Alternative Methods of Frying and Antioxidant Stability in Soybean Oil

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Abstract: A study on shallow and parfrying in soybean oil as alternatives to deep frying and evaluation of stability of a formulated antioxidant administered to the oil was conducted. Potato wedges were deep, shallow and parfried in soybean oil for optimized time and temperature. A citric acid based antioxidant using BHT was formulated and administered to the oils before frying. The performance of antioxidant was assessed by studying its physicochemical properties and DPPH radical scavenging activity with repeated frying. In the oils administered with the formulated antioxidant, highest and least values obtained were: FFA (% oleic acid) of 4.90% in deep frying and 4.55% in parfrying, peroxide values (mEq/Kg) of 6.50 in deep frying and 5.39 in parfrying, para-anisidine value of 6.92 in deep frying and 5.91 in parfrying, TOTOX values of 19.93 in deep frying and 16.70 in parfrying, iodine values (g I$_2$/100 g oil) of 98.56 in deep frying and 102.63 in parfrying, conjugated dienes of 4.88% in deep frying and 4.32% in parfrying and conjugated trienes of 5.7% in deep frying and 5.15% in parfrying. The physicochemical tests revealed least oxidation in oils administered with the formulated antioxidant in parfrying and the most in deep frying, indicating parfrying to be the most suitable frying mode. The DPPH radical scavenging activity of the parfried oil showed 31.52% decrease after the fourth fry. From statistical analyses (p<0.05), it was concluded that the formulated antioxidant significantly limited oxidation in the oils with respect to the control until the third fry (8 days).

Key words: Antioxidant formulation, frying protocol, physicochemical properties, soybean oil

INTRODUCTION

India is the world’s largest importer and the third largest consumer of edible oils (Ramesh and Murughan, 2008). In 2007, in India alone, the annual and per capita consumption of edible oils were 11 million Tonnes and 11.50 kg, respectively (MOFPI, 2011). The most common application of edible oils is in frying and also in salad dressings and food emulsions.

Commonly, immersion frying is employed for frying in which food is immersed in oil or fat for frying (Hubbard and Farkas, 1999). The most common type of immersion frying is deep fat frying. It is used both commercially and domestically to produce fried food products of desirable texture and flavour at high temperature regimes with high heat transfer rates and rapid cooking (Farkas et al., 1996). Although deep fat frying is the most cited form of frying, the risk of high fat content in the fried food product is considerable which is a cause of concern for cardio-vascular health (Willet and Mozaffarian, 2007). Besides, it produces acrolein and malondialdehyde, both of which are mutagenic (Bennoin, 1980; Hageman et al., 1988; Hogervorst et al., 2007). However, blanching with calcium chloride reduces the same by 95% (Tareke and Rydberg, 2002; Gökman and Senyuva, 2007) and contributes to lower oil uptake by the fried product (Rimac-Brnić et al., 2004).

Considering the above, there is a need for alternative methods of frying such as shallow frying and parfrying. In both these techniques, a comparatively lower volume of oil is used than deep frying (Oreopoulou et al., 2006). Parfrying involves frying in two stages. The initial frying (pre-frying) involves partial frying followed by storage at subzero temperature which protects the surface oil from rapid oxidation. Subsequently, the product is finish fried without thawing (Burr, 1971). The parfried product is therefore expected to have the least fat content and the oil to undergo minimal oxidative changes.

Antioxidants are administered to the frying oils to protect oils and fried products from degradative changes and thereby enhance their shelf lives. Antioxidants such as Butylated Hydroxy Anisole (Bha), Butylated Hydroxy Toluene (BHT) and Tertiary Butylated Hydroxy Quinone (TBHQ) are used commercially. It is mandatory to administer these antioxidants within approved limits which otherwise produce detrimental pro-oxidants (Barlow, 1990).
Citric acid has been used for its metal sequestering chelating activity (Mahoney and Graft, 1986). Citric acid is administered during processing to edible oils at levels of 0.005 to 0.01% and helps to protect oils from oxidation (Brekke, 1980). Warner and Gehring (2009) have reported significant antioxidant effects of citric acid and adjuvant doses of aluminium silicate and potassium sulphate in extending shelf stability of fried tortilla chips. Our citric acid based antioxidant (consisting of citric acid and a commercial antioxidant) would therefore allow a single dose of administration (which are otherwise administered separately) to the oil. Soybean oil has been chosen in this study since it is used largely globally (Thoenes, 2004).

The objectives of the present study are to perform deep frying along with shallow and par frying as alternative modes of frying, to assess the suitability of soybean oil. The potency of our formulated antioxidant with repeated frying was evaluated by assay of physicochemical properties and DPPH radical scavenging activity of soybean oil. Fried potato wedges (French fries) were selected as model food in the present study.

MATERIALS AND METHODS

The study was carried out between March-April 2011 in the Department of Food Technology and Biochemical Engineering, Jadavpur University, Kolkata, India.

Materials: Soybean oil and raw potatoes Solanum tuberosum (Jyoti variety) were purchased from a local supermarket in Kolkata. All chemicals used for analyses were of AR grade unless specified. A French fry cutter was procured from M/s Jas Enterprises, Ahmedabad, India. The frying was carried out in an electric deep fat fryer of M/s Shiva Kitchen Appliances, Kolkata, India.

Pre-frying processing of potato wedges: The fresh raw potatoes were washed in distilled water and peeled. The potatoes were cut as ‘wedges’ from the pith of the parenchymatous region of potato tubers (with a French fry cutter) of uniform dimension (7 x 1 x 1 cm). The potato wedges were subsequently blanched in two stages: at 90°C for 2 min and thereafter again with 0.2% potassium metabisulphite (w/v) and 2% calcium chloride (w/v) at 90°C for 15 min, with a delay of 2 min between the consecutive processes. Following blanching, the wedges were dried in a tray dryer at 65°C for 90 min (optimized through several trials) before frying.

Initial frying of potato wedges: Initial frying of potato wedges without administration of antioxidant to the soybean oil was conducted for deep, shallow and par frying to determine the optimum time-temperature regimes in the three different frying modes. Additionally, in par frying, the wedges were ‘pre-fried’ and stored at -18°C overnight and subsequently ‘finish fried’ without thawing. Subsequently, organoleptic evaluation of the fried potato wedges was conducted by ten member semi-trained panel on a 5-point hedonic scale. These results were used to arrive at the optimised frying protocol for the three modes of frying.

The potato wedges were fried (in initial as well as final frying) in batches of 100 g each in a fryer with temperature control of 90-170(±1)ºC. The fryer was filled with 3.51 oil for deep frying and 2l oil for shallow and par frying. After frying, the potato wedges were placed in a strainer to drain off excess oil. The wedges were subsequently placed on blotting paper to remove the excess surface oil on the wedges. The French fries with optimised parameters were then analysed for fat content.

Fat content analysis: The fat content of the fries was determined by AOAC method (1970). Petroleum ether (solvent) was evaporated using a rotary vacuum evaporator (M/s Eyela Corp., Tokyo, Japan) at 40-45ºC and 50 mbar Hg. The leftover fraction was used to calculate the percentage fat content (%w/w basis). The results were used to formulate the antioxidant.

Formulation and administration of antioxidants to frying oils: A citric acid based antioxidant (ATX) was formulated in our laboratory using citric acid, potassium sulphate and aluminium silicate in accordance with that described by Warner and Gehring (2009). BHT was used as an antioxidant in our formulation. The dosage of citric acid and BHT was according to guidelines of LeRoy (1976). Potassium sulphate and aluminium silicate were adjuvants in ATX formulation. ATX was administered to fresh oils using minimum quantity of lipid medium (soybean oil) to facilitate incorporation into the bulk oil.

The final frying: ATX administered oils and respective controls were used to fry in the optimised modes of deep, shallow and par frying. The frying oil was neither replenished nor changed after each successive batch of frying. The frying was carried out for six hours daily, which included different batches and frying methods, with a delay of 30 min (10 min for collection and 20 min for oil cooling) between the two successive batches of frying. The oils were stored for a period of 4 days between two similar and successive batches of frying.

Study of oil characteristics: All oil samples were stored in N2-flushed, airtight, amber coloured glass bottles under refrigerated conditions, prior to analyses.

Viscosity: The viscosity of the three oils both before and after frying was determined using a Brookfield Digital Viscometer (M/s Brookfield Engineering Company, MA, USA) model LVDV-E with spindle no. 2 at 20 rpm and 25(±1)ºC.

Titrimetric assays: Titrimetric analyses of the oils both before and after frying were carried out. The oxidative state (and hence the shelf life) of the oils was determined.
by assays of acid value (reported as FFA (% oleic acid)), peroxide value, iodine value by AOAC methods (1970). Para-anisidine value was determined by IUPAC method (1987). TOTOX value was calculated by

$$\text{TOTOX} = 2 \text{PV} + p-\text{AV}$$  \hspace{1cm} (1)

where, PV is peroxide value, p-AV is para-anisidine value and TOTOX is total oxidation value.

**Absorption spectra and photometric colour index (PCI) of oils:** The spectra of oils for the maximum absorbance wavelength ($\lambda_{\text{max}}$) and PCI were recorded using UV-Vis spectrophotometer (M/s Hitachi Corp., Kyoto, Japan) to assess their purity adopting the method described by Susheelamma et al. (2002).

**Conjugated compounds:** AOCS (1991) method was used to determine the conjugated compounds. The determination of conjugated compounds consisted of estimation of Conjugated Dienes (CD) and Conjugated Trienes (CT).

**Assay of antioxidants:** The antioxidant potential of the administered antioxidants in the oils was determined by the method reported by Karakaya and Şimşek (2011) and expressed as % scavenging activity (of DPPH radicals).

**Statistical analyses:** All the experiments were conducted in triplicate and reported as mean±SD. Statistical analysis of the variation in the results was carried out by one-way ANOVA using STATISTICA 8.0 software (Statsoft, OK, USA).

**RESULTS AND DISCUSSION**

**Optimized frying method:** The optimized frying was carried out by following the procedure shown in Fig. 1. Blanched potato wedges were dried in a tray drier under our optimized conditions of 65°C, 90 min and subsequently fried conditions of deep frying (170°C, 5 min), shallow frying (130°C, 10 min) and parfrying (pre-cooking at 105°C, 4 min and finish frying at 130°C, 4 min).

![Fig. 1: Flowchart for optimized deep, shallow and parfrying in soybean oil](image)
Sharma
oxidative damage with formation of fatty acids affecting
iodine values at all stages of frying.

values of FFA, peroxide, para-anisidine, TOTOX and
significantly lower oxidation (p<0.05) in terms of lower
parfry batches of the oil. ATX administered oils had
anisidine, TOTOX and iodine values in deep, shallow and
the FFA content (as % oleic acid), peroxide, para-
of frying and in different modes of frying. Table 1 shows
the oxidative states of soybean oil in successive batches
Titrimetric assays:
difference with the control.
effectiveness of ATX decreased and had significant
third fry. This indicated that after third frying, the
administered oils and were significantly different until the
in viscosities of control oil samples were more than ATX
oxidation with frying than oils without them. The increase
administered with BHT and citric acid have lesser
with Serjouie
molecular weight polymeric compounds, in agreement
viscosity in fried oils may be due to formation of high
administered oils after the fourth fry. The increase in
fat content (%) of the
frying regimes was determined to formulate the
oxidant. It was observed that fat content (%) of the
wedges were 11.60±0.12 in deep fry, 8.36±0.14 in
shallow fry and 4.52±0.12 in parfry.

Viscosity: In deep frying, viscosity increased the most
and in parfrying the least, possibly due to lower intensity
of frying, minimum frying time and low temperature of
frying in the latter (Fig. 2). The native oil viscosity of 58
mPas increased to 85.36 mPas in deep fry, 81.57 mPas in
shallow fry and 74.99 mPas in parfry, for the ATX
administered oils after the fourth fry. The increase in
viscosity in fried oils may be due to formation of high
molecular weight polymeric compounds, in agreement with Serjouie et al., 2010). Lower viscosities were
observed in oils administered with ATX than in control, in compliance with Ruget et al. (2002) and Sharma et al. (2007), who have reported that oils administered with BHT and citric acid have lesser oxidation with frying than oils without them. The increase
in viscosities of control oil samples were more than ATX
administered oils and were significantly different until the
third fry. This indicated that after third frying, the
effectiveness of ATX decreased and had significant
difference with the control.

Titrimetric assays: The titrimetric assay values indicate the oxidative states of soybean oil in successive batches
of frying and in different modes of frying. Table 1 shows the FFA content (as % oleic acid), peroxide, para-
anisidine, TOTOX and iodine values in deep, shallow and
parfry batches of the oil. ATX administered oils had
significantly lower oxidation (p<0.05) in terms of lower
values of FFA, peroxide, para-anisidine, TOTOX and
iodine values at all stages of frying.

FFA is mainly the product of hydrolysis and depicts
oxidative damage with formation of fatty acids affecting

Analyses of fat content of fries: The fat content in the
French fries (without antioxidants added) in different pre-
frying regimes was determined to formulate the
antioxidant. It was observed that fat content (%) of the
shallow fry control
Deep fry ATX
Deep fry control
Deep fry ATX
Shallow fry ATX
Shallow fry control
Parfry ATX
Parfry control

Fig. 2: Viscosity of soybean oil with frying

TOTOX value represents the oil or fat quality, oxidation status and presence of degradation products
formed from previous oxidation of oils. TOTOX value of
native oil was 3.02 which increased to 19.93 in deep
frying, 19.37 in shallow frying and 16.70 in parfrying
(after the fourth fry in ATX administered oils). Therefore,
deep fried soybean oil had significantly higher TOTOX
value than shallow and parfried oils, which was in
agreement with Wai et al. 2009) who have reported that lower the TOTOX value, the better is the quality of
the oil.

Iodine values decreases linearly with number of
frying which indicated a general loss of unsaturation and
lipid oxidation in agreement with Naz et al. (2004).
Soybean oil had a high initial iodine value and also a
sharp fall with subsequent frying. This observation was in
agreement with the fact that greater the unsaturation
(or high IV), the more rapid the oil tends to be oxidised

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The shelf stability of oil is further governed by its
peroxide and para-anisidine values. Peroxide value
measures the primary products of oxidation
(hydroperoxides) of the reaction between oxygen and
unsaturated fatty acids. The oils with peroxide value
between 1 and 5 mEq/Kg are at low oxidation state and
between 5 and 10 mEq/Kg are at average oxidation state
(O’Brien, 2004). Therefore, oil samples in this study were
mainly in low oxidation state (upto third frying which was
8 days) and they shifted to average oxidation state only
after fourth fry (12 days). The peroxide values (mEq/Kg)
were 0.34 for native oil which increased to 6.50 in deep
fry, 6.38 in shallow fry and 5.39 in parfry (after the fourth
fry in ATX administered oils).

The para-anisidine value accounts for the conversion
of primary oxidation products (hydroperoxides) into
secondary oxidation products (aldehydes) which
contribute almost 50% of volatile compounds during
lipid oxidation (Serjouie et al., 2010). The native oil
para-anisidine value of 2.34 increased to 6.92 in deep fry,
6.61 in shallow fry and 5.91 in parfried batches (after the
fourth fry in ATX administered oils). The para-anisidine
value measures the secondary oxidation and the amount
of α, β-unsaturation present in the oil indicating the
current status and history of the oil (Shahidi, 2005). Thus,
lower para-anisidine values of parfried oils vis-à-vis deep
fry oils indicated a longer shelf life of oil in the former
frying mode. Also, in agreement with our previous
observations, ATX was effective until the third fry.

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Table 1: Chemical properties of soybean oil with frying

<table>
<thead>
<tr>
<th>Type of fry</th>
<th>Antioxidant</th>
<th>No. of frying</th>
<th>FFA [% olate acid]</th>
<th>Peroxide value [mEq/Kg]</th>
<th>Para- anisidine Totox value</th>
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<tbody>
<tr>
<td>Deep Control</td>
<td>0</td>
<td>0.25±0.02</td>
<td>0.34±0.02</td>
<td>2.38±0.02</td>
<td>3.02±0.05</td>
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<tr>
<th>Type of fry</th>
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<th>No. of frying</th>
<th>Iodine value [g I 2/100 g oil]</th>
<th>OD ratio</th>
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<td>0.087±0.006</td>
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<td>112.53±0.84</td>
<td>4.00±0.04</td>
<td>0.107±0.003</td>
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<td>3</td>
<td>106.30±1.01</td>
<td>4.30±0.05</td>
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<tr>
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</tr>
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Values are expressed by mean±SD (n = 3); Different letters in a column in a particular test category and fry type are significantly different (p<0.05)
(Alireza et al., 2010). The iodine values of the oil were 124.31 for native oil, 98.56 in deep frying, 101.07 in shallow frying and 102.63 in parfrying (after fourth fry in ATX administered batches). In all the analyses, it was commonly observed that highest oxidation occurred in deep frying and least in parfrying, which may be attributed to the extent of frying. Also it was commonly observed that there were significant differences (p<0.05) between the control and ATX administered oils, up to third fry (8 days). Titrimetric assay values changed abruptly in all modes of frying after the third fry, indicating higher oxidation. In fourth frying, there was no significant difference between the samples, which indicated reduced ATX activity and loss of antioxidant potential (due to thermal oxidation of BHT and citric acid).

Absorption spectra of oils: The spectrophotometric absorption occurred in the UV region (Table 1), indicating oxidation of polyunsaturated fatty acid accompanied with increase in ultraviolet absorption in agreement with O’Brien (1998). The analyses showed that comparatively greater changes in $\lambda_{max}$ in deep fry than other frying modes with least changes in parfrying (Table 1). The $\lambda_{max}$ of the oil was 260.87 for native oil, 276.80 in deep frying, 273.36 in shallow frying and 270.20 in parfrying (after the fourth fry in ATX administered oils). Also, the values changed abruptly after third fry as observed earlier. Higher $\lambda_{max}$ signified higher oxidation of the oil and possibly polymerisation and other physicochemical changes in the fried product in agreement with Tan et al. (1985).

The absorption ratio (OD ratio) at 233/274 nm has been used as an index of oil oxidation during alkali isomerisation (Appleqvist and Kamal-Eldin, 1991). The OD ratio serves as an index of oil oxidation and hence unsaturation (Susheelamma et al., 2002). From Table 1, the values of the OD ratio were 0.029 in native oil and 0.148 in deep fry, 0.126 in shallow fry and 0.112 in parfry (after the fourth fry in ATX administered oils). Lowest values obtained for parfrying suggested this frying mode to be better amongst others.

PCI and conjugated compounds: PCI served as an index to assess the degradation of the oil by estimation of the colour index of the oil (Fig. 3). Highest values of PCI were observed in deep frying and the least in parfrying with values of 1.85 in native oil and 5.20 in deep fry, 4.77 in shallow fry and 3.83 in parfry (after the fourth fry in ATX administered oils). Therefore, PCI values increased sharply after third fry indicating higher oxidation. This is attributed to differential oxidation of oils during frying (based on frying mode) and accumulation of non-volatile decomposed compounds such as oxidised triacylglycerols and FFA (Paul and Mittal, 1996).

The UV spectral property changes ascertain the content of conjugated compounds (O’Connor, 1960). The method is usually used to determine the changes in oil due to alkali isomerisation. Higher values of conjugated compounds relate to higher oxidation and reduced unsaturation in the oils. It was observed that among the frying techniques, in deep fry, the greatest percentage of conjugated compounds was formed followed by shallow and parfry (Table 1). In accordance with Susheelamma et al. (2002), greater changes occurred in trienes than in dienes. It was observed that in all modes of frying, the increase in conjugated compounds was sharp after the third fry with greatest values in deep fry, followed by shallow fry and parfry. The conjugated dienes (%) in native oil was 1.04 which increased to 4.88 in deep frying, 4.68 in shallow frying and 4.32 in parfrying. Conjugated trienes (%) were 2.68 in native oil, 5.71 in deep fry, 5.48 in shallow fry and 5.15 in parfry (after the fourth fry in ATX administered oils). These conjugated compounds are directly related to hydroperoxides and are often used in addition or as a substitute of peroxide value (Shahidi, 2005). ATX administration to oils, hence, had significant effect on PCI and conjugated compounds (p<0.05) and limited oxidation of oils. The effect of ATX was until the third fry (as reported above) and suggested fresh oil replacement thereafter.
Antioxidant assay: The antioxidant assay was carried out for parfried, since lowest values were obtained in the physicochemical tests for the same (Fig. 4). With increase in number of frying, there was decrease in antioxidant potential (low radical scavenging activity) with radical scavenging activity (%) of 73.84 in native oil which decreased to 45.32 after the fourth fry. The efficacy of ATX in limiting oil oxidation in different frying modes was significant (p<0.05) until the third fry. In fourth fry, no significant difference was obtained in ATX and control oil samples in agreement with the physicochemical results obtained above. This can be attributed to the deterioration of the fried oil with storage which inadvertently became more abused and was susceptible to oxidation (Frankel, 2005). This may be due to the fact that both BHT and citric acid are known to be heat labile and volatile with prolonged frying (Freeman et al., 1973; Warner and Gehring, 2009). It is therefore recommended to replace or replenish the oil with fresh oil after third frying.

CONCLUSION

The present study showed parfrying to be the most suitable frying in soybean oil, based on physiochemical tests and antioxidant assay. The parfried oils had lowest oxidation and accordingly highest antioxidant potency. We recommend ATX (formulated using BHT) best for parfrying, followed by shallow and deep frying, since the oil underwent least oxidation with the same. A higher antioxidant activity has also been obtained in parfrying. From our studies, soybean oil is recommended to be replaced or replenished with fresh oil after third fry (about 8 days from first use). Further, we recommend blending of soybean oil with other oils to impart improved frying characteristics, overcoming the limitations of the individual oils. Alternatively, oils may be rotated to observe for synergistic benefits of individual oils in frying operations.

REFERENCES


