IARJSET

ISSN (Online) 2393-8021
ISSN (Print) 2394-1588

International Advanced Research Journal in Science, Engineering and Technology
Vol. 7, Issue 8, August 2020

DOI 10.17148/IARJSET.2020.7801

Measurement of Total Polar Compounds, Acid and Peroxide Values of Repeatedly Used Frying Oils by Restaurants in Jalgaon City, Maharashtra, India

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Abstract: Reusing cooking oil is a common practice in India. Oxidation and hydrolysis occur when oil is heated repeatedly due to thermal decomposition. It had been suggested that consumption of repeatedly heated oil could be a health hazard. The increasing use of edible oils and fats for the preparation of fried products requires an increasingly strict control in order to maintain the quality and safety of the fried foods. Due to the knowledge that the frying process alters the chemical nature of the heated oil and its consumption represents health risks. In this study, the measurements were performed in daily frying operations of these restaurants and were analysed repeatedly for the relevance of results. The Total polar compounds and peroxide values of some collected frying oil samples from which daily frying main areas of cities were measured by standard procedures. The results showed that the total polar materials in the range of 12.24% to 22.12% and which are within the norms of codex standards. Peroxide values are in the range of 12.36 to 26.65 meq O2/kg which deviated from the Codex standard value of 10 meq O2/kg. Acid values are 0.78-5.98 in the range which deviates safety standards. The results showed degradation in the both the properties of the vegetable cooking oil after repetitive frying. The standard deviation for AV, PV and TMC are in the range of 0.16-0.32 while in case of standard mean error it is in the range of 0.09-0.18. These results provided the basis for choosing the proper rapid-measuring device to control the quality of frying oil in restaurants.

Keywords: Deep Frying Oils, Total Polar Compounds, Acid Value, Peroxide Value.

I. INTRODUCTION

Cooking oil of plant and animal origin or synthetic fat is used in frying, baking, and other types of cooking. It is also used in food preparation and flavouring not involving heat, such as salad dressings and bread dips, also termed edible oil. Cooking oils are liquid, although some oils that contain a high amount of saturated fat, such as coconut oil, palm oil and palm kernel oil, are solid at room temperature. Cooking oils are derived from animal fat, as butter, lard and other types, or plant oils from the olive, maize, sunflower and many other species. Different types of cooking oil include: olive oil, soybean oil, palm oil, canola oil (rapeseed oil), corn oil, pumpkin seed oil, sunflower oil, safflower oil, peanut oil, grape seed oil, sesame oil, rice bran oil and other vegetable oils, as well as animal-based oils like butter and lard. Oil can be flavoured with aromatic foodstuffs such as herbs, chilies or garlic. Lipids in edible oils are susceptible to photo-oxidation and auto-oxidation during processing and storage[1], which is a major problem for the oil industry. Oxidation may cause undesirable flavours and taste, decomposing the nutritional quality, and leading to production of toxic compounds. Oxidation of oils may be influenced by different factors such as the degree of unsaturation, heat, light, oil processing, antioxidants and transition metals. Another important issue is the reusing of fried oils. This practice is not only restricted to roadside food stalls, and reputable food outlets in large cities also use this technique to lower their costs. The repeated heating of cooking oil result in oil that is more prone to lipid peroxidation [2]. Furthermore repeated frying of oils darken the oil at different rates, and the oil is discarded only when the oil becomes foamy or smelly[3]. Auto-oxidation, where peroxide is the main product that gives rise to objectionable flavour in food products, proceeds through the free radical chain reaction, where it attacks on the double bond at room temperatures. Photo-oxidation is a much faster reaction that involves attack at double bond [4]. Rancidity of food items can be the result of auto and photo-oxidation, which are natural oxidation and chemical degradation processes of edible oils, where fatty acid esters of oils are converted into FFA giving a smell observed in many vegetable oils[5]. Indicators of poor oil quality include elevated FFA, low smoke point, change of colour, low iodine value, peroxide value, total polar material, high foaming properties and increased viscosity [6]. The double bonds found in fats and oils play an essential role in autoxidation.

The increasing use of edible oils and fats for the preparation of fried products requires an strict control in order to maintain the quality and safety of the fried foods. Due to the knowledge that the frying process alters the chemical nature of the heated oil and its consumption represents health risks [7-8]. studies on the assessment of the quality of frying oils, which studies are used by the industry of fried products of immediate consumption, have shown the need for measures to reduce the degree of degradation of oils and fats. In this sense, by seeing that it is a public health problem, many countries have adopted regulations, recommendations and legal standards in order to protect consumers by limiting the use of frying oils and fats for human consumption [9-10].

Laws and regulations to control the quality of frying oil were adopted by some countries, including Belgium, France, Germany, Switzerland, the Netherlands, the United States and Chile. In Brazil, discontinuous frying processes are widely used both in home preparations as in restaurants and cafeterias. The oil is used in a large number of times with minimum replacement, which may result in high levels of change. However, Brazil does not yet have rules for monitoring and disposal of frying oils. These facts demonstrate the importance of studies to get to know the behavior of oil in discontinuous frying processes and their degree of change[11].

Several authors have sought to identify the compounds formed in the frying oil and the biological importance. The importance of the volatile compounds, partially eliminated during frying, is closely related to the sensory characteristics of oil and fried products,[8]causing deterioration of flavour, aroma and visual appearance, besides the formation of potentially toxic polymeric compounds[12-13].

II. LITERATURE REVIEW

For frying operations, the temperature which should be in the range of 160 - 180°C.The highest temperatures were observed for vegetable cooking fat (173.6°C) while the lowest temperatures were examined for using vegetable shortening oil (124.1°C)[14]. Aladedunye and Przybylski (2009) concluded that the extent of oxidative deterioration, as measured by the TPM formation, was faster during frying at 215°C compared to 185°C. Soriano et al(2002) recommended that the continuous heating as the intermittent heating is much deleterious due to an increased rate of oil breakdown[15].

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 ^{o}C. The hot oil serves as a medium of heat transfer into the food, while the moisture migrates out and the oil is absorbed [16]. Frying causes complex physicochemical reactions such as starch gelatinization, protein denaturation, browning, crust formation, textural and flavour changes. These depend on either the frying process itself or the nature of the food or type of frying oil[17]. 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 [18]. The popularity of fried foods has at no time been reported to decrease. This is certainly due to the smooth mouth feel, distinct flavour, palatability, and aesthetic appeal of fried foods.

When edible fats and oils are heated for deep- and pan frying, several kinds of decomposition compounds are produced. Free fatty acids and di- and mono-acylglycerols produced by the hydrolysis of triacylglycerols, and hydroxy- and oxo-fatty acids and polymerized compounds produced by the thermal oxidation are all polar compounds. Polar compounds are measured by column chromatography using silicic acid[19].

The formation of the degradation compounds such as monomers, dimers, polymers and cyclic compounds with different polarities, with or without oxygen, under the physiological and nutritional points of view, since such compounds become part of the diet when they remain dissolved. Apart from the nutritional aspect, there is an analytical interest, since the content of these compounds, accumulated in the oil since the start of frying, is related to its total change. Among the parameters that measure change in oils and fats used in frying is the percentage of total polar compounds, formed from the triacylglycerides[20].

Measurement of total polar components (TP) is useful in estimating heat misuse in frying oils. Evaluating TP has been characterized as one of the best indicators of the overall quality of frying oils, providing critical information about the total amount of newly formed compounds having higher polarity than triacylglycerols [21]. TP in fresh frying oil include sterols, tocopherols, mono- and diglycerides, free fatty acids, and other oil-soluble components that are more polar than triglycerides [22]. Other authors [23-24] also reported an increase in total polar components with heating, results that concur with findings in this study. Oxidation of oil is caused by aeration during frying that is promoted by bubbling of water provided by food. When the amount of total polar components reaches 25% levels, oil is considered to be thermally degraded and should be replaced with fresh oil[25].

Total polar materials reflect the total level of breakdown products from the frying process. The amount and character of these products are affected by some frying parameters such as fat and food composition, frying conditions (temperature, oxygen exposure, heating time, turnover rate) and the design and material of frying equipment [26-27].According to Bracoo et al(1981),the significant parameter that influences the formation of polar compounds in heated oils is the ratio of the surface oil area to, oil volume in the fryer. The specific surface also plays an important role in behaviour of oils during frying, as the overall deterioration is an oxidation process rather than an interaction with frying foods [28]. The differences in temperatures do not cause significant changes in frying oils [29].

The presence of excess polar compounds in repeatedly used frying oil has been associated with increased risk of developing hypertension [30]. Consumption of repeatedly heated cooking oil might increase the risk of developing atherosclerosis. Lipid per oxidation products induce oxidative stress in endothelial cells, resulting in endothelial dysfunction that could eventually lead to the formation of atherosclerosis [31]. Consumption of repeatedly heated cooking oil is also associated with increased total serum lipid and low density lipoprotein (LDL) levels[32]. Moreover, thermally oxidized lipids enhance per oxidation of membrane macromolecules, contributing to their mutagenicity and genotoxicity which could potentially lead to carcinogenesis.

Peroxide value is a measure of oxidation during storage and freshness of lipid matrix. Peroxide values are used to indicate rancidity of oils. Oils with high degree of unsaturation will have greater peroxide values. It is also used for assessing the quality of oil. It is the amount of peroxide oxygen present in 1 kilogram of oil. It is expressed in units of mill equivalents [33-34]. In general fresh oils have a peroxide value of less than10 mEq/Kg Rancid oil forms harmful free radicals in the body which increase the risk of cancer, heart disease ,cellular damage and have been associated with diabetes, Peroxides accelerates ageing, raised cholesterol levels, obesity etc.[33-35].Peroxides are unstable and decompose at frying temperature. PV is generally not a very reliable parameter to determine deterioration of frying oil quality[36-37].Poly-unsaturated oils have reduced stability at elevated temperatures; unsaturated fatty acids easily react with oxygen to form peroxides[38].

The content of total polar compounds and acid value are the most predominant indicators for oil quality and are widely used in many international regulations[39-40]. For public health concerns, the content of total polar compounds and acid value in frying oil are regulated at not more than 25% and 2.0 mg KOH/g, respectively, in Taiwan[41].Determination of total polar compounds in frying oil provides a more robust measurement on the extent of deterioration in most situations[39] due to its higher accuracy and reproducibility. The contents of free fatty acid (FFA) and total polar compounds were commonly used for initial oil quality assurance and after-use frying oil quality assessment, respectively [41]. Nevertheless, the standard analytical procedure for oil quality evaluation needs to be done in a laboratory with proper equipment by skilled technicians[42].

This study has aimed to analyze the degree of degradation of frying oil in electric frying pans used in commercial restaurants in Jalgaon city, Maharashtra.Therefore, it is important to understand the factors affecting the deterioration of frying oil and to monitor the quality of oils with the help of total polar compounds and peroxide value determination. The mechanism of thermal degradation of frying oil is complicated. Variables involved in the process include frying conditions, replenishment of fresh oil, original oil quality.

2. Material and Methods

The frying oils collected from different restaurants of main areas of Jalgaon city. In total 26 oil samples are collected (200ml each in clean plastic bottle) and coded A to P according to areas which performed daily frying operations. The most of restaurants used only one type of frying fat during measurements. the collected oil samples were analysed for acid, peroxide values and total polar matter using standards procedures. The obtained results are compared to each other with codex safety standards and are summarised in table 1. All the chemicals reagents and glassware used in this analytical work are analytical grade.

III. EXPERIMENTAL PROCEDURES

3.1 Determination of polar compounds[43-45]

Semi-solid and solid samples were heated at temperature just above their melting point and filtered to remove visible impurities. Then 2.5 g sample precisely weighed was placed in a 50 mL flask and dissolved with 20 mL of a solvent mixture composed of 87% petroleum ether and 13% diethyl ether with slight heating. After cooling at room temperature and adjusting to volume with the same solvent mixture, polar and nonpolar components were separated by chromatography by pouring the sample at the top of the column. Elution was done with 150 mL of the previous solvent mixture. The eluate was collected in a round bottom flask then concentrated by distilling the solvent on a rotary evaporator at about 40°C to about 5 ml. The remaining solvent was then evaporated to dryness under stream of analytical grade nitrogen (99.999%). Each sample was analyzed in triplicate.The estimation and calculation of the TPC of the oil samples were done according to the method and equation.

TPC(%)= oil mass (mg)- nonpolar compounds (mg)/oil mass(mg)*100

3.2 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 colour appeared. The acid value was estimated using the following equation:

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

Where W is weight of oil that equals 5 grams, V is titre value of 0.1N NaOH [43-45].

3.3 Determination of peroxide value

The peroxide value method is referenced in both the American Oil’s Chemist Society (AOCS) and the Association of Analytical Chemists (AOAC) as methods 965.33 (AOAC) or Cd-8b (AOCS) 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 colour was gone and after that 1mL of starch solution indicator was added and we continued titration by vigorous shaking to release all I_2 from CH3Cl layer until blue colour disappeared. The peroxide value was estimated using the following equation:

$$\text{Peroxide value} = V \times N \times 100/W, \ \text{-------------} \ (2)$$

Where V is volume of sodium thiosulphate, N is normality used for titre and W is weight of the sample [43-45].

Table 1. Analysis of AV, PV and TPM of frying oils

Sr.No	Code no	AV***(mgKOH/g)**	PV***(meq/kg)**	TPM*(%)
1	A	2.48	20.83	16.0
2	B	3.77	24.24	15.5
3	C	1.29	20.14	17.98
4	D	0.56	24.30	22.12
5	E	1.21	21.78	17.34
6	F	2.25	18.56	12.24
7	G	5.98	26.65	16.14
8	H	3.77	24.18	19.5
9	I	1.74	21.16	16.0
10	J	0.85	20.69	13.5
11	K	2.67	20.82	14.98
12	L	3.25	26.65	15.54
13	M	1.83	17.58	18.28
14	N	2.67	12.36	14.68
15	O	3.26	21.72	16.46
16	P	0.74	20.69	13.0
17	Total	38.32	342.35	259.26
18	Mean	2.4	21.4	16.20
19	SD	0.16	0.31	0.2
20	CV	6.59	1.46	1.23
21	SEM	0.09	0.18	0.12

(*AV-acid value, PV-peroxide value, TPM-total polar material, SD-standard deviation, CV-coefficient of variation, SEM standard error)

Table2.Test results of after frying and codex standards

Sr.no	Test	After frying	Codex Alimentarius commission standard	FSSAI
1	Acid value	0.78-5.98 mg KOH/g	0.6 mg KOH/g	0.5-6.0 mg KOH/g
2	Peroxide value	12.36 to 26.65 $MeqO_{2/Kg}$	10.0 $MeqO_{2/Kg}$	1-10 $MeqO_{2/Kg}$
3	Total polar compounds%	12.24-22.12 %	Upto 24%	Not more than 25%

IV. STATISTICAL ANALYSIS

The data obtained from the experimental measurements and accuracy of different parameters for different frying oils have been analysed and the Statistical parameter like standard deviation, coefficient of variance and standard mean error were calculated for AV, PV and TPM for different frying oils. All the experiment was carried out in triplicate and the results are presented as the mean ± SD, CV, ± SEM. Accuracy and descriptive Statistics of different frying oils from different parts of India as shown in figure1to2.

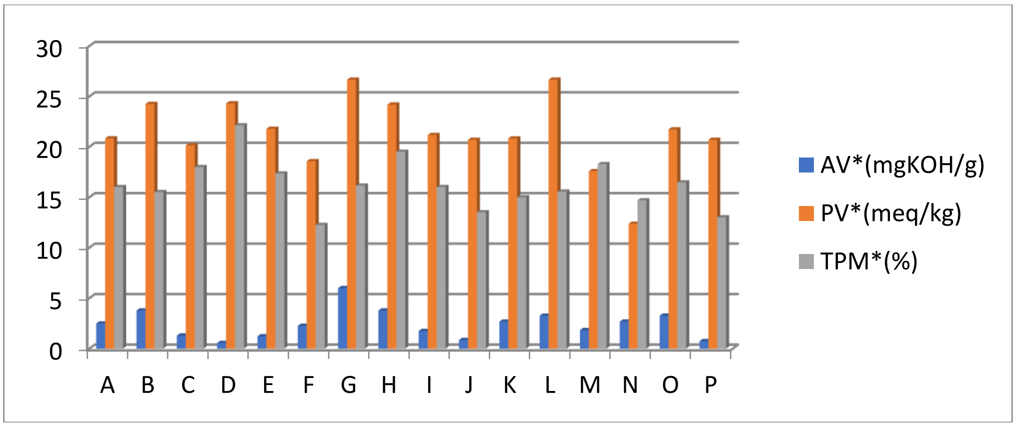

Fig1.shows the AV, PV and TPM of different edible vegetable collected from different parts of city

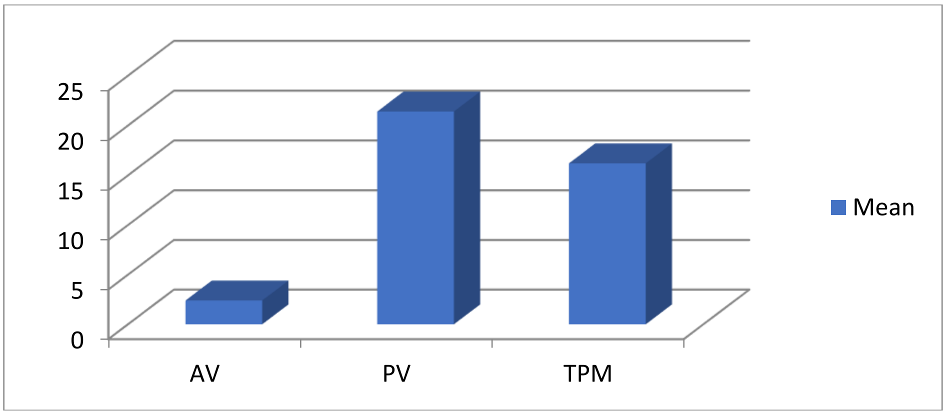

Fig 2. Accuracy and descriptive Statistics of different oils from different parts of India

V. RESULTS AND DISCUSSION

The experimental results of acid value, peroxide value and total polar matter of frying oils collected from different restaurants of main areas of Jalgaon city .In total 26 oil samples are collected (200ml each in clean plastic bottle) and coded A to P according to their areas which performed daily frying operations and have been analysed and summarised in table 1-2.The descriptive statistics and graphical representation of different oils are shown in figures 1-2. The codex standards for these parameters are given in Table2 and compared with limits of codex quality and safety standards. Acid values of all oils are in the range between 0.78-5.98 mg/KOH/g. PV ranges between 12.36-26.65Meq/kg as compared to codex and FSSAI standards as all the oils having more PV than the limit of 10 meq/kg. Hence all the oils deviates the standards of codex and FSSAI. Lipid oxidation results in peroxides which are responsible for primary oxidation. Peroxides are unstable and decompose at frying temperature. It is generally not a very reliable parameter to determine

DOI 10.17148/IARJSET.2020.7801

deterioration of frying oil quality [38]. In case of total polar compounds of all the frying oil samples are in the range of 12.24-22.12 %, it is less than the codex and FSSAI limit of 25% . Formation of total polar components, which indicates during frying, oil deterioration is strongly related to primary and secondary oxidation. Thermal decomposition of lipids is generally observed during heating to temperatures above 200 °C and results in the appearance of cyclic polymers and monomers [47].The plot of AV, PV and TPM against the obtained analysed value are shown in the Figure 1, which explains the variation of AV ,PV and TPM. The peroxide value of frying oils gradually increases were recorded as shown in the Table 1. This increase is due to the formation of peroxide at double bond which on simultaneous cleavage results in formation of aldehydes and ketones. The variation in the AV,PV and TMP were as plotted against mean number of obtained values(Fig. 2).The standard deviation for AV,PV and TMC are in the range of 0.16-0.32 and standard mean error in the range of 0.09-0.18.

VI. CONCLUSION

From the obtained experimental results, the repetitive use of vegetable oils used for frying should be avoided since changes in oxidative stability properties of the oil affect oil quality for human consumption and deviates codex safety standards. Oil is part of the daily diet of the population, for knowing the quality of oil as per its degree of degradation,. In this regard, many countries have adopted regulations, recommendations and legal standards in order to protect consumers by limiting the use of frying oils and fats for human consumption. The awareness of the general public in India regarding the usage of repeatedly heated cooking oil needs to be increased. More publicity and exposure about this little-known health issue should be given in the mass media.

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