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Studies on the Quality Indices of Processing of Edible Vegetable Oils

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Abstract: This study shows the quality Indices of edible vegetable oils. The quality of deep-fried oil is affected by several processes such as hydrolysis, oxidation, and polymerization, which in turn alters the flavor stability, and reduces tocopherols and fatty acids in Oil. Palm olein (PO), Refined sunflower oil (RSO), Sesame oil (SO), Groundnut oil (GO), Rice bran oil (RBO), Coconut oil (CO), Virgin coconut oil (VCO), Cold press sesame oil (CSO) and Cold press groundnut oil (CGO) were used in the current study. Oils were fortified with α-tocopherols, retinol, calciferol, and phytonadione of fat-soluble vitamins and were heated at 220°C. Physicochemical characteristics (Primary, secondary, tertiary oxidation) were studied to determine the stability of fortified oil samples. Acid value (mg NaoH/g) of deep-fried coconut oil, groundnut oil, sesame oil, rice bran oil, Palmolein oil, and Refined sunflower oil at 200-220°C is 1.43, 1.55, 7.3, 1.2, 1.13, 1.6 respectively. Peroxide value (meq of active O_2/Kg) of deep-fried dried coconut oil, groundnut oil, sesame oil, rice bran oil, Palmolein oil, and refined sunflower oil at 200-220°C is 1.25, 2.6, 3.2, 1.5, 6.98, and 2.25. Iodine value (g of iodine per 100 g oil) of deep-fried coconut oil, groundnut oil, sesame oil, rice bran oil, Palmolein oil, and refined sunflower oil at 200-220°C is 10.6, 99.09, 121.1, 104.45, 63.01, 144.23. After processing at the temperature of 200-220°C, the fortified vitamins have deteriorated.

Keywords: Tocopherol, Edible Oil, Antioxidant, Deep Frying, Degradation

1. Introduction

Oil is commonly exploited in the trendy culinary technique known as frying, both in industrial and household food preparation. Oils are substrates for the production of biological membranes, such as phospholipids and cholesterol, which are essential for the formation of cell membranes involved in human metabolism [8]. In India consumption of vegetable oils in the year 2021 was over 22 million metric tons and 19-19.80 kg per person per annum which include coconut oil, palm oil, sunflower oil, groundnut oil, and sesame oil. Unsaturated fatty acids and the lack of cholesterol in vegetable oils make them the better alternative to animal fat [4]. The most significant use of oils in our diet is to provide desired organoleptic features including flavor, aroma, texture, and mouth feel, which make our food pleasant and convey a sense of satisfaction [1].

The primary component of fried food products is edible vegetable oil. Fried food consumption results in the consumption of highly oxidized fatty acids. For frying, oils with a high amount of saturated fatty acids, such as coconut oil and Palmolein, or oils with a high amount of mono-unsaturated fatty acids, such as groundnut oil, refined rice bran oil, and high oleic sunflower oil, are preferred. In order to maximize efficiency and save costs, vegetable oil is heated multiple times. The oil provides a heat transfer medium and even a carrier for fat-soluble vitamins A, D, E, and K. As a fat-soluble vitamin, oil is an ideal matrix for vitamin fortifications. As commercial edible vegetable oils were intended to minimize vitamin deficiency in people, it is crucial to understand the condition of vitamin fortification in products [9]. Excessive reuse of the same cooking oil causes chemical reactions that increase the foaming and darkening of the oil, which can lead to degradation. During deep-fat frying, mass transfer results in the loss of oil, protein, carbohydrates, vitamins, and moisture from the fried food and the absorption of oil by the product [10].

Consequently, both frying oil and fried food have an effect on one another and increase the frequency of complicated reaction pathways. Oxidation, polymerization, isomerization, and hydrolysis are the main chemical processes that take place during deep-fat frying; as a result, the oil quality degrades to the point that it is no longer suitable for frying [2]. The objective of this study is to examine the quality changes in oil at different temperatures and times, when oil reaches maximum safe during frying, and also assess the current vitamin fortification status of commercially available oils.

2. Materials and Methods

2.1. Raw Material

Initially, frying Physico-chemical tests were performed using six commercial oils namely Palm olein oil, Ground nut oil, Sesame oil, Rice bran oil, Coconut oil, and refined Sunflower oil was carried out. Several batches of potato chips were fried using fried at different intervals of time.

2.2. Oil Sample

Following each successive frying temperature, 25ml of oil was extracted for analysis until a high degree of frying was reached. Throughout the frying operations of the present designations, the oil amount was not refilled.

2.3. Differential Processing of Oil

Potatoes were Procured from the local market (Chennai), thoroughly washed and cleaned manually. Fresh Indian potato was cut into 3-5cm length of shoestring size 0.5cm*0.5cm at different temperatures. Fry potato chips until the oil stops bubbling (estimated time of 2-3min). Several batches of potato chips were fried for 5 minutes at varying temperatures.

2.4. Preliminary oil Analysis / Chemical Analysis

AOACS, ISO, and FSSAI recommended methods were used to determine Moisture content and other impurities (FSSAI 02.001:2021), Free fatty acid content (FSSAI 02.009:2021, AOAC method 940.28 (AOAC, 2005)), Iodine value (AOAC 920.158, FSSAI 02.010:2021), Acid value (FSSAI 02.009:2021), Peroxide value (FSSAI 02.042:2021, AOAC 965.33 (AOAC, 2005)), P-Anisidine value (ISO/FDIS 6885).

Color (FSSAI 02.005: 2021) was analyzed using the Lovibond Tintometer model FX [11]. The fatty acid composition was determined according to the method of AOAC Method 996.06 using Gas chromatography/Flame ionization detector (GC-FID) Using the AOCS-approved technique, fatty acid methyl esters (FAME) were prepared. Celi-07 (AOACS, 2017).

2.5. Statistical Evaluation

Oil samples were evaluated in triplicate and the standard deviation (SD) was recorded. Microsoft Office Excel was used for general statistical analysis (MS Excel 2007). The correlation coefficients were found to be significant.

2.6. Gas Chromatography- Flame Ionization Detector (GC-FID) Instrumental Condition

Using a gas chromatograph (Shimadzu GC-14B, Japan) outfitted with a flame ionization detector and a fused silica capillary column (FAMEWAX, Cross bond polyethylene glycol), the composition of fatty acids was examined. It was injected using a split-less approach using nitrogen as the carrier gas at a constant flow rate of 20 ml/min. The oven's beginning temperature was 150°C, and the injector temperature was 250°C for five minutes. The temperature was raised to 190°C at a rate of 8°C/min and then kept at 200°C for 10 minutes at a rate of 2°C/min. The automated GC program was used to identify the fatty acids using the appropriate fatty acid methyl ester standards (FAME mix), which were then displayed as relative percentages (Mass Hunter) as described in the determination of Trans fatty acids, Modification to AOAC 996.06 (the research) [16].

2.7. Analysis of Fatty Acid Composition

Fatty acid (FA) from the oil sample's relative concentration was calculated as corresponding methyl esters. In a 15 ml test tube, 5-7 droplets of oil were placed, and 3 ml of 0.5 M sodium methoxide (produced by mixing metallic sodium in methanol) was added and digested for about 15 minutes by stirring in a boiling water bath. It was allowed to cool to ambient temperature before slowly adding 1 ml of petroleum ether (b.p 40-60 C) and 10 ml deionized water, which was gently mixed and allowed to settle for 5-6 minutes. The distinct top layer of methyl ester in petroleum ether was carefully isolated and analyzed in a sealed bottle. In a series of screw-capped test tubes, 200 mg of each fatty acid standard in its corresponding methyl ester form were dissolved individually in 10 ml petroleum ether (b.p 40-60 C). Aliquots of 1 µL fatty acid methyl ester (FAME) were injected, and the peaks of fatty acids were recorded by the data processing unit of the GC for their respective retention time and areas [6].

2.8. Abbreviations

The abbreviations terms of oil used in processing are Palm olein (PO), sunflower oil (RSO), sesame oil (SO), groundnut oil (GO), Rice bran oil (RBO), Coconut oil (CO), Virgin coconut oil (VCO), Cold press sesame oil (CSO) and Cold press groundnut oil (CGO), Iodine Value (IV), Peroxide value (PV), Gas chromatography/Flame ionization detector (GC-FID), Free fatty acid (FFA).

3. Result and Discussion

There are various oxidation parameters. During frying, physicochemical reactions such as oxidation, hydrolysis, and polymerization occur. As oil oxidizes, it creates a series of breakdown products in three stages: (1) primary oxidation (peroxides, dienes, and FFA); (2) secondary oxidation (carbonyls, aldehydes, and trienes); and (3) tertiary oxidation (carbonyls, aldehydes, and trienes) (polymerization of secondary oxidation products). The physical properties like Moisture content and other impurities and color of various edible

vegetable oil used in deep fat potato frying have been described.

Groundnut oil is 45.07% and Linoleic acid in refined sunflower oil shows higher as 60.13%, respectively. Oils having a high amount of mono-unsaturated fatty acids (oleic acid) are preferred due to the health advantages correlated with coronary heart disease. As a consequence, multiple attempts at processing various oils to enhance the monounsaturated fatty acid concentration are done.

3.1. Evaluation of Physical Characteristics of Fried Oil

The initial value of moisture & other impurities content of different edible vegetable oil was found and noted. The moisture content of oils and fats is the mass loss of the sample when heated at 105 ± 1 °C under the given operating conditions. This moisture is derived from the lubricating oil progressively interacting with ambient air humidity over time. The more additives in the oil, the more hygroscopic (water-attracting) it becomes. Typical acceptable dissolved moisture levels are 50-300 ppm (or 0.0050 percent – 0.0300 percent). A maximum moisture level of 0.2% is allowed in edible oils.

The change in color was visible to the naked eye and this was supported by the Lovibond Tintometer values obtained and noted. Even the naked eye could see the discoloration of the oil throughout the frying process. The various causes for the darkening of oil color when heated as stated in the literature [11].

3.2. Oxidation Parameter

During frying, physicochemical reactions such as oxidation, hydrolysis, and polymerization occur. The breakdown of oil results in three different types of breakdown products: primary oxidation (peroxides, dienes, and FFA); secondary oxidation (carbonyls, aldehydes, and trienes); and tertiary oxidation (carbonyls, aldehydes, and trienes) (polymerization of secondary oxidation products).

3.3. Fatty Acid Profile

Oils involved in the frying experiment contained different fatty acid contents shown in Table 1. The different types of processed oils such Cold pressed ground nut oil, Palmolein oil, Virgin coconut oil, Rice bran oil, refined sunflower oil, and Sesame oil. The most eminent fatty acids in the oil are Palmitic acid (13.81%, 40.52%, 9.18%, 21.44%, 7.03%, and 10.79%) as saturated fatty acid, Mono Unsaturated fatty acid of oleic acid (45.07%, 39.86%, 5.51%, 40.91%, 27.83%, and 39.20%) and polyunsaturated fatty acid of Linoleic acid (30.67%, 11.69%, 0.87%, 32.22%, 60.13%, and 43.08%) which are found in a differential variety of processed oils, respectively. Palmitic acid was found higher in Palmolein oil at 452%, Oleic acid was found higher in cold-pressed.

Table 1. *Differential processing of FFA as Oleic acid of different oil.*

Frying Time-30 mins					
Types of oils	**Frying temperature (°C)**				
	Fresh oil (without frying)	**140-160**	**160-180**	**180-200**	**200-220**
CO	0.51	1.50	2.12	3.56	4.03
SO	0.91	1.51	2.05	2.80	4.01
GO	0.91	1.85	2.15	3.35	4.30
PO	0.87	1.83	2.71	3.20	3.92
RSO	0.15	0.63	1.65	3.34	5.01
RBO	0.02	0.19	0.23	1.35	2.52
VCO	0.43	0.55	1.98	2.54	3.82
CPSO	0.51	1.50	2.12	3.56	4.03
CPGO	0.81	1.61	2.01	3.20	3.95

*All values are expressed as %.

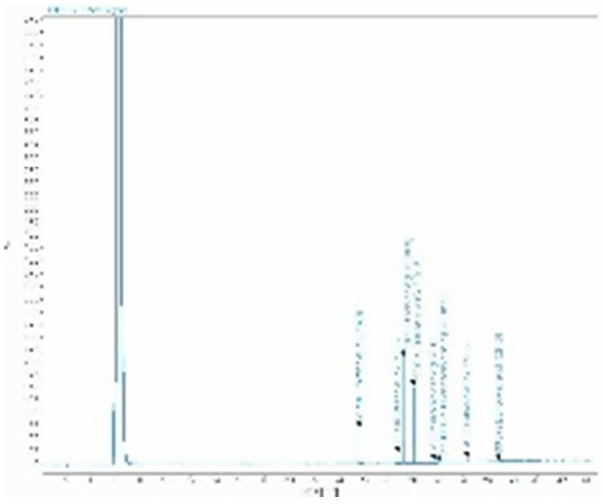

Figure 1. *Fatty acid profile of groundnut oil.*

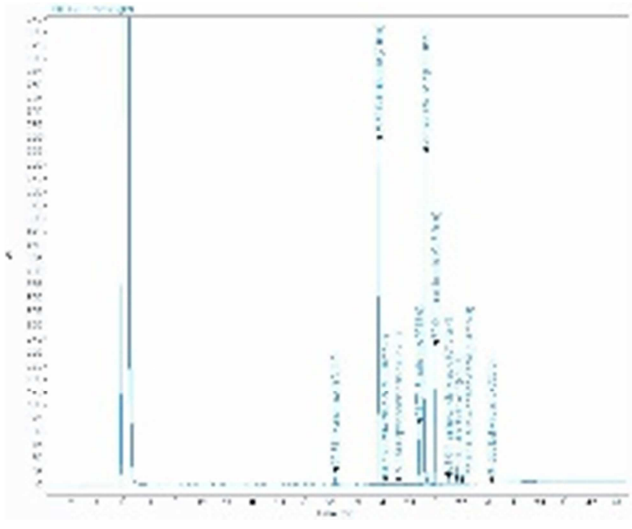

Figure 2. *Fatty acid profile of Palmolein oil.*

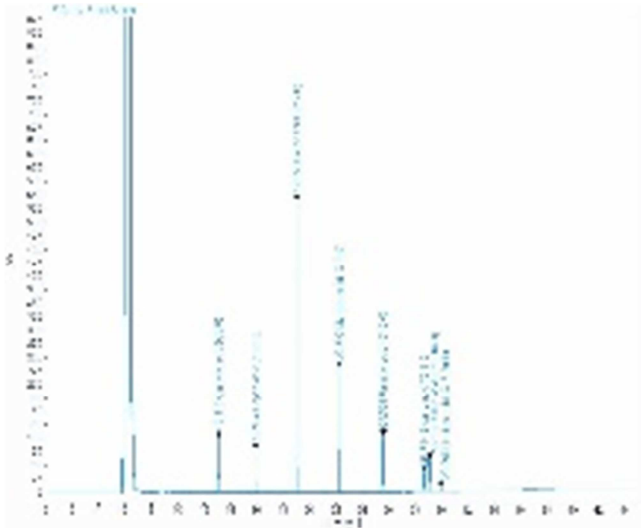

Figure 3. *Fatty acid profile of Coconut oil.*

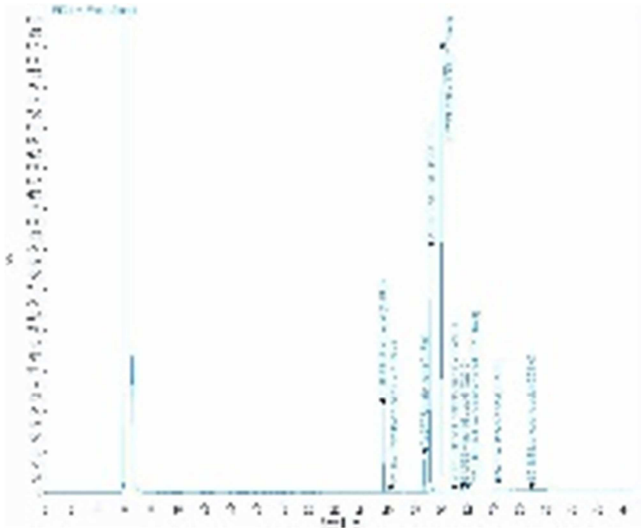

Figure 4. *Fatty acid profile of Rice bran oil.*

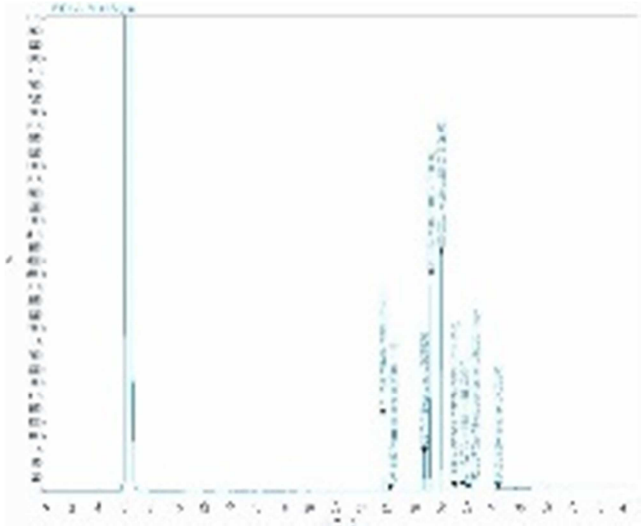

Figure 5. *Fatty acid profile of Refined Sunflower oil.*

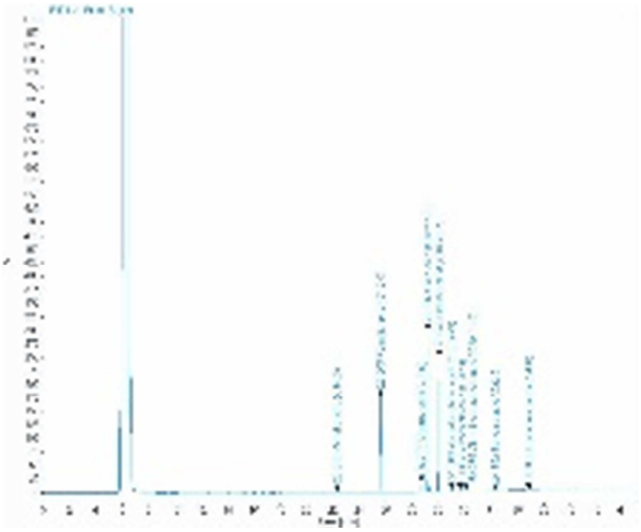

Figure 6. *Fatty acid profile of Sesame oil.*

3.4. Changes in Free Fatty Acid Content (FFA)

To estimate the amount of FFA in fats or oils the level to which they have deteriorated due to the hydrolysis of Triacylglycerol or the oxidation of double bonds [2]. Although initial FFA as oleic acid values of the oil was different for VCO, CSO, CGO, PO, RSO, RBO, CO, GO, and SO as (0.72%, 3.67%, 0.756%, 0.564%, 0.81%, 0.605%, 0.75%, 0.8105%, and 3.719%), respectively, at the end of frying temperature of 220°C. The overall change in FFA levels ranges from the initial to the final temperature of frying. While the frying process continues, the FFA value rises [12]. On sesame oil and ground nut oil. Moreover, the value of these variations in food products alters. They noticed that the FFA of potatoes was greater than the FFA of deep-frying oil. Potatoes have 78% moisture by weight. It is caused by the release of fatty acids from foods that contain fat, and their concentration in the frying oil rises over time. The FFA value increases with the number of heating and frying cycles. With frying, the changes in FFA are higher than that when cooking [13]. Water can increase the hydrolysis of TBA to generate a mixture of free fatty acids, which is why moisture from fried foods promotes hydrolysis. When combined with other approaches, it can be a useful predictor of the level of fat misuse. Nevertheless, because titration to determine free fatty acids is a quantitative method, it is hard to establish how much of the increase in free fatty acids is due to oxidation or hydrolysis [3].

3.5. Changes in Peroxide Value

The peroxide value is a valuable early indication of oxidation; however, it is related to the time of frying. In the determination of this value, the rate of change in PV is shown in Table 2. The PV of the PO oil is increasing rapidly from the initial stage of raw oil to frying. The PO has higher values of PV (6.986 meqO_2/kg) of oil with a frying temperature of 220°C and the lowest of 3.30 meq O_2/kg of SO. The PV shows the least values of 1.5 meq O_2/kg of RBO,

respectively. This was mostly owing to the high levels of Linoleic acid, which demonstrated poorer oxidation stability. The quick increase in PV of various oils demonstrated extremely unstable oxidative degradation. As compared to other oils, the levels of C18:2 and C18:3 in VCO and RSO are 0.87 meq O_2/Kg and 0.08 meq O_2/Kg, respectively. PV is not an accurate measure for determining the amount of oil degradation [3]. An increase in PV during the frying time indicates increased peroxide generation due to oxidation. Nevertheless, peroxide levels are unstable under deep-frying conditions due to the hydroperoxides degrading into carbonyl and aldehydes molecules when the oil deteriorates, leading peroxide values to fall.

Table 2. *Differential processing on peroxide value of different oil.*

Frying Time-30 mins					
Types of oils	**Frying temperature (°C)**				
	Fresh oil (without frying)	**140-160**	**160-180**	**180-200**	**200-220**
CO	0.88	1.05	1.20	1.22	1.28
SO	0.64	1.60	2.40	2.61	3.30
GO	0.50	0.81	1.55	2.28	2.60
PO	0.14	1.99	2.60	3.57	6.99
RSO	0.79	0.83	1.50	2.01	2.25
RBO	0.56	0.6	0.89	1.02	1.50
VCO	0.85	1.00	1.13	1.20	1.25
CPSO	0.63	1.51	2.33	2.59	3.20
CPGO	0.50	0.83	1.52	2.15	2.57

*All values are expressed as a unit of peroxide value meq of active O_2/Kg

3.6. Changes in Iodine Value

The iodine value of oil serves as a direct indicator of the oil's degree of unsaturation [14]. The changes in Iodine value for different oil is shown In Table 3. The breakdown of double bonds by oxidation and polymerization results in a decrease in Iodine value. Changes in Iodine value at the initial stage of raw oil for SO, RSO, and CSO are 107.05 g/100ml, 105.12 g/100ml, and 105.3 g/100ml, respectively. The IV of RSO, SO and CSO shows a drastic increase at frying temperature 220°C as 144.23 g/100ml, 121.5 g/100ml, and 121.1 g/100ml respectively. Other oils were analyzed and evaluated as well. As a result, deep frying enhances the oxidation of the oil, resulting in the greatest drop in iodine levels. This indicated that VCO and CO were the least oxidation-resistant.

Table 3. *Differential processing on iodine value of different oil.*

Frying Time-30 mins					
Types of oils	**Frying temperature (°C)**				
	Fresh oil (without frying)	**140-160**	**160-180**	**180-200**	**200-220**
CO	8.15	8.56	9.62	9.89	11.01
SO	107.05	110.1	112.12	115.1	121.5
GO	86.00	89.3	92.01	96.32	99.09
PO	55.01	58.15	60.2	61.16	63.01
RSO	105.12	118.2	125.8	130.7	144.23
RBO	95.20	98.23	101.5	103.38	104.45
VCO	7.50	8.01	8.21	9.35	10.53
CPSO	105.3	108.2	111.01	115.08	121.1
CPGO	85.5	88.1	90.22	96.32	99.09

*All Values are expressed as g of iodine/100 ml of oil.

3.7. Changes in the p-Anisidine Value

This technique for determining secondary changes in oils is described as 100 times the optical density measured at 350 nm in a 1 cm cell containing 1g of oil in a 100 ml combination of solvent and reagent [4]. It's used to determine where the aldehydes are in animal fats and vegetable oils. To indicate the degree of oxidative rancidity, this approach is combined with the peroxide value.

$$TOTOX = 2PV + p\text{-}AV$$

Hence, determining TOTOX Value has been used widely to calculate the rate at which dietary lipids oxidize. This number indicates the level of product deterioration and the quality of the oil or fat. The result of this analysis is shown in Table 5. Frying at 220°C, the TOTOX values of PO (17.893) show higher when compared to CSO (10.54), RSO (9.510), and CGO (9.82), respectively. The higher TOTOX values in CSO, RSO, and CGO were due to the high percentages of polyunsaturated fatty acids. They contain a high amount of Linoleic acids and Linoleic acids. In contrast, RBO, on either hand, includes a large amount of monounsaturated fatty acid (oleic acid), which enhances oxidative stability and reduces TOTOX levels. The greatest TOTOX level indicates a significant decrease in stability [5].

The study found that AnV increased dramatically during frying with RSO, with the highest increase seen in Table 4. AnV levels were often much lower in heated oils than those found in frying oils. AnV observed in RSO, GO, and CO during frying was substantially greater than during heating. As a result, the loss of aldehydes during oxidation and polymerization to produce higher molecular weight compounds from fatty acids counterbalanced the formation of more aldehydes.

Table 4. *Differential processing on the p-Anisidine value of different oil.*

Frying Time-30 mins					
Types of oils	**Frying temperature (°C)**				
	Fresh oil (without frying)	**140-160**	**160-180**	**180-200**	**200-220**
CO	0.51	1.50	2.12	3.56	4.03
SO	0.91	1.51	2.05	2.80	4.01
GO	0.91	1.85	2.15	3.35	4.30
PO	0.87	1.83	2.71	3.20	3.92
RSO	0.15	0.63	1.65	3.34	5.01
RBO	0.02	0.19	0.23	1.35	2.52
VCO	0.43	0.55	1.98	2.54	3.82
CPSO	0.51	1.50	2.12	3.56	4.03
CPGO	0.81	1.61	2.01	3.20	3.95

*All values are expressed as Absorbance (Å).

3.8. Determination of Total Oxidation (TOTOX Values)

p-AV can be used to calculate the total oxidation value, and it's generally used in industry for the evaluation of the TOTOX value in combination with PV.

Table 5. *Differential processing on TOTOX value of different oil.*

Frying Time-30 mins					
Types of oils	**Frying temperature (°C)**				
	Fresh oil (without frying)	**140-160**	**160-180**	**180-200**	**200-220**
CO	0.51	1.50	2.12	3.56	4.03
SO	0.91	1.51	2.05	2.80	4.01
GO	0.91	1.85	2.15	3.35	4.30
PO	0.87	1.83	2.71	3.20	3.92
RSO	0.15	0.63	1.65	3.34	5.01
RBO	0.02	0.19	0.23	1.35	2.52
VCO	0.43	0.55	1.98	2.54	3.82
CPSO	0.51	1.50	2.12	3.56	4.03
CPGO	0.81	1.61	2.01	3.20	3.95

*All values are expressed as no unit.

3.9. Analysis of Vitamins

Commercial oils such as rice bran oil, sesame oil, Palmolein oil, and groundnut oil are fortified with essential vitamins A, D, and natural antioxidant vitamin E (*tocopherols*), which are present in many vegetable oils [7]. The fortified oils typically contain 2500-3000 IU of vitamin A, 11.25-12.5 mcg of vitamin D, and 17.7-35 mg of vitamin E per gram. However, after processing at high temperatures (200-220°C), the fortification levels of these vitamins were not found in the oils. According to FSSAI regulations, all edible oils should contain a vitamin fortification level of 15-30 ppm. Unfortunately, the vitamin content of these fortified oils did not meet the FSSAI criteria for fortified oil. It is crucial to further explore processing methods that minimize the loss of essential vitamins in fortified oils, to ensure that consumers receive the intended nutritional value from these products [15].

4. Conclusion

The purpose of this study was to determine the effects of heat deterioration on the four most often-used oils. These analyses have shown that the quantities of FFA, PV, p-AV, TV, and TPC in oil blends before frying are significantly affected. In general, palm olein outperformed the other oils in frying because it contains more saturated and unsaturated fatty acids, making it less vulnerable to oxidation. A significant correlation was observed between quality index parameters such as free fatty acids, iodine value, fatty acid composition, p-Anisidine value, and peroxide value, according to statistical analysis. Because they are less likely to break down at high temperatures, high-oleic oils often produce results in frying that are similar to those produced by palm olein.

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