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Combination of Gas Chromatography-Mass Spectrometry and Electron Spin Resonance Spectroscopy for Analysis of Oxidative Stability in Soybean Oil During Deep-Frying Process

Ying Liu[1] · Yuanpeng Wang[1] · Peirang Cao[1] · Yuanfa Liu[1]

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Abstract
Lipid oxidation of edible oil during frying process is a complex process and involves free radical chain reactions. Soybean oil with high amount of unsaturated fatty acids was used to investigate the impact of frying time on oxidative stability of oil. Electron spin resonance (ESR) spectroscopy technique was applied to identify and quantify the formed radicals, along with the assessment of physicochemical parameters including peroxide value, oxidative stability, fatty acid composition, and volatile profile. Results showed that the amount of formed free radicals determined by ESR in frying oil increased with the prolongation of frying time. The availability of this method was compared with physicochemical properties and the well correlation coefficients were obtained. Besides, main volatile aldehyde compounds produced by β-scission homolytic cleavage of peroxide group in frying oil during thermal oxidation were derived from oxidation of oleic and linoleic acid.

Keywords Soybean oil · Frying · Lipid oxidation · Gas chromatography-mass spectrometry · Electron spin resonance

Introduction

Deep-frying has become one of the most popular procedures in both industrial and domestic scale for food preparation at a high temperature about 180 °C. Deep-fried foods are highly appreciated by consumers because of their unique organoleptic and sensorial properties, such as flavor, color, texture, and appearance (Li et al. 2016a; Santos et al. 2013). However, the chemical stability of the frying oil can be affected by the high temperatures of deep-frying. Thermal oxidation is the main cause of oil deterioration resulting in the formation of hydroperoxides and their degradation products, which naturally influence the sensory, physical, chemical, and nutritional properties (Juárez et al. 2011; Esposto et al. 2015). Besides, lipid oxidative products induce negative biological effects, such as inducing nonalcoholic fatty liver disease and nonalcoholic steatohepatitis (Feldstein et al. 2010), stimulating the endoplasmic reticulum stress response (Haberzettl and Hill 2013).

Lipid oxidation is a complex process, which involves in a series of reactions including degradation, hydrolysis, and polymerization. Vegetable oils with high amounts of unsaturated fatty acids are susceptible to oxidation in the presence of catalytic systems such as light, heat, enzymes, metals, and microorganisms resulting in complex processes of autoxidation, photooxidation, and thermal or enzymatic oxidation. Autoxidation is the most common and main process and the spontaneous reaction of lipid with oxygen via a chain reaction mechanism of free radicals includes the initiation, propagation, and termination steps (Zhang et al. 2012; Shahidi and Zhong 2010; Zribi et al. 2016). Soybean oil is one of the most widely used vegetable oils by consumers for its nutritional and industrial attributes. Soybean oil contains about 55% linoleic acid which makes it highly susceptible to oxidation (Jung and Min 1990; Hou et al. 2012).

Electron spin resonance (ESR), also called electron paramagnetic resonance (EPR), has been widely applied to detect lipid oxidation (Raitio et al. 2011; Papadimitriou et al. 2006) owing to its simple, high-efficient and portable properties. ESR is a magnetic resonance technique allowing the specific detection and quantification of free radicals with unpaired

✉ Yuanfa Liu
yfliu@jiangnan.edu.cn

[1] State Key Laboratory of Food Science and Technology, School of Food Science and Technology, Jiangnan University, 1800 Lihu Avenue, Wuxi 214122, Jiangsu Province, People's Republic of China

electrons in an applied magnetic field (Li et al. 2016b). However, lipid-derived radicals are so reactive and unsteady that they could not be detected by ESR with detection limit of 10^{-9}–10^{-8} M under optimal conditions (Schaich and Borg 1980). Consequently, the spin trapping technique is used to yield stable radicals and to improve the detectable concentrations ($> 10^{-7}$–10^{-6} M) through the reaction of transient radicals with diamagnetic compounds (Kalogeropoulos et al. 2007). Most of the spin-trapping agents used have a nitrone-type group to form a nitroxide spin adduct. Among these nitrones, 5,5-dimethyl-1-pyrroline N-oxide (DMPO) is preferred because it can not only form stabilized spin adducts but also trap carbon-centered and oxygen-centered radicals generated in chemical and biochemical systems (Rota et al. 1997; Qian et al. 2000).

A few studies focused on the ESR spin trapping technique for analyzing lipid oxidation in oils (Papadimitriou et al. 2006; Chen et al. 2017), but there is little information on detection of radical development of lipid oxidation by ESR spectroscopy techniques for assessing quality of frying oil. The thermo-oxidative changes of frying oil are characterized by a decrease in oxidative stability and the amount of unsaturated fatty acids with an increasing peroxide value (PV). Secondary oxidation products which degrade into hydrocarbons, aldehydes, ketones, and so on tend to be volatile and are responsible for the flavor impairments and degradation of lipids in oils after frying for a long time (Castejón et al. 2017). The aim of this study was to evaluate the lipid oxidation and quality degradation of soybean oil after frying process at high temperature, which is based on an EPR spectroscopy spin-trapping technique and the evaluation of physicochemical appreciation.

Materials and Methods

Chemicals and Oils

DMPO (high purity, ≥ 99%) was purchased from J & K Chemical Technology (Shanghai, China). DMPO was further purified with activated carbon/benzene and then was dissolved in toluene at a concentration of 200 mM and stored at − 80 °C in darkness before use.

Methyl heneicosanoate (C21:0) and 37 component FAME mix analytical standards (C4-C24) were supplied by Supelco (Bellefonte, PA, USA). Standards of n-alkanes (C8–C40) and 2-octanol were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). Hexane (99% purity) was purchased from J & K Chemical Technology (Shanghai, China). Boron trifluoride, methanol, and all other chemical reagents were of analytical grade and were obtained from Sinopharm Chemical Reagent Company.

Soybean oil was purchased from Wilmar International Ltd. (Shanghai, China).

Preparation of Frying Oils

Five liters of oil was placed in a domestic electrical fryer (24 × 30 × 14 cm) with a 10-L-volume vessel and was heated to and keep at 180 ± 5 °C for 10 h per day for 5 continuous days. Different batches of 100 ± 1 g fresh potato sticks (40 × 7.2 × 7.2 mm) were fried for 4 min in succession every 20 min. Frying oil (50 mL) was collected every 5 h with 15 frying cycles and then stored at − 20 °C in darkness until analysis.

ESR Spectroscopic Analyses

EPR spin trapping measurement was carried out on a BrukerEMXplus-10/12 spectrometer (Bruker, Germany) running at 9.43 GHz with a variable temperature control unit (Bruker ER4141 VT-I). Twenty-five microliters of DMPO in toluene (200 mM) was immediately dissolved into 100 μL of oil samples to obtain 40 mM mixed solution. The oil samples and DMPO in toluene were mixed and then were transferred to ESR tubes with 3-mm inner diameter followed by being stirred at room temperature. The exact sample masses and heights in the ESR tubes were noted to ensure the sample cavity of the spectrometer to be completely full with the sample. After the resonant cavity reached the set temperature, the tubes were put into the resonant cavity. EPR spectra were then recorded every 2 min after the resonant cavity reached 120 °C. All analyses were performed in triplicate and special care was taken to avoid the presence of light. The parameters applied were as follows: center field, 3350 G; sweep width, 200.0 G; resolution, 1024 points; microwave power, 20 mW; modulation amplitude, 1.0 G; modulation frequency, 100 kHz; conversion time, 1.28 ms; and time constant, 20.48 ms. The parameters used were kept constant in each determination, and only receiver gain was adjusted and the results from the measurements were accordingly corrected.

Simulation of ESR Spectra

Computer simulation of experimental ESR spectra was employed to calculate g value and hyperfine coupling constants. Hyperfine splitting constants of experimental spectra were calculated by Bruker Xenon software after the optimal signal-to-noise ratios. The precision in the EPR parameters was ~ 3%.

Calculation of Amounts of Spins

The amounts of spins in the frying soybean oil were calculated by Bruker Xenon software (Bruker, Rheinstetten, Germany). The area under the curve of the absorption spectra was obtained by double integration of the spectra over the scan sweep.

Determination of peroxide value, oxidative stability, and fatty acid composition

Peroxide value (PV) of samples was measured according to the AOCS official method AOCS Cd 8b-90 (AOCS 2003).

Oxidative stability was determined on a Rancimat instrument of Metrohm 743 (Metrohm Ltd., Herisau, Switzerland). 3.0 g of oil samples was weighted into Rancimat reaction vessels and heated to 110 °C by applying a continuous air flow rate of 20 L/h until the termination of oil oxidation.

Fatty acids were first converted to FAMEs by derivatization (Firestone 1989) and then were determined by GC-2010 PLUS (SHIMADZU, Japan) equipped with a TR-FAME fused-silica capillary column (60 m × 0.25 mm I.D. × 0.25-μm thickness) and a FID detector (FID-14C, SHIMADZU, Japan). The samples were injected in split mode with a 100:1 split ratio at 250 °C. The flow rate of carrier gas was 1 mL/min. The oven temperature program was as follows: initial 60 °C for 3 min, raised to 175 °C at 5 °C/min, and held for 15 min, then increased to 220 °C at 2 °C/min and then held at 220 °C for 10 min. The injection volume of sample dissolved in hexane was 1 μL.

Volatile Compounds Analysis

Four grams of frying oil samples was hermetically sealed in 20 mL headspace vial for 40 min under stirring at 60 °C. Volatile compounds were extracted by an automatic headspace solid phase microextraction (HS-SPME) device equipped with the 50/30 μm DVB/CAR/PDMS fiber. Before extraction, the fiber was pre-conditioned by inserting into the injector port of the GC system and keeping at 270 °C for 2 h in the stream of helium and samples were equilibrated at 60 °C for 15 min. After extraction, the SPME device was carried out in the GC injector at 250 °C for 5 min in splitless mode.

The volatile compounds in frying oil were analyzed by a GC-MS/MS instrument (TSQ Quantum XLS, Thermo Fisher Scientific, USA) equipped with a HP-5MS silica capillary column (30 m × 0.25 mm × 0.25 μm, Supelco Co., USA). The flow rate of helium (99.999% purity) was 1.0 mL/min.

For the programed sequence of the column, the initial temperature of 45 °C was held for 2 min, then raised to 180 °C at ramp rate of 3 °C/min, followed by increasing to 240 °C at 10 °C/min and maintained for 7 min. The mass spectrometer parameters were as follows: electron impact mode, 70 eV; ion source temperature, 230 °C; and mass to charge ratio, 50–550 m/z. Identification of the volatile compounds detected was based on comparison of retention indices (RIs) and on computer matching with the reference mass spectra of the MS library of NIST 14 and Wiley 8.0,

Statistical Analysis

All the determinations were carried out in triplicate and the results were expressed as mean ± standard deviation of replicated measurements. The data were analyzed by using the SPSS statistical package (Version 19.0, SPSS Inc., Chicago, Illinois, USA).

Results and Discussion

ESR Analysis of Free Radicals of Frying Soybean Oil

Thermal oxidation of oil in deep-frying process could induce free radical chain reactions and generate free radicals, whose mechanism is the same as autoxidation mechanism. ESR signals were detected only in samples containing DMPO which could react with transient radicals to form stable and detectable spin adducts because of the short-lived nature of free radicals in frying oil. The control DMPO solution has a negligible EPR signal (Fig. 1a), while the intense ESR signals of experimental spectra of frying oil as well as corresponding spectra were fitted by using Bruker Xenon software (Fig. 1b).

The addition of DMPO in frying soybean oil led to an ESR signal resulting from the trapping of transient radicals including alkyl, peroxyl, and alkoxyl radicals by the nitrone function. The formations of these spin adducts were as follows. In the initiation step, unsaturated lipid molecules lose a hydrogen radical to form the alkyl radicals. In one of the propagation steps of peroxidation, molecular oxygen reacts with the carbon-centered alkyl radicals to generate peroxyl radicals. Peroxyl radical adducts trapped by DMPO are very unstable and further decompose to form new alkoxyl radicals to be trapped by DMPO (Yin et al. 2011). The splitting constants were $aN = 13.80$ G, $aH_\beta = 7.96$ G, $aH_\gamma = 1.46$ G, g value = 2.00732 for alkoxyl spin adducts and $aN = 14.38$ G, $aH_\beta = 20.89$ G, g value = 2.00670 for alkyl radical adducts.

Total Amount of Spin Adducts in Frying Soybean Oil

Total amount of spins in frying soybean oil is given in Fig. 2a. The results showed that the concentration of total radical adducts in frying soybean oil increased with the increase of frying time from 0 to 50 h. In the initial stage of frying process ranging from 0 to35 h, total amount of spin adducts of the samples slightly increased and maintained at a low level, which indicated lipid oxidation rate showed an increasing trend. After that, total amounts of spins increased sharply from 35 to 50 h of frying. Total amount of spins in frying oil samples at the late frying period of 50 h were 3 to 12 times higher than those of 0 h. The continuous increase indicated that decay rate of spin adducts was lower than generation rate during the detection period.

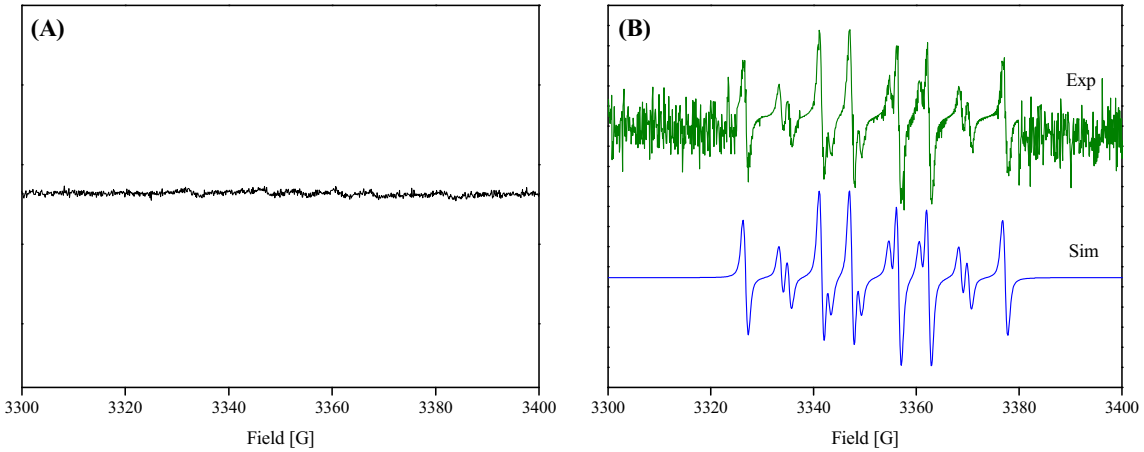

Fig. 1 ESR spectrum of DMPO solution (**a**) and frying oil sample (**b**) heated at 120 °C. Exp, experimental spectrum; Sim, computer simulation of the experimental spectrum

As displayed in Fig. 2a, change of total amounts of spins in frying oil was monitored within 36 min and was recorded every 2 min. Results showed the amounts of spin adducts increased with the increasing detection time from 0 to 28 min, peaking at 28 min. After that, spin amounts decreased because higher total amount of spins leads to higher decay rates, high decay rates therefore cause the decrease of the total amount of spins. Total amount of spins of soybean oil

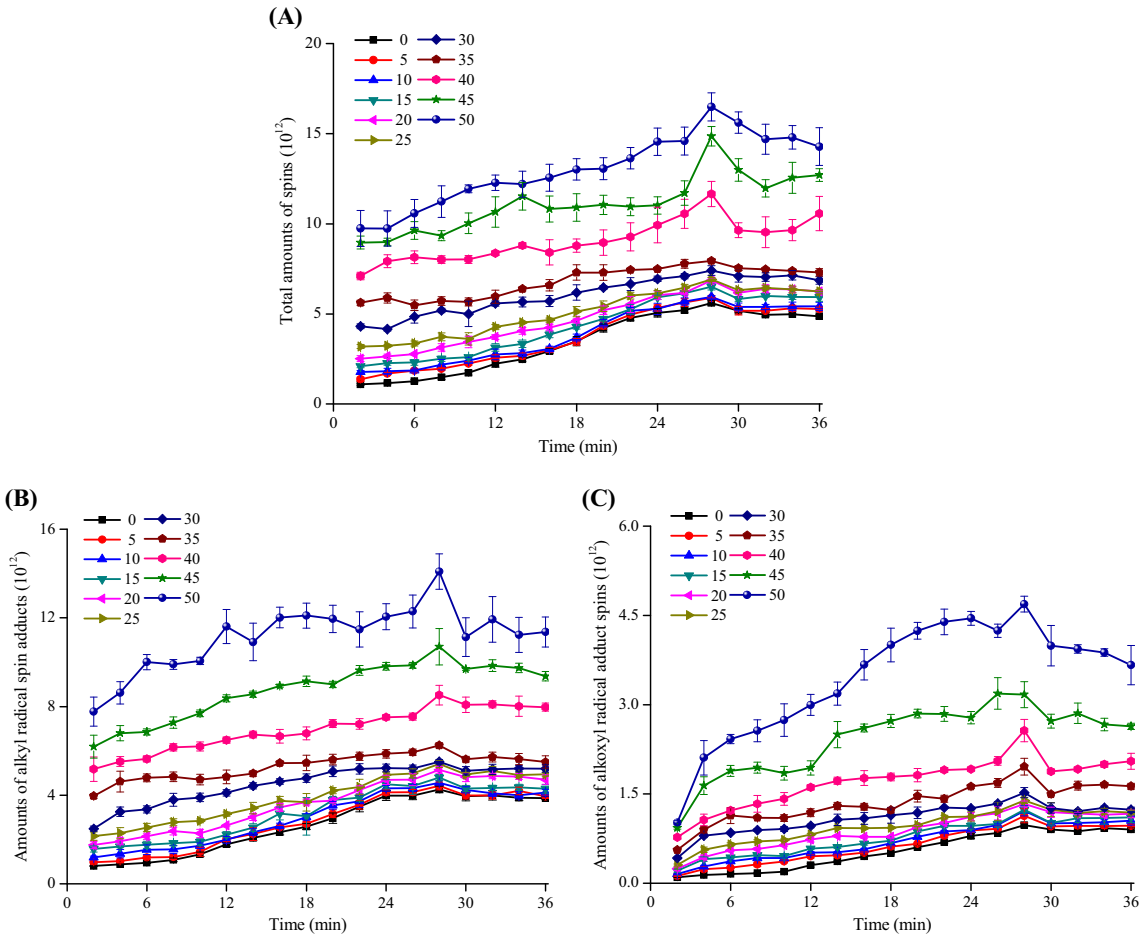

Fig. 2 The amounts of total spin adducts (**a**), alkyl (**b**), and alkoxyl (**c**) spin adducts of frying oil samples detected in 36 min at different frying periods

decreased about 12% at 36 min compared with peak value. The decrease amount of spins in frying oil after 28 min indicated that the silence of the signal intensities arose because newly formed free radicals reacted with stable spin adducts. Additionally, the total amount of spins kept in a certain level and no longer decreased largely from 28 to 36 min of detection, which demonstrated a balance between the formation and decay of the radical adducts was achieved.

Amounts of Alkyl and Alkoxyl Spin Adducts in Frying Oil

Free radical chain reactions of lipid oxidation produce three forms of radicals, among which peroxyl radicals were unstable, alkyl and alkoxyl adducts were therefore the main spin adducts in oil samples detected by ESR. The figures for these two adducts accounted for a large proportion total amounts of spins adducts by computing simulation (Qian et al. 2000), especially alkyl radical adducts. Amounts of alkyl and alkoxyl radical adducts are shown in Fig. 2b, c, respectively. The amounts of both adducts which had a similar trend with the total amounts of adducts increased from 0 to 50 h of frying. During the first 35 h of frying, amounts of two adducts in the samples increased slightly and maintained at a low level. Subsequently, a rapid increase of two adducts arose in frying oil samples frying for more than 35 h. The amount changes of two adducts within 36 min at an interval of 2 min could also be seen in Fig. 2b, c. Results demonstrated that the low amounts of alkyl and alkoxyl spin adducts existed in the first 8 and 10 min of detection, respectively. The amounts of alkyl and alkoxyl adducts reached a plateau at 28 min of detection period in soybean oil. After that, the figures for alkyl and alkoxyl adducts reached a steady state in the last 6 min of detection, which indicated the formation and decay of the radical adducts were in a balance. It could be evident from Fig. 2b, c that the amount of alkyl spin adducts was higher than that of alkoxyl radical adducts, this is due to a very short lifetime of alkoxyl radicals in lipid thermal oxidation, especially at high temperature.

Physicochemical Analysis

Lipid oxidation could cause lipid degradation and produce oxidation products. The increasing rate of oxygen consumption during oxidation process generates an increasing amount of peroxides. As could be seen from Fig. 3, PV of frying soybean oil increased as the frying time prolonged. Definitely, with a longer period of frying or heating process, lipid and oil have higher degree of oxidation. PV detection of soybean oil coupled with free radical measurement by ESR could better characterize the oxidative events in frying oil at different times. The increasing PV of oil samples verified the ESR results. A well linear correlation ($r = 0.950$) was found between the ESR and PV result of frying soybean oil, which indicated ESR could provide effective information associated with the lipid oxidation in frying oil system.

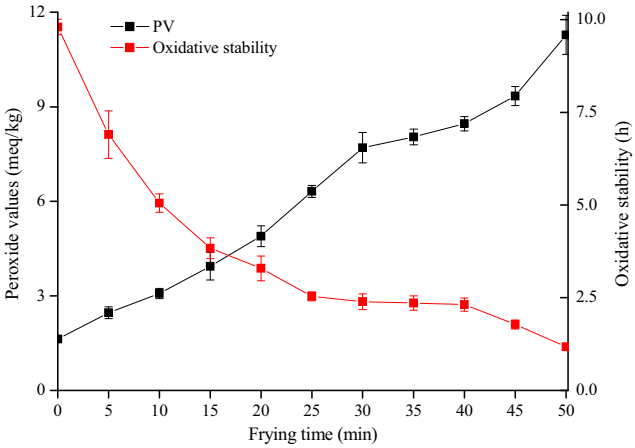

Fig. 3 Peroxide value and oxidative stability of frying oil samples at different frying periods

Rancimat method was employed to study oxidative stability of soybean oil after different frying time. Results from Fig. 3 showed that the induction time obtained was within the range of 1–10 h. Induction time of oil samples fried from 0 to 25 h declined rapidly, while it decreased slightly from 25 to 40 h, after that it fell off sharply to the end of frying time. The linear correlation coefficient between the induction time and total radical adduct concentration was − 0.742. The negative linear correlation between the two methods agreed with the previous study by Velasco (Velasco et al. 2004), which indicated that EPR spin trapping technique could be used as an evaluation of lipid oxidation. Detection of free radicals in frying soybean oil allowed mild conditions to be used in a rapid and sensitive method for determining of oxidative stability.

The fatty acid composition of frying soybean oil is shown in Table 1. Results indicated that the frying oil samples were rich in unsaturated fatty acids (UFA), having the oleic acid and linoleic acid as major fatty acids. The content of unsaturated fatty acids decreased with the increase of frying time because unsaturated fatty acids are prone to degrade to oxidation compounds, while the amount of saturated fatty acids decreased slightly from 0 to 50 h of frying process. Besides, when the frying time ranging from 0 to 5 h and 40 to 45 h, the degradation of unsaturated fatty acids in frying oil increased aggressively, while it slightly increased with the frying time from 5 to 40 h. It is supposed that oil with high content of unsaturated fatty acids at high temperature is more likely to occur oxidative degradation under frying long hours. This was in agreement with the results obtained from the ESR measurements that high unsaturated fatty acid content was likely to produce many free radicals.

Table 1 Fatty acid composition of frying soybean oil at different frying periods

Fatty acid composition (g/100 g)	Frying time (h)											
	0	5	10	15	20	25	30	35	40	45	50
C16:0	10.64 ± 0.62	10.41 ± 0.62	10.25 ± 0.44	10.11 ± 1.09	10.08 ± 0.99	9.50 ± 0.71	10.68 ± 0.48	10.24 ± 1.11	10.18 ± 1.82	7.94 ± 1.02	10.90 ± 0.2
C16:1	0.07 ± 0.002	0.08 ± 0.01	0.09 ± 0.02	0.07 ± 0.01	0.09 ± 0.01	0.11 ± 0.01	0.08 ± 0.01	0.10 ± 0.01	0.10 ± 0.02	0.08 ± 0.01	0.08 ± 0.01
C18:0	3.99 ± 0.36	3.85 ± 0.21	3.95 ± 0.11	3.76 ± 0.30	3.88 ± 0.17	3.40 ± 0.25	3.52 ± 0.11	3.45 ± 0.34	3.53 ± 0.29	3.07 ± 0.24	3.47 ± 0.23
C18:1	22.99 ± 1.26	21.95 ± 0.53	21.46 ± 1.60	18.98 ± 1.06	19.35 ± 1.12	18.92 ± 1.25	19.20 ± 1.24	19.74 ± 1.02	18.43 ± 2.97	15.46 ± 0.36	18.31 ± 2.97
C18:2	43.39 ± 1.80	38.92 ± 1.57	37.64 ± 1.57	34.83 ± 0.86	37.10 ± 2.51	32.95 ± 0.89	32.20 ± 1.65	31.63 ± 1.85	30.33 ± 1.71	25.32 ± 2.12	26.50 ± 1.65
C18:3	5.06 ± 0.26	4.56 ± 0.65	4.83 ± 0.17	3.65 ± 0.16	3.95 ± 0.17	3.33 ± 0.16	3.24 ± 0.21	3.17 ± 0.16	2.92 ± 0.18	2.76 ± 0.17	2.36 ± 0.08
C20:0	0.44 ± 0.02	0.40 ± 0.02	0.47 ± 0.02	0.36 ± 0.03	0.43 ± 0.02	0.38 ± 0.01	0.37 ± 0.01	0.39 ± 0.01	0.37 ± 0.03	0.39 ± 0.01	0.37 ± 0.02
C20:1	0.25 ± 0.04	0.28 ± 0.01	0.30 ± 0.02	0.25 ± 0.01	0.27 ± 0.02	0.23 ± 0.01	0.23 ± 0.01	0.24 ± 0.01	0.23 ± 0.02	0.23 ± 0.01	0.23 ± 0.01
C22:0	0.54 ± 0.03	0.52 ± 0.02	0.54 ± 0.02	0.46 ± 0.02	0.48 ± 0.03	0.44 ± 0.02	0.43 ± 0.02	0.44 ± 0.02	0.45 ± 0.02	0.23 ± 0.01	0.43 ± 0.02
∑SFAs	16.12 ± 0.59	15.50 ± 0.47	15.92 ± 0.57	14.69 ± 0.59	15.98 ± 0.56	14.93 ± 0.41	15.02 ± 0.52	15.22 ± 1.63	15.34 ± 2.07	13.37 ± 0.51	14.96 ± 2.12
∑MUFAs	24.79 ± 0.72	23.27 ± 0.78	23.36 ± 0.34	21.43 ± 1.83	21.56 ± 1.33	21.05 ± 1.12	20.78 ± 0.39	21.21 ± 0.38	20.52 ± 0.68	17.69 ± 2.15	17.9 ± 2.25
∑PUFAs	50.76 ± 1.62	45.01 ± 4.28	45.09 ± 1.84	42.63 ± 4.78	43.65 ± 0.90	38.84 ± 2.49	37.70 ± 1.24	37.24 ± 1.36	35.29 ± 0.91	29.01 ± 3.18	29.53 ± 1.26

Analysis of Volatile Profiles from Lipid Oxidation of Frying Oil

Hydroperoxides and polyunsaturated aldehydes produced during frying process could further decompose into volatile constituents. These components could be divided into six groups: aldehydes, ketones, alcohols, acids, hydrocarbons, and other volatiles (such as furanic compounds). Among the volatiles produced by the hemolytic β cleavage of O–O, C–C, and C–O of peroxide group of free radicals (Porter et al. 1995), saturated and unsaturated aldehydes were the major significant compounds, followed by alcohols and hydrocarbons, while the figures for ketones and acids were minor. Table 2 shows the main aldehyde volatile compounds of frying soybean oil.

The major aldehyde volatile constituents identified in frying oil are derived from the decomposition of lipid oxidation products, especially degradation of fatty acids. The main volatile decomposition products formed from oleic acid by homolytic cleavages on the alkoxyl intermediate group are decanal, 2-undecenal, nonanal, and octanal, while 2,4-decadienal and hexanal are produced from autoxidized linoleic acid and (2*E*,4*E*)-2,4-heptadienal is generated from linolenic acid (Frankel 1998). In frying soybean oil, hexanal, (2*E*)-heptenal, nonanal, (2*E*)-decenal, and (2*E*,4*E*)-decadienal were the most abundant aldehydes, which increased consistently with the increase of frying time. Content of hexanal, heptanal, (2*E*)-decenal, and (2*E*,4*E*)-decadienal in frying oil samples increased rapidly with the increasing frying time. This significant increase of these compounds may have an effect on sensory quality of frying oil. Additionally, the amount of (2*E*,4*E*)-decadienal was the highest among all aldehydes because soybean oil was rich in linoleic acid and oils with higher amounts of unsaturated fatty acids were more prone to be oxidized and produce oxidation products.

Conclusion

This study demonstrated the relationship between frying time and oxidative stability of soybean oil. The ESR results showed that frying for long hours not only promoted the hydrolysis and oxidation of soybean oil, but also promoted the oxidation of fatty acids, which agreed with physicochemical results. Besides, HS-SPME-GC-MS/MS was used to study decomposition products of lipid oxidation. Results indicated that the figures for hexanal, heptanal, (2*E*)-decenal, and (2*E*,4*E*)-decadienal in oil samples increased rapidly due to the decomposition of hydroperoxides and polyunsaturated aldehydes and oxidation of fatty acids produced by thermal oxidation during frying process. The study provides a new idea to characterize oil oxidation during frying process.

Table 2 The main aldehyde compounds of frying soybean oil at different frying periods

Aldehyde compounds (μg/kg)	Frying time (h)					
	0	5	10	15	20	25
Hexanal	117.18 ± 28.54	287.21 ± 41.80	355.03 ± 44.42	461.87 ± 39.34	552.30 ± 33.48	560.87 ± 23.24
Heptanal	32.52 ± 8.24	68.33 ± 13.76	82.76 ± 17.81	136.99 ± 17.91	230.55 ± 47.65	331.95 ± 74.10
(2*E*)-hexenal	38.21 ± 8.52	63.48 ± 4.52	93.50 ± 9.64	98.30 ± 9.98	125.32 ± 10.05	120.11 ± 22.58
Octanal	87.27 ± 5.27	108.54 ± 8.76	112.69 ± 16.71	138.80 ± 20.40	155.00 ± 27.36	201.67 ± 44.78
(2*E*)-heptenal	240.16 ± 45.06	423.95 ± 17.53	613.00 ± 27.03	694.96 ± 56.63	810.22 ± 46.96	1064.55 ± 255.83
Nonanal	671.39 ± 73.76	742.37 ± 56.60	802.34 ± 102.01	860.93 ± 56.14	911.13 ± 39.96	1198.15 ± 133.17
(2*E*)-octenal	102.34 ± 22.36	212.69 ± 45.96	295.39 ± 33.09	371.79 ± 22.44	407.09 ± 42.29	509.82 ± 32.17
Undecanal	14.55 ± 1.44	18.26 ± 4.00	18.65 ± 0.96	16.17 ± 3.07	20.48 ± 1.33	20.76 ± 0.17
(2*E*,4*E*)-heptadienal	97.50 ± 14.31	193.69 ± 35.71	351.49 ± 59.94	359.79 ± 24.70	382.27 ± 28.18	349.90 ± 36.17
Decanal	175.39 ± 18.46	174.31 ± 14.14	223.37 ± 19.68	248.96 ± 13.28	285.83 ± 10.78	302.40 ± 26.62
(2*E*)-nonenal	75.58 ± 15.05	95.13 ± 5.93	126.64 ± 15.30	167.50 ± 21.13	181.66 ± 15.14	199.74 ± 33.53
(2*E*,4*E*)-nonadienal	17.04 ± 3.20	24.95 ± 3.95	30.93 ± 3.87	41.83 ± 5.80	46.69 ± 7.46	56.39 ± 2.07
(2*E*)-decenal	71.22 ± 4.69	125.93 ± 11.90	253.97 ± 16.08	355.93 ± 25.95	393.77 ± 15.09	566.65 ± 40.50
2-undecenal	55.45 ± 4.27	70.30 ± 2.65	83.18 ± 10.14	161.25 ± 24.16	177.01 ± 16.32	178.65 ± 15.89
(2*E*,4*E*)-decadienal	364.71 ± 17.56	876.55 ± 42.73	1301.92 ± 63.14	1567.06 ± 180.31	1674.71 ± 239.14	2126.60 ± 395.07

Aldehyde compounds (μg/kg)	Frying time (h)			
	5	30	35	40
Hexanal	287.21 ± 41.80	646.03 ± 16.08	682.62 ± 86.18	924.21 ± 27.63
Heptanal	68.33 ± 13.76	288.49 ± 55.39	483.15 ± 84.97	465.85 ± 12.88
(2*E*)-hexenal	63.48 ± 4.52	134.24 ± 15.32	135.37 ± 18.78	191.56 ± 34.07
Octanal	108.54 ± 8.76	197.28 ± 8.55	262.97 ± 84.10	308.86 ± 33.18
(2*E*)-heptenal	423.95 ± 17.53	962.08 ± 57.33	1213.65 ± 108.79	1563.28 ± 282.76
Nonanal	742.37 ± 56.60	1032.75 ± 43.00	1252.29 ± 144.31	1355.17 ± 113.55
(2*E*)-octenal	212.69 ± 45.96	509.64 ± 103.27	733.59 ± 50.72	739.54 ± 62.10
Undecanal	18.26 ± 4.00	24.60 ± 2.48	21.37 ± 3.08	21.21 ± 3.61
(2*E*,4*E*)-heptadienal	193.69 ± 35.71	352.12 ± 53.37	408.74 ± 65.34	483.16 ± 72.41
Decanal	174.31 ± 14.14	304.35 ± 42.55	302.36 ± 21.23	360.03 ± 14.11
(2*E*)-nonenal	95.13 ± 5.93	202.09 ± 25.82	219.64 ± 26.50	237.72 ± 30.93
(2*E*,4*E*)-nonadienal	24.95 ± 3.95	63.39 ± 6.31	75.79 ± 15.46	83.15 ± 16.56
(2*E*)-decenal	125.93 ± 11.90	752.28 ± 53.09	867.65 ± 33.72	1077.87 ± 93.25
2-undecenal	70.30 ± 2.65	196.97 ± 13.52	197.94 ± 12.03	206.62 ± 28.02
(2*E*,4*E*)-decadienal	876.55 ± 42.73	2976.60 ± 524.17	3270.26 ± 331.53	3878.18 ± 222.95

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Compliance with Ethical Standards

Conflict of Interest Ying Liu declares that she has no conflict of interest. Yuanpeng Wang declares that he has no conflict of interest. Peirang Cao declares that he has no conflict of interest. Yuanfa Liu declares that he has no conflict of interest.

Ethical Approval This article does not contain any studies with human participants or animals performed by any of the authors.

Informed Consent Not applicable.

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