International Journal of Engineering, Science and Mathematics
Vol. 13 Issue 8, Aug 2024,
ISSN: 2320-0294 Impact Factor: 6.765
Journal Homepage: http://www.ijmra.us, Email: editorijmie@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal - Included in the International Serial Directories Indexed & Listed at: Ulrich's Periodicals Directory ©, U.S.A., Open J-Gage as well as in Cabell's Directories of Publishing Opportunities, U.S.A

EFFECT OF DEEP-FRYING ON PHYSICO-CHEMICAL CHARACTERISTICS OF VEGETABLE OILS

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Abstract

Vegetable oils for deep frying such as potato chips, French fries etc. The physico-chemical properties of sunflower, groundnut and rice bran oil during deep frying at 180℃ were studied. The deep frying substantially changes the physico-chemical properties of oil.Deep frying is a well-known cooking method and worldwide method used for cooking foods. Deep frying is done by submerging a portion of food in boiling oil (150-190℃) until it reaches a safe minimum internal temperature. The simultaneous heat and mass transfer of oil, food and air provide fast foods desirable and unique quality during frying.This study aims to investigate the effect of deep frying on the physico-chemical properties of three selected edible oil such as sunflower oil, rice bran oil and ground nut oil.

Keywords: Deep frying, vegetable oils, physicochemical properties

Introduction

Deep frying is one of the most common methods used for preparation of food [1]. In frying due to hydrolysis, oxidation and polymerization process the composition of the oil changes which in turn changes the flavour and stability of its compound [2]. In deep frying, different reactions depend on some factors such as replenishment of fresh oil, frying condition, original quantity of frying oil and decrease in their oxidative stability [3]. Atmospheric oxygen reacts instantly with lipid and other organic compounds of the oil which leads to loss of quality of odour and is harmful to human health [4].

Therefore, for retaining the quality of oil, 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 [5].

Santos et.al[6] stated that deep frying is the most common and one of the oldest methods of food preparation worldwide. To reduce the expenses, the oil tend to be used repeatedly for frying. When heated repeatedly changes in physical appearance of the oil occur such as increased viscosity and darkening in colour, which alter the fatty acid composition of the oil.Heating causes the oil to undergo a series of chemical reactions like oxidation, hydrolysis and polymerisation. During this process many oxidative products such as hydroperoxide and aldehydes are produced which can be absorbed into the fried food.The oxidation and chemical changes in oils during heating are characterized by an increase in free fatty acid content and decrease in the total unsaturation of oils [7]. The deep frying is carried out at elevated temperature ranging from 150-200°C. In this type of frying, the food is submerged in frying oil and at the frying temperature a lot of reactions occurs in the oil. The oil gets hydrolysed to free fatty acids, glycerol, monoglycerides and diglycerides. The oil gets oxidised to hydroperoxides, hydroxide, ketones, epoxides and conjugated dienoic acids. 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. Repeated frying causes overall oxidative and thermal reactions which results in change in the physico chemical, nutritional and sensory properties of the oil. 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.

Sunflower, groundnut and ricebran oils are the most widely used edible oils in India for frying purpose. It is selected and analysed to determine the effect of frying on the quantity of oil and vice versa and to recommend safe number of frying of a specific product in oil for making recommendation to be used safely and commercially.

Materials And Methods

Materials Used

Sunflower (RBD) Oil Refined, bleached and deodorized sunflower oil was purchased from the local market and was used in the experiments.

Groundnut (RBD) Oil

Refined, bleached, and deodorized groundnut oil was purchased from local market and was used in the experiment.

Rice bran (RBD) oil

Refined, bleached and deodorized rice bran oil was purchased from local market and was used in the experiment.

Potatoes

The potatoes used during the frying experiments were also obtained from local market. The average moisture content of the potatoes was 75%.

Chemicals Used

All the chemicals used for analytical work were of AR grade.

Methods

Determination Of Physico-Chemical Characteristics Of Frying Oils

Physico-chemical characteristics of experimental oil samples of deep frying were determined by using the following procedures.

Determination of Refractive Index

Abbe refract meter was used to determine the refractive index of oil samples during deep frying.

The prism of the refract meter was cleaned by the acetone and dried. The temperature of the refract meter was adjusted to 30 ± 1°C. A few drops of the sample was placed on the lower prism and the prism was closed, tightened firmly with the screw-head and allowed to stand for one or two minutes. Thereafter the instrument was adjusted to obtain the most distinct reading possible.

Whenever required, the temperature correction was made using the following formula

R = R' + K(T'-T)

Where

R= The reading of the refractometer reduced to the specified temperature, T°C

R'= The reading at T'0C

K = Constant 0.000385 for oils

T' = The temperature at which the reading R' is taken

T = The specified temperature

Determination of Specific Gravity

Specific gravity of the original and recovered deep fat fried oil samples was determined against water at 30 °C using a specific gravity bottle of 10.0 ml capacity.[8]

Perfectly dried specific gravity bottle was taken and filled with water. The stopper was inserted to exclude the extra water. After wiping the bottle dry it was weighed accurately with on Dhona 200D electrical balance. After weighing with water, replaced the water from bottle and dried and filled with oil samp[le as above and weighed accurately. The specific gravity was calculated as follows

Specific gravity (at 30°C) = Weight of oil / Weight of water

Further this was corrected to 30°C by the following factor

Specific gravity at TC/T°Cs'+ 0.00041 (T1-T)

Where

S = Specific gravity atT /T°C

T = Temperature at which the specific gravity was determined

And

T=Standard temperature,30°C

Determination of Acid Value

The acid value of the deep-frying oil samples was determined by method [8]. Accurately weighed sample of oil (2 to 3 g) was mixed with neutral ethyl alcohol, warmed, and titrated against standard sodium hydroxide solution using phenolphthalein as indicator. The acid value was calculated using the following relationship.

$$\text{Acid Value} = \frac{5.61 \times N \times V}{W}$$

Where

N = Normality of aqueous sodium hydroxide solution

W = Weight in gm of the sample

and

V = Volume in ml of sodium hydroxide solution consumed

Determination of Iodine Value

Iodine values of the oil samples during deep frying of chips were determined by using method [8]. The oil sample (0.2-0.3 g) was weighed accurately into the 500 ml Iodine value flask and 25 ml of carbon tetrachloride was added to dissolve the contents. Then 25 ml of Wijs solution (Iodine monochloride in glacial acetic acid) was added and glass stopper was replaced after wetting it with potassium iodide solution (freshly prepared by dissolving 10 g potassium iodide, free from potassium iodate, in 90 ml water). The flask was swirled and was allowed to stand in dark for 45 minutes. Thereafter the flask was taken out and 15 ml of potassium iodide solution was added followed by addition of 100 ml distilled water rinsing the stopper also. The Iodine, which liberated, was titrated against standard sodium thiosulphate solution until the colour of solution was straw yellow. At this stage 1 ml of starch solution (1%) was add to flask and titration was confirmed until the blue colour formed on addition of starch disappeared after through shaking with the stopper on. A blank determination was also made simultaneously under similar conditions and the iodine value of the relationship. sample was calculated using the following

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

Where

B = Volume in ml of the standard sodium thiosulphate solution used up in the blank determination.

S = Volume in ml of standard sodium thiosulphate solution

N = Normality of the solution of sodium thiosulphate and

W = Weight of the sample (in gm)

Determination of Peroxide Value

Peroxide value of RBD sunflower oil RBD groundnut oil and RBD Rice Bran Oil sample grown during deep-fat frying of Potato chips were determined by using method [8]. The oil sample (5.00+ 0.05 g) was weighed accurately in to a glass stoppered conical flask of 250 ml of capacity and then 30 ml acetic acid chloroform solution was added. The flask was swirled to completely dissolve the sample and then 0.5 ml of saturated potassium iodide solution was added. The solution was allowed to stand exactly one minute with occasional shaking and then 30 ml of distilled water was added. Thereafter the contents of the flask were titrated with 0.1 N sodium thiosulphate solution with constant and vigorous shaking. The titration was continued up to the almost disappearance of yellow colour. The end point was determined by using starch indication and judged with disappearance of blue colour. A blank determination was also made simultaneously under similar condition and peroxide value as milli equivalent per 1000 grams of sample was calculated using following relationship.

$$\text{Peroxidevalue} = \frac{(S-B) \times N \times 1000}{W}$$

Where

S = Volume in ml of standard sodium thiosulphate solution

B = Volume in ml of the standard sodium thiosulphate solution used up in the blank determination.

N = Normality of sodium thiosulphate solution and

W = Weight of g of the

Determination of p-Anisidine Value

p-Anisidine Value is a measure of the secondary oxidation products that are formed by break down of the primary oxidation product during extensive oxidation. p-Anisidine values were determined according to ISO 6885-2006. A test solution is prepared in isooctane. It is reacted with an acetic solution of p-Anicidine. The increase in absorbance at 350nm is measured.

Fatty Acid Composition

Methyl esters are prepared of RBD sunflower, RBD groundnut oil and RBD ground nut oil. Oil samples recovered after 36 h of frying for determination of the fatty acid composition of the samples in question and then subjecting them to gas - liquid chromatography.

Preparation of Methyl Esters (FAME)

Saponification and esterification process are used to prepare the methyl esters of the oil samples (5). About 10 gm of oil were refluxed with 50 ml of alcoholic potassium hydroxide (78%) in ethanol, w/v) for 3 hrs. After that the content were

transferred in separatory funnel with addition of 50 ml of cold distilled water. Their content of the unsaponifiable were extracted out twice with 50 ml aliquots of petroleum ether. The soap solutions were acidified with requisite amount of 2N sulphuric acid to obtain free fatty acids. The free fatty acids were extracted with 5 x 10 ml portions of diethyl ether. The combined ether extracts of each sample were dried using anhydrous sodium sulphate and filtered. The fatty acid of the samples was recovered by distilling of the ether under moderate vacuum from dried extracts.

The fatty acids recovered from the samples were esterified by refluxing 4 h, with 5 volume of acidified methanol (100 ml methanol containing 1 ml concentrated sulphuric acid). The esterified contents of the flask were transferred into separating funnels with equal volume of distilled water. The methyl esters were extracted with 5 x 10 ml portion of diethyl ether. The combined ether extracts of each sample were washed thrice first with 50 ml aliquots of 10% sodium bicarbonate solution and then with 50 ml of aliquots of distilled water. Anhydrous sodium sulphate is used to dry the ether extracts and then filtered. The methyl esters of the fatty acids of the samples were recovered by distilling off the ether under moderate vacuum from the dried extracts. The recovered extracts were dissolved in diethyl ether in desired quantity and subjected in gas liquid chromatograph by micro syringe for determination of their fatty acid composition.

Gas-Liquid Chromatography

Fatty acid composition was determined chromatograph (TREMETRICS 540, USA) having flame with gas ionization detector. The column used for analysis was 3 mm x 2 m stainless steel column packed with 15% DEGS on chromosorb W (80 100 mesh). Chromatographic grade purified nitrogen gas was used as carries. Hydrogen gas of extra high purity was used as the flame ionization detector. The flow rate of hydrogen and nitrogen were kept 30 ml/min. The oven and injector temperature were 190°C and 225°C respectively. The methyl ester of fatty acids was dissolved in diethyl ether to a specific concentration (10%) and 0.4 µl of this solution was injected to the gas chromatograph. The percentage of fatty acids were obtained from computerized data processor.

Experimental

Deep Frying Of Potato Chips

Refined sunflower, rice bran and groundnut oil were purchased from a local market.

The frying of a known weight (50g) of potato chips was carried out by drawing 500ml of oil sample from sample from pure oil in a frying pan (diameter 17cm, depth 5cm) at a deep fat frying temperature of 180℃ for 9 sec. After frying, the oil samples from pure oil were cooled to room temperature and stored in PET bottles for three days for further frying. After 3 days oil samples were taken from pure oils for physico chemical parameters. After every frying cycle, the volume of all oil samples was again made up to 500ml by adding oil. The same frying processes were repeated with each and every oil sample.

Result And Discussion

The results of physico-chemical analysis tabulated in Table 1-5 discussed below:

Table 1: Change In Physico Chemical Properties Of Sunflower Oil During Deep-Frying

Quality Parameters	Before Frying the Oil	Result for Fried Oil - 1	Result for Fried Oil - 2	Result for Fried Oil - 3	Result for Fried Oil – 4
Peroxide Value(Meq/kg)	0.59	1.82	5.83	5.52	1.98
p-Anisidine	8.3	19.26	19.8	20.3	21.85
Iodine value(mg/g)	113.4	108.5	107.8	107.5	106.4
Acid value(mg/KOH)	0.022	0.025	0.028	0.041	0.043
Rf Value at 50C	1.4679	1.4686	1.46701	1.46709	1.46716
Specific Gravity	0.9121	0.9168	0.9171	0.9183	0.9188
Saponification (mg/g)	189.13	190.84	207.35	234.98	253.52
Colours(Y+5R)	2.5	3.5	4.4	4.6	2.3

Table 2: Changes In Physico Chemical Properties Of Ricebran Oil During Deep Frying

Quality Parameters	Before frying the oil	Result for Fried Oil - 1	Result for Fried Oil - 2	Result for Fried Oil - 3	Result for Fried Oil – 4
Peroxide Value(Meq/kg)	0.38	1.08	1.59	2.14	3.08
p-Anisidine	5.0	8.0	12.5	16.8	18.3
Iodine value(mg/g)	95.40	95.0	94.2	93.5	91.5
Acid value(mg/KOH)	0.163	0.170	0.188	0.196	0.198
Rf Value at 50C	1.4171	1.4181	1.4192	1.4208	1.4224
Specific Gravity	0.914	0.918	0.923	0.927	0.931
Saponification(mg/g)	191.33	198.32	207.11	231.00	238.21
Colour(Y+5R)	26	27	27.2	27.2	34

TABLE 3: CHANGE IN PHYSICO CHEMICAL PROPERTIES OF GROUNDNUT OIL WITH DEEP FRYING

Quality Parameters	Before Frying the Oil	Result for Fried Oil - 1	Result for Fried Oil - 2	Result for Fried Oil - 3	Result for Fried Oil – 4
Peroxide Value(Meq/kg)	0.787	2.21	5.6	4.98	3.96
p-Anisidine	5.2	9.61	15.81	17.98	18.19
Iodine value(mg/g)	112.05	110.43	109.5	107.32	106.2
Acid value(mg/KOH)	4.98	17.98	107.32	108.32	1.4700
Rf Value at 50C	1.4673	1.4681	1.4693	1.4700	1.4708
Specific Gravity	0.911	0.923	0.941	0.952	0.957
Saponification(mg/g)	189.90	191.20	193.60	195.20	196.10
Colour(Y+5R)	15	22	28	29	32

Table 4: Major Saturated Fatty Acids Composition Of Sunflower, Rice Bran And Groundnut Oil During Depp Frying

% FATTY ACID COMPETITION	OILS	INITIALLY	AFTER 1ST FRYING	AFTER 2ND FRYING	AFTER 3RD FRYING	AFTER 4TH FRYING
C14:0	**RBO**	0.23	0.23	0.25	0.28	0.29
	SFO	0.03	0.06	0.10	0.13	0.13
	GO	0.1061	0.12	0.15	0.19	0.20
C16:0	**RBO**	18.09	18.12	18.30	18.30	18.34
	SFO	5.45	5.65	5.67	5.80	5.83
	GO	20.12	20.39	20.58	20.73	20.79
C18:0	**RBO**	3.22	3.34	3.45	3.50	3.51
	SFO	4.45	4.49	4.53	4.63	4.65
	GO	2.90	3.25	3.75	3.82	4.00

Table 5: Major Unsaturated Fatty Acids Compositions Of Sunflower Oil Rice Branoil And Groundnut Oil During Deep Frying

% FATTY ACID COMPETITION	OILS	INITIALLY	AFTER 1ST FRYING	AFTER 2ND FRYING	AFTER 3RD FRYING	AFTER 4TH FRYING
C18:1	**RBO**	45.02	44.92	44.37	44.54	44.55
	SFO	51.61	51.54	51.61	50.60	50.15
	GO	53.12	53.21	53.38	53.45	53.49
C18:2	**RBO**	30.99	30.97	30.88	30.62	30.58
	SFO	37.47	37.34	37.22	37.20	37.10
	GO	27.30	27.28	27.39	27.43	27.61
C18:3	**RBO**	0.76	0.76	0.75	0.63	0.61
	SFO	0.41	0.39	0.37	0.36	0.35
	GO	0.34	0.38	0.39	0.42	0.45

Saturated and unsaturated fatty acids can influence the degradation of frying oils. Oils havinghigh amount of polyunsaturated fatty acids (sunflower, ground nut) are suitable for cooking.It has also been shown that the presence of large quantities of polyunsaturated fatty acids,mainly alpha -linolenic, is positively correlated to the oxidative degradation affecting the oxidation resistance between different oils. During deep frying it is recommended an oil or fat with low unsaturation degree.Indeed, a higher percentage of oleic acid indicates a better resistance to thermal and oxidative degradation during deep frying. The oxidative stability of the oil increase during deep frying and thatan oil or fat with low unsaturation is the best choice.

Discussion

1. Acid Value – The acid value increases progressively with increase in number of frying oil is triglyceride, composed of three molecules of fatty acids joined to one molecule of glycerol.
   When oil is heated with moist food, it gets hydrolysed to the free fatty acid and glycerol, thus increases acidity and free fatty acids. The re-heating of oil produces toxic byproducts such as trans fatty acids, aldehydes, polymerized and oxidized lipids which have health impacts. The trans fatty acid formation begins with fifth frying oil.
2. Iodine Number or Value – It decreases with increase in number of frying. The sunflower oil is rich in linoleic acid, a polysaturated fatty acid. During frying process, the double bonds in the acid get destroyed by oxidation and polymerisation. This decreases the degree of unsaturation causing decreased iodine value.
3. Peroxide Value – It is an index to measure the level of peroxide and hydroperoxide, the primary oxidized product of fat and oil. It increases with increase in number of frying. The presence of moisture and reheating increases the rate of peroxidation of poly unsaturated fatty acids, thereby increasing the peroxide value.
4. Saponification - Saponification value is an index of the molecular weights of triglycerides in the oil. It is inversely proportional to the average molecular weight or chain length of the fatty acids [9]. It increases with increase in number of frying. Repeated heating of oil may cause breakdown of long chain fatty acids into short chain fatty acids, thereby increasing the saponification value. Higher the saponification value, greater is the percentage of the oil.
5. Refractive Index – There was a significant increase in Refractive Index with increment in the number of frying. This is attributed to increase in opaqueness of oil, increase in viscosity due to polymerisation and product of high level of non-volatile decomposition products which accumulate in oil, leading to darkening of the oil.
6. Specific Gravity - During frying due to hydrolysis, oxidation and polymerisation the composition of oil degrades, which affect the specific gravity. It increases with increase in number of frying.This is because oxidation and polymerisation make the oil more and more dense.
7. Colour - The colour of oil deteriorates during deep frying.It is due to amino-carbonyl reaction between thermally oxidised oil and amino acids exuded by fried

stuffs. Colouring of oil itself influenced by mineral content. As the number of frying increases the oil become darken.

8. The anicidine value in oils is a measure of the aldehyde and therefore the level of secondary oxidation that occurred and is used as an indicator of quality. Secondary oxidation occurs when the peroxides decompose to form aldehydes and it is these compounds that generates the characteristic odour. Higher the anisidine value more is the rancidity of oil. During repeated frying sunflower oil, rice bran oil and ground nut oil awful smell comes out due to high anicidine value.

Conclusion

The result of this study shows that repeated use of vegetable oil for frying reduces the quality of the oil via changes in the composition of the oil. The values of all the parameters measured increased with frying line except the iodine values that decreased. This shows deterioration of the oil. Among the three selected vegetable oils, the peroxide value of sunflower oil after fourth frying round is least, which is the indicator less oxidation and higher stability. The repeated use of vegetable oil should be discouraged and further research should also be carried out for larger heating period.

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