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## Changes of Headspace Volatile Constituents of Palm Olein And Selected Oils after Frying French Fries

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**Abstract:** Changes of aroma constituents of palm olein and selected oils after frying French fries have been studied. The aroma constituents of used oils were collected using a solid-phase microextraction (SPME) headspace technique with an absorbent of a divinylbenzene/carboxen (DVB/CAR) (50/30  $\mu\text{m}$ ) on polydimethylsiloxane (PDMS) fibre. The extracted volatiles were desorbed from the fibre in the injection port of the gas chromatograph at 250°C and the aroma constituents were identified by GC-MS. Analytical data showed that volatile constituents of palm olein, soybean oil, corn oil and sunflower oil changed while frying continued from 2 to 40 h, respectively. In palm olein, the 2t,4t-decadienal content decreased from 14.7 to 5.5  $\mu\text{g g}^{-1}$  (40 h) whilst hexanal increased from 7.9  $\mu\text{g g}^{-1}$  (2 h) to 29.2  $\mu\text{g g}^{-1}$  (40 h), respectively. Similar result was also obtained from soybean oil after frying French fries. The 2t,4t-decadienal content decreased from 15.9  $\mu\text{g g}^{-1}$  (2 h) to 3.2  $\mu\text{g g}^{-1}$  after 40 h frying whilst hexanal increased from 10.2  $\mu\text{g g}^{-1}$  (2 h) to 34.2  $\mu\text{g g}^{-1}$  (40 h). Meanwhile, in corn oil, it was found that 2t,4t-decadienal decreased from 15.6  $\mu\text{g g}^{-1}$  (2 h) to 3.2  $\mu\text{g g}^{-1}$  (40 h) whilst hexanal increased from 11.3  $\mu\text{g g}^{-1}$  (2 h) to 33.8  $\mu\text{g g}^{-1}$  when frying time reached 40 h. In sunflower oil, it was found that 2t,4t-decadienal, decreased from 16.8  $\mu\text{g g}^{-1}$  (2 h) to 1.2  $\mu\text{g g}^{-1}$  (40 h) while hexanal increased from 9.5  $\mu\text{g g}^{-1}$  (2 h) to 32.4  $\mu\text{g g}^{-1}$  when frying time reached 40 h. It also showed that used oils exhibited off-odour characteristics due to the increasing amount of hexanal while their freshness characteristics diminished due to the decreasing amount of 2t, 4t-decadienal.

**Key words:** Aroma volatiles, french fries, palm olein and selected oils

### INTRODUCTION

It is generally accepted that frying oils are easily decomposed when heated at frying temperature. During frying, the degradation process, i.e., autoxidation, involves the formation of various primary and secondary degradation compounds. These compounds affect the flavour quality of fried products which can influence consumer acceptance of the finished products. For example, the oxidation product of linoleic acid, such as 2t, 4t-decadienal influences the freshness of fried potato chips. This compound probably plays a greater role in terms of shelf life and stability of fried products. Other compounds, i.e., aldehydes and ketones, are responsible for various unpleasant odours which lead to rancidity (Robards *et al.*, 1998; St. Angelo, 1996; Grosch, 1987; Frankel, 1993a). Some headspace volatiles, i.e., hexanal and pentanal, have been commonly used to measure the extent of lipid oxidation, particularly in fish oil (Frankel, 1993b), since these off-flavour components have very low

threshold values (Horiuchi *et al.*, 1998). Other volatiles, such as 1-penten-3-one, 4c-heptenal, 2t,4t- heptadienal and 2t, 6c-nonadienal, have been characterized as very potent contributors to the unpleasant fishy smell in fish and meat products (Koelsch *et al.*, 1991; Karahadian and Lindsay, 1989; Milo and Grosch, 1995).

Volatile substances can be trapped from the headspace (HS) of the oil by numerous techniques, i.e., static, dynamic and adsorption techniques. Among the HS adsorption techniques, solid-phase microextraction (SPME) headspace trapping is widespread in the field of environmental chemistry and toxicology (Belardi and Pawliszyn, 1989; Arthur *et al.*, 1992), but in lipid chemistry there is still no standardised method. SPME is a technique developed by investigators at the University of Waterloo (Arthur *et al.*, 1992). It is an innovative, solvent free technology that is fast, economical and versatile. However, there are only limited publications on the utilisation of the SPME techniques for characterizing the origin and oxidative state of the oil

based on the determination of the aroma and volatile compounds (Bentivenga *et al.*, 2001; Keszler and Heberger, 1998; Doleschall *et al.*, 2002).

## MATERIALS AND METHODS

**Materials:** Processed palm olein, soybean, corn and sunflower oils were obtained from various local stores and analysed initially for volatiles.

**Frying procedures:** The oil was heated to  $180 \pm 2^\circ\text{C}$  in electrically heated open fryer (Frymaster, Split Pot, USA) of 11.5 L capacity. About 200 g of frozen French fries were defrosted to room temperature and fried at the above temperature for 4 min at interval of 30 min. Each oil was subjected to a total of 40 h of frying and heating, i.e., 8 h a day for five consecutive days. For analysis, the oil was collected at 0, 2, 8, 16, 24, 32 and 40 h of frying and the volatile flavour constituents were collected using a SPME headspace adsorption technique.

**Headspace extraction of volatiles:** Five grams of sample was weighed into a 15 mL headspace vial, closed with aluminium seal with a PTFE liner and heated at corresponding temperature for 45 min. The internal standard solution, i.e., *n*-dodecane ( $5 \mu\text{g g}^{-1}$ ) was injected into the headspace vial for the purpose of quantification of the volatile constituent. The volatiles from the oil were collected using a SPME headspace sampling system as previously described (Doleschall *et al.*, 2003). The PDMS fibre containing DVB/CAR was placed for 30 min in the headspace vial 3 mm above the surface of the oil.

## ANALYSIS AND IDENTIFICATION OF VOLATILE COMPOUNDS

**Gas chromatographic analysis:** The polydimethylsiloxane (PDMS) fibre was injected into a HP 5890 Gas Chromatograph (Agilent, Palo Alto, USA) equipped with a fused silica capillary column (Ultra 1, 50 m x 0.32 mm x 0.52  $\mu$ , Agilent, Palo alto, USA) and FID detector. Helium was applied as a carrier gas at a constant flow rate of  $1.0 \text{ mL min}^{-1}$  and the peak areas were calculated by a HP 3396B integrator (Agilent, Palo Alto, USA). Quantitative analysis of the volatile constituent was calculated using *n*-dodecane as an internal standard according to method previously reported (Snyder *et al.*, 1985; Snyder *et al.*, 1988). Operating condition: Injector and detector temperatures were 250 and  $250^\circ\text{C}$ , respectively; the oven temperature was programmed from 70 to  $220^\circ\text{C}$  at a rate of  $4^\circ\text{C/min}$ .

**GC-MS analysis.** A HP 5890 model gas chromatograph equipped with the same column as GC analysis was directly interfaced to the ion source of a HP 5971A mass spectrometer. Working condition: GC as above with He column head pressure 25 kPa, MS: transfer line temperature  $280^\circ\text{C}$ , ion source temperature  $182^\circ\text{C}$  and MS identification of the compounds was made according to the mass spectra of the standards and by applying NIST 98 library.

## RESULTS AND DISCUSSION

### Changes of volatile constituents of palm olein, soybean oil, corn oil and sunflower oil during frying of French fries:

Figure 1 shows that 2t, 4t-decadienal, the flavour contributing compound of French fries, decreased from  $14.7 \mu\text{g g}^{-1}$  (2 h) to  $5.5 \mu\text{g g}^{-1}$  after 40 h frying whilst hexanal increased from  $7.9 \mu\text{g g}^{-1}$  (h) to  $29.2 \mu\text{g g}^{-1}$  when frying time reached 40 h. Similar result was also obtained when soybean oil was used to fry French fries (Fig. 2). The hexanal content increased from  $10.2 \mu\text{g g}^{-1}$  (2 h) to  $34.2 \mu\text{g g}^{-1}$  (40 h) whilst 2t, 4t-decadienal decreased from  $15.9 \mu\text{g g}^{-1}$  (2 h) to  $3.2 \mu\text{g g}^{-1}$  when frying continued for 40 h. Wu and Chen (1992) observed a similar situation when soybean oil was used as a frying oil in deep frying process.

The data (Fig. 3) indicated that 2t, 4t-decadienal decreased from  $15.6 \mu\text{g g}^{-1}$  (2 h) to  $3.2 \mu\text{g g}^{-1}$  after 40 h frying whilst hexanal increased from  $11.3 \mu\text{g g}^{-1}$  (2 h) to  $33.8 \mu\text{g g}^{-1}$  (40 h). The decreasing amount of 2t, 4t-decadienal might contribute to the freshness of the French fries while off-odour developed when the hexanal content increased.

In sunflower oil, 2t, 4t-decadienal decreased from  $16.8 \mu\text{g g}^{-1}$  (2 h) to  $1.2 \mu\text{g g}^{-1}$  after 40 h frying whilst hexanal increased from  $9.5 \mu\text{g g}^{-1}$  (2 h) to  $32.4 \mu\text{g g}^{-1}$  when frying time reached 40 h (Fig. 4).

Figure 5 shows that the hexanal content in palm olein was significantly low compared to other liquid oils. The lower in hexanal concentration indicated that palm olein was more stable towards degradation at higher temperature due to lower content in linoleic acid (Boskou *et al.*, 2006). Meanwhile, the concentration of 2t, 4t-decadienal showed that palm olein contained less amount of this constituent at the beginning of frying compared to other oils (Fig. 6). It showed that the quantity of this compound was closely related to the unsaturation degree of the oils. Palm olein was expected to produce lower quantity of decadienal as compared to other liquid oils (Boskou *et al.*, 2006). However, when frying prolonged up to 40 h, the 2t, 4t-decadienal content in olein

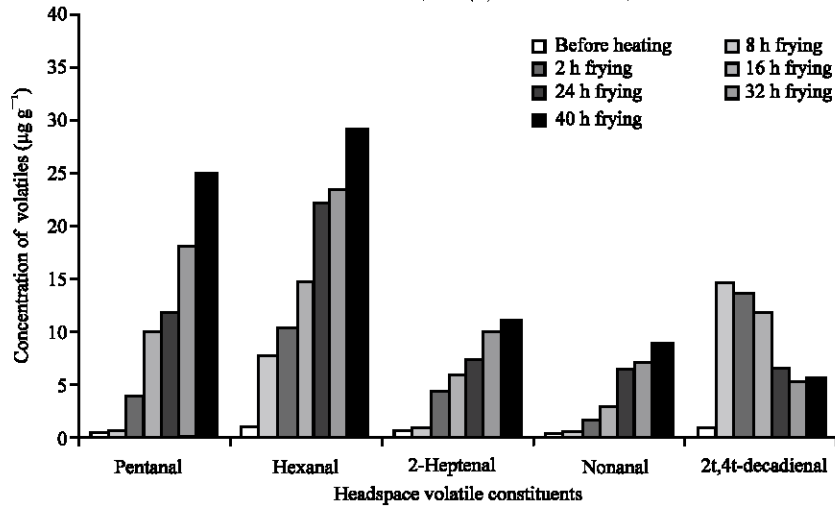


Fig. 1: Headspace volatiles of palm olein

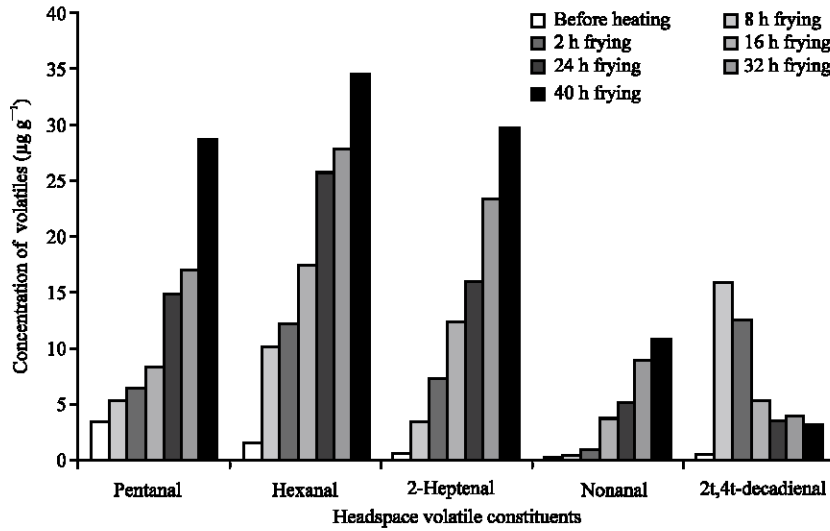


Fig. 2: Headspace volatile of soybean oil

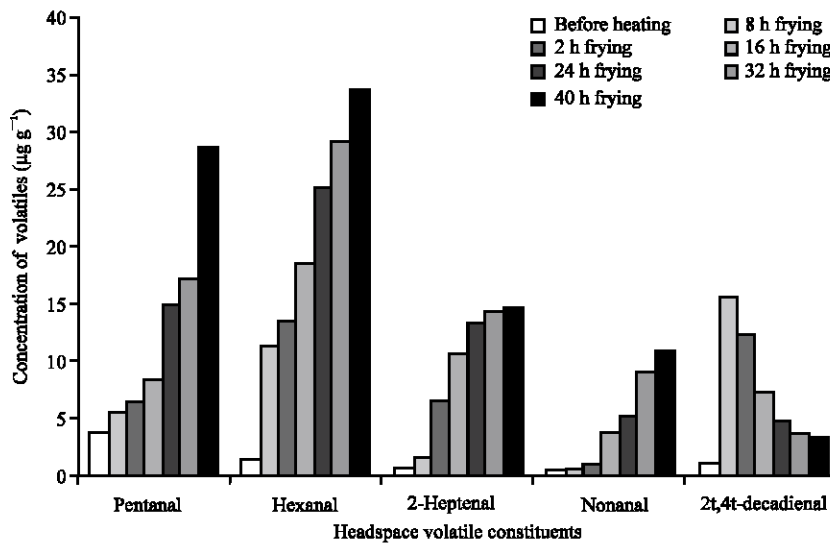


Fig. 3: Headspace volatiles of corn oil

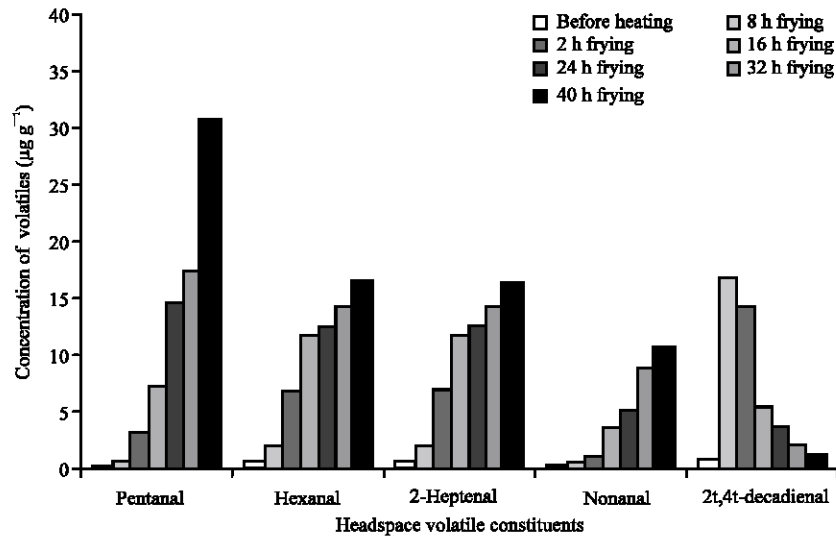


Fig. 4: Headspace volatile of sunflower oil

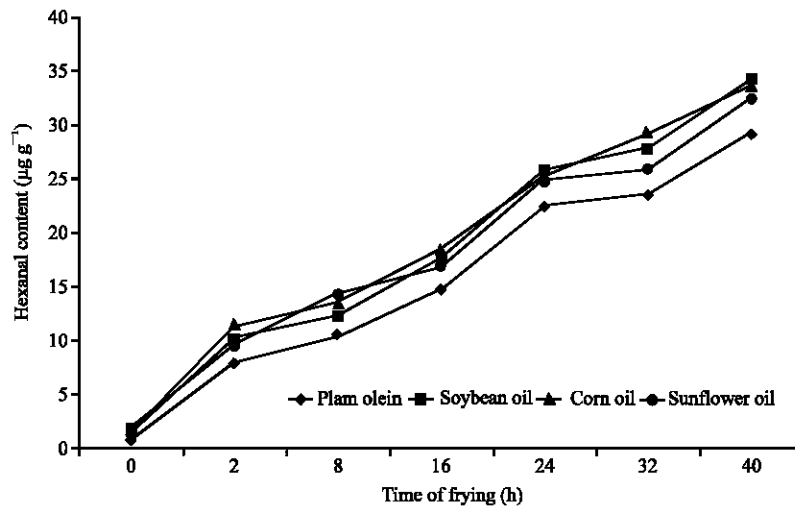


Fig. 5: Hexanal content of palm olein and selected oils

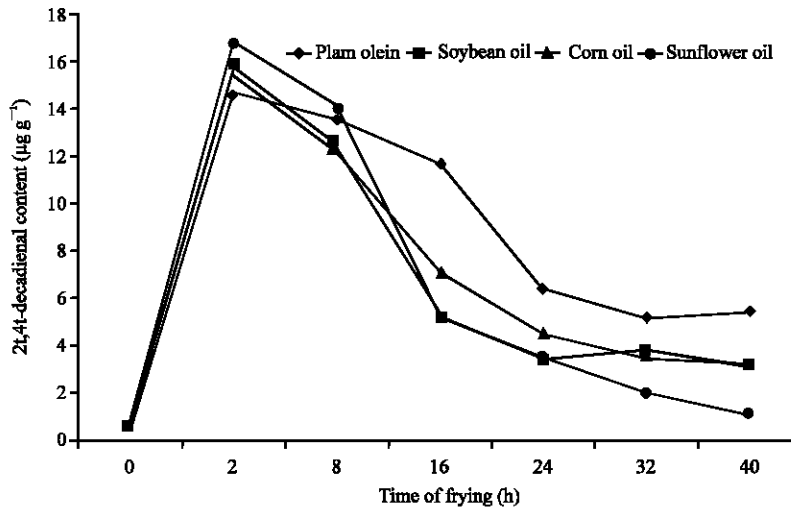


Fig. 6: Concentration of 2t, 4t-decadienal in palm olein and selected oils

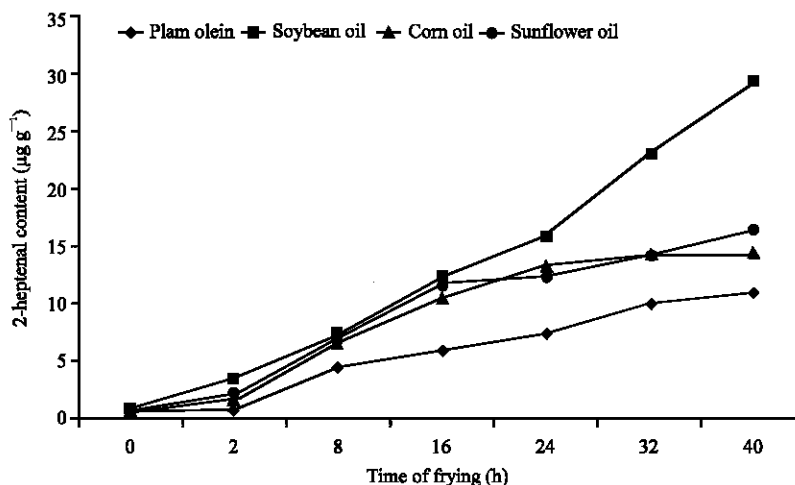


Fig. 7: The 2-heptenal content in palm olein and selected oils

was higher compared to other selected oils. This data concluded that during frying a small amount of decadienal was absorbed by French fries (Boskou *et al.*, 2006), while high amount of this compound remained in palm olein.

The result showed that the 2-heptenal content in soybean oil after 40 h of frying was significantly high compared to palm olein, corn oil and sunflower oil (Fig. 7). The higher content of this constituent may contribute to fishy odour in French fries as previously reported (Abdullah, 2003).

### CONCLUSIONS

Volatile flavour constituents of heated palm olein, soybean oil, corn oil and sunflower oil have been characterized and identified using SPME headspace adsorption technique followed by GC-MS analysis.

During frying, changes of volatile constituents influenced the aroma quality of heated oils. It showed that used oils exhibited off-odour characteristics due to the increasing amount of hexanal while their freshness characteristics diminished due to the decreasing amount of 2t,4t-decadienal.

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