Evaluation of the Quality of Commonly Used Edible Oils and The Effects of Frying

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ABSTRACT

Oils and fats hold paramount importance in our diet. Today, as the expense factor is significant, the population finds itself repeatedly using the same fried oil. Reusing cooking oils increases the risk to type-2 diabetes, acidity, and the presence of free radicals in the body which causes inflammation. The present study aims to showcase the numerical data of the deleterious effects caused by reusing oils, and thereby educate the population to halt this practise. Commonly consumed oils namely Refined Sunflower oil, Extra Virgin Olive oil, Refined Groundnut oil and Refined Palm oil were subjected to various tests; physical parameters involving pH, density, specific gravity and viscosity; and chemical parameters such as saponification value, iodine number, peroxide, acid, p-anisidine value and totex value were determined. The decreasing trend of iodine values and increasing trend of all the other parameters highlights the oxidative nature and introduction of free radicals in the samples.

Keywords: Cooking oil, deep frying, free radicals, nutritional value, rancidity

INTRODUCTION

Edible oils used for cooking, frying and food formulations are derived from plant sources such as sunflower seeds, olives, peanuts palm fruits etc. These are liquids at room temperature and are majorly comprised of triacyl glycerides. Frying time, food surface area, moisture content of food, types of breading or battering materials, and frying oil influence the amount of absorbed oil to foods (Moreira et al., 1997). The nutritional and physio-chemical properties of edible oils are highly dependent on the nature of fatty acids present in the oil. Vegetable oil provides vitamins, antioxidants and energy. It also functions as a transporter of several fat-soluble vitamins to the body cell.

Although high content of unsaturated fatty acid is associated with healthier oils, yet, these are prone to quick oxidation, leading to quality deterioration during processing, handling and storage. It is extremely crucial to check the purity and quality of edible oils in order to reduce various types of health hazards. As it is well known, oils containing higher proportions unsaturated fatty acids are easier to be oxidized (Kamal-Eldin., 2006; Sathianathan et al., 2014). The deteriorated frying oil can lead to adverse health effect on the human system due to accumulated toxic substances in the oil and fried product (Tena et al., 2009). The oil may thicken and become more viscous as it is heated. This seems to be due to the process of polymerisation and also to oxidation, hydrolysis and isomerization (Lin et al., 1998). The amount of FFA, mono- and diacylglycerols and glycerols in oils increases during hydrolysis. Hydroperoxides and low molecular weight volatile compounds such as aldehydes, ketones, carboxylic acids, and short chain alkanes and alkenes are produced during oxidation. Dimers or polymers are either acyclic or cyclic depending on the reaction process and kinds of fatty acids consisting of the oil (Cuesta et al., 1993; Sánchez-Muniz et al., 1993; Takeoka et al., 1997; Tompkins et al., 2000). Dimers and polymers are formed as a result of exposure to high temperatures during cooking and frying.

The economy of commercial deep-fat frying has been estimated to be $83 billion in the United States and at least twice the amount for the rest of the world (Pedreschi et al,. 2005). Oil is an essential ingredient for any type of cooking process. And while its replacement is not possible, studies have shown that people revert to reusing the same oil again and again to substantiate the high cost. Reheating cooking oil deteriorates its quality, releases toxins, trans fats and free radicals, ultimately taking a toll on the consumer's health. Long-term intake of diet comprising reheated is the main ground of most common diseases such as obesity, heart diseases, diabetes, endothelial dysfunction, and lowers immunity.

During frying, myriads of complex reactions such as hydrolysis, isomerization, cyclization, oxidation and polymerizations occur which changes the flavour and decompose the compounds in the oil (Gomez et al., 2003), thereby affecting the quality of oil and fried food. Consumption of repeatedly heated edible oils should be restricted due to its detrimental consequences. This study, aims to access the quality of four commonly used edible oils- sunflower oil, olive oil, groundnut oil and palm oil- which have not been compared before. Each oil was reheated for four times and the quality was analysed using various physical parameters such as pH, density, specific gravity, viscosity measurement and chemical parameters such as saponification value, iodine number, peroxide value, acid value, para anisidine value and totex value.

ABBREVIATIONS

FFA: Free Fatty Acid; **SV:** Saponification Value; **IV:** Iodine Value; **PV:** p- Anisidine Value; **AV:** Acid Value.

MATERIALS AND METHODS

Oil samples and Reagents

Commonly used vegetable oil samples, namely Sunflower Oil, Olive Oil, Groundnut Oil and Palm Oil were purchased. The samples were then subjected to cooking, carried out using foods like potatoes for 4 consecutive times.

Potassium hydroxide (KOH), ethanol (C_2H_5OH), hydrochloric acid (HCl), phenolphthalein indicator, powdered potassium iodide (KI), glacial acetic acid (CH_3COOH), chloroform (CH_3Cl), sodium thiosulphate ($Na_2S_2O_3$), sodium carbonate (Na_2CO_3), starch, potassium dichromate ($K_2Cr_2O_7$) and Hannus iodide solution were purchased. All the chemicals used were of analytic grade.

PHYSICAL PARAMETERS

pH Determination

The pH of the oil samples before and after the frying processes were determined using Elico (LI 120) pH meter. The instrument was first calibrated with standard buffers of 4.0 and 9.2 pH. Later, the fresh and fried oil samples were tested for pH.

Density Measurement

10 ml of oil was taken in a weighed beaker and mass was determined. The following equation was used to determine the density for each of the 20 samples.

$$\rho = \frac{M}{V}$$

where ρ =density of the oil sample (g/cm3), M= mass of the oil sample(g) and V= Volume of the oil sample taken(ml).

Specific Gravity Measurement

The empty beaker was first weighed (wo), followed by weight of the beaker with 10ml distilled water(w2). This was followed by the determination of weight of the beaker with 10ml oil sample(w1). Specific gravity was calculated using the formula:

$$Specific\ Gravity = \frac{w1 - wo}{w2 - wo}$$

Viscosity Measurement

The viscosity of all the oil samples was determined using an Ostwald's Viscometer. The flow time was recorded using a stopwatch. Viscosity was calculated using the following formula:

$$\eta = dt$$

where η = viscosity, d= density of the oil sample and t= flow time.

CHEMICAL PARAMETERS

Saponification Value Measurement

Saponification value was determined using the following procedure with a few modifications from (ASTM 2020). 0.5N HCl was standardized using standard sodium carbonate solution. 1g of oil was mixed with solvent mixture (Ethanol: Ether in ratio 2:1) and 0.5N alcoholic KOH was added. The conical flask was attached to a reflux condenser and the contents were heated for 30 minutes. Cooled mixture was then titrated against standard HCl in the burette. Endpoint was determined by change in the phenolphthalein indicator from pink to colourless. Blank was determined in the same manner without the sample. The procedure was repeated for all the 20 samples. Saponification Value was calculated using the following formula:

$$S.V. = \frac{A - B * N * 56.1}{W}$$

where, A= volume of HCl (ml) for blank, B= volume of HCl (ml) for sample, W= weight of sample (g), N= normality of HCl.

Iodine Value Measurement

Iodine number was determined using Hubl method with a few modifications. 0.1N sodium thiosulphate was standardized using standard potassium dichromate solution. 1g of the oil sample was taken in a dry iodination flask and dissolved in 10ml of chloroform. To this, 30ml of Hannus iodide reagent was added and the flask was stoppered. Flask was then placed in dark for 30 minutes. 10ml of 15% KI and 100ml distilled water was added and the contents were titrated against standard sodium thiosulphate in the burette till a faint yellow colour appeared. 2ml of starch was added and titration was continued till blue colour disappeared. Blank titration was carried out without the oil sample. Iodine value was determined using the following formula:

$$Iodine\ Value = \frac{(X-Y)12.7}{10}$$

Where X = volume of sodium thiosulphate (ml) for blank and Y = volume of sodium thiosulphate (ml) for sample.

Peroxide Value Measurement

Peroxide value was determined using the method described by (Nduka et al., 2021). 1g of powdered KI and 20ml of solvent mixture (glacial acetic acid: chloroform in ratio 2:1) was added to 1g of oil and the boiling tube was allowed to stand on a boiling water bath for 30 seconds. The contents of the boiling tube were added to a conical flask containing 20ml of 5% KI solution and 35ml of distilled water. The mixture was titrated against 0.002N sodium thiosulphate solution in the burette till a pale-yellow colour appeared. 0.5ml starch was added and the titration was continued till the solution turned colourless. Blank titration was carried out without the oil sample. Peroxide value was determined using the following formula:

$$Peroxide\ Value = \frac{(A-B)*1000}{W}$$

where, A= volume of sodium thiosulphate (ml) for oil sample, B= volume of sodium thiosulphate (ml) for blank titration, W= weight of oil sample (g).

Acid Value Measurement

Acid Value was determined using (ISO 660). 2g of oil was taken in a conical flask and 10ml of ethanol and 2 drops of phenolphthalein indicator were added. The contents were heated over a boiling water bath for 5 minutes and then titrated with 0.1N KOH till a pale pink colour appeared. Acid value was calculated using the following equation:

$$Acid\ Value = \frac{T*N*56.1}{W}$$

$$FFA = Acid\ Value * 2$$

where, T= volume of KOH (ml), N= normality of KOH, W= weight of oil sample (g), FFA= Free Fatty Acid.

p- Anisidine Value

PV was determined using the method (Moigradean et al., 2012). 100mg of the oil sample was first dissolved in 25ml isooctane. The absorbance of the mixture was measured at 350nm using a UV-visible spectrophotometer. Next, to 2.5ml of the mixture, 0.5ml of 0.5% (w/v) p- anisidine in isooctane was added. The mixture was allowed to stand at room temperature for 10 minutes and then absorbance was read at 350nm. Value of PV was calculated using the following formula:

$$PV = \frac{25(1.2*A2 - A1)}{W}$$

where A1 is the absorbance of the mixture before the addition of p-Anisidine (at 350nm), A2 is the absorbance after the addition of p-Anisidine (at 350nm) and W is the weight of the oil sample taken (in g).

Totex Value

The totex value provides an assessment of the oxidative deterioration of the oil samples. It is calculated as follows:

where PV= p- Anisidine Value and AV = Acid Value.

Statistical Analysis

Results were calculated according to the respective formulae and the trends in change for each parameter was observed using graphical data.

RESULTS AND DISCUSSIONS

pH and Density

In accordance to edible oils, the pH value indicates the variance of organic molecules in the sample and not the fatty acid composition. The pH range of all four samples remained at a constant range without any appreciable variance as shown in Table 1. The values fell between pH 6.0-8.25 for all the samples.

Table 1. pH And Density Measurement

	Sunflower Oil		Olive Oil		Groundnut Oil		Palm Oil	
	pH	DENSITY (g/cm³)	pH	DENSITY (g/cm³)	pH	DENSITY (g/cm³)	pH	DENSITY (g/cm³)
Fresh Oil	8.24	0.901	6.28	0.887	6.40	0.796	6.26	0.863
1X fried	7.01	0.88	6.30	0.894	6.33	0.902	6.14	0.923
2X fried	7.30	0.918	6.22	0.86	6.42	0.862	6.13	0.916
3X fried	7	0.911	6.61	0.874	6.48	0.836	6.39	0.842
4X fried	6.88	0.903	6.55	0.88	6.38	0.826	6.23	0.986

Table 2. Saponification Value (Mg Koh/G) And Iodine Value

	Sunflower Oil		Olive Oil		Groundnut Oil		Palm Oil	
	SV	IV	SV	IV	SV	IV	SV	IV
Fresh	105.18	45.72	110.5843	45.339	98.4555	44.958	102.7639	42.545
1X	103.4035	45.339	106.7695	45.086	105.1875	44.45	111.2912	38.1
2X	108.1496	44.831	110.5843	45.085	94.248	43.18	106.7695	9.525
3X	110.001	44.323	108.5647	44.958	110.3038	38.1	110.001	15.875
4X	111.4819	44.069	111.7961	44.5	111.078	36.195	111.078	29.845
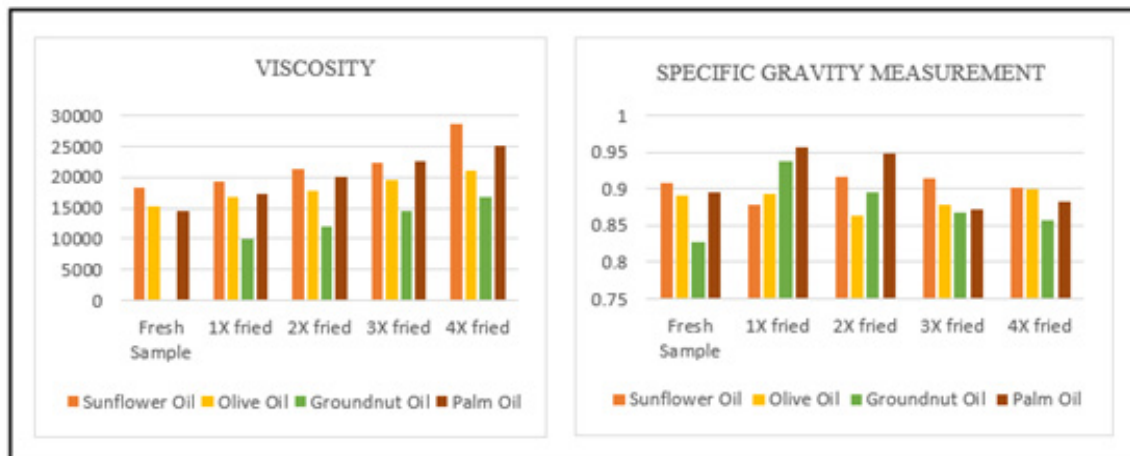
Figure 1: Viscosity Measurement & Specific Gravity Measurement

The densities, showed similarities in value across the samples irrespective of the variance due to heating. The value fell in the range 0.79-0.98 g/cm3 as shown in Table 1.

Specific Gravity and Viscosity

Specific gravity is the heaviness of a substance compared to that of water and it is expressed without units (Idun-Acquah et al., 2016). The specific gravity of all the samples remained in the range 0.8-0.9, Figure 1. There was no great significance in the change in specific gravity with frying.

Viscosity is the resistance to flow offered by a liquid. Viscosity is one of the most important physical properties of a liquid system; the change in viscosity is linked to physicochemical oil properties (Belgharza et al., 2015). The viscosities of the samples gradually increased. The

Figure 1 shows the increasing trend of viscosities among the 4 samples.

Increasing viscosities may be due to a hidden effect of free fatty acids produced by hydrolysis reactions and other small molecular weight decomposition products produced during frying (M. Sharoba et al., 2017).

Saponification Value

Saponification value gives the measure of the fatty acids present in the oil sample. High SV indicates the presence of shorter fatty acids on the glycerol backbone (Marina et al., 2009). Table 2 depicts an overall increase in the SV with the frying process. The highest SV was observed in 4 times fried oils of all samples.

This indicates that continuous supply of heat caused triglyceride breakage and increase in free fatty acid of oil;

resulting in decrease in unsaturated fatty acid composition (Ayoola et al., 2016).

Iodine Number

Iodine value indicates the degree of unsaturation of an oil or fat sample. It is given by the amount of iodine absorbed by 100g of fat sample. On the average, the iodine values of the samples ranged from 9.5-45.72, as shown in Table 2. steady decrease in iodine values was seen in sunflower oil, olive oil and groundnut oil samples. This trend was quite unsteady in palm oil.

Deep frying of oils decreases its unsaturated fatty acid content. The low degree of unsaturation leads to higher resistance to oxidative rancidity (Nduka et al., 2021). Thus, highest IV was recorded in the fresh sample of Sunflower oil and the lowest in fried sample of palm oil. The greater the degree of unsaturation, (or high IV) the more rapid the oil tends to get oxidised, particularly during deep frying process (Chebe et al., 2016).

Peroxide Value

The peroxide value indicates the amount of peroxide oxygen per 1kg of fat or oil sample. Unsaturated fatty acids form peroxides on oxidation. In the initial stages of lipid oxidation, peroxides and hydroperoxides are formed. The number of peroxides present in vegetable oils reflect its oxidative level and thus its tendency to become rancid (Sebastian et al., 2014). According to the results, the Figure 2 highlights an overall increasing trend of the peroxide values upon repeated frying. The highest value was seen in 4 times fried groundnut oil sample.

Large increase in peroxide values indicate that the sample are relatively unstable to oxidation. While this increasing trend was gradual in olive oil, the other oils showed a sharp increase as seen in fig 2. At high temperatures, the hydroperoxides break down and subsequently form secondary oxidation products on cooling (Park et al., 2016).
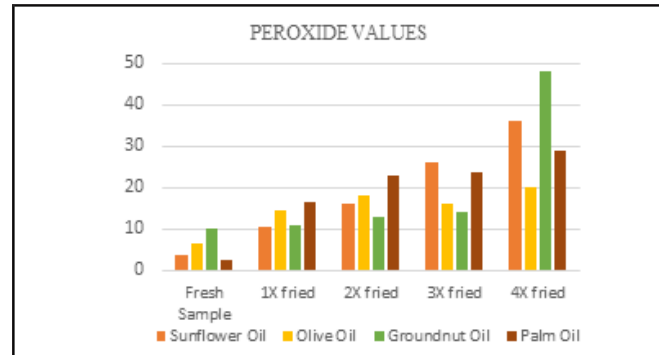

Figure 2: Peroxide Value Measurement

Acid Value

A gradual increase in the acid value is seen in Figure 3. Greatest acid value was observed in Groundnut oil samples. The overall increase is attributed to the increase in fatty acid content of the samples as the oil is subjected to the process of repeated frying.

Acid value measures the content of free fatty acid formed upon the hydrolytic degradation of free lipid molecules, thus contributing the reduction of shelf life of oil (Pardeshi 2020). Frying oil breaks the fatty acid, glycerol backbone of triglycerides and thereby increases the acid value of oils. This increase is regardless of the type of oil tested. The lower the acid value of oil, the better the quality, fresh degree and degree of refining (W. Zhang et al., 2015).
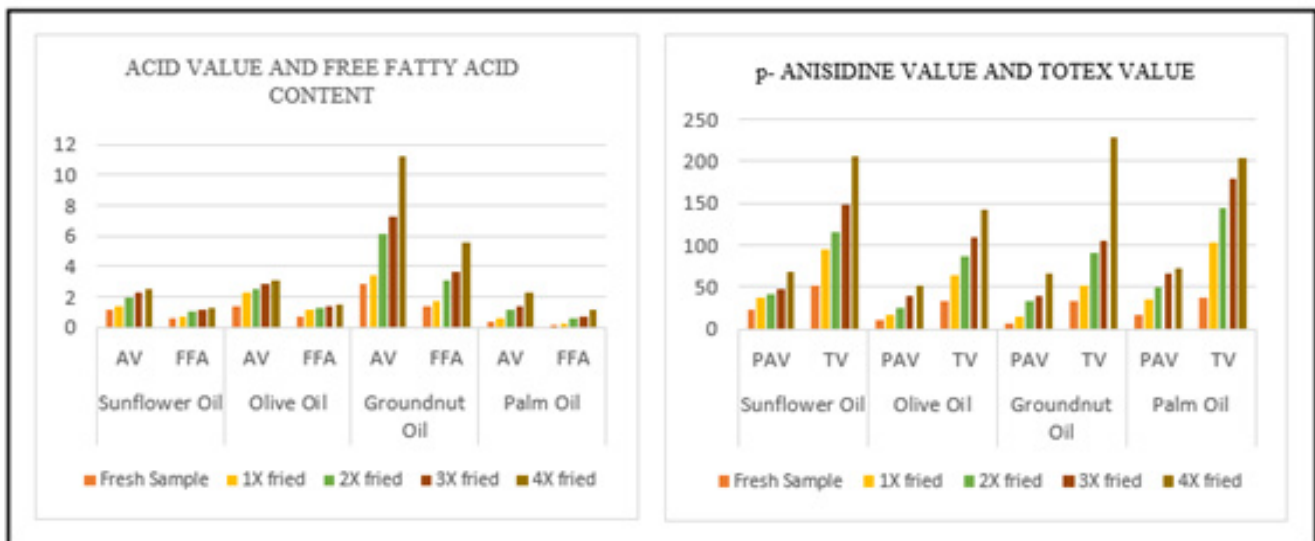

Figure 3: Acid Value - FFA & P- Anisidine Value-Totex Value Measurement

p-Anisidine Value and Totex Value

The secondary oxidation of oils produces aldehydes such as 2-alkenals and 2,4-dienals. p-AV values showed a gradual increase as the sample was subjected to repeated frying. The greatest value was found in 4 times fried sunflower oil. Olive oil showed the least p-AV values compared to the other three samples as illustrated in Figure 3. The totex values increased in the similar trend.

The primary oxidation of products such as hydroperoxides are unstable and those compounds decompose to the secondary oxidation products during frying process which contributes to increase in PAV (Sebastian et al., 2014).

CONCLUSION

Oils and fats are inevitable parts of our existence. On investigation of the results, it was evident that the quality of edible oils substantially decreases upon reuse. Oil becomes thicker, denser and more viscous upon repeated frying. Saponification value, peroxide value, acid value, p-anisidine value and totex values significantly increased and iodine value decreased highlighting the detrimental effects of using repeatedly fried oils on health. Extra Virgin Olive Oil was less prone to sudden changes, in comparison to the other refined oils tested. Palm oil was the most viscous and contained highest peroxide value after subjected to 4 times frying. Oils become oxidised and turn rancid and thereby pose a variety of health hazards. Prolonged consumption of repeatedly heated oil has been shown to increase blood pressure and total cholesterol, cause vascular inflammation as well as vascular changes which predispose to atherosclerosis (Ng et al., 2014). Today, more than ever, during these pandemic times, the topic of health and wellness has attained spotlight. Thus, it is the right time to be mindful of our choices and discontinue this age-old practice.

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CONFLICT OF INTEREST

The authors declare no conflict of interests.

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