Frying Stability of Sunflower Oil and Palmolein Oil

Abhilash Babu G

Junior Research Officer, Government Analysts Laboratory, Trivandrum – 35, Kerala, India

Abstract: ***Deep-fat frying at high temperature under normal pressure is one of the oldest, simplest and fastest methods of preparing dishes in Indian culinary practice. Fried foods have desirable flavor, color, and crispy texture, which make them verypopulartothe consumers. The most common fried snack products include potato chips, banana chips, vadas, samosas etc. The frying process is also applied to meat and fish. This work was intended to evaluate the quality attributes of two common edible vegetable oils viz., sunflower oil and palmolein oil during the frying process. The frying was applied to sliced potatoes. The samples were subjected to frying for eight minutes. The product is removed, oil is cooled and a portion is taken for analysis. The process is repeated with remaining portion of oil and a total of six times the frying is conducted. The process is conducted separately with each oil. The physio-chemical properties such as refractive index, specific gravity, acid value, saponification value, iodine value, peroxide value and total polar compounds were analysed before and after frying process. All these parameters have significant changes during the frying process. A comparison of these physio-chemical properties between sunflower oil and palmolein is also made.***

Keywords: Deep-frying, RI, AV, IV, TPC, fatty acid, peroxide value

Abbreviations: RI-Refrativeindex, 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

1. Introduction

The edible fats and oils are used for frying different foods .The fried foods 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. 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.Moisture from food starts to form steam which gets evaporated with a bubbling action that gradually subsides as the food becomes cooked. 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.

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 dienoicacids. 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.

In this work, the following physical and chemical characteristics of two most common edible oils viz., sunflower and palmolein oil are analysed separately before and after frying and are compared.

2. Materials & Methods

2.1 Materials

***Study Setting*:** The sunflower oil, palmolein oil and potatoes used in this study were purchased from local market and analysed in Government Analysts Laboratory.

***Sample Preparation*:** The potatoes were peeled, washed and then sliced into thin pieces, as done for French frying. Exactly 500 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. The same frying procedure is repeated with palmolein oil.

Apparatus and Reagents

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

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.

2.2 Methods

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

Refractive Index: The refractive index (RI) was measured by using the instrument **ATAGO RX-5000i** Refractometer by IS 548 (Part-1) 1964: Reaffirmed 2015 method. The instrument was cleaned with rectified spirit, calibrated with distilled water, again cleaned with rectified spirit and then dried. A drop of oil was put into the sampling part of instrument and wait for the temperature to reach 40^0C.Then the direct reading of RI was recorded for each oil sample. The corresponding Butyro Refractometer Reading (BRR) was obtained from the conversion table given in the IS 548 (Part-1) 1964: Reaffirmed 2015 method.

Specific gravity: It is measured by pycnometer method.

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.

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 gets completely saponified (equation-4). The unreacted KOH is back titrated with standardized HCL (0.5 normal), using phenolphthalein as indicator. A blank test is conducted. The saponification value is calculated by the expression

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

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.

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, dissolved in carbon tetrachloride, is reacted with known excess of Wij's solution (25 ml) and kept in dark for half an hour. Halogen addition to double bond take place. Add 15 ml of potassium iodide solution (10 % w/w) and 100 ml distilled water. The KI reduces excess ICl to free iodine and the liberated iodine is then titrated with sodium thiosulphate solution using starch indictor. A blank test is carried out in the same way.

The iodine value is calculated by the equation

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

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: The peroxide value (PV) of oil was determined by IS 548 (Part-1) 1964: Reaffirmed 2015 method. 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. Conduct a blank. The peroxide value is calculated by the equation

$$PV = \frac{(S\text{-}B) \times N \times 1000}{W} \text{ milli-equivalents / 1000 g}$$

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

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.

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.

3. Results & Discussion

The analytical values of different physio-chemical characteristics of refined sunflower and refined palmoleinoils before deep-frying are given in table-1. The values are in agreement with the range prescribed in the Food Safety and Standards (Food Products Standards and Food Additives) Regulations 2011, the mandatory regulation for domestic and imported foods, issued by Food Safety and Standards Authority of India (FSSAI).The prescribed limits under FSS Regulation is given in table-2 as a reference.

Table 1

S No	Parameters	Refined Sunflower Oil	Refined Palmolein Oil
1	Refractive Index	1.46579	1.45863
2	Butyro Refractometer Reading	59.8	48.9
3	Specific Gravity	0.9121	0.9097
4	Acid Value	0.18	0.12
5	Saponification Value	189.13	196.33
6	Iodine Value	115.85	56.74
7	Peroxide Value	0.41	
8	Total Polar Compounds	9.0	8.5
9	Baudouin Test	Negative	Negative
10	Halphen Test	Negative	Negative
11	Test for Mineral Oil	Negative	Negative
12	Added Colouring Matter	Absent	Absent

Table 2

S No	Parameters	Refined Sunflower Oil	Refined Palmolein Oil
1	Refractive Index	1.4640-1.4691	1.4550-1.4610
2	Butyro Refractometer Reading	57.1 – 65.0	43.7 – 52.5
3	Specific Gravity	-------	-------
4	Acid Value	Not more than 6.0 Not more than 0.5(refined)	Not more than 6.0 Not more than 0.5(refined)
5	Saponification Value	188 - 194	195 - 205
6	Iodine Value	100 - 145	54 - 62
7	Peroxide Value	-----------	-----------
8	Total Polar Compounds	-----------	-----------
9	Baudouin Test	Shall be negative	Shall be negative
10	Halphen Test	Shall be negative	Shall be negative
11	Test for Mineral Oil	Shall be negative	Shall be negative
12	Added Colouring Matter	Shall be negative	Shall be negative

The fatty acid compositional analysis indicates that sunflower oil contains more unsaturated fatty acids (14.0 to 39.4 % oleic acid and 48.3 to 74.0 % linoleic acid) than palmolein oil (39.8 to 47.0 % of oleic acid and 10.0 to 13.5 % linoleic acid).Hence, the refractive index, specific gravity and iodine values of sunflower oil is higher than palmoleinoil.The high aponification value of palmoleinthan sunflower oil may be due to higher proportions of short chain fatty acids in palmolein(palmolein oil-lauric acid 0.1 to 0.5 %, myristc acid 0.5 to 1.5 %, palmitic acid 38.0 to 43.5 %, stearic acid 3.5 to 5.4 %) (sunflower oil-lauric acid and myristic acid ND to 0.3 % each, palmitic acid 4.0 to 8.0 % an stearic acid 1.0 to 7.0 %)

Effect of Deep-Frying on Refractive Index

The statistical data regarding the Refractive Index of oils has been presented in Table – 3 and the corresponding BRR values in Table-4.

Table 3

S No	Nature of Oil	RI of Sunflower Oil	RI of Palmolein Oil
1	Pure Oil	1.46579	1.45863
2	Fried Oil-1	1.46676	1.45896
3	Fried Oil-2	1.46701	1.45901
4	Fried Oil-3	1.46709	1.45913
5	Fried Oil-4	1.46716	1.45927
6	Fried Oil-5	1.46727	1.45938
7	Fried Oil-6	1.46752	1.45989

Table 4

S No	Nature of Oil	BRR of Sunflower Oil	BRR of Palmolein Oil
1	Pure Oil	59.8	48.9
2	Fried Oil-1	61.4	49.5
3	Fried Oil-2	61.7	49.5
4	Fried Oil-3	61.8	49.7
5	Fried Oil-4	62.0	50.0
6	Fried Oil-5	62.2	50.1
7	Fried Oil-6	62.5	50.8

The results show that, there was a significant 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 (NVDP), which accumulate in oil, leading to darkening of oil.

The sunflower oil is more unsaturated and is more prone to oxidation than palmolein oil. Understandably, the fat oxidation tendency decreases from sunflower oil to palmoleinoil. This indicates that more increase in RI was observed for sunflower oil than palmolein oil. A similar trend exist for BRR values.

Effect of Deep-Frying on Specific Gravity

The statistical data regarding the specific gravity of oils is presented in Table-5.

Table 5

S No	Nature of Oil	SG of Sunflower Oil	SG of Palmolein Oil
1	Pure Oil	0.9121	0.9097
2	Fried Oil-1	0.9168	0.9131
3	Fried Oil-2	0.9171	0.9142
4	Fried Oil-3	0.9185	0.9150
5	Fried Oil-4	0.9193	0.9156
6	Fried Oil-5	0.9205	0.9167
7	Fried Oil-6	0.9219	0.9178

The data reveals that the specific gravity increases progressively with number of frying. The palmolein oil remains more stable with respect to specific gravity than sunflower oil in food frying. This may be due to higher level of saturation and monounsaturation in palmolein oil as compared to sunflower oil. Moreover, the variation further reveals that the more the poly unsaturation in oil, the more will be increase in specific gravity.

Effect of Deep-Frying on Acid Value

The acid value of an oil, fat, or wax is a measure of the free fatty acidity, and represents the number of milligrams of potassium hydroxide required to neutralise the free fatty acids in 1 gram of the substance. The statistical data regarding the acid value of oils is presented in Table-6.

Table 6

S No	Nature of Oil	AV of Sunflower Oil	AV of Palmolein Oil
1	Pure Oil	0.18	0.12
2	Fried Oil-1	0.18	0.14
3	Fried Oil-2	0.26	0.21
4	Fried Oil-3	0.39	0.32
5	Fried Oil-4	0.45	0.40
6	Fried Oil-5	0.58	0.48
7	Fried Oil-6	0.71	0.54

The data reveals that there was a significant increase in acid value with number of frying irrespective of the nature of oil.The initial acid value of sunflower and palmolein oils are comparatively much less ;because both are refined oils and refining reduces free fatty acids.

Oil is a triglyceride, an ester composed of three molecules of fatty acids joined to one molecule of glycerol. When oil is heated with moist food, it gets hydrolyzed to free fatty acids and glycerol. Thus hydrolysis (lipolysis) increases free fatty acid and acid value.

Hydrolysis is more preferable in oil with short and unsaturated fatty acids than oil with long and saturated fatty acids because short and unsaturated fatty acids are more soluble in water than long and saturated fatty acids. Water from foods is easily accessible to short-chain fats and oils for hydrolysis(Nawar1969).Since both acids contain negligible proportions of short chain fatty acids; palmolein has higher levels of saturation and mono unsaturation while sunflower oil has higher level of poly unsaturation.The more the poly unsaturation in oil, the more will be increase in acid value. As a result, the rate of formation of free fatty acids for refined sunflower oil was higher which increases from 0.18 to 0.71 compare to refined palmolein oil which was from 0.12 to 0.54.

The development of high levels of free fatty acids during frying is usually associated with decrease in smoke point and surface tension of the oil and a reduction in quality of fried foods. Furthermore, free fatty acids are more susceptible to oxidation than are the fatty acids esterified to glycerol.

Effect of Deep-Frying on Saponification Value

The saponification number is defined as the number of milligrams of potassium hydroxide required to saponify 1g of fat. Very high saponification number implies preponderance of fatty acids with very short chains (very low molecular weights). The statistical data regarding the saponification value is given in Table-7.

Table 7

S No	Nature of Oil	SV of Sunflower Oil	SV of Palmolein Oil
1	Pure Oil	189.13	196.33
2	Fried Oil-1	190.84	214.02
3	Fried Oil-2	207.35	226.84
4	Fried Oil-3	234.98	235.30
5	Fried Oil-4	253.52	244.52
6	Fried Oil-5	278.76	256.60
7	Fried Oil-6	300.42	268.77

The saponification value increases with increase 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.

Since sunflower oil contains more proportions of long chain fatty acids than palmoleinoil, the increase in saponification value is more in case of sunflower than palmolein oil.

Effect of Deep-Frying on Peroxide Value

It is an index to measure the level of peroxide and hydroperoxide, the primary oxidized product of fat and oil. The statistical data regarding the peroxide value is given in table -8

Table 8

S No	Nature of Oil	PV of Sunflower Oil	PV of Palmolein Oil
1	Pure Oil	0.41	Nil
2	Fried Oil-1	3.73	1.82
3	Fried Oil-2	4.01	2.13
4	Fried Oil-3	4.60	3.05
5	Fried Oil-4	5.58	4.22
6	Fried Oil-5	6.16	4.87
7	Fried Oil-6	6.57	5.46

The peroxide value increase with increase in number of frying. The presence of moisture and reheating increases the rate of peroxidation of fatty acids, thereby increasing the peroxide value.

The presence of higher levels of saturated fatty acids and monounsaturated fatty acids make oils more resistant towards oxidation at elevated temperatures during deep frying and more polyunsaturated fatty acids are rapidly oxidised. The more increase in PV for sunflower oil is due to the presence of considerable amounts of polyunsaturated fatty acids, which get readily oxidised to form peroxides.

Effect of Deep Frying on Iodine Value

The degree of unsaturation of the fatty acids in a fat or oil can be quantitatively expressed by the Iodine Value of the fat. Iodine value refers to the number of grams of iodine absorbed by 100 g of fat. Since the iodine reacts at the sites of unsaturation much as would hydrogen in hydrogenation, the higher the iodine value the greater the degree of unsaturation in the fat.

The statistical data regarding the iodine value is given in Table-9

Table 9

S No	Nature of Oil	IV of Sunflower Oil	IV of Palmolein Oil
1	Pure Oil	115.85	56.74
2	Fried Oil-1	108.38	53.56
3	Fried Oil-2	97.97	48.11
4	Fried Oil-3	88.15	43.96
5	Fried Oil-4	76.04	39.80
6	Fried Oil-5	70.96	36.43
7	Fried Oil-6	64.69	32.89

The iodine value decreased significantly with increase in number of frying. This is probably because the double bonds in unsaturated fatty acids get destroyed by oxidation and polymerization. This decreases the degree of unsaturation causing decreased iodine value.

Sunflower oil showed more decrease in iodine value because of more unsaturation.

Effect of Deep Frying on Total Polar Compounds

The statistical data regarding the total polar compounds of different oils are given in table-10.

Table 10

S No	Nature of Oil	TPC of Sunflower Oil	TPC of Palmolein Oil
1	Pure Oil	9.0	8.5
2	Fried Oil-1	9.5	9.0
3	Fried Oil-2	10.0	9.5
4	Fried Oil-3	10.5	10.0
5	Fried Oil-4	11.5	10.5
6	Fried Oil-5	12.5	11.0
7	Fried Oil-6	14.5	12.0

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. In India, a regulatory limit of 25% of TPC is used as a basis for the assessment of end point of frying oil. The TPC remained under this limit during deep-frying of food even after 6th frying in the present study.

The oils deteriorated faster at frying temperatures through the formation of polar compounds and generally oils with higher levels of unsaturated fatty acids produced more polar compounds compared to more saturated ones.Sunflower oil showed more increase in TPC because of more unsaturation.

4. Conclusion

Both sunflower oil and palmolein showed decreasing oxidative stability after frying process. Sunflower oil showed higher increment in refractive index, acid value, saponification value and peroxide value compared to palmolein. Decrease in IV for sunflower oil was found greater than palmolein due to its high degree of unsaturation compared to palmolein leading to increased rate of oxidation and break down of double bonds in fatty acid during frying. In conclusion, palmolein shows better stability than the sunflower oil in deep frying of potato chips.

References

[1] Essentials of Food Science 3rd Edition by Vickie. A. Vaclavik and Elizabeth W. Christian

[2] Food Chemistry 4th revised and extended edition by H.-D. Belitz · W. Grosch · P. Schieberle

[3] Blumenthal MM. 1991. A new look at the chemistry and physics of deep-fat frying. Food Technol45(2):68–71, 94.

[4] Boskou D. 1988. Stability of frying oils. In: Varela G, Bender AE, Morton ID, editors. Frying of food: principles, changes, new approaches. New York: VCH Publishers. P174–82.

[5] Chloe, E. and Min, D.B. (2007). Chemistry of Deep - Fat Frying Oils. Journal of Food Science.72:77-82

[6] Tyagi, V. K. and Vasishtha, A. K. (1996). Changes in the characteristics and Composition of oil During Deep- fat frying. Journal. American.

[7] Abhilash Babu.G (2020) Effect of Deep-Frying on Physio-Chemical Characteristics of Sunflower Oil. Journal IJISRT volume-5, issue-2, February 2020.

[8] Food Safety and Standards(Food products Standards and Food Additives) Regulation, 2011

[9] IS 548 (Part-1) - 1964:Reaffirmed 2015

[10] IS 548 (Part-2) – 1976: reaffirmed 2010