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



Qing Zhang<sup>a,\*</sup>, Chong Wan<sup>a</sup>, Chenzhi Wang<sup>a</sup>, Hong Chen<sup>a</sup>, Yaowen Liu<sup>a</sup>, Suqing Li<sup>a</sup>, Derong Lin<sup>a</sup>, Dingtao Wu<sup>b</sup>, Wen Oin<sup>b</sup>

- <sup>a</sup> College of Food Science, Sichuan Agricultural University, No. 46, Xinkang Road, Ya'an 625014, Sichuan, China
- b Institute of Food Processing and Safety, Sichuan Agricultural University, No. 46, Xinkang Road, Ya'an 625014, Sichuan, China

#### ARTICLE INFO

# 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)

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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, alkones, 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.

#### 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

E-mail address: zhangqing@sicau.edu.cn (Q. Zhang).

<sup>\*</sup> Corresponding author.

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(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% linoleic 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  $\times$  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  $\pm$  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  $50/30~\mu m$  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  $\times$  0.25 mm  $\times$  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  $250\,^{\circ}\text{C}$  at  $10\,^{\circ}\text{C/min}$  and then maintained at  $250\,^{\circ}\text{C}$  for  $10\,\text{min}.$  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  $\mu$ L. 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 et al., 2003).

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