

Assessment of Quality of Some Edible Cooking Oils before and after Frying Sold in Local Market

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Abstract— Chemical reactions like oxidation and hydrolysis occur when oil is heated repeatedly due to thermal decomposition. During frying, oil or fat is exposed to heat. Therefore, thermal, oxidative, and hydrolytic decomposition of the oil may occur. Fats and oils are oxidized to form hydro peroxides, the primary oxidation products. These peroxides are extremely unstable and decompose and formation of chemical products, such as alcohols, aldehydes, ketones, acids, dimers, trimers, polymers, and cyclic compounds. In this research There are five types of vegetable oils before and after frying were analysed using standard procedures, the physicochemical properties such as saponification, acid, peroxide, ester value, specific gravity viscosity and P-anisidine values were investigated. saponification and ester values were ranged between 170.22-191.44 and 167.89-192.02 mg KOH/g oil in fresh oils respectively and between 191.26-205.28 and 184-205mg KOH/g oil in frying oils respectively. Acid values were ranged between 0.33-2.23 in fresh oils and 0.88-7.76 mg KOH/g of groundnut, cottonseed, mustard, soyabean and sunflower oil samples specific gravity and viscosity values were ranged between 0.9071-0.9084 in fresh oils, 0.9902-0.9987 after frying and 34-39 in fresh and 96-132 in frying oils respectively. In case of P-anisidine values it is in the range of 1.02-1.92 in fresh oils while 2.11-3.15Meq/kg in frying oils respectively. Furthermore, Acid and Peroxide values ranged from 0.33-7.76 and from 9.25-20.24Meq/kg in frying oils were exceeding in the range of the permitted value of 5 mg/KOHg and 10 meq/Kg. The percentage increase in acid value in after frying are in the range between 43.18-71.26 while in case of peroxide value, it increases after frying is 29.51-53.31%.

Keywords: Edible Cooking Oils, Frying, Specific Gravity, Viscosity, PV and P-Anisidine Values

I. INTRODUCTION

Fats and oils are parts of normal daily consumptions. As a major source of energy, fats and oils are considered as important nutrients in human diets. The edible oils are used in cooking as well as in traditional medicine for the treatment of colds, coughs, bronchitis, edema and burns, also play an important role in the body as carriers of essential fatty acids which are not synthesized in the body but are needed through the diet to maintain the integrity of cell membranes. They are also needed for the synthesis of prostaglandins which have many vital functions to perform in the body [1-2]. Vegetable oils are beneficial and popular due to their cholesterol-lowering effect. In contrast to animal fats, which are predominantly saturated and hence do not react readily with other chemicals, especially oxygen, unsaturated vegetable oils are more reactive. Vegetable oils are essential in global nutrition depending on the regional

conditions, a variety of oils are produced in different qualities [1-3].

II. LITERATURE REVIEW

Oils are very rich source of energy. When oils are exposed to high temperatures the omega 3 fatty acids are affected and therefore damage the oils. Deep frying is the most common and one of the oldest methods of food preparation worldwide. It involves heat and mass transfer. To reduce the expenses, the oils tend to be used repeatedly for frying. When heated repeatedly, changes in physical appearance of the oil will occur such as increased viscosity and darkening in colour, which may alter the fatty acid composition of the oil. Heating causes the oil to undergo a series of chemical reactions like oxidation, hydrolysis and polymerization. During this process, many oxidative products such as hydroperoxide and aldehydes are produced, which can be absorbed into the fried food [4]. Chronic consumption of repeatedly heated vegetable oils could be detrimental to health. It was shown to demonstrate genotoxic and preneoplastic change in the rat liver [5]. It also impaired fluid and glucose intestinal absorption in rats [6]. In rats given alcohol plus heated sunflower, an apparent liver damage as well as increased cholesterol level was observed and found an independent positive association between the risk of hypertension and intake of heated cooking oil. These accumulating data suggest chronic intake of heated cooking oils increases the risk of cancer and cardiovascular diseases [7-8].

Atmospheric oxygen reacts instantly with lipid and other organic compounds of the oil to cause structural degradation in the oil which leads to loss of quality of food and is harmful to human health [9]. During frying, due to hydrolysis, oxidation and polymerization processes the composition of oil changes which in turn changes the flavor and stability of its compounds [10].

As deep fat frying is normally carried out at high temperatures (between 150°C and 190°C) and in the presence of air and moisture, these frying oils and fats will undergo physical and chemical deterioration which will affect their frying performance and the storage stability of the fried products [11]. During deep-frying, the fat and oil decompose forming volatile, non-volatile, monomeric and polymeric, oxidised or non-oxidised compounds [12]. These products are formed as a result of oxidation of unsaturated fatty acids. The intensity of these reactions depends on duration, method of heat treatment, frying medium and type of product [13].

Deep frying is one of the most common methods used for the preparation of food. Repeated frying causes several oxidative and thermal reactions which results in change in the physicochemical, nutritional and sensory properties of the oil [14].

Deep-fat frying is the process of cooking by completely immersing foods in hot oil. It is a simultaneous heat and mass transfer process. Frying oils are usually maintained at elevated temperatures ranging from 150 to 200 °C. The hot oil serves as a medium of heat transfer into the food, while the moisture migrates out and the oil is absorbed [15]. Frying causes complex physicochemical reactions such as starch gelatinization, protein denaturation, browning, crust formation, textural and flavor changes. These depend on either the frying process itself or the nature of the food or type of frying oil [16]. Atmospheric deep-fat frying is usually practiced. At high frying temperatures and in the presence of oxygen, thermo-oxidation and breakdown occur especially if the oil is polyunsaturated. These reactions lead to the formation of volatile and non-volatile oxidative compounds that affect the quality of frying oil and fried products. Foaming also occurs when products with high initial moisture content are fried. Repeated and continuous use of frying oils produces undesirable compounds that may compromise the quality of the food and pose a potential risk to human health and nutrition [17]. The popularity of fried foods has at no time been reported to decrease. This is certainly due to the smooth mouthfeel, distinct flavor, palatability, and aesthetic appeal of fried foods.

During deep frying different reactions depend on some factors such as replenishment of fresh oil, frying condition, original quality of frying oil and decrease in their oxidative stability [18].

Thermal deterioration of fats and oils due to oxidation, cyclization, polymerization and hydrolysis occurs during heat cooking, although pan- and deep-frying process impart the desirable flavor and taste to foods. Various low- and/or high-molecular weight chemicals are formed during heat cooking. Particularly, by-products harmful to human health, such as hydro peroxides and polymers are formed during frying, which reduce the nutritional value of fats and oils. Moreover, some volatile low-molecular weight compounds with functional groups aldehydes, ketones and alcohols may impart undesirable flavor. Fats and oils in oil foods are also susceptible to auto- and photo-oxidation reactions during storage, and the products may lead to undesirable flavor and taste. Thus, it is very important to evaluate the degree of deterioration in fats and oils during heat cooking and storage to ensure and maintain the quality of the food products. Some internationally known standard methods are used to evaluate the quality of edible fats and oils such as the AOCS official methods, IUPAC standard methods and Standard Methods for Analysis of Fats, Oils and Related Materials published by Japan Oil Chemists Society named as the JOCS standard methods [19-21].

Fried oil changes in the stability of the taste or quality of the oil by hydrolysis, oxidation, and polymerization. Tocopherols, essential amino acids, and fatty acids in the diet degraded during frying. Changes frying oil depends on factors like the freshness of the oil, frying conditions, the original quality of cooking oil, fried foods, types of frying, antioxidants, oxygen concentration. Frying temperature is high, the amount of fried oil, free fatty acids, polyvalent metal, and unsaturated fatty acids decrease the stability of the oil due to oxidation and the taste quality

of the oil. Frying oil with high temperatures can degrade the effectiveness of antioxidants.[1]

Several chemical reactions such as hydrolysis, oxidation, polymerization, fission and isomerization take place, during frying. The presence of oxygen, moisture, trace elements and free radicals at the high temperatures used in frying accelerate the breakdown process. These reactions change the oil from a medium that is almost pure triacylglycerol when fresh to one that contains literally thousands of different degradation compounds. These can compromise the texture, taste, flavor, and the overall perception of the fried product. Additionally, potential risk to human health and nutrition may arise [22]. Oils with higher amounts of PUFA are not stable to oxidation and the products fried using such oils have shorter shelf-life. PUFA oils quickly break down at frying temperatures to form gums. Some physical changes such as increased viscosity and foaming, color changes and decreased smoke-point, also occur. Also, a vast number of volatile compounds are formed during the frying process, depending on the nature of the oil used and the frying conditions employed. The volatiles cover different classes of compounds, like alkanes, alkenes, alcohols, saturated and unsaturated aldehydes/ ketones, and short chain fatty acids. These compounds are responsible for the distinctive pleasant odor and the unpleasant flavor of abused frying oil and can be used as markers of frying oil quality [23-25].

Therefore, it is essential to monitor the quality of oil to avoid the use of abused oil due to the health consequences of consuming foods fried in degraded oil, to maintain the quality of fried foods and to minimize the production costs associated with early disposal of the frying medium [26].

Total FFA depends on the amount of water introduced into the frying medium by the food, the food composition, the frying temperature, the oil turnover time, and the accumulation of burnt food particles. Thus, heated and unheated oils must be monitored by means of analysis. However; FFA only reflects hydrolytic changes, comprising only part of the complex degradation process that occurs during frying. FFA levels in frying oil increase with the number of frying cycles and are therefore used to monitor the quality of the frying oil[27,28]. The peroxide value is used to determine the level of oil damage. The peroxide value standard for vegetable oils that do not undergo rancidity should be well below 10 meq/kg. Saponification value is a rough index of the molecular weight of the fat or oil. The smaller the saponification value higher molecular weight. It also shows the magnitude of the amount of alkali required to convert the amount of fat or oil to be soap. It can be used for checking the purity of fats or oils [2].

Moreover, poly-unsaturated oils have reduced stability at elevated temperatures; unsaturated fatty acids easily react with oxygen to form peroxides [29]. Peroxide value is useful as an indicator of oxidation at the initial stages; however, it is not related to the frying duration, but to the formation and breakdown of oxidation products. Peroxides are unstable and decompose at frying temperature. They may even increase after the sample is taken from the fryer. Hence, it is generally not a very

reliable parameter to determine deterioration of frying oil quality [30,31].

The aim of present study was to evaluate the effect of frying on the chemical properties such as specific gravity (SV), viscosity (V), acid value (AV), iodine value (IV), peroxide value (PV), ester value (EV) and saponification value (SV) of some edible cooking oils were measured before and after frying and to assess whether these oils could be re-used or not.

III. MATERIALS AND METHODS

All the chemicals reagents and glassware used in this analytical work are analytical grade. Edible oil samples of groundnut, cottonseed, mustard, soyabean and sunflower oils before and after frying were purchased from some food supply markets in Jalgaon city of Maharashtra, India and home kitchen uses. In this study, cooking oil samples of different brands were subjected to controlled heating and frying in the laboratory at 180 °C to 200 °C for 6 hr. The specific gravity, viscosity, acid value, peroxide value, ester value and saponification value and P-anisidine values of edible oil before and after frying were measured according to the AOCS and AOAC [32-35]. The results are summarized in table 1.

A. Determination of Specific Gravity of the Oil at 30°C

The specific gravity of the oils are also determined by specific bottle method. The specific gravity of the oil samples was determined using a 25 ml specific gravity bottle. The specific gravity bottle was weighed empty and then filled with the oil sample up to the mark on the bottle. The bottle with oil sample was weighed again. The weight of the empty bottle was subtracted from the total weight of the bottle and oil sample. The weight of the empty bottle was divided by the total weight of the bottle and oil to obtain the weight of the oil sample. The weight of the oil sample was then divided by the weight of an equal volume of water to get the specific gravity of the oil sample. specific gravity of oil was calculated by using the following formula

$$\text{Specific gravity} = \frac{\text{Weight of bottle with sample} - \text{Weight of empty bottle}}{\text{Weight of bottle with water} - \text{Weight of empty bottle}}$$

B. Determination of viscosities

Measured Viscosity of various brands of vegetable oil before and after frying using Haake Rheowin Viscometer: flow characteristics for viscosity, Take 50ml sample of the original oil in the container set the instrument with water circulating for control of temperature thermostat as per manuals ,the viscosity determine at the 27 °C temperature. Take the reading of pure vegetable oils before and after frying which are shown in Table 1.

C. Method for Determination of Acid Value.

Each cooled oil sample was weighed (5gms) in 250mL of conical flasks and 50 mL of freshly neutralized ethyl alcohol (ethanol) was added to the samples and then shaken well to dissolve sample. The sample solution was boiled for about five minutes and cooled and then 1mL of phenolphthalein indicator was added to the sample solution. The sample solution was titrated with 0.1N sodium hydroxide solution

until permanent pink light color appeared. The acid value was estimated using the following equation:

$$\text{Acid value} = 56.1 \times V \times 100/W \quad \text{----- (1)}$$

Where W is weight of oil that equals 5 grams, V is titer value of 0.1N NaOH [4, 7].

D. Method for Determination of Saponification Value.

Known gms of each oil sample was weighed in 250mL Erlenmeyer flasks; then 25mL of alcoholic potassium hydroxide solution was added into the flasks. The blank determination was conducted along with the sample. The samples flask and the blank flask were connected with air condensers and boiled gently in the water bath, steadily until the saponification was completed, indicated by absence of oily matter and the appearance of clear solution. Clarity was achieved in half hour boiling. After the flask and the condenser cooled, inside of the condensers was washed down with about 10mL of ethanol and then 1mL of phenolphthalein indicators was added to the solution. Excess potassium hydroxide was titrated with 0.5N hydrochloric acid until cloudy solution was formed. The saponification value was estimated using the following equation:

$$\text{Saponification value} = 56.1 \times (b - a) \times N/W, \quad \text{----- (2)}$$

Where W is weight of sample that equals 2 grams, b is blank titer value, a is sample titer value, and N is 0.5 normality of HCl [32-35].

E. Method for Determination of Peroxide Value.

A known oil sample was weighed in 250mL of conical flask; then, 30mL of acetic acid and chloroform solvent mixture (3:2) was added to each oil sample and swirled to dissolve. Then, 1mL of potassium iodide solution was added to the solution. The solution was kept for 1min in dark room with occasional shaking and then 30mL of distilled water was added. Slowly, titrate liberated iodine in 0.01N sodium thiosulphate solution until vigorously shaking yellow color was gone and after that 1mL of starch solution indicator was added and we continued titration by vigorous shaking to release all I₂ from CH₃Cl layer until blue color disappeared. The peroxide value was estimated using the following equation:

$$\text{Peroxide value} = V \times N \times 100/W, \quad \text{----- (4)}$$

Where V is volume of sodium thiosulphate, N is normality used for titer and W is weight of the sample [32-35].

F. Method for determination of ester value:

The ester value is the 'mg' of KOH required to react with glycerol/ glycerin after saponify 1 g of oil sample. Ester value is calculated by the following relation

$$\text{Ester Value} = \text{Saponification Value} - \text{Acid Value}$$

G. Determination of P-Anisidine Value (p-AV):

The carbonyl content in oils was determined by standard method according to AOCS. It measures the reactivity of the aldehydes carbonyl bond on the p-anisidine amine group forming a Schiff's base which absorbs at 350 nm. 2g (W) of each soy bean and sun flower oil was dissolved in 25 ml isooctane and absorbance A₁ was measured at 350nm against a blank isooctane. An aliquot (5ml) of this solution, respectively 5 ml of isooctane (as blank) was transferred to

each of two test tubes of 10ml and 1ml anisidine solution (0.25% g/v glacial acetic acid) was added to each. After 10 minute the absorbance A2 was measured at 350nm against

isooctane containing p-anisidine. The p-AV is determined as; $p-AV = 25 \times 1.2 \times (A2-A1) / W$.

Groundnut oil				FSSAI standard	% Increase/decrease
Sr. no.	Characteristics	Before frying	After frying		
1	Saponification value, mg KOH / g oil	191.44	202.88	188-196	+5.64
2	Acid value, mg KOH / g oil	2.10	4.84	6.0	+52.48
3	Peroxide value Meq/Kg	9.27	17.32	10	+46.48
4	Ester value, (S.V - A.V) mg KOH) /g oil	191.96	203.02	-	+5.45
5	Specific gravity	0.9084	0.9987	-	-
6	Viscosity (CP)	36.0	96.0	-	-
7	P-anisidine Meq/Kg	1.82	3.15	-	-
Cottonseed oil					
1	Saponification value, mg KOH / g oil	191.18	205.28	190-198	+6.87
2	Acid value, mg KOH / g oil	0.5	0.88	0.5	+43.18
3	Peroxide value Meq/Kg	5.56	9.98	10	+44.29
4	Ester value, (S.V - A.V) mg KOH) /g oil	190.28	203.03	-	+6.28
5	Specific gravity	0.9081	0.9969	-	-
6	Viscosity (CP)	34.0	135.0	-	-
7	P-anisidine Meq/Kg	1.02	2.16	-	-
Mustard oil					
1	Saponification value, mg KOH / g oil	170.22	191.26	168-177	+11.0
2	Acid value, mg KOH / g oil	2.23	7.76	6.0	+71.26
3	Peroxide value Meq/Kg	9.45	20.24	10	+53.31
4	Ester value, (S.V - A.V) mg KOH) /g oil	167.89	184	-	+8.76
5	Specific gravity	0.9082	0.9972	-	-
6	Viscosity (CP)	36.0	132.0	-	-
7	P-anisidine Meq/Kg	1.92	2.64	-	-
Soyabean oil					
1	Saponification value, mg KOH / g oil	191.64	203.28	189-195	+5.73
2	Acid value, mg KOH / g oil	0.44	0.98	2.5	+55.10
3	Peroxide value Meq/Kg	6.52	9.25	10	+29.51
4	Ester value, (S.V - A.V) mg KOH) /g oil	192.02	203.8	-	+5.78
5	Specific gravity	0.9081	0.9980	-	-
6	Viscosity (CP)	37.4	109.3	-	-
7	P-anisidine Meq/Kg	1.22	2.11	-	-
Sunflower oil					
1	Saponification value, mg KOH / g oil	190.86	204.18	188-194	+6.52
2	Acid value, mg KOH / g oil	0.33	0.78	6.0	+57.69
3	Peroxide value Meq/Kg	5.75	11.35	10	+49.34
4	Ester value, (S.V - A.V) mg KOH) /g oil	191.19	205	-	+6.74
5	Specific gravity	0.9071	0.9902	-	-
6	Viscosity(CP)	39.0	110.0	-	-
7	P-anisidine Meq/Kg	1.62	2.15	-	-

Table 1: Chemical characteristics of different brands of cooking oil before and after frying

Sr.no	Test	Before frying	After frying	Codex Alimentarius commission standard	FSSAI standard
1	Saponification value, mg KOH / g oil	170.22-191.44 mg KOH/g	191.26-205.28 mg KOH/g	--	168-198 mg KOH/g
2	Acid value, mg KOH / g oil	0.33-2.23 mg KOH/g	0.88-7.76 mg KOH/g	5.0(0.6 mg KOH/g in case of refined oil)	0.5-6.0 mg KOH/g
3	Peroxide value Meq/Kg	5.56-9.56	9.25-20.24	10.0 MeqO ₂ /Kg	1.0-10 MeqO ₂ /Kg
4	Ester value, (S.V - A.V) mg KOH) /g oil	167.89-192.02 KOH/g	184-205 KOH/g	--	-
5	Specific gravity	0.9071-0.9084	0.9902--0.9987	0.899-0.920	--
6	Viscosity(CP)	34.0-39.0	96.0-132.0	--	--

7	P-anisidine MeqO ₂ /Kg	1.02-1.92 MeqO ₂ /Kg	2.11to3.15 MeqO ₂ /Kg	20 MeqO ₂ /Kg	20 MeqO ₂ /Kg
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Table 2: Test results before and after frying and codex standards

IV. STATISTICAL ANALYSIS:

The data obtained from the experimental measurements and accuracy of different parameters for different varieties of oils have been analysed and the physicochemical parameter like AV,IV,SV,EV, specific gravity ,viscosity and P-AV were investigated for different brands of oils before and after frying. All the experiment was carried out in triplicate and the results are presented as the % increase/decreases in mean analysed values as per FSSAI standards. Accuracy and descriptive Statistics of different oils from different parts of India as shown in figure1to5.

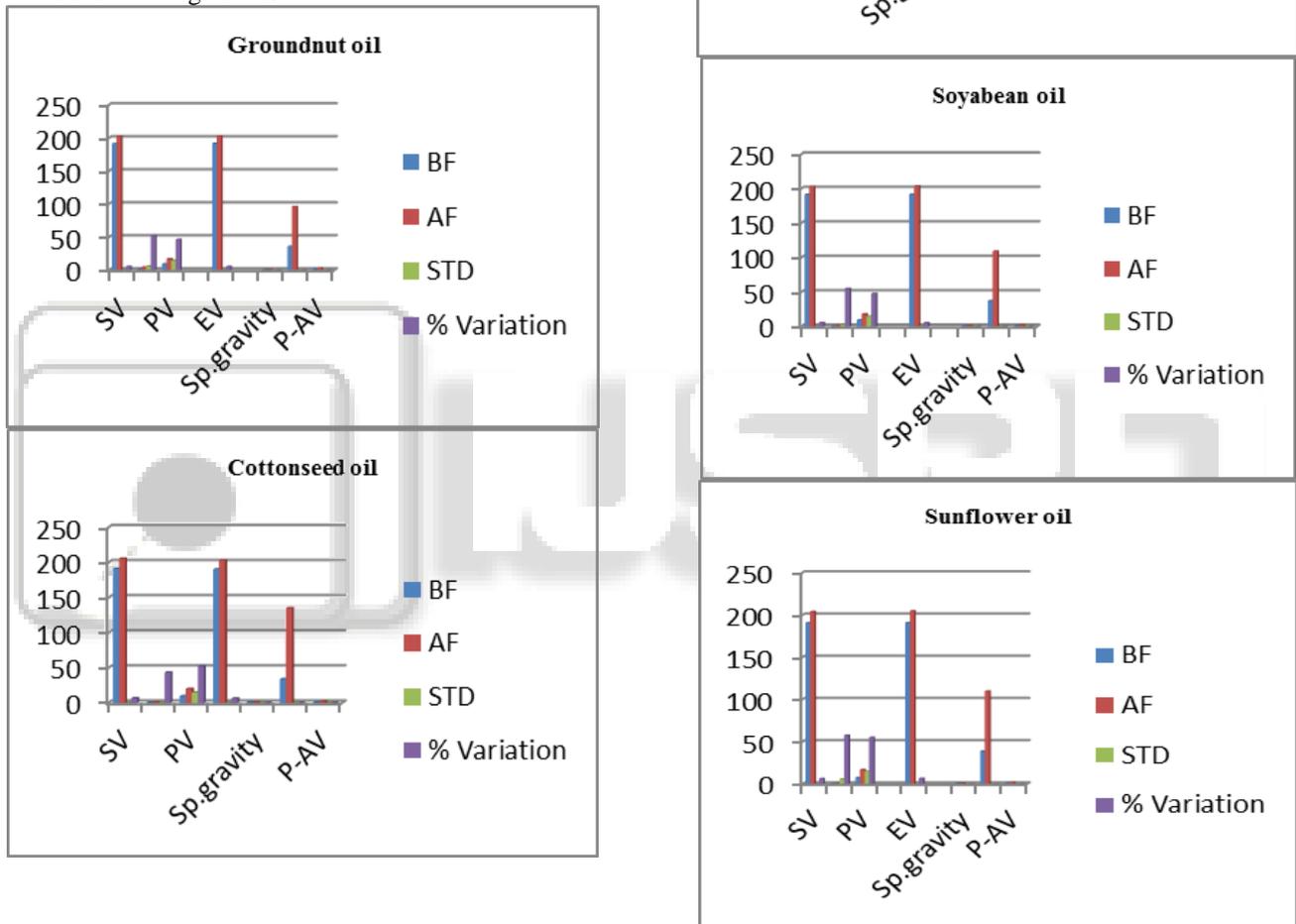


Fig 1 to 5 represents the graphical representation of AV,PV,SV, EV, Sp.gravity, viscosity and P-anisidine value and compare with standard value and % variation before and after frying.

V. RESULTS AND DISCUSSION

Some physicochemical characteristics such as saponification values, acid value, peroxide value, ester value, specific gravity viscosity and P-anisidine values of groundnut, cottonseed, mustard, soyabean oil and sunflower oils before frying and after frying have been extensively investigated. The experimental results of analysed paramters of given oils are illustrated in Tables 1-2 and graphical representation are shown in figures 1-4. It can be seen from the last tables and

figure 1 that, saponification value of groundnut, cottonseed, mustard, sunflower, and soyabean oils before and after frying were almost the same range of 170.22-205.28 in all the oils which are 191.44-202.88 in case of groundnut oil, 191.88-205.28 mg KOH/g for cottonseed oil, 170.22-191.26 for mustard, 190.86-204.18 for sun flower and 191.64-203.28 for soyabean oil. On the other hand, the acid value of groundnut, cottonseed, mustard, sunflower, and soyabean oils after frying 4.84, 0.88, 7.76, 0.98 and 0.78 respectively, had slightly higher value compared with that before frying 2.1, 0.5, 2.23, 0.44 and 0.33, also It can be noticed that the acid value of groundnut and mustard oils before and after frying had higher values 4.84 and 7.76 mg KOH/g oil compared with the remaining oils such as cottonseed oil soyabean and sunflower oils before and after frying 0.88, 0.98 and 0.78 mg/KOH/g. Generally, the slight increase of the acid value of the investigated samples may attribute to the complete inhibition of enzymes activity. The obtained data indicated that the ester values of groundnut, cottonseed, mustard, sunflower, and soyabean oils after frying had slightly higher value compared with that before frying as seen in table 1. Also, it is clear from the obtained results (Tables 1, 2 and Figure 1-5) that, peroxide values of groundnut, cottonseed, mustard, sunflower, and soyabean oils in the range of 5.56-9.56 in case of before frying while in case of after frying it is in the range of 9.25-20.24 which are 9.27-17.32 for groundnut, 9.56-19.98 for cottonseed, 9.45-20.24 for mustard, 9.52-18.25 for soyabean and in case of sunflower oil it is 7.75-17.35 Meq/Kg increased after frying respectively. The specific gravity value of respective oils are compared with that before and after frying in the range of 0.9071-0.9084 and 0.9902-0.9987. The viscosity of all the given oils which are in the range of 34-132 (cp) before and after frying. In case of P-anisidine value of all the frying oils which are in the range of 1.02-1.92 and 2.11-3.15 Meq/kg respectively, causing undesirable odor of oil sample after frying. These results might be due to the effect of high frying temperature causing destruction of some glycerides. The percentage increase in acid value in after frying are in the range between 43.18-71.26 while in case of peroxide value, it increases after frying is 29.51-53.31%.

VI. CONCLUSION

The edible oil before and after frying (groundnut, cottonseed, mustard, soyabean and sunflower oils) collected from super markets in Jalgaon city of Maharashtra, India and home kitchen use as samples in this study. The saponification values, acid value, peroxide value, and ester value, specific gravity, viscosity and P-anisidine values of given oils before and after were investigated. It is clear from the obtained results that, the acid and peroxide values of edible oil increased after frying compared with that before frying (might be due to the effect of high frying temperature causing destruction of some glycerides). All the parameter after frying are in the range of codex and FSSAI standards. It is concluded that all the oil samples are suitable for frying and cooking purposes.

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