

The changes in the volatile aldehydes formed during the deep-fat frying process

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Abstract Volatile aldehydes (VAs) formed during soybean oil (SBO) heating, wheat dough (WD) frying, and chicken breast meat (CBM) frying processes were comparatively investigated by solid-phase micro-extraction-gas chromatography–mass spectrometry (SPME-GC-MS). The results showed that relative amounts (RAs) of the most detected VAs were firstly increased to maximum values in oil samples collected at the second hour of the seventh day and the values were then decreased with the increase in the time of oil heating process (control). However, for food frying processes, the time needed for reaching maximum RAs of VAs was shorter and the values were decreased with the increase in frying time. Significant change in contents of the VAs was observed for oil samples fried with CBM due to the high contents of water, protein, and lipid content compared to oil samples fried with WD. Based on the obtained results, free radical reaction, particularly positional isomerization and *cis-trans* isomerization, was deduced to occur when WD or CBM was fried in SBO. The relatively high RAs of VAs formed during the deep-fat frying process presented certain invaluable measures for evaluating of frying oil and fried food quality and safety.

Keywords Soybean oil · Deep-fat frying · Frying oil · Volatile aldehyde · Solid-phase micro-extraction-gas chromatography–mass spectrometry

Introduction

In addition to attractive golden appearance and crispy structure, pleasant flavor is important for the popularity of fried food. However, the fume generated during food frying process is usually harmful to the health due to the generation of detrimental compounds, such as polycyclic aromatic hydrocarbons (Lee and Gany 2013), heterocyclic amines (Cao et al. 2013), and varying types of aldehydes (Dung et al. 2006). Therefore, the characterization of the aldehydes formed during the deep-fat frying process is very important from the viewpoint of food quality and food safety.

Generally, high amount of aldehydes can be formed during food frying process or oil heating process (Jerković et al. 2007; Ramirez et al. 2004). These aldehydes are mainly generated from the thermal oxidation of the polyunsaturated triacylglycerols (TAGs) (Zhang et al. 2012). However, the reaction substrates involved in the complex reactions are not only the constituents of frying oil, but also the components of fried food and the reactive intermediates. The Maillard reaction, for instance, occurred between amino-containing compound and carbonyl-containing product is the primary reaction involving the constituents of the fried food and frying oil (Zamora and Hidalgo 2005). Therefore, studying the composition of VAs during deep-fat frying process is important for understanding the mechanism of aldehydes formation.

Many studies have been carried out to characterize the types of VAs formed during deep-fat frying process (Katsuta et al. 2008; Katragadda et al. 2010). However, few studies have investigated the difference in VA profiles of varying

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types of food fried with SBO. Furthermore, a small number of systematical research studies have been done on the mechanisms of the typical VAs formation. Therefore, the contents of the volatile VAs formed during the thermal treatment of SBO without or with foods were comparatively investigated by SPME-GC-MS in this work.

Materials and methods

Materials and chemicals

Refined SBO, wheat flour, and chilled CBM were purchased from a local market. The major FAs of refined SBO expressed in mass ratio are as follows: 4.49 % stearic acid, 22.49 % oleic acid (O), 50.15 % linoleic acid (L), and 10.54 % linolenic acid (Ln).

Propyl propionate (99 %) and n-alkanes (C5-C20) standard solvent were purchased from Sigma-Aldrich. Chromatographically pure n-hexane was purchased from MREDA technology Ltd.

Sample preparation

WD was made by mixing the wheat flour and deionized water with a mass ratio of 2:1 in a mixer. WD was placed in a refrigerator at 4 °C overnight and was kneaded to a shape of 10 cm-diameter disc and thickness of 0.6 cm before the frying treatment. Fresh CBM samples were purchased according to the daily use amount and were manually cut into uniform strips with a sectional area of 0.6×0.6 cm. The gross chemical composition of the initial food was determined and expressed in mass percentage as follows: water, 39.00 %; protein, 9.11 %; lipid, 0.03 %; carbohydrates, 51.52 %; and ash, 0.34 % for WD; water, 72.20 %; protein, 19.80 %; lipid, 4.59 %; carbohydrates, 2.31 %; and ash, 1.10 % for CBM.

A deep-fat frying process was performed in a domestic scale electric fryer with double cylinder (HY-82EX, Guangzhou Huili Food Machinery Co., Ltd., China). Specifically, 5 L of SBO were put into the cylinder and heated to the set temperature (180 °C). No replenishment of fresh SBO was carried out during the whole deep-fat frying process. Food materials (100 g) were placed in a stainless screen frame and fully immersed into the heated SBO. Frying time was set as 10 min for WD and 5 min for CBM due to the difference in the nature of foods. The time interval between the frying batches in the WD-frying treatment was 5 min and was 10 min for the CBM-frying treatment. The frying process was performed for 8 h/day over a period of 7 consecutive days. SBO was heated under the same conditions as a control. Oil samples were collected in triplicate at 2 h intervals. Cold

water was used to cool the oil samples to the room temperature prior to the SPME treatment.

SPME treatment of volatile aldehydes

Propyl propionate and hexane were mixed (1:9, v/v) to be used as the internal standard. Extraction of VAs was performed by using a 50/30 μm polydimethylsiloxane/divinylbenzene/carboxen SPME fiber mounted to an SPME manual holder assembly (Supelco, Bellefonte, PA, USA) and a constant temperature magnetic stirrer (PC-420, Corning Inc., Acton, MA, USA).

Oil sample (5 g) and internal standard solution (0.0060 g) were precisely weighed into a 15-mL SPME vial with a 1-cm rotor. The sample-loaded vial was sealed with a specialized cap and was then placed into a water bath maintained at 60 °C on a stirrer. Then, the manual holder assembly was inserted into the vial to expose the SPME fiber at the position of 1 cm over the oil surface. The sample loading and SPME fiber insertion were completed as quickly as possible. A total time of 50 min was taken to perform the VAs extraction and the oil sample was maintained under stirring at scale 5 on a magnetic stirrer. The headspace volatiles of the fresh SBO were also extracted under the same conditions.

GC-MS analysis of volatile aldehydes

Analysis of VAs was carried out by an Agilent gas chromatography mass spectrometer (7890A-5975C). After SPME extraction, the fiber was inserted into the injection port and desorbed for 2 min at the temperature of 250 °C. Helium (99.999 %) was used as the carrier gas at 1 mL/min. Separation of VAs was performed on a DB-5MS column (30 m×0.25 mm×0.25 μm, J&W Scientific) and in splitless mode for the best separation efficiency. The temperature program was set at 40 °C for 2 min and was then raised to 160 °C at ratio of 5 °C/min and held for 2 min, and was then raised to 250 °C at ratio of 10 °C/min and held for 10 min. Temperatures of the transfer line, ion source, and quadrupole mass filter were set at 250, 230, and 150 °C, respectively. The mass spectrum was acquired over a range of m/z30–450 by electron impact mode with ionization energy of 70 eV. The n-alkanes (C5-C20) standard were separated and analyzed under the same conditions in liquid injection mode with an injection volume of 1 μL.

VAs were qualitatively analyzed by consulting both the NIST08.L MS library (match quality >80 %) and the Flavornet and LRI&odour Database according to the calculated relative retention index (RI) (Bianchi et al. 2007). The relative quantification of the VAs was achieved by using the internal standard method.

Statistical analysis

Analysis of variance (ANOVA) was used to study the changes in contents of VAs during the deep-fat frying process. Data processing and analysis were carried out by SPSS 17.0 for Windows (SPSS Corp., Chicago, USA).

Results and discussion

As the major volatile compounds, aldehydes showed a large proportion of the detected volatiles in both the heat-treated oil (control) and the food frying oils (71.25, 66.54, and 71.77 % in the oil sample of 7–8 h of processes for oil heating, WD frying, and CBM frying, respectively). As shown in Table 1, both saturated aldehydes (alkanals and substituted alkanals) and unsaturated aldehydes (n-alkenals and alkadienals) were

observed. Moreover, both *cis* and *trans* configurations are presented in the detected aldehydes.

Based on the FA composition of SBO, all VAs are related to the free radical reaction occurred in the unsaturated FAs. Generally, the breakdown of ester bond in TAGs, such as thermal degradation and hydrolysis, easily occurs under frying condition to produce the free FAs (Chung et al. 2004). Therefore, the expression of primary oxidation product is in the form of free FAs. Different types of hydroperoxide are formed in the oxidation reaction of O, L, and Ln according to the varying reaction sites around the carbon-carbon double (C=C) bonds (Yin et al. 2011). Each hydroperoxide would further decompose into low-molecular-mass products, such as hydrocarbons, alcohols, aldehydes, ketones, and acids. Therefore, most of the detected aldehydes are either the direct products of oxidation of unsaturated FAs or the reaction products of the oxidative intermediates.

Table 1 The volatile aldehydes detected during the processes of soybean oil heating (control), WD frying, and CBM frying ^{a,b}

No.	RT (min)	Compounds (Systematic name)	MQ (%)	RI	Possible precursor	Proposed mechanism
1	6.729	3-Methylbutanal	83	917	Ln	oxidation
2	8.180	<i>Trans</i> -2-pentenal	86	771	Ln-9-hydroperoxide	further oxidation
3	9.289	Hexanal	91	2203	L-13-hydroperoxide; L-12-hydroperoxide	β -homolysis; keto-enol tautomerism
4	10.941	<i>Trans</i> -2-hexenal	96	931	Ln-12-hydroperoxide	keto-enol tautomerism; isomerization
5	12.274	Heptanal	87	16126	O-11-hydroperoxide	further oxidation
6	14.002	<i>Trans</i> -2-heptenal	93	1023	L-12-hydroperoxide	β -homolysis
7	14.051	<i>Cis</i> -2-heptenal	97	1031	<i>trans</i> -2-Heptenal	<i>cis-trans</i> isomerization
8	14.456	Benzaldehyde	96	1131	L; 2,4-decadienal	oxidation, dehydration; further oxidation
9	15.561	<i>Trans,trans</i> -2,4-Heptadienal	95	1006	Ln-12-hydroperoxide	β -homolysis
10	17.206	<i>Trans</i> -2-octenal	82	1149	L-9-hydroperoxide; L-10-hydroperoxide	further oxidation
11	18.550	Nonanal	86	1105	O-10-hydroperoxide; O-9-hydroperoxide	β -homolysis; keto-enol automerism
12	20.196	<i>Trans</i> -2-nonenal	93	1256	L-9-hydroperoxide; 2-undecenal	position isomerization; further oxidation
13	21.466	Decanal	84	1205	O-8-hydroperoxide	keto-enol tautomerism
14	21.778	<i>Trans,trans</i> -2,4-nonadienal	95	1220	L-9-hydroperoxide; <i>trans</i> -2-nonenal	further oxidation
15	22.645	4-Oxononanal	90	1298	L	further oxidation
16	23.058	<i>Trans</i> -2-decenal	91	1387	O-9-hydroperoxide	β -homolysis
17	24.315	<i>Trans,trans</i> -2,4-decadienal	96	1315	L-9-hydroperoxide	β -homolysis
18	25.663	<i>Trans</i> -2-tridecenal	80	1476	<i>trans</i> -2-undecenal	combining reaction
19	25.741	<i>Trans</i> -2-undecenal	80	1500	O-8-hydroperoxide	β -homolysis; <i>cis-trans</i> isomerization
20	25.741	<i>Trans</i> -2-dodecenal	82	1500	<i>trans</i> -2-undecenal	combining reaction
21	27.260	<i>Trans,trans</i> -2,4-undecadienal	88	1430	<i>trans</i> -2-undecenal	further oxidation; desaturation
22	27.260	<i>Trans,trans</i> -2,4-dodecadienal	84	1430	<i>trans</i> -2-dodecenal	further oxidation; desaturation
23	28.127	Cyclohexanecarboxaldehyde, 4-(hydroxymethyl)-	80	1519	structure-similar alkanes, alkenes	oxidation
24	32.747	<i>Cis,cis</i> -10,12-hexadecadienal	93	1890	unsaturated radicals	combination reaction
25	32.976	<i>Trans</i> -14-hexadecenal	84	2191	unsaturated FAs	decarboxylic reaction; free radical reaction

^a Abbreviations: *WD* wheat dough, *CBM* chicken breast meat, *RT* retention time, *MQ* matching quality, *RI* relative retention index, *O* oleic acid, *L* linoleic acid, *Ln* linolenic acid

^b MQ was consulted from NIST08.L MS database. RI values calculated in relation to the C5-C20 n-alkanes for a DB-5 MS column

It is interesting that no volatile aldehyde was observed in the fresh SBO. Therefore, all the detected volatile aldehydes were probably produced during the oil heating or food frying treatments. Due to the continuity of the changes in RA of VAs, RAs of VAs of the oil samples which were collected at the fourth and sixth hour during the 7-days treatments were omitted for the succinct expression of the data.

Changes in alkanals content

As the β -homolysis cleavage product of L-13-hydroperoxide, hexanal can also be formed by keto-enol tautomerism of the combination product between 1-hexenyl radical degraded by β -homolysis of L-12-hydroperoxide and hydroxyl radical. As shown in Table 2, hexanal was first presented in the heat-treated oil sample of 2–8 h, meaning that it had not been formed or the yield was too low to be detected at the initial stage of the oil heating process (control). As the processing time increased, the RA of hexanal was significantly increased and reached a maximum value of 10.28 mg/kg in oil sample of 7–2 h. In contrast, hexanal was early detected in the food-fried oil samples, indicating that the reaction rate for formation of hexanal was higher at the early stage of the food frying process than that of the oil heating process (control). Relatively slow increase in RA of hexanal was observed in the WD-fried oil samples as the processing time increased. However, no obvious change in RA of hexanal was found for oil samples fried with CBM. This may be attributed to the relatively stable reaction environment during the heating process and the involving of more reaction substrates during the frying process. In other words, the formation of hexanal was influenced by the food components during the frying process.

Heptanal is not the direct product of triolein, trilinolein, and trilinolenin oxidation (Selke and Rohwedder 1983; Selke et al. 1977, 1980). Therefore, heptanal was not observed during both the oil heating process (control) and the food frying processes except the last stage of these treatments (oil sample of 7–8 h). Based on the possible oxidation products of unsaturated FAs, the precursor of heptanal might be heptanol decomposed from O-11-hydroperoxide.

Nonanal is not only the β -homolysis product of O-10-hydroperoxide but also the keto-enol tautomerism product of the combination product between 1-nonenyl radical degraded from O-9-hydroperoxide and hydroxyl radical. The RAs of nonanal during the oil heating process (control) were greater than those during the food frying process, indicating that the formation of nonanal was also influenced by the food components. Therefore, the formation rate of nonanal was firstly increased and was then decreased to be lower than the reaction rate of consequent reactions of nonanal as the processing time increased.

As a keto-enol tautomerism product of the combination product between 1-decenyl radical decomposed from O-8-

hydroperoxide and hydroxyl radical, decanal was discontinuously observed in the heat-treated oil samples (control) and was not present in the food-fried oil samples. Therefore, decanal is unstable and can easily contribute to the consequent reactions during the thermal treatment of SBO (particularly the deep-fat frying process).

Changes in n-alkenals content

As presented in Table 3, *trans*-2-pentenal was only observed in a relatively low amount in few heated oil samples during the oil heating process (control). *Trans*-2-pentenal was previously considered the decomposition products of Ln (Soheili et al. 2002). However, according to the composition of secondary oxidation products (SOPs) of Ln-9-hydroperoxide, *trans*-2-pentenal might be the further oxidation product of *cis,cis*-3,6-nonadienal, which is unstable under conditions of high temperature and oxygen. *Trans*-2-pentenal was not observed during the frying process, which could be attributed to its high volatility under the increased reaction intensity condition.

Based on the classical lipid oxidation mechanism (Yin et al. 2011), *trans*-2-hexenal is not the direct SOP of unsaturated FAs. Due to the features of lipid oxidation, *trans*-2-hexenal might be formed from *cis*-3-hexenal by *cis-trans* isomerization and electronic rearrangement. *Cis*-3-hexenal can be formed by the keto-enol tautomerism of the combination product between 1,3-hexadienyl radical degraded from Ln-12-hydroperoxide and hydroxyl radical. Therefore, the RAs of *trans*-2-hexenal formed during the heating and frying processes are lower than those of other major directly oxidative degraded 2-alkenals. The RA of *trans*-2-hexenal was increased to a maximum value of 1.30 mg/kg in the oil sample of 7–2 h and was then decreased as the processing time increased during the oil heating process (control). However, reduced RAs of *trans*-2-hexenal were observed during the frying process, especially in the CBM-fried oil samples. It is interesting that the RA of *trans*-2-hexenal was increased during the WD frying process; however, it was decreased during the CBM frying process as the processing time increased. This might be attributed to the relatively more reaction substrates involved in the CBM frying process.

Trans-2-heptenal, β -homolysis product of L-12-hydroperoxide, might be transformed to *cis*-2-heptenal by *cis-trans* isomerization under the adopted experimental conditions (Frankel 2005a). Furthermore, 2-heptenal can also be formed from the decomposition of 2,4-decadienal (Matthews et al. 1971). *Cis*-2-heptenal was observed during the whole CBM frying process and the interim (from the oil sample of 2–8 h to 5–8 h) of the WD frying process; however, *trans*-2-heptenal was found during the whole oil heating process (control) and the early and the last stages of WD frying process. This discrepancy might be related to the differences in nature of the reaction substrates involved in the treatments of control, WD-

Table 2 The changes in amounts of alkanals formed during the soybean oil heating process and food frying process^{a,b}

Alkanals	Treatments	1–2 h	1–8 h	2–2 h	2–8 h	3–2 h	3–8 h	4–2 h
Hexanal	Oil heating	ND	ND	ND	0.48±0.01b	1.23±0.03a	1.25±0.01b	2.28±0.04a
	WD frying	0.70±0.38b	0.73±0.22b	0.81±0.19a	1.07±0.23a	1.03±0.32a	1.73±0.13a	1.48±0.23b
	CBM frying	ND	1.11±0.36a	1.11±0.22a	1.11±0.23a	1.03±0.32a	0.88±0.32c	1.46±0.26b
Heptanal	Oil heating	ND	ND	ND	ND	ND	ND	ND
	WD frying	ND	ND	ND	ND	ND	ND	ND
	CBM frying	ND	ND	ND	ND	ND	ND	ND
Nonanal	Oil heating	2.54±0.20b	3.44±0.32a	4.21±0.22a	6.12±0.27a	5.53±0.28a	6.45±0.32a	7.06±0.23a
	WD frying	3.11±0.34a	3.56±0.51a	4.59±0.42a	4.27±0.54c	3.95±0.49b	6.02±0.54a	4.87±0.65b
	CBM frying	1.89±0.22c	3.64±0.22a	4.30±0.26a	5.25±0.28b	5.21±0.24a	4.71±0.25b	4.61±0.28b
Decanal	Oil heating	ND	ND	ND	ND	0.41±0.10	0.70±0.07	0.63±0.11
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Alkanals	Treatments	4–8 h	5–2 h	5–8 h	6–2 h	6–8 h	7–2 h	7–8 h
Hexanal	Oil heating	1.93±0.02a	4.45±0.02a	8.54±0.07a	4.02±0.01a	4.45±0.04a	10.28±0.08a	8.10±0.05a
	WD frying	1.37±0.19b	1.30±0.24b	1.18±0.11b	1.35±0.22b	1.43±0.22b	1.61±0.36b	1.93±0.20b
	CBM frying	1.28±0.37b	0.99±0.35b	1.06±0.14c	0.97±0.38b	1.10±0.33b	1.00±0.20c	0.96±0.10c
Heptanal	Oil heating	ND	ND	ND	ND	ND	ND	3.89±0.080a
	WD frying	ND	ND	ND	ND	ND	ND	0.07±0.01c
	CBM frying	ND	ND	ND	ND	ND	ND	1.29±0.45b
Nonanal	Oil heating	8.38±0.31a	9.09±0.26a	7.04±0.41a	10.20±0.32a	9.99±0.28a	8.34±0.21a	8.38±0.32a
	WD frying	5.06±0.19c	5.54±0.68b	5.05±0.17b	6.29±0.54b	6.24±0.52b	5.80±0.63b	6.52±0.63b
	CBM frying	5.57±0.24b	5.65±0.23b	4.45±0.32c	4.66±0.22c	5.15±0.34c	5.75±0.37b	5.46±0.23b
Decanal	Oil heating	ND	ND	ND	1.14±0.11	0.95±0.07	0.87±0.08	0.81±0.06

^a Abbreviations: *WD* wheat dough, *CBM* chicken breast meat, *I–2 h*, oil sample collected at the second hour of the first day, *ND* not detected

^b The relative contents of alkanals were expressed as average value ± confidence interval. The lowercase (a,b,c) behind the content represents the significant difference among the three thermal treatments ($p < 0.05$, $n = 3$)

Table 3 The changes in amounts of n-alkenals formed during the soybean oil heating process and food frying process^{a,b}

n-Alkenals	Treatments	1–2 h	1–8 h	2–2 h	2–8 h	3–2 h	3–8 h	4–2 h
<i>Trans</i> -2-pentenal	Oil heating	ND	ND	ND	ND	ND	ND	ND
	Oil heating	0.40±0.09b	0.34±0.11b	0.52±0.10a	0.41±0.14a	0.33±0.11a	0.29±0.10b	0.75±0.13a
<i>Trans</i> -2-hexenal	Oil heating	0.32±0.06b	0.24±0.07b	0.03±0.02c	0.33±0.04a	0.27±0.09a	0.49±0.05a	0.45±0.04b
	WD frying	0.60±0.08a	0.59±0.06a	0.26±0.06b	0.22±0.04b	0.19±0.06a	0.22±0.04b	0.25±0.08c
<i>Cis</i> -2-heptenal	CBM frying	12.17±1.31a	14.29±1.09b	15.75±0.93a	16.89±1.39a	17.90±1.23a	21.11±1.94a	24.81±1.26a
	Oil heating	ND	ND	ND	15.88±0.82a	14.23±0.72b	21.82±1.53a	14.92±1.06b
<i>Trans</i> -2-heptenal	WD frying	12.64±0.09a	17.14±0.10a	15.46±0.06a	16.10±0.03a	14.14±0.04b	13.19±0.05b	12.78±0.03c
	CBM frying	20.31±0.72	19.13±1.07	19.29±1.16	ND	ND	ND	ND
<i>Trans</i> -2-octenal	WD frying	6.73±0.51c	10.25±0.42b	11.48±0.62b	12.06±0.46a	12.71±0.34a	14.34±0.41a	16.01±0.51a
	Oil heating	11.05±0.72a	11.63±0.67a	13.10±0.82a	10.27±0.82b	9.12±0.65b	13.12±0.63b	10.03±0.91b
<i>Trans</i> -2-nonenal	WD frying	7.60±0.28b	7.47±0.18c	7.74±0.17c	8.50±0.14c	7.78±0.17c	7.07±0.26c	6.97±0.10c
	CBM frying	0.91±0.20a	1.40±0.18a	1.92±0.18a	2.75±0.19a	2.67±0.20a	3.83±0.20a	4.56±0.18a
<i>Trans</i> -2-decenal	Oil heating	0.76±0.13a	1.24±0.31ab	1.59±0.32a	1.36±0.29b	1.33±0.37c	2.55±0.29b	2.11±0.38b
	WD frying	0.28±0.05b	0.88±0.06b	1.21±0.05b	1.67±0.13b	1.93±0.08b	2.30±0.06b	2.21±0.10b
<i>Trans</i> -2-undecenal	CBM frying	3.09±0.69a	5.15±0.67a	5.61±0.51a	8.62±0.94a	7.85±0.88a	10.54±1.08a	11.51±1.00a
	Oil heating	2.66±0.33b	3.27±0.28b	4.21±0.37b	3.12±0.40b	2.38±0.34c	3.73±0.29b	3.69±0.27b
<i>Trans</i> -2-dodecenal	WD frying	1.10±0.04c	2.73±0.09c	3.02±0.05c	3.13±0.07b	3.29±0.08b	2.67±0.08c	2.47±0.06c
	CBM frying	1.55±0.33a	ND	ND	5.87±0.73a	4.70±0.44a	7.32±1.07a	8.00±1.01a
<i>Trans</i> -2-tridecenal	Oil heating	1.19±0.04b	2.43±0.05a	3.04±0.07a	2.17±0.08b	1.56±0.08c	2.55±0.05b	2.52±0.06b
	WD frying	0.44±0.04c	1.59±0.05b	2.26±0.06b	1.95±0.05c	1.95±0.07b	ND	ND
<i>Trans</i> -14-hexadecenal	Oil heating	ND	2.87±0.41	3.27±0.49	ND	ND	ND	ND
	WD frying	ND	ND	ND	ND	ND	ND	ND
<i>Trans</i> -2-tetradecenal	CBM frying	ND	ND	ND	ND	ND	1.55±0.04	1.34±0.05
	Oil heating	0.02±0.01	ND	ND	ND	ND	ND	ND
<i>Trans</i> -2-pentenal	WD frying	ND	ND	0.05±0.02	0.02±0.01	0.27±0.03	ND	ND
	CBM frying	ND	ND	ND	ND	ND	ND	ND
n-Alkenals	4–8 h	5–2 h	5–8 h	6–2 h	6–8 h	7–2 h	7–8 h	
<i>Trans</i> -2-pentenal	ND	ND	0.09±0.01	0.03±0.01	ND	ND	ND	0.11±0.02
	1.13±0.34a	0.66±0.44a	0.89±0.13a	0.54±0.11a	0.89±0.24a	1.30±0.31a	0.41±0.12b	0.41±0.12b
<i>Trans</i> -2-hexenal	0.33±0.05b	0.20±0.05c	0.41±0.07b	0.19±0.04b	0.13±0.08b	0.24±0.09b	0.61±0.07a	0.61±0.07a
	0.35±0.07b	0.37±0.04b	0.21±0.06c	0.40±0.07a	0.17±0.06b	0.33±0.05b	0.14±0.06c	0.14±0.06c
<i>Cis</i> -2-heptenal	23.09±1.48a	23.86±1.33a	27.94±1.29a	22.86±1.40a	22.10±1.46a	25.22±2.01a	23.66±1.36a	23.66±1.36a
	14.61±0.49b	14.51±0.82b	13.40±0.10b	ND	ND	ND	ND	ND
<i>Trans</i> -2-heptenal	10.07±0.7c	11.46±0.03c	8.72±0.06c	9.01±0.03b	7.87±0.05b	8.40±0.05b	6.63±0.05b	6.63±0.05b
	ND	ND	ND	14.32±0.92	12.87±0.49	12.97±1.00	12.79±0.82	12.79±0.82
<i>Trans</i> -2-octenal	12.68±0.57a	14.24±0.41a	19.08±0.57a	13.63±0.58a	13.33±0.44a	19.89±0.71a	17.09±0.61a	17.09±0.61a
	9.38±0.37b	9.71±0.72b	8.42±0.76b	9.54±0.73b	8.57±0.78b	7.83±0.58b	8.65±0.67b	8.65±0.67b
<i>Trans</i> -2-nonenal	8.30±0.24c	8.11±0.36c	6.17±0.19c	6.05±0.17c	5.91±0.46c	6.23±0.33c	5.37±0.16c	5.37±0.16c
	3.52±0.18a	4.91±0.20a	5.52±0.23a	4.75±0.22a	4.48±0.22a	6.65±0.16a	5.20±0.18a	5.20±0.18a

Table 3 (continued)

n-Alkenals	4–8 h	5–2 h	5–8 h	6–2 h	6–8 h	7–2 h	7–8 h
<i>Trans</i> -2-decenal	2.18±0.32c	2.34±0.24c	2.12±0.26b	2.99±0.29b	2.77±0.33b	2.45±0.31c	3.28±0.22b
	3.15±0.10b	3.25±0.30b	2.43±0.10b	2.52±0.11c	2.60±0.22b	3.12±0.17b	2.61±0.10c
	9.59±1.03a	12.23±1.09a	11.15±0.10a	11.06±1.26a	9.64±1.11a	18.41±1.15a	9.11±0.10a
	3.54±0.28b	3.41±0.31b	2.66±0.32b	3.90±0.32b	3.61±0.41b	2.44±0.44b	3.30±0.31b
<i>Trans</i> -2-undecenal	3.2±0.07b	ND	ND	ND	ND	ND	ND
	6.71±0.88	ND	ND	7.78±1.34	6.37±1.01	15.48±2.01	ND
	ND	ND	ND	ND	ND	ND	ND
<i>Trans</i> -2-dodecenal	ND	8.83±1.01	7.57±1.04	ND	ND	ND	6.23±0.99
	2.49±0.05a	2.41±0.08a	1.64±0.04a	2.84±0.08a	2.37±0.09a	2.48±0.06a	2.05±0.07a
<i>Trans</i> -2-tridecenal	1.88±0.07b	2.13±0.06b	1.21±0.05b	1.22±0.06b	1.11±0.09b	1.44±0.10b	0.89±0.07b
	ND	ND	ND	ND	ND	0.25±0.02	ND
	ND	ND	ND	ND	ND	ND	ND
<i>Trans</i> -14-hexadecenal	ND	ND	ND	ND	ND	ND	ND
	ND	ND	ND	ND	ND	ND	0.04±0.01

^a Abbreviations: *WD* wheat dough, *CBM* chicken breast meat, *T–2 h* oil sample collected at the second hour of the first day, *ND* not detected

^b The relative contents of n-alkenals were expressed as average value ± confidence interval. The lowercase (a,b,c) behind the content represents the significant difference among the three thermal treatments ($p < 0.05$, $n = 3$)

frying, and CBM-frying, and can be also explained by the difference in composition of products formed during the frying process of varying types of food. The RAs of *cis*-2-heptenal were gradually increased and was then decreased during the oil heating (control) and CBM frying processes. The difference between these two treatments was the occurrence time of maximum value of this product.

The formation of *trans*-2-octenal can't be fully explained by the classical oxidation of unsaturated FAs. Therefore, *trans*-2-octenal was regarded as the oxidative decomposition product (ODP) of 3-nonenal which was formed by the β -homolysis of L-9-hydroperoxide (Frankel 2005b). Oxidation occurred in the methylene between carbonyl and C=C bonds, shortening the carbon chain and forming the 2-octenal. On the other hand, oxidation could also take place in the hydroxyl of *cis*-2-octen-1-ol, which is the β -homolysis product of L-10-hydroperoxide, producing *trans*-2-octenal under the conditions of high temperature and occurrence of oxygen. Based on the RAs of *trans*-2-octenal, the oxidation can intensively take place in the unsaturated SOP of frying oil. Similar trend of change in RA of *trans*-2-octenal, which was first increased and was then decreased as the processing time increased, was observed during the varying frying treatments. The major difference was the time needed for reaching the maximum value of *trans*-2-octenal, which also reflect the complexity of the food frying process compared to the control.

3-Nonenal, the combination product of 1,3-nonadienyl radical decomposed from L-9-hydroperoxide and hydroxyl radical, can be converted into *trans*-2-nonenal by positional isomerization of C=C bonds under the high temperature condition (Frankel et al. 1981). Additionally, *trans*-2-nonenal was also considered the ODP of 2-undecenal (Warner et al. 2001). An increase and then a decrease in RA of *trans*-2-nonenal were also observed during the oil heating process (control) and CBM frying process. However, the RA of this aldehyde was increased as the processing time increased during the WD frying process.

Trans-2-decenal is the β -homolysis product of O-9-hydroperoxide. As a direct SOP of O, the RA of *trans*-2-decenal was increased to a maximum value of 18.41 mg/kg for the oil sample of 7–2 h during the oil heating process (control). Along with the proceeding of heating, *trans*-2-decenal could contribute to the subsequent reactions, resulting in a decrease in its RA in the frying oil. The RA of *trans*-2-decenal during the WD frying process was increased to a maximum value of 4.21 mg/kg for the oil sample of 2–2 h and then no significant changes were observed during the rest frying treatment. This might be attributed to the balance between the production and the consumption rate of this aldehyde during the WD frying process. The change profile of *trans*-2-decenal was different for the CBM frying process. *Trans*-2-decenal was not observed after the maximum value of 3.32 mg/kg at oil sample of 4–8 h. In addition, the unsaturated SOP could be fully

involved in the subsequent reactions during the CBM frying process when the frying treatment was carried out in a certain time.

Similar to *trans*-2-decenal, *trans*-2-undecenal is the SOP of O-8-hydroperoxide. Therefore, the RA of *trans*-2-undecenal was first increased and was then decreased as the processing time increased during the oil heating process (control). Interestingly, *trans*-2-undecenal was not observed in some oil samples (1–8 h, 2–2 h, 5–2 h, 5–8 h, and 7–8 h) and *trans*-2-dodecenal was alternatively observed in these samples. First, *trans*-2-dodecenal might be regarded as the reaction product of *trans*-2-undecenal under the high temperature condition. Second, due to the same retention time of these two aldehydes, the detected RA might be the total value of these two compounds. An increase and then a decrease (or absence) in RA of *trans*-2-undecenal was also observed during the frying process. This reflected the major influence resulted from the food components on the unsaturated SOP of frying oil. Thus, *trans*-2-tridecenal was observed in the food-fried oil samples where no *trans*-2-undecenal was detected. Furthermore, the RA of *trans*-2-tridecenal was first increased and was then decreased along with the proceeding of food frying. Comparing with the changes in RA of *trans*-2-tridecenal and *trans*-2-undecenal, *trans*-2-tridecenal might be the ODP resulted from the combination between *trans*-2-undecenal and alkyl radicals formed under high temperature condition. This can also explain that the addition of food components makes the reactions more intensive and the products more complex during the frying process.

Changes in alkadienals content

Polyunsaturated aldehydes with conjugated diene structure were largely formed during both the oil heating (control) and the food frying processes, which is in agreement with previous studies (Katragadda et al. 2010; Ramírez et al. 2004). Polyunsaturated aldehydes observed in this study included 2, 4- and 10,12-alkadienals based on the position of C=C bonds. 2,4-Alkadienals are the most important aldehydes formed during the food frying process from the viewpoint of fried food safety (Dung et al. 2006).

As presented in Table 4, the RA of *trans,trans*-2,4-heptadienal was first increased to a maximum value of 42.53 mg/kg in oil sample of 5–8 h and was then decreased along with the proceeding of oil heating. However, the maximum RAs of *trans,trans*-2,4-heptadienal were 38.00 mg/kg in oil sample of 1–2 h and 24.55 mg/kg in oil sample of 1–8 h for the WD and CBM frying processes, respectively. In addition, the time for reaching the maximum value of *trans,trans*-2,4-heptadienal was significantly short. This can also be attributed to the formation and consumption rates of this aldehyde when the food components were added during the frying process. As a direct β -homolysis product of Ln-12-

Table 4 The changes in amounts of 2,4- and 10,12-alkadienals formed during the soybean oil heating process and food frying process^{a,b}

2,4- and 10,12-Alkadienals	Treatments	1–2 h ^a	1–8 h	2–2 h	2–8 h	3–2 h	3–8 h	4–2 h
<i>Trans,trans</i> -2,4-heptadienal	Oil heating	29.74±1.36b	32.25±1.73a	33.18±0.22b	36.27±2.14a	35.42±2.12a	36.80±1.81a	40.02±1.94a
	WD frying	38.00±0.98a	34.48±1.26a	36.70±1.04a	27.26±1.00b	21.90±0.87b	33.93±1.23b	26.16±2.19b
	CBM frying	19.84±1.98c	24.55±1.31b	23.74±2.10c	23.89±1.22c	22.36±1.45b	19.53±1.82c	18.88±0.89c
<i>Trans,trans</i> -2,4-nonadienal	Oil heating	0.31±0.11a	0.48±0.15b	0.75±0.10b	1.48±0.35a	1.33±0.37a	2.49±0.32a	3.06±0.42a
	WD frying	0.26±0.10a	0.77±0.05a	1.35±0.10a	1.00±0.21a	0.86±0.22ab	1.00±0.15b	1.26±0.33b
	CBM frying	ND	ND	0.61±0.06b	0.73±0.05b	0.79±0.08b	0.59±0.05c	0.58±0.02c
<i>Trans,trans</i> -2,4-decadienal	Oil heating	46.13±4.15a	78.77±2.32a	85.87±4.76a	127.46±2.08a	104.60±3.23a	133.13±3.81a	139.70±4.22a
	WD frying	35.66±3.11b	46.27±1.66b	58.98±3.62b	40.93±1.34b	30.09±3.12c	48.82±2.94b	49.67±1.49b
	CBM frying	15.76±1.98c	36.46±1.56c	40.02±2.03c	37.83±1.88c	39.90±3.00b	35.29±1.35c	31.80±3.00c
<i>Trans,trans</i> -2,4-undecadienal	Oil heating	ND	ND	ND	0.47±0.09	0.14±0.07	0.43±0.10	ND
	Oil heating	ND	ND	ND	ND	ND	ND	0.41±0.04
	WD frying	ND	ND	ND	0.06±0.02	0.27±0.05a	ND	ND
<i>Trans,trans</i> -2,4-dodecadienal	CBM frying	0.01±0	ND	ND	ND	0.03±0.01b	0.05±0	ND
	Oil heating	ND	ND	ND	0.10±0.03	0.12±0.04	0.09±0.03	0.15±0.04
	WD frying	ND	ND	ND	ND	ND	ND	ND
<i>Cis,cis</i> -10,12-hexadecadienal	CBM frying	ND	ND	ND	ND	ND	ND	ND
	Oil heating	ND	ND	ND	ND	ND	ND	ND
	WD frying	ND	ND	ND	ND	ND	ND	ND
2,4- and 10,12-Alkadienals	4–8 h	5–2 h	5–8 h	6–2 h	6–8 h	7–2 h	7–8 h	
	<i>Trans,trans</i> -2,4-heptadienal	33.12±1.54a	36.80±2.36a	42.53±2.00a	33.52±1.70a	27.81±1.91a	41.92±2.09a	27.16±1.44a
		23.09±0.98b	23.45±1.52b	18.87±1.67b	21.73±1.55b	18.38±1.56b	16.39±1.29b	15.65±2.17b
16.23±1.76c		18.33±1.42c	10.56±0.88c	12.78±1.02c	11.71±1.01c	12.39±0.88c	9.83±0.98c	
<i>Trans,trans</i> -2,4-nonadienal	2.13±0.28a	3.11±0.29a	3.61±0.10a	3.10±0.33a	2.72±0.18a	6.40±0.25a	2.74±0.32a	
	1.30±0.16b	1.40±0.25b	1.02±0.09b	1.58±0.22b	1.40±0.20b	0.96±0.26b	1.24±0.15b	
	0.76±0.06c	0.94±0.05c	0.54±0.02c	0.55±0.02c	0.55±0.03c	0.56±0.04c	0.41±0.06c	
<i>Trans,trans</i> -2,4-decadienal	109.29±4.08a	140.03±3.34a	109.67±4.00a	119.60±2.77a	89.94±3.72a	185.07±1.29a	80.39±3.12a	
	44.05±2.19b	42.46±3.61b	28.17±2.44c	44.35±3.20b	38.73±2.16b	23.44±3.47b	31.08±2.20b	
	43.26±1.85b	44.12±2.11b	22.21±1.87c	22.71±1.02c	20.03±2.00c	25.20±1.25c	16.00±3.11c	
<i>Trans,trans</i> -2,4-undecadienal	0.36±0.08	ND	ND	0.67±0.11	0.35±0.09	1.10±0.10	0.65±0.08	
	ND	0.74±0.05	0.34±0.05	ND	ND	ND	ND	
	ND	ND	ND	ND	ND	ND	ND	
<i>Trans,trans</i> -2,4-dodecadienal	ND	ND	ND	ND	ND	ND	ND	
	ND	ND	ND	ND	ND	ND	ND	
	ND	ND	ND	ND	ND	ND	ND	
<i>Cis,cis</i> -10,12-hexadecadienal	0.13±0.04a	0.29±0.05a	ND	0.16±0.03	ND	0.71±0.04	ND	
	ND	ND	0.04±0.01	ND	ND	ND	ND	
	0.06±0.01b	0.06±0.02b	ND	ND	ND	ND	0.05±0.02	

^a Abbreviations: *WD* wheat dough, *CBM* chicken breast meat, *1–2 h* oil sample collected at the second hour of the first day, *ND* not detected

^b The relative contents of 2,4- and 10,12-alkadienals were express as average value ± confidence interval. The lowercase (a,b,c) behind the content represents the significant difference among the three thermal treatments ($p < 0.05$, $n = 3$)

hydroperoxide, *trans,trans*-2,4-heptadienal were also quantitatively reported during the heating of extra virgin olive oil at temperature above 180 °C (Katragadda et al. 2010). Therefore, other formation mechanism for the generation of *trans,trans*-2,4-heptadienal during the heating or frying process is potential.

The changes in RA of *trans,trans*-2,4-nonadienal were similar during both the oil heating (control) and food frying processes except for the occurrence time of the maximum RA of this aldehyde. *Trans,trans*-2,4-nonadienal is not the direct reaction product of the unsaturated FAs based on the classical lipid oxidation mechanism, resulting in relatively lower RAs of this type of conjugated aldehyde than those of other SOP during the oil heating (control) and food frying processes. It was proposed that *trans,trans*-2,4-nonadienal was the peroxidation product of 3-nonenal generated from the decomposition of L-9-hydroperoxide (Warner et al. 2001). Hydroperoxidation occurs at the C5 position of 3-nonenal and intramolecular rearrangement of electronic then takes place to form 2-nonenal-4-hydroperoxide. Loss of a hydrogen peroxide leads to produce *trans,trans*-2,4-nonadienal. Furthermore, the aforementioned *trans*-2-nonenal can be directly formed from 3-nonenal. Comparing the changes in RAs of *trans,trans*-2,4-nonadienal and *trans*-2-nonenal, the same trend of change was observed for these two aldehydes. Therefore, *trans,trans*-2,4-nonadienal could be directly formed by the hydroperoxidation of *trans*-2-nonenal under the conditions of high temperature and oxygen. Briefly, hydroperoxidation occurs at the C4 position of *trans*-2-nonenal to form the *trans*-2-nonenal-4-hydroperoxide and the loss of hydrogen peroxide then occurs to directly produce the *trans,trans*-2,4-nonadienal. According to this proposed mechanism, the formation of *trans,trans*-2,4-heptadienal can be considered the peroxidation product of *trans*-2-heptenal during the processes of oil heating and food frying.

In general, because the *trans,trans*-2,4-decadienal is the decomposition product of L-9-hydroperoxide (Porter et al. 1995), its RA was the highest among the detected VAs during the heating of SBO. In addition, according to the above-mentioned formation mechanism of 2,4-dienal from 2-enal, *trans,trans*-2,4-decadienal can also be formed by the peroxidation of *trans*-2-decenal. It's worth noting that hydroperoxidation and decomposition reaction can also take place in 2,4-decadienal under the conditions of high temperature and occurrence of oxygen to form some lower-molecular-weight decomposition products, such as pentanal, 2-octanal, and 2-nonenal (Yu et al. 1994). This might be the reason for the changes in RAs of *trans,trans*-2,4-decadienal during the oil heating (control) and the food frying processes (Shown in Table 4). Oil samples of 7–2 h, 2–2 h, and 5–2 h showed the highest RAs of *trans,trans*-2,4-decadienal during the oil heating (control), WD frying, and CBM frying processes,

respectively. However, the changes in RA of *trans,trans*-2,4-decadienal could be described as the alternation of the increase and the decrease during all the thermal treatments. The food components intensified the frying-induced chemical reactions to make *trans,trans*-2,4-decadienal contribute to the consequent reactions. The occurrence time of the maximum RA of *trans,trans*-2,4-decadienal for the CBM frying process was later compared with that for the WD frying process, which might be attributed to the relatively high content of in CBM lipids. Furthermore, the relatively lower RA of *trans,trans*-2,4-decadienal detected during the CBM frying process may be attributed to the relatively high content of CBM proteins due to the possible Maillard reaction taken place between this 2,4-dienal and the amino-containing compounds. Moreover, the absorption of *trans,trans*-2,4-decadienal by the fried food might lead to a decrease in its RAs in the frying oil (Boskou et al. 2006).

It is interesting that *trans,trans*-2,4-undecadienal and *trans,trans*-2,4-dodecadienal showed the same retention time and were alternatively presented during the oil heating process (control). However, *trans,trans*-2,4-dodecadienal was only observed for some oil samples during the frying process. A maximum RA of 1.10 mg/kg was found for *trans,trans*-2,4-undecadienal in the oil sample of 7–2 h. The RAs of *trans,trans*-2,4-dodecadienal were relatively low. Based on the aforementioned mechanism of 2,4-dienal from the 2-enal, *trans,trans*-2,4-undecadienal and *trans,trans*-2,4-dodecadienal could be the desaturation products of *trans*-2-undecenal and *trans*-2-dodecenal, respectively. Along with the addition of food components, such as water, protein, carbohydrate, and lipid, the oxidation intensity of unsaturated FAs was increased and the SOP were more prone to be involved in further oxidation or been reacted with each other. Therefore, the precursors of these two 2,4-dienals might be involved in the formation of other products. The formation of *trans*-2-tridecenal is the case for the other reaction occurred in *trans*-2-undecenal during the food frying process.

Cis,cis-10,12-hexadecadienal is the sole polyunsaturated aldehyde with two *cis* configurations. As presented in Table 4, *cis,cis*-10,12-hexadecadienal was mainly observed during the oil heating process (control) and reached a maximum RA of 0.71 mg/kg in the oil sample of 7–2 h. However, *cis,cis*-10,12-hexadecadienal was only presented in the oil sample of 5–8 h for the WD frying process and in the oil samples of 4–8 h, 5–2 h, and 7–8 h for the CBM frying process. From the molecular structure of this aldehyde, *cis,cis*-10,12-hexadecadienal is not the ODP of any unsaturated FAs contained in SBO. Nevertheless, based on the structures of the reaction substrates and the main reaction type (i.e., free radical reaction) involved in the heating and frying processes, *cis,cis*-10,12-hexadecadienal could be the combined product of the unsaturated radicals. *Cis,cis*-10,12-hexadecadienal might be unstable under the conditions of high temperature

and oxygen; therefore, it is rarely to be observed during the frying process.

Changes in substituted alkanals content

Except for the linear chain aldehydes, several aldehydes with substituent were observed during the thermal treatments of SBO. As shown in Table 5, four substituted aldehydes belong to the saturated aldehydes were detected. Comparing to the above-mentioned aldehydes, the substituted aldehydes are not the direct products of the unsaturated FAs oxidation but are related to the free radical reaction.

Benzaldehyde was formed by a series of oxidation and dehydration reactions of L under the conditions of heating and occurrence of oxygen in previous study (Kawada et al. 1967). The RA of benzaldehyde in the volatiles released from the heating of trilinlein was higher than that in the volatiles released from the heating of triolein, corn oil, and hydrogenated cottonseed oil (Matthews et al. 1971). In addition, benzaldehyde was also detected during the autoxidation treatment of 2,4-decadienal. Therefore, both of these two formation mechanisms can be used to explain the formation and detection of benzaldehyde in this study due to the high amounts of L and Ln in SBO. The RA of benzaldehyde was first increased to a maximum value of 2.04 mg/kg in the oil sample of 7–2 h and was then decreased as the processing time increased during the heating process. However, benzaldehyde was not observed or detected in lower RA in the food-fried oil samples, especially for the WD-fried oil samples. This is mainly attributed to the instability of benzaldehyde when high temperature, oxygen, and food components are present. Relatively higher RAs and more detection frequency of benzaldehyde were found during the CBM frying process than those during the WD frying process, which could be related to the higher content of CBM lipids.

4-(Hydroxymethyl)cyclohexanecarbaldehyde was only observed at the last day of the heating process. This hydroxyl-containing aldehyde has the property of instability due to its molecular structure. That's why this compound was detected at the last stage of the oil heating process (control) and was not observed during the food frying process. Based on the possible free radical reaction and the detected cyclic alkanes (such as ethylidene cyclohexane and 3-propyl-cyclohexene, data are not shown) during the long-time thermal treatments, 4-(hydroxymethyl)cyclohexanecarbaldehyde could be generated by the oxidation of the structure-similar alkanes, alkenes, and other compounds.

3-Methylbutanal was regarded as the degradation product of leucine by a nonenzymatic strecker reaction in previous study (Meynier et al. 1999). However, 3-Methylbutanal was obviously observed in the middle and later stages of the heating process and in the late stage of the frying processes. Therefore, 3-methylbutanal could be produced from the

reactions occurred in lipid components. According to the properties of SBO constituents, 3-methylbutanal might be formed through the oxidation decomposition reaction of Ln under the high temperature condition. The contribution of the food components affected the production and the consumption rate of 3-methylbutanal during the food frying process.

Similar to 4-oxo-2-alkenal (C7-C14), 4-hydroxy-2-alkenal (C6-C9), and 4,5-epoxy-2-alkenal (C7 or C10), 4-oxononanal which belongs to 4-oxo-alkenal (C6-C10) is also considered a type of toxic aldehyde formed during the deep-fat frying process (Guillén and Uriarte 2012). Therefore, the formation of 4-oxononanal are very important in terms of fried food and frying oil safety. As presented in Table 5, the RA of 4-oxononanal was first increased to a maximum value of 9.00 mg/kg in the oil sample of 7–2 h and was then decreased during the oil heating process (control) as the processing time increased. However, a decrease in RAs of 4-oxononanal was found during the food frying process and advancing to earlier stages in time needed for reaching the maximum RAs was observed. The food components might not only hinder the formation of 4-oxononanal but also accelerate the consumption of 4-oxononanal. 4-Oxononanal, for instance, can be reacted with amino acids to form the imine linkage-containing compounds (Zamora and Hidalgo 2005). The formation mechanism of 4-oxononanal has been proposed as the consecutive oxidation reactions of L and its SOPs (Neff et al. 1983). Briefly, 9-hydroperoxy-10,13-epidioxy-11-octadecenoic acid is formed by photooxidation of L at the presence of photosensitizer. This 6-membered hydroperoxy epidioxides can decompose to 4-oxo-2-nonenal by β -homolysis and breakage of oxygen-oxygen single bond under the heating condition. 4-Oxononanal is generated from the further hydroperoxidation of 4-oxo-2-nonenal. Due to the diversity of the reaction sites in the unsaturated aliphatic chain, the types of the oxidation products could be diverse. Moreover, interaction could occur among the formation mechanisms of these oxidation products, which could be reflected by the decrease in RA and the time for reaching the maximum RA of 4-oxononanal during the food frying process.

Based on the molecular structure, all the detected VAs are generated from O, L, and Ln through a series of oxidation or free radical reactions when SBO was thermally treated without or with food. During the heating process, most of the RAs of the detected aldehydes were gradually increased to the maximum in the oil sample of 7–2 h and were then decreased as the processing time increased. However, similar trend of change in RA of these aldehydes was observed during the frying processes, but relatively lower RA and shorter time for reaching the maximum RA values of these aldehydes were found when SBO was fried with WD and CBM compared with the control. Therefore, the fried food has a significant influence on the formation of the detected aldehydes. Firstly, the intensity and complexity of the occurred reactions were

Table 5 The changes in amounts of substituted alkanals formed during the soybean oil heating process and food frying process^{a,b}

Substituted alkanals	Treatments	1–2 h	1–8 h	2–2 h	2–8 h	3–2 h	3–8 h	4–2 h
Benzaldehyde	Oil heating	0.63±0.01b	1.16±0.01	1.34±0.02a	1.45±0.02a	0.65±0.01	1.55±0.02	1.83±0.03
	WD frying	ND	ND	ND	0.22±0.03b	ND	ND	ND
	CBM frying	0.79±0.03a	ND	0.96±0.04b	ND	ND	ND	ND
Cyclohexanecarboxaldehyde, 4-(hydroxymethyl)-3-Methylbutanal	Oil heating	ND	ND	ND	ND	ND	ND	ND
	Oil heating	ND	ND	ND	ND	ND	0.17±0.04	0.05±0.02
	WD frying	ND	ND	ND	ND	ND	ND	ND
4-Oxononanal	CBM frying	ND	ND	ND	ND	ND	ND	ND
	Oil heating	0.95±0.32ab	1.46±0.38b	2.01±0.49b	4.52±0.71a	2.92±0.48b	5.17±1.17a	5.53±1.12a
	WD frying	1.38±0.15a	2.41±0.38a	3.26±0.29a	2.19±0.17c	1.73±0.38c	2.76±0.45b	2.76±0.17b
Substituted alkanals	CBM frying	0.61±0.05b	2.38±0.06a	3.30±0.06b	3.65±0.03b	4.12±0.05a	2.95±0.04b	2.67±0.09b
	4–8 h	5–2 h	5–8 h	6–2 h	6–8 h	7–2 h	7–8 h	
Benzaldehyde	1.83±0.02a	1.91±0.01 ac	1.97±0.02a	1.86±0.01a	1.89±0.04a	2.04±0.08a	1.60±0.01a	
	ND	0.72±0.02b	ND	0.09±0.04c	0.65±0.06b	0.08±0.08c	ND	
	0.83±0.05b	0.63±0.01c	0.67±0.04b	0.70±0.07b	0.73±0.06b	0.76±0.08b	0.70±0.08b	
Cyclohexanecarboxaldehyde, 4-(hydroxymethyl)-3-Methylbutanal	ND	ND	ND	ND	ND	ND	0.80±0.04a	0.25±0.04b
	ND	0.28±0.03	0.43±0.03	0.49±0.03	ND	ND	0.02±0.01c	ND
	ND	ND	ND	ND	0.34±0.07a	0.43±0.07a	0.39±0.07a	
4-Oxononanal	5.52±0.88a	6.99±1.01a	4.82±0.81a	7.34±1.15a	5.55±0.72a	9.00±1.35a	4.52±0.92a	
	2.49±0.10c	2.42±0.46b	1.74±0.56b	3.19±0.62b	2.40±0.37b	1.73±0.35b	1.93±0.62b	
	2.89±0.07b	2.86±0.07b	1.37±0.05b	1.64±0.10c	0.86±0.12c	1.21±0.13c	0.48±0.02c	

^a Abbreviations: *WD* wheat dough, *CBM* chicken breast meat, *1–2 h* oil sample collected at the second hour of the first day, *ND* not detected

^b The relative contents of substituted alkanals were expressed as average value ± confidence interval. The lowercase (a,b,c) behind the content represents the significant difference among the three thermal treatments ($p < 0.05$, $n = 3$)

increased by the addition of food components, which resulted in an increase in production of the aldehydes. However, the formation of aldehydes might be influenced or inhibited to a certain degree and most of the aldehydes easily volatilized away under the boiling condition. Secondly, under the conditions of high temperature and occurrence of oxygen, further hydroperoxidation could take place in these unsaturated aldehydes (such as *trans,trans*-2,4-decadienal), which reflected by the reduction in RAs of the detected aldehydes. Finally, the detected aldehydes might react with the food component (such as the Maillard reaction) to expedite the reaction consumption of these unstable aldehydes. According to the RAs of the detected aldehydes and their change profiles, components of CBM showed the most significant influence on the formation of aldehydes during the frying processes.

On the other hand, many of the aforementioned aldehydes have been considered the mutagenic compounds associated with the genotoxicity, carcinogenicity, and oxidative stress (Dung et al. 2006). According to the data in this study, the potential harmful aldehydes, such as nonanal, *trans*-2-octenal, *trans,trans*-2,4-decadienal, and 4-oxononanal, were detected in significant amounts during both the heating process and the frying process. Because of the effect of boiling and the intensified chemical reactions and the incomplete extraction of the adopted SMPE method, the practical amount of these aldehydes formed during the deep-fat frying process might be higher than those measured values. In other words, a large amount of harmful aldehydes could release into the environment during the deep-fat frying process, especially the CBM frying process. Therefore, more attention should be paid to the safety measures of the fried food.

Conclusion

VAs were significantly formed from the unsaturated FAs when SBO was used as the frying medium of WD and CBM. Free radical reaction, particularly the *cis-trans* isomerization and positional isomerization of C=C bonds, might be the main reaction occurred during the deep-fat frying process. According to these reaction mechanisms, alkanals, n-alkenals, alkadienals, and substituted alkanals were generated. Furthermore, based on the molecular structures of the detected VAs, some of them were the further oxidation products of the SOPs of O, L, and Ln under the conditions of high temperature and oxygen.

The RAs of VAs were firstly increased to a maximum value in oil sample of 7–2 h and was then decreased as the processing time increased during the oil heating process (control). However, RAs of the typical aldehydes were mostly reduced and the time for reaching the maximum RAs was advanced to the earlier or medium stages of the treatments during the frying process. Therefore, the food component, such as water,

protein, lipid, and carbohydrate, intensified the chemical reactions taken place in the unsaturated FAs. Significant changes were observed during the CBM frying process, which might be related to the relatively high contents of water, protein, and lipids. In view of the health risks of the studied VAs (such as *trans,trans*-2,4-decadienal, *trans*-2-decenal, and 4-oxononanal) and their relatively high content during the frying process, improvement of measures for determining of fried food quality and safety is very important. Further studies should be carried out to investigate the amounts of these aldehydes in the fried food to help in evaluation of the safety of the whole deep-fat frying process.

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