

Thermal Degradation of Soybean and Palm Olein during Deep Fat Frying

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Abstract

The current study examines the physicochemical characteristics of two brands of vegetable oils i.e. soybean and palm olein that are available in Nepal. The oils were employed as a frying medium to fry dried finger chips 2h each day up to 5 days. The oils were assessed using standard techniques for determining the deterioration of used frying oil, such as changes in free fatty acids (FFA), acid value (AV), peroxide value (PV), refractive index (RI), saponification value (SV), iodine value (IV), and total polar compounds (TPC). The free fatty acid ranged between 0.18 ± 0.02 to 0.44 ± 0.01 and the acid value lies between 0.85 mg KOH/g to 0.87 mg KOH/g for the oils used at the end of frying period respectively. The initial IV values of the oils were 131 and 60.58 for SBO and PO, respectively and at the end of the frying period the iodine value decreased to 117 and 49 for the oils respectively, suggesting a notable level of unsaturated bonds in the oil samples. At the end of the frying period the peroxide value of SBO decreased to 3.04 meqO₂/kg and that PO increased to 4.43 meqO₂/kg whereas the TPC level increased to 33.3% and 22.5% for the oils respectively. The FFA, AV value, iodine values, PV and TPC of the final 5 days were statistically significant different ($p < 0.05$). At the end of the frying period the saponification value increased to 190.81 mg KOH/g and 214.55 mg KOH/g. There is no significant difference entire 5 days ($p > 0.05$). The refractive index of the oils increased with that of soybean oil going from the initial 1.46738 of the original oil to 1.46915 on frying of the final dried finger chips batch, palm olein's refractive index increased from 1.45902 of the original oil to 1.46071 after frying the fifth batch. The elevated refractive index observed in the oil specimens signifies a significant presence of carbon atoms within their fatty acid composition. All these parameters adhered to the Nepal standards for edible oil, indicating the high quality and suitability of the sample oils for consumption up to five days of frying.

Keywords: Deep Fat Frying; Thermal Degradation; Soybean Oil; Palm Olein

Abbreviations

FFA: Free Fatty Acids; PV: Peroxide Value; AV: Acid Value; RI: Refractive Index; SV: Saponification Value; TPC: Total Polar Compounds

Introduction

Deep fat frying is characterized as a traditional and prevalent unit operation utilized in the production of a variety of fried food items, including potato chips, French fries, extruded snacks, fish sticks, donuts, and fried chicken products [1]. This approach encompasses the process of preparing food through immersion in hot edible oil or fat at a temperature range typically exceeding 140 - 180. Such a method facilitates dehydration, starch gelatinization, protein denaturation, aromatization, color development via Millard reactions, and

eventual oil absorption [2,3]. The process of oil absorption in deep-fat frying is a multifaceted occurrence that arises from the interplay between the oil and the food product, leading to various physical, chemical, and structural alterations [1]. The refractive index is one of the physical metrics used to track the breakdown of frying fats, while the chemical technique measures total polar compounds (TPMs), saponification value (SV), acid value (AV), iodine value (IV), and free fatty acids (FFA) [4]. Palm olein is considered a prevalent choice for frying oil globally due to its notable concentration of palmitic acid [5]. Soybean oil is regarded as the optimal choice for frying purposes due to its elevated concentration of fatty acids. Furthermore, it boasts a notably high smoke point of 460°F (210°C), surpassing that of all other vegetable oils [6]. Many studies have been conducted on the physical and chemical changes that occur in soybean oil and palm olein during the frying process. Installing a management system that covers all crucial frying process steps is required to ensure the end product is of a high caliber [4]. This study used quantitative techniques to assess the oxidative stability of palm oil and soybean oil both before and after frying.

Materials and Methods

Materials

Soybean oil and palm olein were purchased from the local market of Dharan, Nepal, which are widely used in households and industries, respectively. Dried rolled finger chips measuring 2×4 mm were gathered from several locations in Biratnagar, Nepal.

Design for deep-fat frying

Two commercial oils, namely palm oil (PO) and soybean oil (SBO), were first subjected to a laboratory-scale frying test. The test was repeated daily after each oil had been fried. For a total of five days, multiple batches of dried finger chips were deep-fried every seven minutes, up to two hours per day.

Analysis of oil samples

Sunsari Technical College, Dharan, Nepal, provided laboratory facilities for the physical-chemical examination of oil. The suggested procedures were followed to ascertain the oil's FFA level, acid value, saponification value, and iodine value [7], refractive index and peroxide value [8]. The TPC of both oil samples were determined as per the protocol suggested by Reder, *et al* [9].

Analytical methods

Free fatty acid and acid value of oil sample by titration method

Free fatty acid and acid value of oil sample by titration method as per the guidelines of FSSAI [7]. Briefly, weigh accurately appropriate amount of the cooled oil sample in a 250 mL conical flask (by difference). Add 50 ml of neutral alcohol. Swirl the contents and place flask on the hot plate. Boil the mixture to about 70°C until the sample is completely dissolved. Swirl the flask occasionally. It nearly takes 5 minutes. Filled the burette with 0.1N KOH. Titrate the warm sample vigorously with 0.1N KOH using few drops of phenolphthalein till persistent pink color appear. Carry out titration in triplicate.

The free fatty acids are frequently expressed in terms of acid value instead of % free fatty acid. The acid value is defined as the number of mg of KOH necessary to neutralize 1 gm of sample. To convert % FFA a (as oleic acid) to acid value, multiply the former by 1.99.

Acid value = % of FFA (as oleic acid) × 1.99

$$\text{Or } \text{Acid value} = \frac{V \times N \times 56.1}{W}$$

Peroxide value of oil sample

Peroxide value of oil sample was determined as per procedure suggested by Ranganna [8]. Briefly, weigh accurately 5g of oil sample in iodine flask. Add 25 ml of solvent and dissolve the fats by shaking. Then add 1 ml of saturated KI solution, stopper the flask, immediately

and stand in the dark for 5 minutes (with gentle shaking). Add 35 ml of distilled water. Add 1 ml of 1% starch solution as indicator. Appearance of blue color on addition of starch indicates presence of free iodine and titrate with standardized sodium thiosulphate solution till blue color just disappears. Note the volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution. Carry out a blank determination simultaneously (omitting oil).

Calculate the peroxide value using the following equation:

$$\text{PV (meq/kg)} = \frac{(V_S - V_B) \times N \times 1000}{W}$$

Where: Normality of sodium thiosulphate; Sodium thiosulphate consumed by sample (ml); Sodium thiosulphate consumed by blank (ml); Weight of fat or volume of extract used (g).

Determination iodine value of oil sample

Iodine value of oil sample by titration method as per the guidelines of FSSAI [7]. Briefly, accurately take soybean oil and palm olein in the range of 0.1700 - 0.2125 mL and 0.5288 - 0.6612 mL respectively in a clean and dry 250 ml IV flask. Add 25 ml of $\text{CCl}_4/\text{CHCl}_3$ in sample flask and blank and close the flask immediately and allow oil to dissolve. 25 ml of Wj's solution was taken and poured into sample and blank flask. Then flask was closed immediately with the stopper and swirled. 5 mL potassium iodide solution was added around surface of the stopper (to moisten). The flask is kept in dark for 30 minutes. 100 mL distilled water was added into sample and blank flask and swirl to mix well. Then both flask were titrated with standardized sodium thiosulphate solution until the mixture turns lighter color. Add 1 ml of starch solution. The mixture immediately turns dark blue. Continue vigorous titration until the blue color disappears and milky white color indicates the end point. Carry out titration for blank omitting the fat/oil. The peroxide value was calculated using the following equation:

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

Where: B = mL Thiosulphate for Blank; S = mL Thiosulphate for Sample; N = Normality of Thiosulphate Solution; W = Weight of Sample.

Determination saponification value of oil sample

Saponification value of oil sample by titration method as per the guidelines of FSSAI [7] with minor modification. Briefly, weigh accurately by difference about 1.5 - 2.0g of sample in a 250 ml round bottom flask. Pipette out 25 ml of alcoholic KOH in sample flask. Conduct a blank determination along with the sample. Gently reflux sample and blank flask until it becomes transparent/clear (this usually takes 1h). After the flask and condenser have cooled, wash down the inside of the condenser with about 10 ml hot ethyl alcohol neutral to phenolphthalein. Titrate the saponified sample with 0.5N HCl adding 1 ml of phenolphthalein and mix well and continue titration till the pink color disappears, which is the end point. Note burette reading and calculation done using following relation:

$$\text{Saponification value} = \frac{56.1 \times N \times (V_B - V_S)}{W}$$

Determination refractive index of oil sample

Refractive index of oil sample by titration method as per the guidelines of FSSAI [7]. Melt the sample if it is not already liquid and filter through a filter paper to remove impurities and traces of moisture. Make sure sample is completely dry. Circulate stream of water through the instrument. Adjust the temperature of the refractometer to the desired temperature. Ensure that the prisms are clean and dry. Place a few drops of the sample on the prism. Close the prisms and allow standing for 1 - 2 minutes. Adjust the instrument and lighting to obtain the most distinct reading possible and determine the refractive index or butyro refractometer number as the case may be.

Determination total polar compound (TPC) by using column chromatography

The total polar compound of oils were determined as protocol suggested by Reder, *et al.* [9]. Briefly, 2.5g sample was weighed with a 0.001 precision and diluted using 20 mL of an 80:20 v/v petroleum ether: diethyl ether solution as the eluent solvent. The nonpolar fraction and the polar fraction of the samples were separated in a glass column using eluent solvent and silica gel. A 150 mL eluent mixture was used to elute the nonpolar fraction for 50 minutes. Following the solvent's evaporation, the percentage of TPC was measured gravimetrically, and the outcome was computed using the following formula:

$$TPC(\%) = \frac{M_s - m_n}{m_s} \times 100\%$$

Where: m_s :Initial sample mass, m_n :Nonpolar fraction mass.

Frying techniques

The techniques suggested by Warner and Knowlton [10] is slightly modified and intermittent frying temperature is adjusted at 185 ± 5 with a total of 10 hours of frying and heating spread across 5 days. For the frying, 1 litre of each oil sample that was to be evaluated was used. Dried finger chips that were cooked for two hours every day in iron pans in 25g batches. The oil was preconditioned by heating it to 185 ± 5 and holding it there for 30 minutes on the first day of frying and the dried finger chips were fried for one to two minutes, or until the oil stopped bubbling [11]. For a total of two hours, batches of dry finger chips were fried seven minutes apart. Before frying starting on next day, fresh oil was added daily to restore the pan's oil to its starting level [11,12].

Preparing an oil sample

Every next day morning, oils cooled for overnight at room temperature ($36 \pm 2^\circ\text{C}$) was taken for analysis. At day 0, day 1, day 2, day 3, day 4, and day 5, six samples of each oil were taken. The identical method utilized for the initial oil analysis was applied to all of the gathered oil samples.

Statistical analysis

The three replicates' means and standard deviations are shown as values. IBM SPSS Statistics Version 27 was used for ANOVA and post hoc test.

Results and Discussion

Variations in the amount of free fatty acid (FFA)

Free fatty acid (FFA) content can be considered as a substrate for total acidity (TAG) hydrolysis as well as fatty acid double bond cleavage and oxidation to estimate the extent of degradation [13]. The initial free fatty acid in soybean oil and palm olein were 0.21%, and 0.18% and at the end of the frying period the TPC level increased to 0.44% and 0.43% for the oils respectively. When the number of frying time cycles increases, the value keeps rising. This suggests that hydrolytic breakdown was occurring in the triacyl glycerol components [6]. The amount of FFA produced by hydrolysis is too tiny to have an impact on food quality in nearly all of deep fat frying operations. Usually, the oxidation of unsaturated fatty acids is the cause of the negative consequences [14].

Day	SBO	PO
0	$0.21^a \pm 0.01$	$0.18^a \pm 0.02$
1	$0.24^a \pm 0.02$	$0.23^b \pm 0.01$
2	$0.28^b \pm 0.01$	$0.27^b \pm 0.02$
3	$0.34^b \pm 0.01$	$0.31^a \pm 0.01$
4	$0.40^c \pm 0.02$	$0.37^b \pm 0.02$
5	$0.44^b \pm 0.01$	$0.43^b \pm 0.01$

Table 1: Changes in free fatty acids (FFA) content of frying oils over time.

Mean values within each column followed different letters (a, b, c) are statistically significant different ($p < 0.05$).

Acid value (AV) variations

The acid value serves as a determinant of the oil’s quality and appropriateness for consumption, as well as its efficacy in paint production, by indicating the level of free fatty acids present within the oil [15]. The initial AV values of the oils were 0.41 mg KOH/g and 0.35 mg KOH/g for SBO and PO, respectively. The acid value reported in this study is lower than documented by Ajai., *et al.* [16] in similar study. At the end of the frying period the acid value increased to 0.87 mg KOH/g and 0.85 mg KOH/g for the oils used respectively. The AV values of the final 5 days showed significant different ($p < 0.05$). These values serve as indicators of the degree to which the glycerides in the oil have undergone decomposition due to lipase activity and other physical transformations experienced by palm oil. The AV value disclosed in this investigation falls below the 3.56 ± 0.20 figure reported previously [16].

Day	SBO	PO
0	0.41 ^a ± 0.24	0.35 ^b ± 0.06
1	0.44 ^a ± 0.15	0.45 ^a ± 0.05
2	0.55 ^b ± 0.09	0.53 ^a ± 0.18
3	0.67 ^c ± 0.03	0.61 ^b ± 0.29
4	0.79 ^b ± 0.61	0.73 ^c ± 0.08
5	0.87 ^c ± 0.04	0.85 ^c ± 0.02

Table 2: Changes in acid value (AV mg KOH/g) content of frying oils over time.

Mean values within each column followed different letters (a, b, c) are statistically significantly ($P < 0.05$) different.

Iodine value (IV) variations

Table 3 illustrates the variations in the induction value (IV) of the oils over a span of 5 consecutive days of frying. The initial IV values of the oils were 131 and 60.58 for SBO and PO, respectively which is higher than the value obtained by Aremu., *et al.* [17], Akubugwo and Ugbogu [15], indicates the appreciable levels of unsaturated bonds in the oil samples. At the end of the frying period the iodine value decreased to 117 and 49 for the oils respectively. The IV values of the final 5 days showed significant different ($p < 0.05$). A decrease in IV can be attributed to the destruction of double bonds by oxidation and polymerization. The result obtained is similar to study made on deep fat frying of banana by Abdulkarim, Frage., *et al.* [18].

Day	SBO	PO
0	131 ^a ± 0.24	60.58 ^a ± 0.06
1	130 ^b ± 0.15	60.31 ^a ± 0.05
2	127 ^b ± 0.09	55 ^b ± 0.18
3	124 ^c ± 0.03	53 ^b ± 0.29
4	121 ^a ± 0.61	50 ^c ± 0.08
5	117 ^c ± 0.04	49 ^c ± 0.02

Table 3: Changes in iodine value (IV (g I₂/100 g oil)) content of frying oils over time.

Mean values within each column followed different letters (a, b, c) are statistically significantly ($P < 0.05$) different.

Peroxide value (PV) variations

Table 4 illustrates the variations in the peroxide value (PV) of the oils from day 0 to 5. The initial PV values of the oils were 3.97 meqO₂/kg and 2.946 meqO₂/kg for SBO and PO, respectively. This recorded value is below the value documented by Aremu., *et al.* [17]. And at the end of the frying period the peroxide value of SBO decreased to 3.04 meqO₂/kg and that PO increased to 4.43 meqO₂/kg. The PV values of the final 5 days shows significant different ($p < 0.05$). PV by itself is not an effective way to evaluate the degree of degradation of fats and

oils. An rise in PV throughout the cooking process signifies more peroxides being formed as a result of oxidation. Peroxides, however, are unstable in deep-frying temperatures; as a result, when oil deteriorates, the hydroperoxides break down and form carbonyl and aldehydic chemicals, which lower the peroxide value [19].

Day	SBO	PO
0	3.97 ^a ± 0.29	2.946 ^b ± 0.02
1	4.32 ^a ± 0.02	3.846 ^a ± 0.01
2	5.09 ^b ± 0.01	4.306 ^b ± 0.02
3	4.87 ^b ± 0.01	4.78 ^c ± 0.01
4	3.14 ^a ± 0.02	4.99 ^b ± 0.02 ^b
5	3.04 ^a ± 0.01	4.43 ^a ± 0.01

Table 4: Changes in peroxide value (PVmeqO₂/kg) content of frying oils over time.

Mean values within each column followed different letters (a, b, c) are statistically significantly (P < 0.05) different.

Variations in total polar compound (TPC)

The alteration in the percentage of total polar compounds (TPC) over the course of the frying duration is depicted in table 5. The most dependable assessment of the level of degradation in frying oils across various scenarios is observed changes in TPC (Fritsch, 1981). The initial total polar compounds in soybean oil and palm olein were 14.5%, and 13.5% respectively. Soybean oil is more prone to oxidation and contains higher concentrations of linoleic acid (51%) and linolenic acid (7%). Olein palm is more stable because it mostly comprises of monounsaturated and saturated fatty acids. When oil was fried, it underwent oxidation and a heat process that produced the polar chemicals. Because of this quicker rate of oxidation, more polar molecules were produced during frying in soybean oil than in palm olein [20]. At the end of the frying period the TPC level increased to 33.3% and 22.5% for the oils respectively. This result is similar to deep fat frying of banana by Kumar Nayak., *et al.* [6]. A statistically significant difference (p < 0.05) was identified in the TPC values between SBO and PO. The total polar compounds (TPC) in heated oils encompassed all substances resulting from oxidation and decomposition processes induced by heat, with the magnitude of the polar component serving as an indicator of the extent of degradation [18].

Days	SBO	PO
0	14.5 ^a ± 0.5	13.5 ^a ± 0.4
1	23 ^b ± 0.3	15.23 ^a ± 0.3
2	24.5 ^b ± 0.2	16.5 ^b ± 0.4
3	26 ^b ± 0.6	18.9 ^c ± 0.2
4	30.1 ^c ± 0.7	21 ^c ± 0.6
5	33.3 ^c ± 0.5	22.5 ^b ± 0.8

Table 5: Chemical changes in total polar compound (TPC) of frying oils over time.

Mean values within each column followed different letters (a, b, c) are statistically significantly (P < 0.05) different.

Variations in saponification value (SV)

Table 6 illustrates the variations in the saponification value (SV) of the oils from day 0 to 5. The initial PV values of the oils were 163.04 mgKOH/g and 200.5 mgKOH/g for SBO and PO, respectively. The saponification value (SV) determined in this study falls within the range as documented by Aremu., *et al.* [17] in certain Nigerian oilseed sources. At the end of the frying period the saponification value increased to 190.81 mgKOH/g and 214.55 meqO₂/kg. There is no significant difference entire 5 days (p > 0.05). The increased

amounts of SV seen in both SBO and PO could be explained by the production of comparatively more secondary oxidation products, namely carbonyl compounds, as a consequence of primary oxidation products being transformed [16]. The volatility of oils rises with an increase in saponification value. Because it demonstrates that 1g of oil contains smaller molecular weight components, which will provide more energy upon combustion, it improves the oil's quality. A low saponification value suggests that the oil might not be good for manufacturing shampoos, oil-based ice cream, or soap [15].

Day	SBO	PO
0	163.04 ^a ± 0.45	200.5 ^a ± 0.24
1	174.60 ^b ± 0.34	204.23 ^a ± 0.32
2	187.84 ^c ± 0.39	207.08 ^b ± 0.19
3	191.01 ^a ± 0.50	210.77 ^b ± 0.41
4	192.50 ^b ± 0.65	212.89 ^c ± 0.30
5	190.81 ^b ± 0.27	214.55 ^c ± 0.31

Table 6: Chemical changes in saponification value (SV mg KOH/g) of frying oils over time.

Mean values within each column followed different letters (a, b, c) are statistically significant (P < 0.05). different.

Variation in refractive index (RI)

Table 7 displays the refractive indices of sunflower oil (SBO) and palm olein (PO) from day 0 to 5. The refractive index is found to be similar to result obtained by Ajai., *et al.* [16], indicating a high number of carbon atoms in the fatty acids oils. There is a significant difference (p < 0.05) in the mean values of RI of SBO and PO. Results in table 7 show that the refractive index of the oils increased with that of soybean oil going from the initial 1.46738 of the original oil to 1.46915 on frying of the final dried finger chips batch, palm olein's refractive index increased from 1.45902 of the original oil to 1.46071 after frying the fifth batch. The results obtained are in agreement with the work of [21]. According to Arya., *et al.* the refractive Index provides an objective way to assess the rancidity of edible oils and fats. Frequent frying causes an ongoing rise in the oil's RI batches show that deep-frying causes the oil to become more rancid. This implies that it is not advisable to fry food in the same vegetable oil repeatedly [21].

Day	SBO	PO
0	1.46738 ^a ± 0.01	1.45902 ^a ± 0.01 ^a
1	1.46772 ^b ± 0.01	1.45925 ^b ± 0.02 ^a
2	1.46825 ^b ± 0.01	1.45948 ^b ± 0.011 ^a
3	1.46852 ^a ± 0.02	1.45988 ^a ± 0.013 ^a
4	1.46891 ^c ± 0.01	1.46029 ^a ± 0.02 ^a
5	1.46915 ^c ± 0.01	1.46071 ^c ± 0.03 ^a

Table 7: Chemical changes in refractive index (RI) of frying oils over time.

Mean values within each column followed different letters (a, b, c) are statistically significantly different (P < 0.05).

Conclusion

The deterioration of vegetable oil during processing at high temperatures is a complicated problem. The physiochemical changes in oil are based on multiple references. Increase in in FFA, acid value Peroxide value, TPC, Iodine Value, Saponification value, refractive index. The changes are not good for people's health. Soybean oil and palm olein are the finest vegetable cooking oil having health benefits turns into health hazardous after being treated to high temperature during deep fat frying.

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