fried in SO. Among the oxidation products of the oils and fats, the decomposition products with groups of hydroperoxyl, peroxyl, carbonyl, or hydroxyl were prone to react with the amino or amide-containing compounds to form the covalent bonding complexes (Pokorný & Kołakowska, 2011). Therefore, many alcohols, aldehydes, and ketones with low molecular weight were not detected in CBM-fried oil samples. Meanwhile, some typical NCVs were detected only in the CBM-fried oil samples.

### 3.6. Nitrogen-containing volatiles

NCVs are well known to be the typical aroma source for thermally treated meat. The formation of these compounds is related mainly to the high content of protein in animal food. As shown in Table 1, no NCVs were observed when WD was fried in SO even though the WD was made of high-gluten wheat flour. This phenomenon might be attributable to the ability of the stable gluten structure to wrap the proteins, preventing them from participating in the reactions occurring during deep-fat frying process and resulting in NCVs being detected solely in the CBM-fried oil samples (see Supplement 6). A total of 23 NCVs were observed and included, mainly

pyridines, pyrazines, pyrroles, pyrazoles, and amines. The appearance and the concentrations of these NCVs revealed that the quantity and concentrations of the detected NCVs increased when SO was repeatedly fried with CBM.

Among these NCVs, as shown in Figure 5, 2-propylpyridine and 2-pentylpyridine were observed in an increasing tendency to the final maximum concentrations of 0.453 and 3.474 mg/kg for the CBM fried-oil sample of 7-8h, respectively. Pyridines and alkylpyridines detected in the CBM-fried oil samples might be formed by Strecker degradation during the Maillard reaction between amino acids and reduced sugars contained in the CBM. However, alkylpyridines might be more likely to be generated from the reaction between amino compounds and the lipid oxidation decomposition products, such as conjugated 2,4-alkadienals in the food frying environment. As shown in Figure 5, aldimines were formed by the dehydration condensation reaction between 2,4-alkadienals and amino compounds. Intramolecular cyclization and homolysis of these unstable Schiff bases then occurred under the high temperature conditions to form 2-alkylpyridines (Adams, Kitrytė, Venskutonis, & De Kimpe, 2011). Based on this proposed mechanism, 2-propylpyridine, 2-butylpyridine, 2-pentylpyridine, and 2-hexylpyridine might be formed via the reactions between 2,4-heptadienal, 2,4-nonadienal, 2,4-decadienal, and 2,4-undecadienal and amino compounds, respectively. These results correspond to the changes in concentrations of these alkadienals formed during deep-fat frying (Zhang et al., 2015b). In addition, the concentration of 2-pentylpyridine increased from 0.071 mg/kg for the oil sample of 1-2h to 3.474 mg/kg for the oil sample of 7-8h, which also corresponded to the

gradually increased concentration of *trans,trans*-2,4-decadienal as the deep-fat frying proceeded (Zhang et al., 2015b).

Another interesting NCV is tricyclo[3.3.1.1(3,7)]decan-1-amine, also known as amantadine, which is well known to be an effective antiviral drug used for preventing the poultry flu (Pabbaraju, Ho, & Wong, 2008). However, the antibody of the influenza virus is easily generated when amantadine is utilized in abundant dose, and adverse reactions, such as nausea and convulsions, could be observed in the subjects (Keyser, Karl, Nafziger, & Bertino, 2000). As shown in Figure 5, amantadine, confirmed by its mass spectrogram, was first detected in the oil sample of 3-8h at 0.457 mg/kg and then gradually increased in concentration until the end of the frying treatment (0.81 mg/kg in oil sample of 7-8h). On the one hand, the fresh CBM used in this study might be contaminated by amantadine, which would dissolve in the frying oil in increasing concentration due to its organic solvent solubility along with the increase of frying batches of CBM. On the other hand, amantadine might be formed under the complex frying conditions, as suggested by the observation of possible structure-like precursors such as 9-methylene-tricyclo[4.2.1.1(2,5)]decane and 4-oxatricyclo[4.3.1.1(3,8)]undecan-5-one. Amantadine was first observed in the CBM-fried oil samples, which gave a new attention of harmful product to producers or consumers for the consumption of fried chickens. However, the specific source of amantadine observed during deep-fat frying process should be investigated further.

3.7. Other volatiles

In addition to the aforementioned typical volatile compounds, acids, furans, antioxidant derivatives, aromatic compounds, and esters were also formed when SO was heated or deep-fat fried with WD and CBM (shown in Supplement 7).

Short-chain SFAs (C6-9) mainly formed by oxidative decomposition of UFAs were discontinuously detected in the collected oil samples, especially hexanoic acid in the late stage of the heating or deep-fat frying process. However, hexanoic acid might be formed by the oxidation of hexanal that was the decomposition product of linoleic acid-13-hydroperoxide. From the changes in concentration, the addition of food components might delay the formation of hexanoic acid. Among the furans, 2-pentylfuran was observed in an approximately increasing trend from 2.021, 2.401, and 1.581 mg/kg in oil samples of 1-2h to 9.399, 9.299, and 4.838 mg/kg in oil samples of 7-8h during the processes of SO heating, WD frying, and CBM frying, respectively. This type of oxidative decomposition product of UFAs was steadily formed during the heating or frying of SO. 2-pentylfuran is a typical oxidative decomposition product of linoleic acid or linolenic acid and was regarded as a factor in the reversion of the flavor of refined SO (Dlugogorski, Kennedy, & Mackie, 2012).

Antioxidants or their derivatives such as butylated hydroxytoluene (BHT) and 2-*tert*-butyl-1,4-benzoquinone (TBBQ), were detected in significant concentration in the first day of heating or deep-fat frying. For example, TBBQ was observed in a decrease trend from 17.630 mg/kg in oil sample of 1-2h to 0.622 mg/kg in oil sample of 2-2h during the heating of SO; however, it was only observed in lower concentrations of 3.074 and 1.449 mg/kg in oil sample of 1-2h during the WD frying

and CBM frying, respectively. This phenomenon also reflected the intense reactions accelerated by food components during the food frying process. TBBQ is formed by oxidation of the hydroxyl group of tertiary butylhydroquinone (TBHQ). No significant change in concentration of BHT and a significant decrease in concentration of TBBQ were observed, which reflected that TBHQ had better antioxidant properties than BHT in the oxidation of SO (Allam & Mohamed, 2002).

Aromatic compounds, including alkylbenzenes and PAHs, were also formed in considerable amount during the heating or deep-fat frying of SO. For example, toluene was observed in the largest concentrations (e.g. 45.03 mg/kg in oil sample of 1-8h) during the heating of SO; however, less quantity of alkylbenzenes in lower concentrations were just observed in the food-fried oil samples. Because of the potential carcinogenicity and genotoxicity of alkylbenzenes and PAHs, their distribution in processed food and cooking oil fumes has been widely studied (Li, Pan, & Wang, 1994; Qin, Leung, Leung, Zheng, & Wong, 2011). Alkylbenzenes, such as ethylbenzene, propylbenzene, butylbenzene, and pentylbenzene, were previously qualitatively and quantitatively studied during the heating of extra virgin olive, sunflower, and virgin linseed oils (Uriarte & Guillén, 2010). Butylbenzene was reported in concentrations of 1.429, 0.287, and 0.102 mg/L in these three oils heated for 20 h, respectively. The same order of magnitude of the concentrations of alkylbenzenes was observed in this study. In addition, alkenylbenzenes were observed in increasing concentration during the heating of virgin linseed oil with a relatively high content of linolenic acid. Therefore, alkylbenzenes and alkenylbenzenes, such as

toluene, 1,2,4,5-tetramethylbenzene, 4-ethyl-1,2-dimethylbenzene, and 2-butenylbenzene could be formed during the heating or deep-fat frying of SO because of its considerable linolenic acid content. In addition, benzene could also be formed by oxidation of cyclohexene (Pitts Jr., 1983). Thus, these alkylbenzenes and alkenylbenzenes might be formed by oxidation of substituted cyclohexenes during the heating or deep-fat frying of SO.

Alkylnaphthalenes, such as 1-methyldecahydronaphthalene and 2-methyldecahydronaphthalene, were the major PAHs observed during the heating or deep-fat frying of SO. On the one hand, alkyl naphthalenes can be formed by Diels-Alder reaction between substituted benzenes and conjugated dienes such as 2,4-octadiene and 1,3-nonadiene decomposed from oxidation of UFAs (Chen & Chen, 1983). On the other hand, benzene-like compounds, such as 1,2-hexenediol (from methyl linoleate), 2-cyclohexene-1-one and 4,4-dimethyl-2-cyclohexene-1-one (from methyl linolenate) could be the precursors for the formation of alkylnaphthalenes (Mestres & Sola, 1998). 4-Isopropenylcyclohexanone and 5-methyl-2-(1-methylethylidene)-cyclohexanone were the typical benzene-like compounds detected in the studied oil samples.

Esters, such as fatty acid methyl esters and phthalates, were the typical volatile compounds observed in this study. Methyl palmitate, a typical fatty acid methyl ester, was detected in a fluctuating variation trend in all of the collected oil samples, especially the deep-fat fried oil samples. Trace amounts of methyl palmitate were previously reported in the volatile constituents of heated corn oil and used frying oil

(Chung et al., 1993; Takeoka, Perrino, & Buttery, 1996). Approximately 10% palmitic acid was contained in the SO and could be formed by hydrolysis of palmitic acid-containing TAGs. Therefore, methyl palmitate could be formed by esterification between palmitic acid and alcohols.

Phthalates, also known as plasticizers, are compounds extensively used to modify plastic moldings in the plastics industry. Because of their good oil solubility, phthalates have been commonly found in various foods, including wines, beverages, and vegetable oils. However, potential harm to human health, such as male reproductive toxicity, was observed when people were expose to these phthalates (Knez, 2013). Therefore, the detection of phthalates in the studied oil samples was interesting and cannot be ignored. Diethyl phthalate was previously found in French fried potatoes; however, its source or formation mechanism was not analyzed (Gillatt, 2001). Although the fresh SO was sold in a plastic bucket, no phthalate was observed among the volatile compounds in fresh SO. In addition, the procedures of sampling and detection were carefully conducted to avoid any plasticizer-containing plastic materials. Therefore, phthalates might be formed from TAGs under high temperature conditions. On the basis of the similarity of their molecular structures, the 1(3*H*)-isobenzofuranone and alkylnaphthalenes might be the precursors of phthalates. These benzene-containing compounds might act as the hydrogen donors to form free radicals that would subsequently participate in the ring-opening reaction or cleavage of carbon-oxygen bonds to form the phthalic acid. Phthalates were then formed by esterification between the phthalic acid and oxidative decomposed alcohols of

unsaturated TAGs. The addition of food components reduced the quantity of phthalates, but increased the quantity of oil samples in which some phthalates were detected, such as dibutyl phthalate in both the WD- and CBM-fried oil samples and butyl octyl phthalate in the CBM-fried oil samples. Therefore, food components promoted the formation of phthalates in the frying oil, which should be further verified because more and more attention was paid on the safety of frying course and fried food.

## 4. Conclusion

In addition to aldehydes, alkanes, alkenes, alkynes, alcohols, ketones, and other volatiles were analyzed during the processes of heating SO, frying WD, and frying CBM. Along with the increase of heating or frying time, most volatiles were observed in increasing concentrations. When the heating or frying proceeded to the late stage, some volatiles such as alkenes were observed in decreasing concentration because of their unstable property and the intense reaction environment. A reduced quantity and concentration of volatiles in the collected oil samples were observed when WD and CBM were fried in SO compared to those observed during the SO heating process, which was primarily due to the intense process of frying food when food components such as water, carbohydrates, and proteins were involved. The influence of CBM components on the frying process was more significant than the influence of WD on the basis of the volatile profiles detected. NCVs were detected solely in the CBM-fried oil samples, and the quantity and concentration of these volatiles showed

an increasing trend as the frying batches of CBM increased.

Among the volatiles formed during deep-fat frying process, some compounds were considered potentially harmful for the frying process and fried foods. The first interesting harmful compound observed in the CBM-fried oil sample from the beginning of 3-8h is amantadine, which might be the further reaction product of the molecular structure-like polycyclic oxidative products of UFAs during the CBM frying process. Alkenylbenzenes and PHAs are the second type of harmful compound that should be considered and might be related to the further oxidation of TAG oxidative decomposition products. The third important type of harmful volatiles when SO is used as the deep-fat frying medium is phthalates, which might be formed by the reactions involving the benzene-containing compounds. Although the specific formation mechanism of these harmful compounds needs to be further confirmed, the safety of the frying process for the cook and of fried food for consumers should not be ignored.

**Conflicts of interest**

The authors declare no conflict of interest.

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**Figure captions**

Figure 1. Total ion chromatograms of the volatiles formed during the heating of SO (A), frying of SO with WD (B), and frying of SO with CBM (C) (SO, soybean oil; WD, wheat dough; CBM, chicken breast meat).

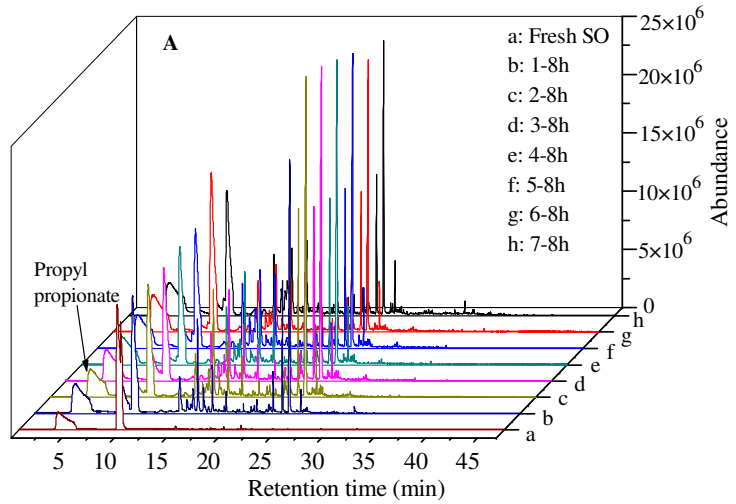
Figure 2. Changes in concentrations of tetradecane (A) and pentadecane (B) during the deep-fat frying process (SO, soybean oil; WD, wheat dough; CBM, chicken breast meat).

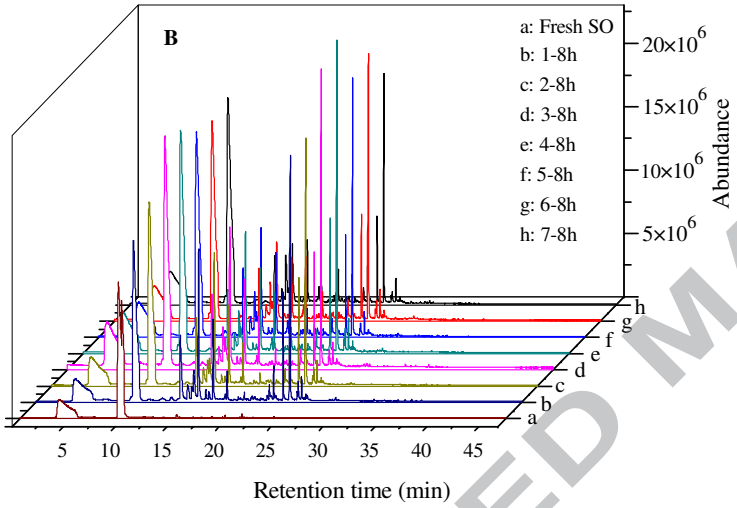
Figure 3. Changes in concentrations of 4-methyl-1,4-heptadiene (A), methyl ethyl cyclopentene (B), 7-methyl-3,4-octadiene (C), and 2-methylbicyclo[2.2.2]octane (D) during deep-fat frying process and the proposed reaction mechanisms for the formation of methyl ethyl cyclopentene from 4-methyl-1,4-heptadiene and 2-methylbicyclo[2.2.2]octane from 7-methyl-3,4-octadiene (SO, soybean oil; WD, wheat dough; CBM, chicken breast meat).

Figure 4. Changes in concentrations of 3-nonen-2-one (A) and 1(3*H*)-isobenzofuranone (B) during the deep-fat frying process (SO, soybean oil; WD, wheat dough; CBM, chicken breast meat).

Figure 5. Changes in concentrations of 2-propylpyridine, 2-pentylpyridine, and tricyclo[3.3.1.1(3,7)]decan-1-amine (also known as amantadine) during CBM frying in SO and the proposed reaction mechanisms for the formation of 2-alkylpyridines from 2,4-alkadienals and amino

compounds (SO, soybean oil; CBM, chicken breast meat).



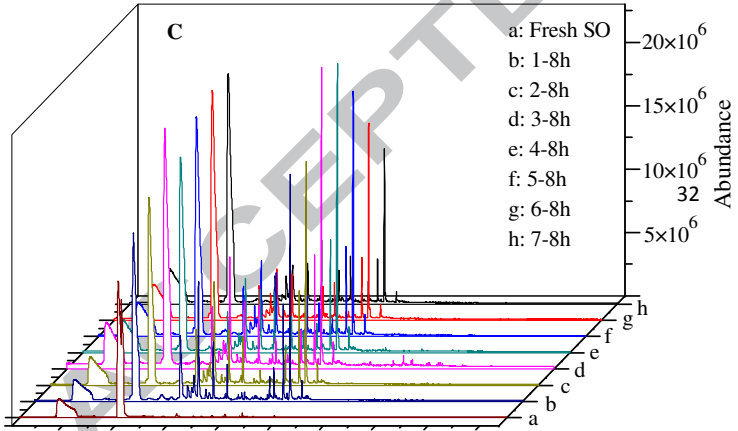



Figure 1.

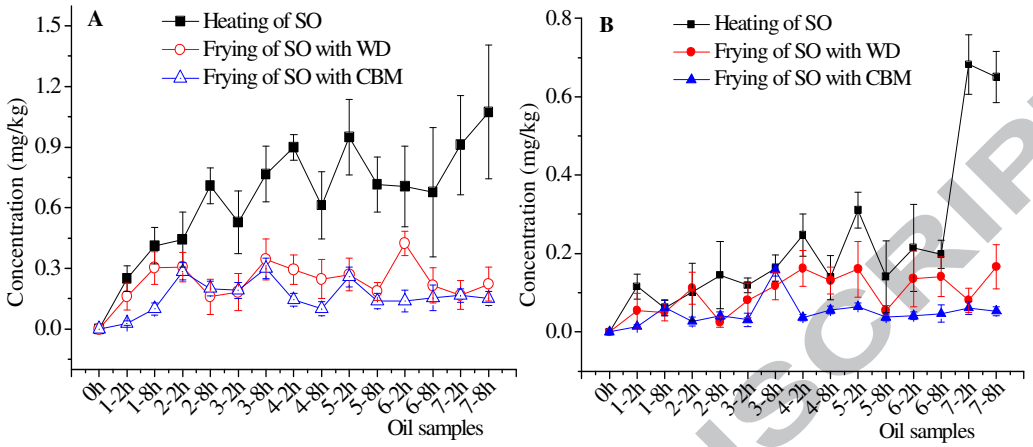
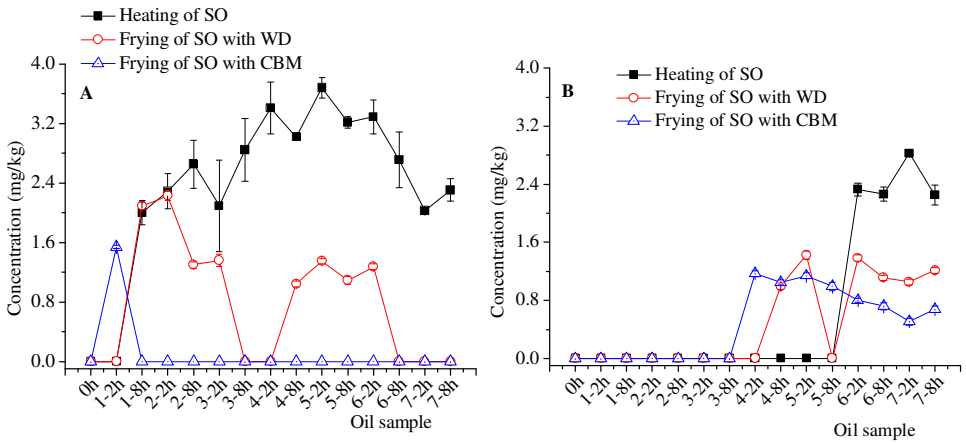
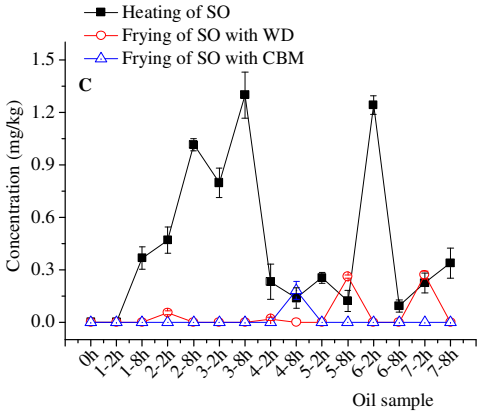


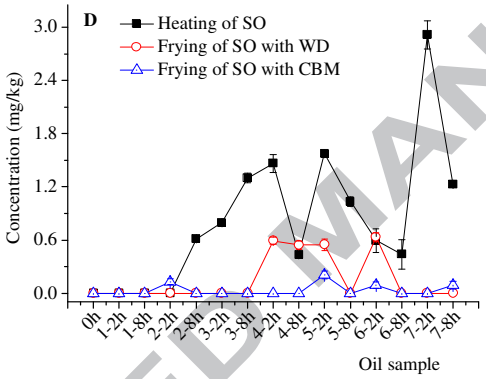

Figure 2.









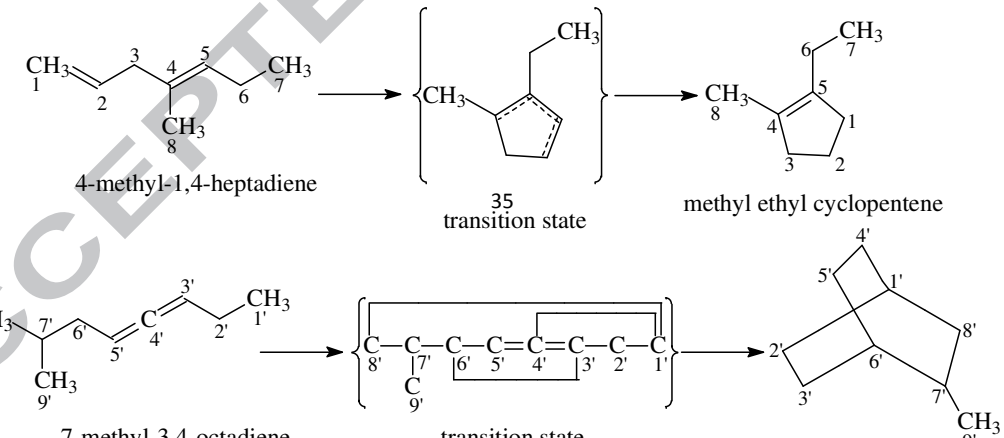



Figure 3.

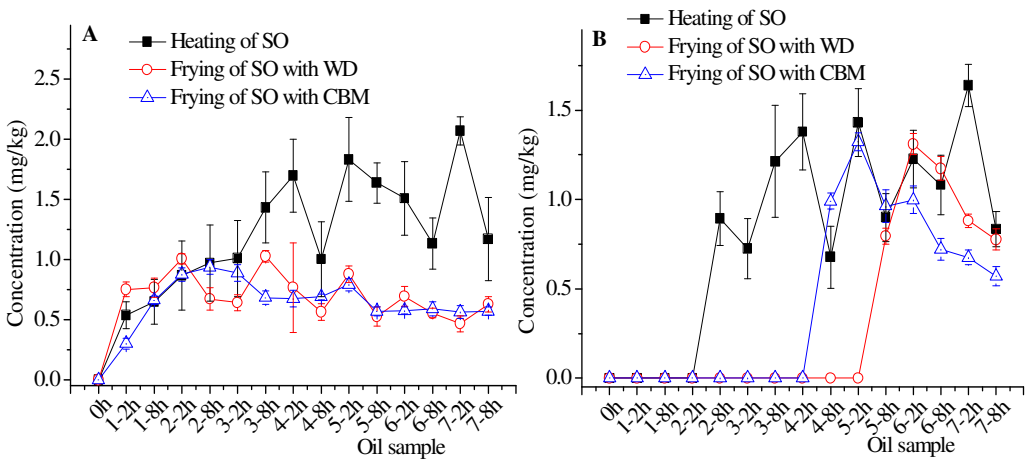
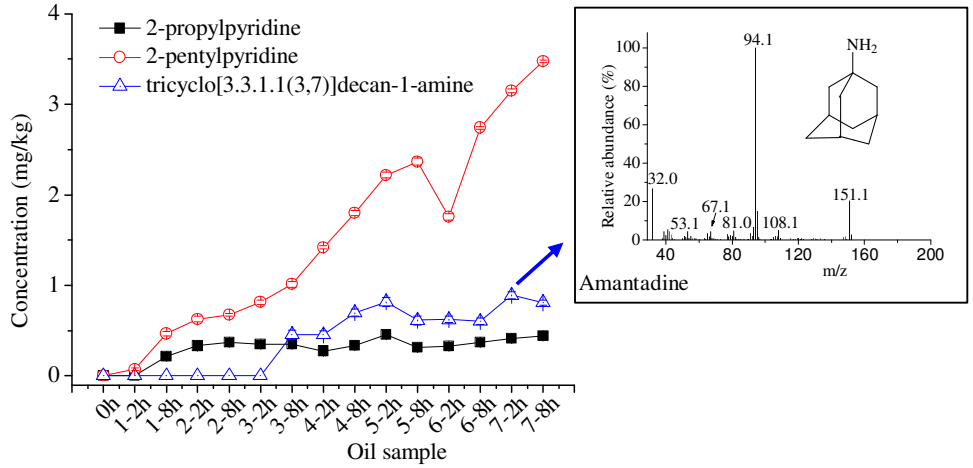



Figure 4.



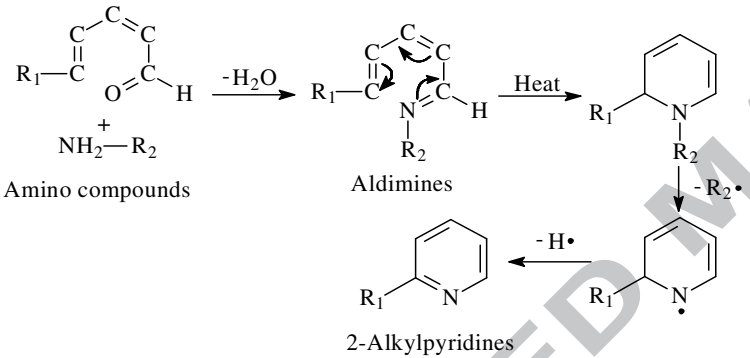




Figure 5.

Table 1 Typical volatile compounds detected during the processes of heating of SO, frying of SO with WD, and frying of SO with CBM [a].

| Volatile compounds | Heating of SO | | Frying of SO with WD | | Frying of SO with CBM | | Possible formation mechanism |
|---|---|---|---|---|---|---|---|
| | First detected | Maximum concentration (mg/kg) | First detected | Maximum concentration (mg/kg) | First detected | Maximum concentration (mg/kg) | |
| **Alkanes** | | | | | | | |
| Undecane | 1-2h | 2.415±0.098 in 3-8h | 1-2h | 1.087±0.056 in 1-6h | 1-2h | 1.049±0.066 in 1-6h | Free radical reaction of both unsaturated and saturated fatty acids |
| Tetradecane | 1-2h | 1.074±0.331 in 7-8h | 1-2h | 0.424±0.059 in 6-2h | 1-2h | 0.300±0.051 in 3-8h | |
| Pentadecane | 1-2h | 0.682±0.076 in 7-2h | 1-2h | 0.302±0.039 in 4-6h | 1-2h | 0.158±0.016 in 3-8h | |
| 2-Methylbicyclo[2.2.2]octane | 2-4h | 2.913±0.156 in 7-2h | 4-2h | 0.633±0.052 in 6-2h | 1-6h | 0.206±0.045 in 5-2h | Concerted reaction of 7-methyl-3,4-octadiene |
| 9-Methylbicyclo[3.3.1]nonane | 1-4h | 0.227±0.033 in 7-2h | 1-8h | 0.258±0.067 in 7-6h | 7-6h | 0.030±0.011 in 7-6h | Cyclization of alkane radicals |
| **Alkenes** | | | | | | | |
| 6-Dodecene, (Z)- | 3-8h | 2.577±0.131 in 4-2h | 1-2h | 0.996±0.077 in 3-4h | 1-2h | 0.579±0.043 in 2-8h | Free radical reaction of unsaturated fatty acids |
| 1,3-Nonadiene, (E,E)- | 1-2h | 4.516±0.316 in 5-4h | 2-2h | 1.309±0.049 in 2-6h | 1-2h | 0.893±0.116 in 2-6h | |
| 4-Methyl-1,4-heptadiene | 1-4h | 3.408±0.351 in 4-2h | 1-4h | 2.828±0.072 in 1-4h | 1-2h | 1.541±0.019 in 1-2h | |
| 7-Methyl-3,4-octadiene | 1-4h | 1.299±0.132 in 3-8h | 2-2h | 0.458±0.035 in 5-6h | 4-8h | 0.182±0.051 in 4-8h | |
| Methyl ethyl cyclopentene | 6-2h | 2.826±0.016 in 7-2h | 4-6h | 1.483±0.035 in 4-6h | 4-2h | 1.205±0.066 in 4-4h | Concerted reaction from 3,4-octadiene, 7-methyl- |
| **Alkynes** | | | | | | | |
| 5-Dodecyne | 3-8h | 0.512±0.0163 in 3-8h | 6-2h | 0.115±0.013 in 6-2h | 5-2h | 0.396±0.063 in 5-2h | Free radical reaction of unsaturated fatty acids |
| 7-Pentadecyne | 1-2h | 0.756±0.163 in 7-2h | 1-8h | 0.334±0.074 in 6-2h | 1-4h | 0.198±0.059 in 5-2h | |
| 9-Octadecyne | 1-2h | 1.227±0.096 in 7-8h | 1-4h | 0.676±0.014 in 3-8h | 2-4h | 0.171±0.072 in 2-6h | |
| **Alcohols** | | | | | | | |
| 1-Octanol | 1-4h | 3.669±0.961 in 7-2h | / | / | 1-4h | 1.498±0.325 in 1-4h | Decomposition of oleic acid-10-hydroperoxide |
| 1-Octen-3-ol | 1-2h | 11.690±0.382 in 5-8h | 1-2h | 5.333±0.317 in 3-8h | 1-2h | 4.434±0.364 in 1-6h | Positional isomerization of hydroxyl and C=C in 2-octen-1-ol |
| 4-Ethylcyclohexanol | 1-8h | 0.594±0.046 in 2-2h | 1-2h | 2.316±0.456 in 1-4h | 2-8h | 0.116±0.052 in 2-8h | Free radical reaction of both unsaturated fatty acids |
| 2,3-Dihydro-2-methyl-1H-inden-1-ol | / | / | 1-2h | 1.380±0.118 in 1-4h | 1-4h | 1.132±0.215 in 1-4h | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Ketones** | | | | | | | |
| 6-Dodecanone | 3-2h | 2.422±0.164 in 7-2h | 2-2h | 0.744±0.082 in 5-4h | 3-2h | 0.535±0.022 in 4-8h | Oxidation of 6-dodecene |
| 3-Nonen-2-one | 1-2h | 2.069±0.116 in 7-2h | 1-2h | 1.026±0.049 in 3-8h | 1-2h | 0.985±0.073 in 1-6h | Oxidation of aldehyde group and positional isomerization of C=C in (*E*)-2-nonenal |
| 1(3H)-Isobenzofuranone | 2-8h | 1.639±0.117 in 7-2h | 5-6h | 1.310±0.059 in 6-2h | 4-6h | 1.195±0.115 in 6-4h | Oxidation of cyclic alkenes or alcohols |
| **Nitrogen-containing compounds** | | | | | | | |
| 2-Pentylpyridine | / | / | / | / | 1-2h | 3.474±0.017 in 7-8h | Reaction between amino compounds and the lipid |
| 2-Propylpyridine | / | / | / | / | 1-6h | 0.453±0.020 in 7-8h | oxidation decomposition products or Maillard |
| Pyrrole-3-butyronitrile | / | / | / | / | 2-6h | 0.422±0.019 in 2-8h | reaction |
| Amantadine | / | / | / | / | 3-8h | 0.891±0.040 in 7-2h | From fresh CBM or its structure-like precursor |
| **Other compounds** | | | | | | | |
| Hexanoic acid | 1-2h | 0.890±0.085 in 1-8h | 4-8h | 1.187±0.077 in 6-4h | 3-2h | 1.177±0.080 in 5-2h | Oxidation of hexanal |
| 2-Pentylfuran | 1-2h | 11.243±0.284 in 7-2h | 1-2h | 9.299±0.999 in 7-8h | 1-2h | 5.064±0.037 in 5-8h | Oxidative decomposition product of linoleic acid or linolenic acid |
| Hexadecanoic acid, methyl ester | 1-4h | 0.134±0.013 in 7-8h | 1-2h | 0.095±0.014 in 3-8h | 1-6h | 0.079±0.019 in 3-8h | Esterification between palmitic acid and alcohols |
| 2-(1,1-Dimethylethyl)-1,4-benzenediol | 1-2h | 11.134±0.086 in 1-2h | 1-2h | 2.332±0.075 in 1-2h | 1-2h | 0.767±0.045 in 1-2h | Artificial antioxidants |
| 1-Methyldecahydronaphthalene | 1-4h | 0.488±0.038 in 4-2h | 2-4h | 0.062±0.032 in 2-4h | 4-8h | 0.083±0.016 in 4-8h | Diels-Alder reaction between substituted benzenes and conjugated dienes |
| 1-Ethyl-2,4-dimethylbenzene | 1-2h | 0.516±0.062 in 3-6h | / | / | 3-8h | 0.086±0.017 in 3-8h | Oxidation of substituted cyclohexenes |
| Dimethyl phthalate | 5-2h | 0.584±0.061 in 7-2h | 3-8h | 0.134±0.029 in 3-8h | 3-8h | 0.088±0.022 in 3-8h | |
| Dibutyl phthalate | 4-2h | 0.080±0.010 in 6-2h | 1-6h | 0.051±0.022 in 2-2h | 1-8h | 0.102±0.013 in 1-8h | Originated from 1(3H)-isobenzofuranone and alkylnaphthalenes or brought from circumstance |
| 1,2-Benzenedicarboxylic acid, butyl octyl ester | 6-4h | 0.030±0.007 in 6-4h | 4-2h | 0.076±0.019 in 4-6h | 2-4h | 0.122±0.025 in 4-8h | |

[a] Abbreviation: SO, soybean oil; WD, wheat dough; CBM, chicken breast meat; 1-2h, oil sample prepared at the second hour in the first day; C=C, carbon-carbon double bonds; Forward slash means not detected.

Highlights

- Non-aldehyde volatiles formed during deep-fat frying of soybean oil were studied.
- Hydrocarbons, alcohols, ketones, N-containing volatiles, and others were identified.
- Less and lower concentration of volatiles were observed in food-fried oil samples.
- N-containing volatiles were observed solely during deep-fat frying with chicken meat.
- Amantadine and phthalates were first detected during deep-fat frying of soybean oil.