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Effect of Deep-Frying on Physio - Chemical Characteristics of Sunflower Oil

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Abstract:- The oils and fats are one of the major constituents of our food since pre-historic time and are also used as a source of heat and light.These are used for frying different foods.Sunflower oil is one of the most important vegetable oils employed for deep-frying.It has been used in the cooking of food such as meat,fish,doughnuts, potatochips,French fries,snacks etc at home, in restaurants and in industry.The frying substantially changes the physio-chemical properties of oil.This paper provides an indepth study on the variations in properties of sunflower oil upon deep frying and health impacts of using frying oil continuously.

Keywords:- *Deep-Frying, Oil, Refractive Index, TPC, Fatty Acid Profile, Transfat, Peroxide Value, Iodine Value Etc.*

Abbreviations:- *RI-Refrative index,BRR-Butyro refractometer Reading,TPC-Total Polar Compounds,IV-Iodine value,FSSR-Food Safety and Standards Regulation,SV-saponification value,PV-Peroxide value,AV-Acid value,SG-Specific gravity,FID-Flame ionisation Detector,FAME-Fatty Acid Methyl Ester,GC-Gas chromatography.*

I. INTRODUCTION

The edible fats and oils are used for frying different foods .The fried foods such as chips,French fries,snacks,fish,meat etc are very popular eventhough there exists serious public health concern such as high cholesterol,calorific value,trans fat etc.

The frying is a process of cooking in which heat is directly transferred from hot fat/oil to cold food.A number of changes occurs when cold food is dropped into hot oil.Moisture from food starts to form steam which gets evaporated with a bubbling action that gradually subsides as the food becomes cooked and a desirable browning or caramalization of the surface of food occurs.During the frying process,the food absorbs oil .The majority of absorbed oil/fat accumulates near the surface of most fried foods , which amount to about 9 – 15 % of the finished weight in the fried product .The amount absorbed depends on the time of frying,surface area of the food,the moisture content of food and the nature of food.

There are two types of frying methods.,viz.,shallow frying and deep frying.The shallow frying is carried out at lower temperature, with small quantities of any available oil.The oil disintegration is minimum during this type of frying.However,the deep-frying is carried out at elevated temperatures ranging from150-200 ^{0}C.In this type of frying,the food is submerged in frying oil and at the frying temperature a lot of reactions occurs in the oil.The visible changes taking place in oils or fats during deep frying include darkened colour,increased viscosity,decreased smoke point and increased foaming.The oil/fat gets hydrolysed to free fatty acids, glycerol, monoglycerides and diglycerides.The oil/fat gets oxidised to hydroperoxides, hydroxides, ketones,epoxides and conjugated dienoic acids.These compounds may undergo pyrolysis or remain in the triglyceride molecule and cross-link each other,leading to polymerization.During deep frying,the cis bonds in omega-3 fatty acids get converted into trans bonds, triggering the formation of trans fat.The double bonds may undergo cross-link reactions and produce sticky and harmful fats.The unsaturated fatty acids also undergo polymerization during heating.All such kinds of complex changes affect the nutritional quality of frying oils.

In India,there is a common practice of using same oil in a number of times for the preparation of different products by deep frying.The repeated deep frying in oils may produce undesirable products.In order to avoid such hazards,it is advised to cook different products in different types of oils and to identify the safe number of frying of a specific food product in oils.

Bearing this in mind,sunflower oil,one of the most widely used edible oil in India for frying purpose,is selected and analysed to determine the effect of frying on the quality of oil and vice versa and to recommend safe number of frying of a specific product in oil for making recommendation to be used safely and commercially.

II. MATERIALS & METHODS

A. Materials

- ***Study Setting***: The analysis was carried out at Government Analysts Laboratory,Trivandrum,Kerala under the Commissionerate of Food Safety,Government of Kerala.

- ***Sample collection*** : The sunflower oil,and potatoes used in this study were procured from local market and analysed in the Food Section (Oil) and Food Section (Quality Control) at Government Analysts Laboratory.

- ***Sample Preparation*** : The potatoes were peeled,washed and then sliced into thin pieces,as done for French frying.Exactly500 ml sunflower oil was taken in a frying pan and heated to frying temperature.Then freshly prepared potatoes chips were submerged and fried in oil till a light brown colour was developed.The frying time was set for 8 minutes.After every frying,the oil is cooled and 50 ml of the oil sample was withdrawn for oil characterization analysis and stored at room temperature.The process repeated six times.The process of frying was carried out at a temperature of 180-190 ^{0}C,monitored using 250 ^{0}C capacity thermometer.

- **Apparatus and Reagents** :

Electronic balance	Sodium hydroxide (0.1 Normal)
Refractometer	Hydrochloric acid (0.5 Normal)
GC	Sodium thiosulphate (0.1 Normal)
Frying oil monitor	Ethanol
Pyknometer	Starch solution
Water bath	Phenolphthalein
Thermometer	

Chromatographic set up such as TLC plate,paper chromatographic sheet and chromatography glass chamber with lid, chemicals such as ethanol,carbon tetrachloride , chloroform , hexane , furfural ,carbon disulphide , sulphur,amyl alcohol, sodium chloride, diethyl ether,n-butanol,petroleum ether ,hexane, 2,7-dichlorofluoresceine etc and glasswares such as specific gravity bottle,conical flask, saponification value flasks with air condenser,iodine value flask, beakers, pipette,burette,funnel etc are also used.

B. Methods :

The following physio-chemical properties are analysed by standard methods.

- **Refractive Index** : The RI is measured using the instrument ATAGO RX-5000 refractometer.The value is directly read from the instrument at 40 ^{0} C. The corresponding BRR value can be obtained from the table in IS 548 (Part 1) 1964:Reaffirmed 2015 method.

- **Specific gravity** : It is measured by pycnometer method.

- **Fatty acid Profile**: The fatty acid profile of oils were determined by Gas Chromatography after derivatization to fatty acid methyl ester (FAME).The instrument is GC-FID by Thermo Scientific.

- **Iodine Value**:The IV is measured by Wijs iodine monochloride method described in IS 548 (Part 1) 1964:Reaffirmed 2015. In this method, a known quantity of oil sample(about 0.3 gram) is dissolved in carbon tetrachloride or chloroform and reacted with known excess of Wij's solution (25 ml). After standing in the dark for half an hour,add 15 ml of potassium iodide solution(10 % w/w) and 100 ml distilled water and then the excess, unreacted iodine is measured by titrating with sodium thiosulphate solution using starch indictor.A blank test is carried out in the same way.The iodine value is measured by the equation

$$\mathbf{IV = \frac{12.69 \times (B\text{-}S) \times N}{W}}$$

Where W- weight of sample,N-Normality of Sodium thiosulphate,B-volume in ml of sodium thiosulphate for blank and S- volume in ml of sodium thiosulphate for sample

- **Peroxide Value**:Accurately weigh about 5 grams of oil into glass stoppered conical flask,add 30 ml of glacial acetic acid-chloroform mixture (3:2 v/v) and swirl to dissolve.Then freshly prepared saturated solution of potassium iodide(0.5 ml) is added and let stand for one minute in dark with occasional shaking.Add 30 ml distilled water and titrate against standard sodium thiosulphate solution (0.1 N) using starch indicator.The peroxide value is calculated by the equation

$$\mathbf{PV = \frac{V \times N \times 1000}{W}}$$

Where W- weight of sample,N-Normality of Sodium thiosulphate and V-volume in ml of sodium thiosulphate solution for sample.

- **Total Polar Compounds**:The TPC is measured by ATAGO Frying Oil Monitor DOM-24 instrument.The value can be read directly from the instrument at specified temperature.

- **Saponification Value**:The SV is measured by IS 548 (Part 1) 1964:Reaffirmed 2015.About 2g of oil is refluxed with a known excess of alcoholic KOH(say,25 ml) until the oil has completely saponified (usually in 30-60 minutes). The amount of KOH consumed can be determined by titrating the excess KOH with standard HCl (0.5 N) using phenolphthalein as indicator.A blank test is conducted. The saponification value is calculated by the expression

$$\mathbf{SV = \frac{56.1 \times (B\text{-}S) \times N}{W}}$$

Where W- weight of sample,N-Normality of hydrochloric acid,B-volume in ml of hydrochloric acid for blank and S- volume in ml of hydrochloric acid for sample.

- **Acid Value**:It is measured by IS 548 (Part 1) 1964:Reaffirmed 2015.A known quantity of oil(approximately 10 grams) is boiled with hot neutral ethanol for 5-10 minutes and titrate with standard NaOH(0.1 N) using phenolphthalein as indicator until pink colour persisted.The acid value is calculated by the formula

$$AV = \frac{56.1 \times V \times N}{W}$$

Where W- weight of sample,N-Normality of Sodium hydroxide and V-volume in ml of sodium hydroxide for sample.

- **Qualitative tests** for the presence of adulterants such as mineral oil (TLC method), argemone oil(Paper Chromatography Method), sesame oil (Baudouin test),cotton seed oil (Halphen test) and added colouring matter are also conducted as described in IS 548 (Part-2) 1976:reaffirmed 2010 method.

III. RESULTS

The pure sunflower oil was analysed for all quality parameters and the results are tabulated in Table-1.The reference values under Food Safety and Standards (Food Products Standards and Food Additives) Regulation,2011 are also given for comparison.

Sl No.	Quality Parameter	Result Obtained	Referenece Values under FSS Regulation
1	Refractive Index at 40 ^{0}C	1.46579	1.4640-1.4691
2	BRR at 40 ^{0}C	59.8	57.1-65.0
3	Total Polar Compounds	9.0	Not more than 25
4	Specific gravity	0.9121	-----
5	Acid Value	0.18	Not more than 6.0 Not more than 0.5(for refined oil)
6	Saponification Value	189.13	188-194
7	Iodine Value	115.85	100-145
8	Peroxide Value	0.41	---
9	Test for Mineral Oil	Negative	Shall be Negative
10	Test for Argemone Oil	Negative	Shall be Negative
11	Baudouin Test	Negative	Shall be Negative
12	Halphen Test	Negative	Shall be Negative
13	Added Colouring Matter	Absent	Shall be Absent

Table 1

All the six fried oils were analysed for all the above quality parameters,the results are tabulated in Table-2.

Sl No	Quality Parameter	Result for Fried Oil-1	Result for Fried Oil-2	Result for Fried Oil-3	Result for Fried Oil-4	Result for Fried Oil-5	Result for Fried Oil-6
1	Refractive Index at 40 ^{0}C	1.46676	1.46701	1.46709	1.46716	1.46727	1.46752
2	BRR at 40^{0}C	61.4	61.7	61.8	62.0	62.2	62.5
3	Total Polar Compounds,%	9.5	10.0	10.5	11.5	12.5	14.5
4	Specific Gravity	0.9168	0.9171	0.9185	0.9193	0.9205	0.9219
5	Acid Value	0.18	0.26	0.39	0.45	0.58	0.71
6	Saponification Value	190.84	207.35	234.98	253.52	278.76	300.42
7	Iodine Value	108.38	97.97	88.15	76.04	70.96	64.69
8	Peroxide Value	3.73	4.01	4.60	5.58	6.16	6.57
9	Test Foe Mineral Oil	Negative	Negative	Negative	Negative	Negative	Negative
10	Test for Argemone Oil	Negative	Negative	Negative	Negative	Negative	Negative
11	Baudouin Test	Negative	Negative	Negative	Negative	Negative	Negative
12	Halphen Test	Negative	Negative	Negative	Negative	Negative	Negative
13	Added Colouring Matter	Absent	Absent	Absent	Absent	Absent	Absent

Table 2

The pure sunflower oil and all fried oils were analysed for fatty acid profile by Gas Chromatography.The fatty acid composition is given in Table-3.

Sl No	Fatty Acid	Pure Sunflower Oil	Fried Oil-1	Fried Oil-2	Fried Oil-3	Fried Oil-4	Fried Oil-5	Fried Oil-6
1	Palmitic acid (C16:0)	6.69 %	6.80 %	6.89 %	6.91 %	6.95 %	6.98 %	7.03 %
2	Stearic acid (C18:0)	3.38 %	3.41 %	3.46 %	3.50 %	3.52 %	3.56 %	3.59 %
3	Elaidic acid (C18:1) **trans**	----	----	---	-----	----	----	-----
4	Oleic acid (C18:1)	26.92 %		32.38		32.53		32.21
5	Linolelaidic acid (C18:2) **trans**	----	-----	----	-----	-----	0.09 %	0.20 %
6	Linoleic acid (C18:2)	60.71 %	58.07 %	57.16 %	56.93 %	56.68 %	56.24 %	55.79 %
7	Arachidic acid (C20:0)	0.32 %	0	0	0	0	0	0.30 %
8	Behenic acid (C22:0)	0.79 %	0	0	0	0	0	0.73 %
9	Lignoceric acid (C24:0)	0.26 %	0	0	0	0	0	0
10	Cis-5,8,11,14,17-Eicosapentaenoic acid (C20:5)	0	0	0	0	0	0	0.25 %

Table 3

IV. DISCUSSION

The result of physio-chemical analysis tabulated in Table-2 is discussed below.

- **RI and BRR** : There was a significance increase in RI and BRR with increments in the number of frying.This is attributed to increase in opaqueness of oil,increase in viscosity due to polymerization and production of high levels of non-volatile decomposition products,which accumulate in oil,leading to darkening of oil.

- **Specific gravity** : The SG increases with increase in number of frying.This is probably because oxidation and polymerization make the oil more and more dense resulting in increase in specific gravity;but it is insignificant.

- **Acid value :** The AV increases progressively with increase in number of frying.Oil is a triglyceride,composed of three molecules of fatty acids joined to one molecule of glycerol.When oil is heated with moist food, it gets hydrolysed to free fatty acids and glycerol; thus increases acidity and free fatty acids.The re-heating of oil produces toxic by-products such as trans fatty acids, aldehydes, polymerized and oxidized lipids which have health impacts.The trans fatty acid formation begins with fifth frying oil.

- **Saponification value** : It increases with increses in number of frying. The SV is inversely proportional to average chain length of fatty acids and hence gives an idea about the average molecular weight of fatty acids.Very high saponification number implies preponderance of fatty acids with very short chains (very low molecular weights). Repeated heating of oil may cause breakdown of long chain fatty acids into short chain fatty acids,thereby increases the saponification value.

- **Iodine value** : It decreases with increase in number of frying.The sunflower oil is rich in linoleic acid,a poly unsaturated fatty acid. During frying process,the double bonds in the acid get destroyed by oxidation and polymerization.This decreases the degree of unsaturation causing decreased iodine value.

- **Total polar compounds**: It increases with increase in the number of frying.Heating may cause hydrolysis of triglycerides into free fatty acids,glycerol , monoglycerides and diglycerides.The presence of diglycerides and other by-products increase the percentage of total polar compounds.As a basis for the assessment of end point of frying oil,a regulatory limit of 25 % of TPC is followed.

- **Peroxide Value**: It is an index to measure the level of peroxide and hydroperoxide,the primary oxidized product of fat and oil.It increase with increase in number of frying.The presence of moisture and reheating increases the rate of peroxidation of poly unsaturated fatty acids, thereby increasing the peroxide value.The fact is supported by decrease in the percentage of linoleic acid on heating(see Table-3).

Fatty acid profile : Interpretation of Fatty acid profile determined by FAME analysis using GC-FID given in Table-3.

The saturated fatty acids in sunflower oil are stearic acid (C18:0) , palmitic acid (C16:0) , arachidic acid (C20:0) ,behenic acid (C22:0) and lignoceric acid (C24:0) ; the stearic acid and palmitic acid are the major saturated acids while others are in insignificant quantities.The percentage of both the major acids increases with increase in number of frying.The sunflower oil is rich in linoleic acid(C18:2),a poly unsaturated fatty acid.It is well known that unsaturated fatty acids are more susceptible than saturated ones to oxygen attack during thermal oxidation.This results in higher levels of saturated fatty acids.Hydrolysis and polymerization also cause an increase in saturated fatty acid contents.

The unsaturated fatty acids present in sunflower oil are oleic acid (C18:1) ,linoleic acid (C18:2) ,with linoleic acid forms the major component.The percentage of monounsaturated fatty acid , oleic acid , increases and that of polyunsaturated fatty acid,linoleic acid, decreases with increase in number of frying.The unsaturated fatty acids are more susceptible to thermal oxidation,hydrolysis and polymerization than saturated acids.This decreases the content of both oleic and linoleic acids.However,increase in the percentage of oleic acid is probably because some linoleic acid get partially saturated to form oleic acid during the frying process.

The continuous heating also cause configurational changes in fatty acids.Consequently,the fifth and sixth frying process produce trans fatty acid in sunflower oil.A samall quantity of linoleic acid configures to linolelaidic acid,its trans isomer.The trans fat raises LDL (bad) cholesterol and lowers HDL (good) cholesterol,resulting in building up of cholesterol in our arteries (blood vessels).This increases the risk for heart disease and stroke.Eating too much trans fat cause weight gain and increase the risk for type-2 diabetes.

The Food Safety and Standards (Food Products Standards and Food Additives) regulation,2011 does not permit the presence of trans fat in edible oils.

V. CONCLUSION

The present study reveals that the refractive index,acid value,free fatty acids,saponification value,peroxide value,total polar compounds and percentage of saturated fatty acids (especially stearic acid and palmitic acid) and mono unsaturated fatty acid (oleic acid) increased significantly with increase in the number of frying whereas iodine value and percentage of poly unsaturated acid (linoleic acid) decreases significantly with the increments in the number of frying of sunflower oil. Eventhough the frying adds a desirable texture to the food and provides a satisfactory eating quality,the danger of the presence of trans fat persists.The percentage of trans fat gradually increases with number of frying;hence it is advisable to avoid the frequent and continuous use of fried oils and fried food products for having a healthy life.

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