

EFFECT OF THE DEEP-FAT FRYING PROCESS ON AROMA COMPOUNDS OF SUNFLOWER SEED OIL

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ABSTRACT

Sunflower seed oil is the fourth largest edible oil in the world and the consumption of it has been increasing due to the aromatic, nutritive and economic reasons. This vegetable oil is mainly used for cooking especially as frying oil. Deep-fat frying is a significant process of food preparation and gives a unique color and desirable flavor to food which is accepted by consumers. Through the process, a variability of chemical reactions result in the formation of extensive aromatic compounds. Likewise any other food product, oil quality is closely related to the aroma detected by consumers, and this attribute will have a great influence on its acceptance or rejection. Therefore, the present study explores the effects of the deep-fat frying process on aroma composition of the sunflower seed oil. The aroma compounds of 1, 5 and 10 times used oils to fry potatoes and non-fried oils were analyzed. Volatile components of the oils were extracted by using of the purge and trap technique with dichloromethane and analyzed by gas chromatography mass spectrometry (GC-MS). Results showed that total aldehydes content increased with the frying treatment due to the Strecker degradation. In this reaction, dicarbonyls or hydroxycarbonyl intermediates deaminate and decarboxylate amino acids to produce the corresponding Strecker aldehydes. Among the aldehyde compounds, (E,E)-2,4-decadienal, (E)-2-heptenal and hexanal were the major aroma compounds in all sunflower seed oils.

Key words: Sunflower, Deep-fat frying, Sunflower seed oil, aroma, GC-MS.

INTRODUCTION

Frying is the cooking of food in oil or another fat. Foods can be fried in a variety of fats and vegetable oils. These oils play a significant role in the food industry due to both their functional and nutritional features and their impact on taste, aroma and health. Refined sunflower oil, especially high-oleic, is very versatile and due to its neutral flavor and heat stability it can be consumed in many ways in the kitchen, such as frying and cooking. Sunflower (*Helianthus annuus* L.) is globally one of the most important oil crops and in

Turkey sunflower oil is commonly used for frying. Especially, deep frying is now the basis of a very large and expanding worldwide industry. During deep-fat frying, fats and oils are continuously or repeatedly heated at high temperatures (up to 190 °C) for prolonged periods of time in the presence of air. Under these conditions both thermal and oxidative reactions of the oils occur, leading to the formation of volatile and nonvolatile decomposition products (Chang et al., 1978). Prolonged deep-fat frying results in poor acceptability and nutritive value owing to the thermal and oxidative reactions in the frying oil. Together with the generation of long-lived bubbles and an increase in viscosity, frying oil begins to generate a noticeable odor attributable to the various volatile decomposition products of the thermally oxidized oil (Fujisaki et al., 2002, Tekelioğlu et al., 2008). Aroma is a main quality factor for edible vegetable oils as a characteristic parameter. During heat treatment by frying beside the aroma compounds formed which are very appreciated by consumers also other compounds which are not desirable get accumulated in the products; those compounds are formed by partial or total alteration of thermolabile nutrients present in food and in the frying oil (Ghidurus et al., 2011). The frying oil decomposition products as well as products formed from reactions between food components (proteins, carbohydrates) and oil constituents may adversely affect the flavor, color, nutritive value, and safety of the fried food (Takeoka et al., 1995; 1996).

Therefore, the aim of the present study was to evaluate the aromatic extracts obtained by purge and trap technique and then investigate the influence of frying process on aroma compounds. In present study, the aroma compounds of 1, 5 and 10 times used oils to fry potatoes and non-fried oils were analyzed.

MATERIALS AND METHODS

Materials

The water used in the study was purified by a Millipore-Q system (Millipore Corp., Saint-Quentin, France). Dichloromethane, 2-octanol, and sodium sulphate were obtained from Merck (Darmstadt, Germany). Dichloromethane was freshly distilled prior to use. Sunflower oil samples were obtained from a local producer in Adana city, Turkey.

Methods

Treatment of Frying Process

Before frying process, potatoes were hand peeled and then cut into strips (1 × 1 × 6 cm) with a stainless steel slicer. A fraction of 200 g of potato strips were used at each frying process. The potatoes were deep fried in sunflower oil using an electrical fryer (Felix FL 269, Turkey) at the 190 °C for 10 minutes. Frying process was repeated 10 times and oil samples were obtained after 1, 5 and 10 times frying.

Extraction of the Aroma Compounds

The volatile compounds of sunflower oils were extracted by purge and trap system which consists in a source of nitrogen, controlled by a flow-meter. For the extraction, 10 g oil sample transferred into 20 mL vial then the sample was pre-incubated at the extraction temperature for 10 min. After purging process, the compounds retained in the cartridge were eluted with dichloromethane. After dehydration by anhydrous sodium sulphate, the pooled

organic extract was reduced to 5 mL in a Kuderna Danish concentrator fitted with a Snyder column at 40°C (Supelco, St Quentin, France) and then to 0.5 mL under a gentle stream of nitrogen. Extracts were then stored at -20°C in a glass vial equipped with a Teflon-lined cap before analysis. Each sample was extracted in triplicate.

Analysis of Aroma Compounds

The GC system consisted of an Agilent 6890 chromatograph equipped with a flame ionization detector (FID) (Wilmington, DE) and an Agilent 5973N -mass selective detector (MSD). Aroma compounds were separated on a DB-Wax (30 m, 0.25 mm, 0.5 mm thickness; J&W Scientific, Folsom, CA) column. Retention indices of the compounds were calculated by using the retention data of a linear alkane series. After identification, the concentrations of aroma compounds were calculated by GC-FID according to the internal standard (2-octanol). The condition details of GC-MS and GC-FID were described in our previous study (Amanpour et al., 2015).

The GC system consisted of an Agilent 6890 chromatograph equipped with a flame ionization detector (FID) (Wilmington, DE) and an Agilent 5973-Network-mass selective detector (MSD) (DE, USA). Aroma compounds were separated on a DB-Wax (30 m length x 0.25 mm i.d. x 0.5µm thickness, J&W Scientific Folsom, CA, USA) column. A total of 3 µL of extract was injected in pulsed splitless (40 psi; 0.5 min) mode. Injector and FID detectors were set at 270°C and 280°C, respectively. The flow rate of carrier gas (helium) was 1.5 mL/min. The oven temperature of the DB-Wax column was first increased from 50° to 200°C at a rate of 5°C min⁻¹ and then to 260°C at 8°C min⁻¹ with a final holds at 260°C for 5 min. The same oven temperature programs were used for the MSD. The mass detector was operated in the electron impact mode at 70 eV. The GC-MS interface and ionization source temperature was set at 250°C and 180°C, respectively. Identification and quantification were performed in full scan mode with a mass/charge range of 30-300 amu at 2.0 scan s⁻¹ scan rate. The compounds were identified by comparing their retention index and Wiley-6 and NIST-98 mass spectral libraries. Standard compounds were injected and analyzed under the same conditions. Retention indices of the compounds were calculated by using an n-alkane series. After identification the concentrations of aroma compounds were calculated according to internal standard (2-octanol) (Kesen et al, 2014).

RESULTS AND DISCUSSIONS

The volatile compounds identified in sunflower oils subjected to different number of frying process were presented in Table 1. Mean values (µg kg⁻¹) of the GC analyses of triplicate extractions were reported. As can be seen in Table 1, the total content of volatile compounds in the non-fried sunflower oil was the lowest and it increased gradually depending on the number of frying. The main reason of this could be taking place of oxidation, polymerization or thermal decomposition reactions in the frying oils used repeatedly at high temperatures. Besides, there are certain proofs that secondary oxidation products such as aldehydes and ketones, polar compounds, and acrolein which are formed in oxidized and degraded oils. Volatile compounds formed in frying oil include aldehydes, ketones, hydrocarbons, alcohols, acids, esters, and aromatic compounds (Chang et al., 1978). The amounts of volatile compounds of non-fried and 1, 5, 10 times fried oils were 2289, 3748, 5074 and 6992 µg kg⁻¹, respectively.

Results showed that total aldehydes content increased with the frying treatment due to the Strecker degradation. In this reaction, dicarbonyls or hydroxycarbonyl intermediates

deaminate and decarboxylate amino acids to produce the corresponding Strecker aldehydes. Among decomposition products during frying process, aldehydes are the most important because they are the most abundant (Frankel, 1985) and their thresholds are lower than those of other secondary products that characterize the flavor of fried foods and oils. As for identified aldehyde compounds in this study, (*E,E*)-2,4-decadienal, (*E*)-2-heptenal and hexanal were the major aroma compounds in all sunflower seed oils and their contents were increased due to number of frying process. The amounts of (*E,E*)-2,4-decadienal, (*E*)-2-heptenal and hexanal were found as 1448.0, 905.6 and 535.6 $\mu\text{g kg}^{-1}$, respectively. Volatile aldehydes are generated mainly from frying oil via β -scission of alkoxy radicals formed by the homolytic cleavage of FA hydroperoxides (Frankel, 1985).

Alcohols which were the other aroma compounds whose amount increased with the frying process. While their concentration in non-fried oil was 463.6 $\mu\text{g kg}^{-1}$, it reached 1417.5 $\mu\text{g kg}^{-1}$ after the tenth frying treatment. The total concentration of pentanol, 2-nonanol, 2-methyl-2-butenol, 1-octen-3-ol and 1H-indole-3-ethanol increased with frying process.

Looking at the acid, lactone, terpene and phenol compounds, it has been observed that the amounts of such compounds decreased with the frying process.

When compared to literature, the different pattern of the aroma compounds of oils that subjected to frying process was determined. In previous studies, Doleschall et al. (2003) showed the aroma compounds of refined sunflower oil before frying and after the 3rd cycle. On the results of the refined oil small amount of hexanal, (*E*)-2-heptenal and nonanal have been observed, while the fried oil contains more types of aldehyde in larger amount. Chang et al. (1978) showed that the volatile products formed from corn oil and hydrogenated cottonseed oil during deep-fat frying. Other researchers have also studied the volatile constituents resulting from the thermal treatment of vegetable oils (Snyder et al., 1985; Macku and Shibamoto, 1991; Wu and Chen, 1992; Chung et al., 1993). These results suggest that frying process can effectively decrease or increase the amount of volatile compounds.

Table 1. Volatile Compounds of Sunflower Oil Under the Influence of Frying Process

Aroma Compounds	Non-fried	Number of frying process		
		1	5	10
Aldehydes				
Pentanal	-	142.0	215.4	344.9
Hexanal	227.4	287.1	304.2	535.6
(<i>E</i>)-2-Hexenal	-	45.8	71.7	124.0
(<i>E</i>)-2-Pentenal	-	-	-	36.5
(<i>E</i>)-2-Heptenal	101.1	766.1	796.8	905.6
Nonanal	-	148.9	175.2	197.1
(<i>E</i>)-2-Octenal	-	259.9	189.5	392.1
(<i>E,E</i>)-2,4-Heptadienal	-	-	128.6	33.3
(<i>E</i>)-2-Decenal	-	-	132.1	137.7
(<i>E,E</i>)-2,4-Nonadienal	-	-	21.5	24.8
(<i>E,Z</i>)-2,4-Decadienal	25.9	171.8	425.5	487.8
(<i>E,E</i>)-2,4-Decadienal	27.8	332.0	1181.1	1448.0
2-Heptedecenal	101.4	-	-	-
Total	483.7	2153.6	3641.7	4667.3
Alcohols				
3-penten-2-ol	129.2	94.3	82.5	72.7
Pentanol	65.0	51.8	123.1	226.3

4-Heptanol	44.4	26.4	25.4	16.7
2-Nonanol	-	-	-	92.6
5-Methyl-2-hexanol	121.1	79.5	71.7	-
2-Methyl-2-butenol	15.4	13.5	17.1	26.9
3-Octanol	30.2	-	-	-
1-Octen-3-ol	-	99.8	116.7	215.6
2-Phenylethanol	58.3	30.4	10.3	7.2
1H-Indole-3-ethanol	-	-	-	759.5
Total	463.6	395.7	446.8	1417.5
Acids				
Pentanoic acid	24.8	43.2	-	-
Hexanoic acid	189.4	138.5	123.3	53.0
Heptanoic acid	45.4	73.2	-	-
Octanoic acid	111.6	92.5	38.2	21.5
Nonanoic acid	73.8	54.5	-	-
Decanoic acid	88.4	43.7	32.9	-
Total	533.3	445.5	194.4	74.5
Ketones				
6-Methyl-2-heptanone	41.0	-	-	-
4-Nonanone	-	19.2	21.1	41.8
4-Hydroxy-4-methyl-2-pentanone	316.9	399.1	348.5	346.3
3-Nonen-2-one	-	48.3	78.7	87.2
2,7-Octanedione	-	37.2	49.4	62.7
Total	357.9	503.7	497.6	538.1
Lactones				
5-Pentyl-2(3H)-furanone	7.9	-	-	-
5-Pentyl-2(5H)-furanone	40.5	26.8	-	-
Total	48.4	26.8	0.0	0.0
Terpenes				
dL-Limonene	140.8	116.0	62.3	23.7
Linalool	-	-	16.2	14.2
Total	140.8	116.0	78.6	37.9
Phenols				
Phenol	20.1	-	-	-
2,3-Dimethyl phenol	93.9	-	-	-
Total	114.0	0.0	0.0	0.0
Esters				
n-Butyl acetate	146.8	107.3	94.8	65.7
Methyl palmitate	-	-	35.8	48.5
Methyl oleate	-	-	83.8	142.5
Total	146.8	107.3	214.4	256.7
GENERAL TOTAL	2288.6	3748.5	5073.5	6991.9

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