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Analytical evaluation of degradation in sunflower oil during thermal oxidation using FTIR and the compositional change analysis by gas chromatography

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ABSTRACT

Atmospheric oxygen can react spontaneously with lipids and other organic compounds causing structural degradation, which is ultimately responsible for the loss of quality in food. When oil is exposed to frying, the triglycerides are converted into myriad. However, this oxidation process can be prevented or retarded by the addition of synthetic or natural antioxidants. Recent developments in Fourier transform infrared (FT-IR) spectroscopy instrumentation extend its application to the field of food research, facilitating particularly the studies on edible oils and fats. Commercial sunflower oil is exposed to repetitive and simulated deep-frying at 250^{0}C for five times. In this work, FT-IR spectroscopy is used as an effective analytical tool to study the saturation and unsaturation composition of heated and unheated oils. In addition, an analytical technique for the measurement of carbonyl compounds in oils, produced after heating, has been employed. A novel methodology in gas chromatography (GC-MS) with an electron impact mass spectrum for the fast analysis of compositional variations of fatty acids and antioxidants in repeatedly heated sunflower oil with minimal sample treatment and the use of non-toxic reagents is also described. It is found that Tocopherol (Vitamin E) disappears in heated oil. The changes in the composition of edible oil confirm the degradation. Especially the unsaturated fractions of fatty acids have been converted to saturated fatty acids due to repeated heating. This conversion is opined to have adverse effect on the antioxidant regulating system of humans.

KEYWORDS

Thermal degradation;
Sunflower oil;
Fourier transform infrared spectroscopy;
Gas chromatography;
Mass spectral analysis.

INTRODUCTION

In the food industry, thermal degradation is the important parameter required to determine the quality and stability of food system. Oils and fats are an important part of the human diet. It elicits important characteristics like flavour, aromas, texture in foods and strong satiety signals to regulate the food intake. Rancidity of lipids in foods produces undesirable effects including loss of fat-soluble vitamins, generation of off-flavours, palatability problems and even production of toxins and cause food poisoning[1]. Atmospheric oxidation is the most important cause of deterioration in fats and oils[2]. Oxidation is accelerated by exposure of heat, light, amount of oxygen available and humidity. The intense frying of oils causes an oxidizing thermal degradation with the formation of decompositional components, such as aldehydes, ketones, free fatty acids and hydroxyl compounds that in high levels can be harmful to human health[3]. When oxygen travels through the fat, it is adsorbed by the fat and reacts mainly in the double links, thus the polyunsaturated (PUFA) components of fats oxidize much faster than unsaturated ones[4]. When the oil is heated to the frying condition, the unsaturation decreases and it becomes saturated due to oxidation.

Mid FT-IR spectra is used to characterize the composition of edible oils and fats. It differentiates the constituents with its intensity and frequency[5]. Moreover infra red spectra show differences in the profile, maximum intensity and position of transmission bands according to the oil composition. Therefore we have used infrared spectral analysis to study the structural changes of edible oils[6]. The FTIR method used to determine the FFA in oils by measuring the carbonyl compound C=O band at 1745.17 cm^{-1} has been reported by Ismail et al.,[7].

FTIR is a non-invasive method to determine the unsaturation in oils which makes it possible to classify them and evaluate their oxidative deterioration which is directly related with the degradation of polyunsaturated fatty acids in the lipids which are indispensable nutrients in human tissue development. The structural variations of the samples are analyzed using FTIR spectrum. Further, GC-MS analysis has been carried out to analyse the changes in the level of unsaturated, saturated fatty acids and antioxidants to infer their degree of degradation.

EXPERIMENTAL

Materials

Commonly available and popular branded sunflower oil has been collected from a local grocery shop located in Thanjavur district of Tamil Nadu, India to assess the possibility of usage of repeatedly heated sunflower oil by common people. Fifty milliliter of sunflower oil has been placed in a copper beaker and heated on an electric device, stirring manually with glass rod. A microcontroller based temperature controller has been designed and has been used to monitor the sample temperature. To mimic the oil oxidation process during frying, the sample has been heated up to 250^{0}C for five times. Initially, the sample was heated to 250^{0}C for half an hour then, it was allowed to cool until room temperature is achieved. Similarly, the sample was subjected to heating up to 250^{0}C for 1 hour, 1½ hours, 2 hours and 2½ hours respectively ensuring that every time the sample is allowed to cool up to room temperature before heating it next time. In order to ensure that the sample has been heated to the temperature greater than its smoke point, it has been exposed to successive heating.

Methods

FTIR analysis

Perkins Elmer Fourier transforms infrared spectrometer with deuterated triglycin sulphate (DTGS) as a detector is used for the analysis. The liquid sample was placed between two KBr pellets with the help of capillary tube. Each pellet was made of 0.2mm thickness and it is placed in the path of the sample beam. The spectra were recorded from 4000 to 450cm^{-1}, the number of scans being 256 at a resolution of 4cm^{-1}. Scan speed 0.20cm/s. Perkins elmer data acquisition and processing software spectrum for windows has been used.

GCMS analysis

For the fatty acid compositional variation determination, an Agilent gas chromatograph from Hewlett-Packard (Palo Alto, CA, USA) equipped with a HP 5971 MS detector was used. Separations were carried out on an Agilent-Hewlet Packard fused silica capillary column HP-5 (30m×0.25mm I.D.; 0.25μm film thickness) (Folsom, CA, USA). The GC-MS interface temperature was maintained at 250^{0}C. 1μl of both heated and unheated sunflower oil samples were injected manually in splitless mode with injector port temperature at 220^{0}C. The helium carrier gas flow rate was 1 ml /min. The column temperature program was as follows: 90^{0}C, held for 1 min, 12^{0}C min^{-1} to 150^{0}C, held for 1 min, 2^{0}C min^{-1} to 230^{0}C, held for 3 min, 10^{0}C min^{-1} to 250^{0}C, held for 25 min. The selective ion mode was used in the analysis. Retention time and abundance of the confirmation ions relative to that of quantification ion were used as identification criteria. Mass Charge range was between 50-500 amu. Oven temperature programmed to 50^{0}C-250^{0}C.

RESULTS AND DISCUSSION

FTIR analysis

Fourier transform spectroscopy is a measurement technique whereby spectra are collected based on measurements of the temporal coherence of an irradiative source. Measurement of a single spectrum is faster for the FTIR technique because the information at all frequencies is collected simultaneously. It provides a quick and accurate way of evaluating thermal degradation of edible oil subjected to intense heat, equivalent to that used in the preparation of food.

FTIR analysis of sunflower oil

Figures 1 and 2 shows the spectra of used and unused sunflower oil. Double bonds or triple bonds are not stronger than single bonds resulting in unsaturated compounds being more chemically reactive than saturated. Unsaturated fatty acids contain double bonds between certain atoms. These bonds may be broken and new atoms attached without disrupting the existing skeleton of the hydrocarbon, though a large majority of lipids are fatty acid tri-esters of glycerol. From the figure, a band shift observed at 3399.23 cm^{-1} can be assigned to the formation of hydrogen peroxide[8]. In compliance with the work reported by R.G.Arnold and T.E.Hartung[5], the degree of increase in saturation has also been confirmed due to the spectral observation at 3010cm^{-1} and at 2854cm^{-1} in the present study which is due to the symmetric stretching vibration of C-H bonds in methylene moiety. A spectrum at 3010cm^{-1} is due to C-H stretching vibration of the *cis*-double bond[9]. Further, the bands at 2924.87 and 2854.53 cm^{-1} have appeared after heating at elevated temperatures due to stretching vibration of CH_2 groups. The bands of carbonyl group showing strong absorption band has been noted at 1745 cm^{-1} which have formed due to stretching vibration of carbonyl groups of Triglyceride esters containing carbonyl groups such as ketones, aldehydes etc.[7,9] which are toxic to the colon. These triglyceride esters have formed due to polymerization of unsaturated fatty acids. Since triglycerides are a by product of oxidation of unsaturated oils, the presence of this peak in the FTIR spectra of used sunflower oil (repeatedly heated) confirms the deterioration in sunflower oil. C=C stretching vibration of cis-olefins has led to the band

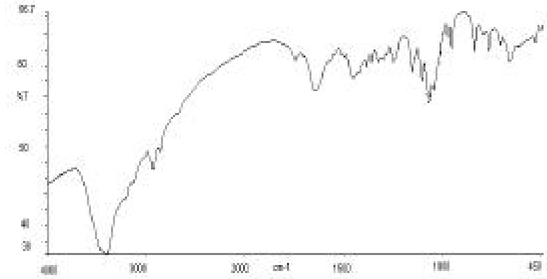

Figure 1 : FTIR spectra of unused sunflower oil

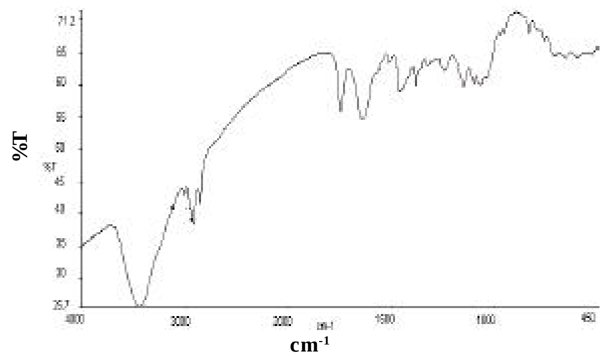

Figure 2 : FTIR spectra of sunflower oil (used)

development at 1651.57cm-1[9]. The spectra observed at 1245.39 and 1153.11 cm^{-1} is due to stretching vibration of the C-O ester groups formed due to the hydrolysis of fatty acids and glycerol during degradation. A significant finding is that the unused oil showed two bands in 974.25 cm^{-1} and 956.02 cm^{-1} which corresponds to C-H out of plane bending in -CH=CH_2[10]. The decreasing of the double bond is further supported by the lack of moderate intensity C-H out of plane bending band near 900 cm^{-1}[10]. Lack of band at 900 cm-^{1} in this study further confirm that the sunflower oil has undergone isomerisation from *cis* form of oleic acid to trans form, which is a unblemished proof for degradation of repeatedly heated sunflower oil. So far, the development of various bands observed at the above mentioned wavelengths have clearly depicted that while successively heating the sunflower oil to higher temperatures, the unsaturated fatty acid components present in the oil have undergone degradation via hydrolysis, isomerisation and polymerization processes.

In order to confirm the compositional degradation of used oils, GC-MS application is inevitable. The following discussion will highlight the results of GC-MS analysis that also confirms the FTIR study results. In consistence with the earlier cited literatures, the GC-

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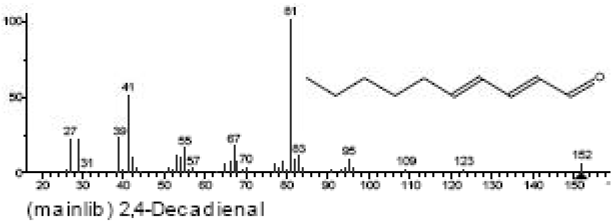

Figure 3 : Mass spectrum of decadienal

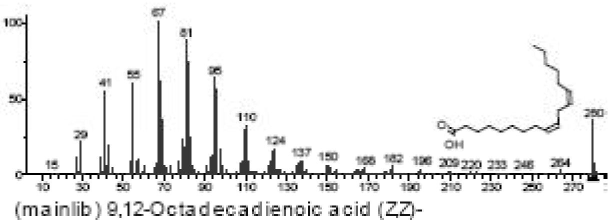

Figure 4 : Mass spectrum of linoleic

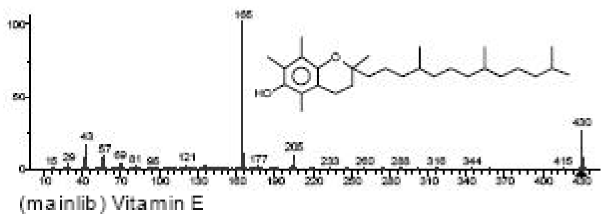

Figure 5 : Mass spectrum of tocopherol

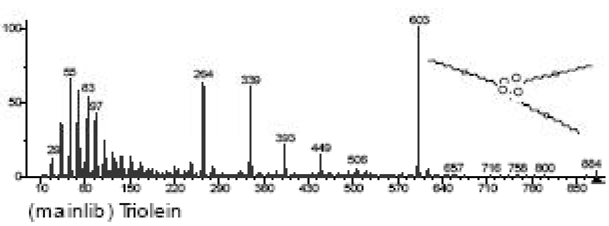

Figure 6 : Mass spectrum of triolein

MS analysis has shown presence of antioxidants, polyunsaturated fatty acids and saturated fatty acids in noral unused sunflower oil[11]. Out of all the components, the polyunsaturated linoleic acid slices off a major contribution to the total constituents of sunflower oil. The characteristic presence of antioxidants such as tocopherol, sitosterol is appreciably 27.67% and is responsible for the cholesterol lowering activities and reduces degradation leading to rancidity in sunflower oil in the unused condition. The respective mass spectrum are presented from figures 3-8. Further, the GC-MS analysis of sunflower oil after heating to 250^{0}C has revealed the presence of sitosterol and absence of tocopherol which supports thermal degradation. TABLE 1 also represents the composition of sunflower oil after thermal degradation that indicates the presence of linoleic

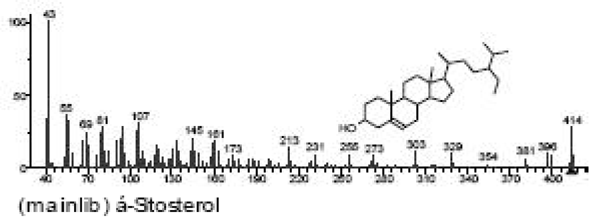

Figure 7 : Mass spectrum of sitosterol

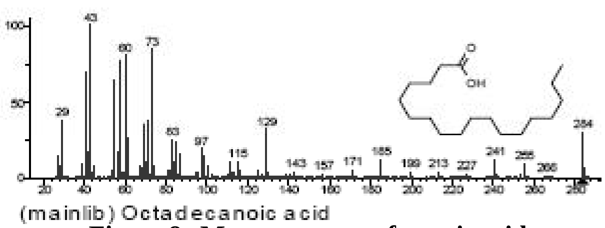

Figure 8 : Mass spectrum of stearic acid

TABLE 1: Composition of sunflower oil before heating from gas gramotogram

S. no.	Peak name	Unused oil		Used oil	
		RT	%Peak area	RT	%Peak area
1	2,4-Decadienal Formula: $C_{10}H_{16}O$ MW: 152	2.78	7.70	-	-
2	Linoleic acid Formula: $C_{18}H_{32}O_2$ MW: 280	6.62	44.48	8.38	36.44
3	Vitamin E Formula: $C_{29}H_{50}O_2$ MW: 430	11.98	14.51	-	-
4	Name: Triolein Formula: $C_{57}H_{104}O_6$ MW: 884	13.60	13.15	-	-
5	Name: á-Sitosterol Formula: $C_{29}H_{50}O$ MW: 414	20.03	20.16	20.9	18.34
6	Stearic acid Formula: $C_{18}H_{36}O_2$ MW: 284	-	-	13.28	24.68
7	Palmitic acid diglycerinester Formula: $C_{35}H_{68}O_5$ MW: 568	-	-	13.93	20.54

acid (36.44 %) that is comparatively less than the unused oil composition. Whereas, presence of saturated compounds such as Palmitic acid diglycerinester (20.54%), stearic acid (24.68%) has been clearly depicted in the spectrum indicating the formation of degradation products in the used condition. The composition of Sitosterol has slightly slipped to 18.34%. Hence, we can confirm that the linoleic acid and sitosterol percentage has decreased after heating. The unsaturated fatty acids present in the unused sunflower oil are Decadienal (7.70%), linoleic (44.48%) acid and triolein (13.15%). Out of these, after repeated heating, triolein has been converted into saturated stearic acid due to thermal reactions at high temperatures. A partial amount of unsaturated fatty acid such as linoleic and the unsaturated compound decadienal have been converted to the saturated compounds such as Palmitic acid diglycerin ester in repeatedly heated sunflower oil. A noteworthy point to remember is that Tocopherol (Vitamin E) has completely disappeared due to repeated heating leading to risky degradation products. The lack of Vitamin E clearly highlights that if sunflower oil is exposed to smoke point temperatures more than two times, then it is rendered unsafe for consumption due to lack of antioxidants.

CONCLUSION

Sunflower oil is found to be more sensitive to thermal treatment. The oil becomes dark, high viscous with unpleasant smell due to thermal elevations. Fourier transform infrared (FT-IR) spectroscopy instrumentation has been used to assess the occurrence of degradation processes such as hydrolysis, isomerisation and polymerization resulting in structural changes of components. High dietary intake of polyunsaturated fatty acids (FA) increases the oxidation of lipoproteins that lead to atherosclerosis, hypertension, coronary artery disease stroke etc. In metabolic activity, saturated fatty acids formed are converted into diacylglycerol which alter colonic epithelial cells that lead to colon cancer. The GC-Ms analysis undertaken clearly outlines the formation of saturated fatty acids due to thermal degradation of unsaturated fatty acids. Moreover, the Vitamin E is totally lost after degradation, whereas, the level of sitosterol has decreased leading to reduced antioxidant property of used sunflower oil. Hence it is recommended to avoid the usage of repeatedly used sunflower oil for culinary purposes.

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