CHEMICAL STABILITY OF COTTONSEED AND GROUNDNUT OIL USED FOR FRYING BHAJIAS AND ITS SENSORY QUALITIES

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ABSTRACT

Deep fried snacks, which evolved as snacks between meals include bhajia, samosa, etc are very popular in India and commercially exploited on a wide scale. Cottonseed and Groundnut oil frequently used in Gujarat for cooking purpose studied for its intermittent frying stability. Indian fried snack popularly known as ‘bhajia’ fried for 5 min at an interval of 1 h, 5 times a day for 5 consecutive days and studied for its various sensory attributes using 9-point hedonic scale. Standard AOCS and AOAC methods were used to determine the quality of oil. Peroxide and p-anisidine values of both oils increased significantly p<0.001 during the 25 h of intermittent frying. Iodine value of cottonseed oil did not decrease throughout the intermittent frying period. Component values increased 25.7% in cottonseed oil (CSO) and 142.9% in groundnut oil (GNO). The saturated and monounsaturated fatty acid content increased significantly with the increase in frying hours. No significant change was seen in linoleic/palmitic acid ratio of both the oils during bhajias frying. The sensory qualities of bhajia fried at different intervals did not change significantly for various attributes namely flavor, taste, crispness, greasiness, odor, color, appearance and overall acceptability.

Keywords: Edible oil, bhajia, frying, fatty acid profile, oxidation, sensory quality

INTRODUCTION

The popularity of foodstuffs covered with tempura-type frying battered products has increased worldwide (Patton, 2011). In this type of food, a chemically leavened batter serves as the outer coating of the food piece; giving good visual and structural characteristics to the product (Loewe, 1993). Popularity and simultaneous increase in demand of these products amongst the consumers ensure good sensory acceptability of battered foods. The deep fried snacks, which evolved as snacks between meals in India, have been known over a period of time, and are commercially exploited on a wide scale. These include a variety of foods including bhajia, samosa, bread rolls etc. Many existing studies on frying batters mainly analyze the characteristic of the basic ingredient, wheat flour for their sensory qualities (Cunningham et al., 1981; Hisia et al., 1992).

Deep-fat frying is a popular method employed in cooking various culinary preparations. This process may be defined as cooking by immersion of food in edible oil or fat at a temperature above the boiling point of water (Hubbard et al., 2000). During frying, the material undergoes chemical and physical transformation at a high operating temperature range of 160–180°C. The process starts with frying the raw product followed by starch gelatinization, protein denaturation, aromatizing and coloring via maillard reactions and finally leading to dehydration (Ziaifar et al., 2008). Repeated series of frying at elevated temperature may lead to undesired degraded reactions and decomposed constituents which results in oxidative rancidity; and/or hydrolysis and formation of polymerized and polar compounds and trans fats. Particles of food materials, as well as particles from breaded or battered food surface coatings, contaminate the frying oil in fairly large quantities. These particles remain in the frying oil until they are caramelized and finally become charred to fine suspending particles of black carbon. This is an important factor contributing to the darkening of the oil.

Deep fat frying imparts good taste, flavor, pleasing golden brown color, and crisp texture to food products along with excellent mouth feel. Number of studies on the modifications of fats and oils during heating and frying under very different conditions has been carried out on the assumption that acceptability of fried foods depends on the quality of the used frying oil or fat (Paul et al., 1997). Deteriorated oils are not only insidious causes of cancers, hypertension and coronary heart diseases but also result in foods with poor texture, flavor and shelf stability (Sagy et al., 2002).

The broad objective of this study was to investigate the intermittent frying stability of groundnut and cottonseed oil used for frying bhajias, in terms of its breakdown products. Consequently to assess the sensory quality of bhajias fried in these oils.

MATERIAL AND METHODS

Procurement of raw material

Double filtered groundnut oil (GNO) and refined cottonseed oil (CSO) were used for frying within one month of manufacture, procured from Ankur Oil Industries (Ahmedabad). For the preparation of bhajias Bengal gram flour (Gaaya) and other ingredients like sodium bicarbonate (Tata), salt (Tata), turmeric powder, red chili powder and bishop seeds were purchased from the local market. Potatoes of Kufri Surya variety were procured from Potato Research Station, Deesa (Gujarat).

Preparation of batter for Bhajia

Bhajias were prepared by deep frying thinly sliced circular potatoes that were dipped in a batter prepared out of 75 g Bengal gram flour with 70 ml water, a pinch of sodium bicarbonate, salt to taste, ¼ tsp turmeric powder, ¼ tsp red chilli powder and ½ tsp bishop seeds were added to the batter (Pasricha, 2004).

Frying procedure and sampling of fried oil

Frying experiment was performed in triplicates. Frying was conducted in 2-L capacity hindalium domestic deep frying pans (diameter-12”, depth-7.2”). Mitsubishi (ISI) mark auto ignition stainless steel LPG Stove was used during entire frying experiments. 1.5L GNO and CSO were placed in separate deep frying pans and heated at 180°C for each frying. Batches of bhajias were fried for 5 min at an interval of 1 h; five times a day for 5 consecutive days. The frying temperature was monitored after every minute with the help of mercury thermometer. Frying pans were not covered during the frying experiment. Oils were not topped up during frying. At the end of each day an aliquot of cooled 75 ml oil was pipette out from each fryer, stored in amber color glass air tight bottles and kept at -4°C in a deep freezer for further analysis.
Analytical Methods

Fatty acid methyl esters were prepared according to the analytical method of AOAC 996.01 (AOAC, 1995). Fatty acid composition was determined at 0, 5, and 10 h interval. GC (NUCON-5765) with 30m x 0.25 mm id, 0.2 µm film, non- bonded 90% cyanopropyl, 10% phenyl silicone capillary column with flame ionization detector was used for determination of fatty acids. Operating conditions: injector temperature 250°C, detector temperature was adjusted at 275°C, hydrogen flow 34 ml/min, air flow ca 300 ml/min, split ratio was 100:1. Helium as a carrier gas was used in flow rate of 2.4 ml/min at 175°C was adjusted. Initial oven temperature was adjusted to 120°C hold for 4 min and increased up to 230°C. Standard methyl esters of fatty acids were used as authentic samples and peak identification for samples was done by comparing relative retention times. Total Polar Components (TPC) was determined by gravimetric method at 0, 5 and 10 h interval. TPC were determined after column chromatography separation of non-polar fraction. Peroxide value (PV), Iodine value (IV), Reactive Index (RI), Acid value (AV), p-anisidine (p-AV), and Color determined at 0, 5, 10, 15, 20, 25 h interval. PV was evaluated following titration method. PV was expressed as milliequivalents of active oxygen per kilogram of oil (meq O₂/kg).

The IV of the samples was determined as Wij’s method. RI was determined using Abbe refractometer (ATAGO DR-A1, US). Readings were taken at 40°C temperature was regulated by using steam circulation (AOAC, 1995).

AV was defined as the number of milligrams of potassium hydroxide required to neutralize the free fatty acids present in one gram of fat. p-AV value was determined as the secondary oxidation products of the oil. Absorbance was measured at 350 nm, using Shimadzu 1201 UV-VIS spectrophotometer. The totox (total oxidation products) value used for evaluation of oils was calculated as: TTV = 2PV+αAV. PV was multiplied by a factor 2 because it has more pronounced effect on the stability of refined oil. Color was determined by Lovibond Tintometer (model F). Oil sample color was matched by adjusting yellow (Y) and red (R) racks of the instrument in the ratio of 5:Y5. A glass cell was filled with the sample and placed inside the illuminated cabinet (AOCS, 1998).

Fatty acid profile

The secondary decomposition products assessed by p-anisidine (p-AV) are significant (p<0.001) values when compared with suggested PFAlimit i.e. <10meq O₂/kg than groundnut oil at 0 h (PFA, 2007). At 5 h of intermittent frying 56.6% increase in PV of GNO was observed. However, CSO showed 34% decrease in peroxide value at 5 h of intermittent frying. CSO showed a progressive decrease then started decreasing thereafter. Despite increase at 5 h of intermittent frying in sunflower oil; Similar superscripts in each row indicate no significant difference at p<0.05.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Fatty acid profile (g/100 g fat) of GNO at different intervals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty acid</td>
<td>0 h</td>
</tr>
<tr>
<td>Palmitic</td>
<td>10.91±0.60*</td>
</tr>
<tr>
<td>Stearic</td>
<td>3.07±0.09a</td>
</tr>
<tr>
<td>Oleic</td>
<td>59.40±0.09b</td>
</tr>
<tr>
<td>Linoleic</td>
<td>22.48±0.18*</td>
</tr>
<tr>
<td>Behenic</td>
<td>4.14±0.01*</td>
</tr>
<tr>
<td>Table 3</td>
<td>Peroxide value (PV) of GNO and CSO at different intervals of intermittent frying. Primary oxidation in cottonseed oil showed significant higher (p&lt;0.001) values when compared with suggested PFA limit i.e. &lt;10meq O₂/kg than groundnut oil at 0 h (PFA, 2007). At 5 h of intermittent frying 56.6% increase in PV of GNO was observed. However, CSO showed 34% decrease in peroxide value at 5 h of intermittent frying. CSO showed a progressive decrease by 50.3% in PV up to 15 h of frying. Study by Rani et al (2008) reported that PV of sunflower oil increased from 2.0 to 28.65 after 22 h of discontinuous frying and then started decreasing thereafter. Despite increase at 5 h of intermittent frying in PV of GNO, it decreased significantly (p&lt;0.001) at 10 h of intermittent frying. In the present study, peroxide values of oils showed rise and fall as the duration of frying increased. Indication of instability of peroxides is reported by other studies who stated parallel results when various vegetable oils were used for frying. Use of PV for following the oxidative deterioration of fats and oils during deep-frying is problematic because peroxides are destroyed by heating temperature and during cooling new peroxides are formed (Rani et al, 2010; Farooqui et al, 2009; Augustin et al, 1983).</td>
</tr>
</tbody>
</table>
interval, which continued to increase up to 25 h of intermittent frying. Further, when potato fritters were fried in refined rapeseed oil for continuous 9 days (15 cycles each day), p-AV increased from 3.8 to 186 (Hazuka et al., 2000).

Acid value

Acid value (AV) of GNO oil at 0 h was significantly (p<0.001) high because of different grades viz, filtered (GNO) and refined (CSO). However, significant increase in AV of CSO was noticed at 5 h of intermittent frying (Table 3). According to PFA, suggested AV for GNO was <6 mg KOH/g and 0.5 mg KOH/g for CSO (PFA, 2007). During frying increase in this parameter is used to assess hydrolytic degradation in oils. GNO at 10 h of intermittent frying showed 24.35% increase in AV however; CSO showed two folds increase as compared to GNO. Refined rapeseed oil used for frying cod fillets, AV showed 1.64 units increase after 6.2 h of intermittent frying (Tynek et al., 2001). After 5 days (25 h) of bhajia frying significant (p<0.001) increase in AV with frying time was observed in both the oils. In some countries of the European Union (EU) greater than 2.5 disqualifies the oil for any further use (Firestone, 1993). However, in the present study none of the oils reached the discarding limit set by EU.

Iodine value

It was found that iodine value (IV) of CSO altered significantly (p<0.05) after 5 days of intermittent frying, indicating decrease in unsaturated fatty acids shown in Table 3. However, bhajia frying in GNO showed no significant change after 25 h of intermittent frying. Reduction in IV is due to complex series of chemical reactions characterized by a decrease in the total unsaturated content of the oil due to abstraction of hydrogen adjacent to the double bond, oxidation, scission, and polymerization (Tyagi et al., 2001; Narasimhamurthy et al., 1998).

Refractive Index

The refractive index (RI) of fried oils is reported in Table 3. RI recommended by PFA in GNO was 1.4620-1.4640 and in CSO was 1.4630-1.4660 (PFA, 2007). The RI of GNO and CSO at 0 h was 1.4624 and 1.4641 respectively. Refractive index of both the oils increased significantly (p<0.001) at the end of 25 h of intermittent frying. In another study similar pattern was observed when pooris were fried in blend of cottonseed and mustard oil (Premavalli et al., 1998). Both oils were within the recommended limit at the end of 25 h of intermittent frying.

Color

Change in red and yellow color of fried oil is shown in Table 3.ANOVA analysis indicated significant increase in red and yellow color in both the oils during 25 h of intermittent frying. Student ‘t’ showed significant (p<0.05)increase in yellow and red color of both the oils up to 5 h of bhajia frying duration. In a study by Rani et al. (2010) reported fat become darker at the end of 24 h of heating. Increase in color of both the oils was noticed up to 25 h of intermittent frying. In a study by Ogunsina et al. (2011) showed 52% increase in color intensity of refined groundnut oil when potato slices were fried in 10 repeated sequences spanning a total time of 2 h. Rise in color intensity of fried oils is indicative of increase in its oxidation (redden the oil, the more oxidized it is) thus reducing its stability (Hack et al., 2009).

### Table 3 Changes in chemical and physical characteristics of frying oil at intermittent intervals

<table>
<thead>
<tr>
<th>Chemical Parameter</th>
<th>Oil</th>
<th>Duration of frying (hours)</th>
<th>0 h</th>
<th>5 h</th>
<th>10 h</th>
<th>15 h</th>
<th>20 h</th>
<th>25 h</th>
<th>F-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peroxide value (meq O₂/kg)</td>
<td>CSO</td>
<td>13.85±0.40a</td>
<td>9.13±0.62b</td>
<td>8.1±0.08a</td>
<td>6.88±0.49a</td>
<td>7.2±0.48a</td>
<td>10.38±0.15a</td>
<td>155.48***</td>
<td></td>
</tr>
<tr>
<td></td>
<td>GNO</td>
<td>8.38±0.25a</td>
<td>13.13±1.28b</td>
<td>8.45±0.40a</td>
<td>9.38±0.45a</td>
<td>9.63±0.68a</td>
<td>9.48±0.57a</td>
<td>25.61***</td>
<td></td>
</tr>
<tr>
<td>p-anisidine value (mg I₂/kg)</td>
<td>CSO</td>
<td>8.71±0.27a</td>
<td>62.09±0.64a</td>
<td>85.47±3.53a</td>
<td>109.22±1.74a</td>
<td>123.18±3.17a</td>
<td>129.87±4.28a</td>
<td>1125.62***</td>
<td></td>
</tr>
<tr>
<td></td>
<td>GNO</td>
<td>0.58±0.28a</td>
<td>61.53±1.42b</td>
<td>82.64±3.32a</td>
<td>91.92±1.09a</td>
<td>95.64±0.77a</td>
<td>108.82±2.14a</td>
<td>1879.97***</td>
<td></td>
</tr>
<tr>
<td>Iodine value (mg I₂/g)</td>
<td>CSO</td>
<td>98.76±0.16a</td>
<td>101.34±4.19a</td>
<td>100.89±4.86a</td>
<td>99.21±3.10a</td>
<td>104.99±0.66a</td>
<td>104.3±1.57a</td>
<td>29.69***</td>
<td></td>
</tr>
<tr>
<td></td>
<td>GNO</td>
<td>82.96±0.51a</td>
<td>85.75±4.65a</td>
<td>87.32±0.74a</td>
<td>87.7±1.06a</td>
<td>85.85±4.95a</td>
<td>83.03±5.03a</td>
<td>1.37***</td>
<td></td>
</tr>
<tr>
<td>Acid value (mg KOH/g)</td>
<td>CSO</td>
<td>0.12±0.02a</td>
<td>0.15±0.01a</td>
<td>0.18±0.01a</td>
<td>0.26±0.02a</td>
<td>0.35±0.01a</td>
<td>0.47±0.03a</td>
<td>207.68***</td>
<td></td>
</tr>
<tr>
<td></td>
<td>GNO</td>
<td>0.78±0.07a</td>
<td>0.85±0.04a</td>
<td>0.97±0.01a</td>
<td>1.04±0.02a</td>
<td>1.22±0.05a</td>
<td>1.29±0.06a</td>
<td>74.87***</td>
<td></td>
</tr>
</tbody>
</table>

**Physical parameters**

| Color (V) | Yellow | CSO | 2.18±0.24a | 3.9±0.12a | 6.03±0.51a | 7.03±0.64a | 7.55±0.70a | 9.13±0.19a | 120.95*** |
|           | GNO    | 3.4±0.08a | 4.03±0.40a | 4.53±0.13a | 5.3±0.24a | 6.98±0.35a | 7.85±0.37a | 144.06*** |
| Color (R) | Red    | CSO | 1.63±0.05a | 2.50±1.71a | 3.25±0.29a | 5.00a | 6.38±0.29a | 14.25±2.87a | 44.68*** |
|           | GNO    | 1.88±0.25a | 4.53±1.68a  | 5.58±0.05a | 5.55±0.14a | 5.83±1.44a | 7.3±0.22a | 25.73***  |
| Refractive Index | CSO | 1.4641±0c | 1.4646±0b | 1.4648±0c | 1.4650±0d | 1.4652±0e | 1.4653±0f | 4.44***   |
|           | GNO    | 1.4624±0c | 1.4627±0d  | 1.4629±0e | 1.4631±0f | 1.4633±0g | 1.4635±0h | 24.51***  |

**Note:** Mean±standard deviation (SD), a, p<0.05, b, p<0.01, c, p<0.001; CSO-Cottonseed oil, GNO-Groundnut oil; Similar superscripts in each row indicate no significant difference at p<0.05.

### Total polar components

Figure 1 shows the total polar components (TPC) of CSO and GNO. TPC increased almost linearly with the frying time similar to that reported by Rani et al. (2010). The initial TPC of GNO and CSO was 3.12 and 4 respectively, which was significantly increased to 7.58 and 14.38 after 25 h of intermittent frying. Results of both the frying medium, showed increased polar compounds as a result of thermo oxidative transformation during the experimental period of frying. Similar results were reported by Rani et al. (2010) and Kimet et al. (2008), when Gulab Jamun and wheat flour dough containing egg yolk powder were repeatedly fried in vanaspati and sunflower oil respectively.

Figure 1: Total polar components (TPC) (%) of CSO (cottonseed oil) and GNO (groundnut oil) at intermittent frying intervals

**Note:** Values are mean of duplicate values conducted in triplicate

### Sensory qualities of bhajias fried in CSO and GNO at different intervals

Bhajias fried in CSO and GNO at different intervals were assessed for various sensory qualities like appearance, color, crispiness, greasiness, flavor, taste, odor and overall acceptability shown in Table 4. F-test showed no significant difference in appearance, color, and crispiness of bhajias fried in CSO and GNO. However, color of intermittently fried bhajias increased from 5.9 to 6.3 and 5.6 to 6.3 in CSO and GNO respectively. An insignificant increase was observed in
Oil uptake

As shown in Table 5 intermittent frying of bhajias in CSO showed 15.6% oil uptake, whereas GNO fried bhajias showed 19.5% uptake of oil. Similar results were obtained in a study conducted on legumes and cereal based deep-fried snacks fried in different vegetable oils. Highest oil uptake was observed by peanut oil (35.9%) and lowest by cottonseed oil (30.6%) (Annapure et al., 1997). Kita (2007) reported that fat absorption is greatly influenced by frying temperature. However, frying at higher temperature (190°C) in peanut oil decreased the oil uptake in potato crisps.

Table 5 Total oil used after 25 h of intermittent french fries frying

<table>
<thead>
<tr>
<th>Oil</th>
<th>Initial level of oil for frying</th>
<th>Total oil removed for chemical analysis</th>
<th>Actual amount of oil used for frying</th>
<th>Amount of oil left after 25 h of intermittent frying</th>
<th>Amount of oil absorbed (mean) for 25 batches of frying</th>
<th>Amount of oil used /batch for 200g bhajias</th>
<th>% Oil uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSO</td>
<td>1354</td>
<td>280</td>
<td>1074</td>
<td>293.8</td>
<td>780.2</td>
<td>31.2</td>
<td>15.6%</td>
</tr>
<tr>
<td>GNO</td>
<td>1348</td>
<td>280</td>
<td>1068</td>
<td>84.6</td>
<td>983.4</td>
<td>39.3</td>
<td>19.5%</td>
</tr>
</tbody>
</table>

CONCLUSION

To conclude, during frying thermal-oxidation of GNO and CSO was indicated by alteration in PV and p-AV beyond the acceptable limits. In terms of acid value, iodine value, and 18:2/16:0 (linoleic/palmitic) ratio CSO showed less stability than GNO. Bhajias showed no significant change in sensory qualities when fried intermittently up to 21 h. Bhajias fried in GNO had higher oil uptake as compared to CSO fried bhajias.

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