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Lipid profile of foods fried in thermally polymerized palm oil

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Abstract

Lipids extracted from foods fried in thermally polymerized palm oil were evaluated in *papads,* French fries and fish fry (Bombay duck) with moisture content ranging between 10% and 75%, in an attempt to investigate the effect of moisture content on lipid quality indices such as free fatty acids, conjugated dienes, *p*-anisidine value, viscosity, total polar materials and colour values. The quality of lipids in products with high moisture content (50% or more) was found to be inferior to that of the oil left after frying, as evidenced in Bombay duck and French fries from potatoes with initial moisture content of 52–77%. A reverse trend was observed in *papads* and French fries prepared from dehydrated potatoes with moisture content of 12% or less. The results indicate the moisture content of food plays a definite role in the distribution of the lipid constituents during frying in thermally polymerized oil.

Keywords: French fries; Fish fry; *Papads*; Moisture; Lipid; Quality

1. Introduction

Fats and oils undergo deteriorative changes during deep fat frying such as oxidative, hydrolytic, and polymerization. These are influenced by the temperature of frying, and also by factors such as emulsifiers, trace metals, food scraps, free fatty acids and alkaline-reacting materials in the frying oil. Various compounds are released from the substrate into the frying oil, enhancing discoloration or formation of off-flavors. For instance, fatty fish release fat during frying so that the frying oil becomes contaminated with fish oil (Sanchez-Muniz, Viejo, & Medina, 1992). As fish oil is highly polyunsaturated, the frying oil contaminated with fish oil deteriorates rapidly. During frying of cabbage and other green vegetables, glucosinolates are decomposed, and their decomposition products, such as nitriles, indolyl derivatives or vinyl oxazolidinethione contaminate the frying oil (Rossell, 2001). Chlorophylls and their decomposition products (mainly pheophytins) have been reported to pass into the frying oil producing absorption peaks between 600 and 700 nm (Taha, Helmy, & EI-Nokrashy, 1988). On the contrary, pigments present in frying oil may be adsorbed on the surface of the fried substrate.

Maillard browning products and their precursors are the major contributing substances to the discoloration of frying oil; lysine, γ-aminobutyric acid and glycine being the most potent precursors of brown pigments. The discoloration is highly pronounced in fish fried in used frying oil, as polyunsaturated fatty acids of fish oil participate in the formation of brown pigments (Pokorny, 1981). Vitamins, such as thiamin, pyridoxin, riboflavin and ascorbic acid decompose on heating, and some oil-soluble decomposition products dissolve in the frying oil, affecting colour and flavour, the decomposition being accelerated by contact with the oxidation products of the frying oil (Pokorny, 1998). Iron and copper salts released from the substrate during frying accelerate the oxidation of frying oil. Sodium and potassium ions are transported to the frying oil to form alkaline soaps, which in turn stimulate foaming. Foaming increases the interface between oil and air and further promotes oxidation (Blumenthal, Stockier, & Summers, 1985).

Mutagens formed during deep-frying of protein-rich foods belong to the polycyclic aromatic heterocycles of the aminoimidazo-azarene and amine-carbolin series (Hatch, Knize, & Felton, 1991). Creatine and creatinine

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are the most important precursors of these aromatic heterocyclic compounds. Maillard products react with creatinine, producing various imidazoquinolines and imidazoquinoxaline mutagens (Dahlqvisl, 1986). The production of mutagens is much lower in the absence of fat so that frying fat is important for their formation.

Oxidation by aerial oxygen is the most important deterioration reaction of frying oil, which is relatively rapid, especially in the case of polyunsaturated oils, such as soybean or sunflower oil. Free peroxyl radicals are unstable intermediates, and hydroperoxides, the primary oxidation products are rather unstable under frying conditions. They react with the substrate, particularly with thiol, sulphide disulphide, and primary amine groups of proteins, and partially remain attached to the protein moiety (Pokorny et al., 1988). Frying fat adsorbed on the surface of the substrate is generally more oxidized than frying oil as oxidized products are selectively adsorbed on protein molecules (Pokorny, 1998).

The extent of hydrolysis of oil triacylglycerols during deep-fat frying is influenced by the moisture from the substrate. When the food material, usually at room temperature, comes in contact with the frying oil preheated to 130–200 °C, the water within the substrate is almost immediately heated to boiling point. The steam so produced partially hydrolyzes the triacylglycerols into free fatty acids and partial glycerol esters (diacylglycerol, monoacylglycerol and even glycerol) in a relatively short period of about 5–10 min of deep fat-frying (Pokorny, 1998). In a study, addition of water to coconut or niger seed oil before frying was found to increase the formation of epoxy acids and stimulate the formation of free fatty acids during subsequent heating (Ramanna & Sen, 1983). The water evaporated was proportional to the square root of frying time, and the difference between the temperature of oil and boiling water (Ashkenazi, Mizrahi, & Berk, 1984). More than the other components, the water present in the substrate was found to greatly affect the quality of frying oil (Barbanti, Pizzirani, & Dalla Rosa, 1994).

The quality of oil in a fried product depends upon pyrolytic degradation of frying oil and interactions that take place within a product between degraded components of frying oil and free functional groups of the ingredients of a product. Assessment of the quality of frying oil and that picked up by the fried product is relevant from the nutritional point of view.

Food processors in unorganized sectors often continue to fry foods in heat-abused oils in batch processes without replenishing with fresh oils. Consumers do experience discomfort on consumption of such foods. However, such foods are poorly characterized. In the present investigation, three fried foods that are very popular in the Indian sub-continent *viz*. fried fish, *papads* and French fries that differ vastly in their composition and moisture content were selected. These were fried in heat-abused palm oil, and evaluated for the quality of the lipid extracted from the said foods, and that left behind in the fryer. Palm oil is used commonly for preparation of fried foods due to its availability and better stability than other vegetable oils and hence was used in this study.

2. Materials and methods

2.1. Oil samples

Heat-abused frying oil (palm oil used for continuous frying of legume-based snacks for 36 h at 170–180 °C without any fresh oil-makeup, and labeled as P36) was obtained from a local processor from a small-scale unorganized sector of Mumbai city.

2.2. Food samples

The raw materials, *papads,* potatoes and fish were obtained from a local market of Mumbai city. The products prepared were diced potato fingers for French fries of initial moisture content of 72.7%, which were dehydrated to 63.09%, 52.05% and 10.14%, respectively, fried *papads* (initial moisture content, 11.84%), and fish fry (Bombay Duck having an initial moisture content of 74.52%).

2.3. Frying of the selected foods

Raw *papads* were deep-fried in the frying oil. Potatoes were peeled, thin-sliced (0.95 cm wide, 4–5 cm long, straight-cut), and further dipped in 4% salt water to prevent browning. The slices were drained and divided into four portions, of which three portions were subjected to drying at 60 °C to achieve the required moisture levels as stated above, and one portion was air-dried at room temperature. All the four portions after the respective treatments were deep-fried. Fish (100 g) was cleaned, dipped in 150 ml of a 9% solution (comprising of 1% turmeric, 7% chilli powder, and 2% salt) for 10 s, well drained and deep-fried for 90 s.

For frying, 200 ml of oil were heated to smoke point (180 °C) and about 100 g of each of the materials were fried separately in P36 for times, as judged subjectively to be sufficient for completion of frying. The oil left behind in the fryer and the products were stored at −18 °C until further analysis.

2.4. Sampling procedures

Fifty grams of the products were cut into small pieces and macerated to obtain a uniform mass, which was dried in a hot air oven at 60 °C for 30 min and subjected to fat extraction. The extracted fat was stored at −18 °C until analysis.

2.5. Analytical methods

2.5.1. Total lipid content

Total lipid content of the fried food was determined by the Soxhlet extraction using petroleum ether (60–80 °C) as the solvent.

2.5.2. Percent free fatty acids (FFA)

FFA was determined by the AOCS (1989) method with few modifications (AOCS, 1989). Thirty millilitres ether/ethanol/water 3:3:2 (v/v/v) were used to dissolve 5 g of the sample and titrated against 0.1 N sodium hydroxide solution (Foglia, Petruso, & Feairheller, 1993). FFA was expressed as %oleic acid.

2.5.3. Total polar materials (TPM)

TPM was determined using the method of AOCS (1998). A chromatographic column (21 mm i.d., 450 mm long with stopcock and ground glass joint) was filled with about 30 ml of a mixture of light petroleum and diethyl ether (87:13, v/v). A wad of glass wool was introduced at the lower end of the column with the aid of a glass rod. Twenty five grams silica gel were slurried in about 80 ml of the solvent mixture and poured into the column. The elution solvent was drained through the column until its level was 10 cm above the silica gel level. About 4 g of sea sand was added and the supernatant was drained up to the sand layer.

For the determination of TPM, 2.5 g of the oil sample were dissolved in 20 ml of the solvent mixture containing light petroleum and diethyl ether (87:13, v/v) at room temperature (30 ± 2 °C), with slight warming, if necessary. The volume was then made to 50 ml with the solvent mixture and 20 ml of resulting solution were introduced into the column, and drained off to the level of the sand layer. The non-polar compounds were eluted with 150 ml of the solvent mixture at a flow rate of 2.5 ml/min. TPM was calculated as:

$$\%\text{TPM} = [(m - m_1)/m] \times 100$$

where m_1 is the mass (g) of the non-polar fraction and m is the mass (g) of the sample contained in 20 ml of the solution added to the column.

2.5.4. p-Anisidine value (p-AV)

p-AV was determined as per AOCS (1998). The sample (0.5–4.0 g) was dissolved and diluted to volume with *iso*-octane in a 25 ml volumetric flask. The absorbance (A_b) of the solution was measured at 350 nm. Exactly 5 ml of the fat solution were transferred to a test tube and 5 ml of only the solvent were added to another test tube. One millilitre of *p*-anisidine reagent (2.5 g/l solution in glacial acetic acid) was added to each tube, and shaken. After exactly 10 min, the absorbance (A_s) of the solution in the first test tube was measured at 350 nm, using the solution in the second test tube as blank.

$$p\text{–AV} = [25 \times (1.2A_s – A_b)]/m.$$

2.5.5. Percent conjugated diene (CD)

CD was determined as per AOCS (1998). The sample (90–130 mg) was added to 75 ml of purified *iso*-octane in 100 ml flask. The flask was warmed to completely dissolve the sample, cooled to room temperature, allowed to stand for 15 min, and then diluted to a final concentration of 0.01/l. The absorbance was then measured at 233 nm. % CD was calculated as follows:

$$\%\text{CD} = 0.84[(A_s/bc) - K_o]$$

where K_o = absorptivity by acid or ester groups (0.07 for esters, 0.03 for acids), A_s = observed absorbance at 233 nm, b = cuvette length in cm, and c = concentration of sample, g/l of the final dilution.

2.5.6. Viscosity

Viscosity was determined as per AOCS (1998) using a Brookfield DV111 model digital rheometer at 30 °C using LV 2 spindle at 10, 20 and 50 rpm.

2.5.7. Colour

Colour was determined as per AOCS (1989), measured using a Lovibond Tintometer Model PFX990, using an oil sample of 12 ml and an optical path length of 1 in. Results were expressed on R and Y scale. The oil samples to be analyzed were heated at 45 °C, and shaken well to bring each sample to a homogenous liquid state. To minimize any experimental errors from temperature variations,

Table 1
Quality of oil extracted from *papads* and fish fry and the corresponding fryer oil[C,D,E]

Parameters	*Papad*			Fish fry		
	P36	A	B	P36	A	B
FFA	0.92 ± 0.01^{a}	1.29 ± 0.02^{b}	1.34 ± 0.03^{b}	0.92 ± 0.01^{a}	1.04 ± 0.01^{b}	0.94 ± 0.01^{a}
% CD	0.22 ± 0.02^{c}	0.35 ± 0.03^{d}	0.37 ± 0.03^{d}	0.22 ± 0.02^{c}	0.18 ± 0.02^{c}	0.17 ± 0.01^{d}
p-AV	22.71 ± 0.34^{e}	19.24 ± 0.37^{f}	23.69 ± 0.85^{e}	22.71 ± 0.34^{e}	49.45 ± 0.84^{f}	26.88 ± 0.65^{g}
TPM	18.62 ± 0.53^{g}	30.8 ± 0.53^{h}	32.5 ± 0.95^{h}	18.62 ± 0.53^{g}	24.52 ± 1.28^{i}	19.71 ± 0.35^{j}
Viscosity (cPs, 30 °C)	97.1 ± 0.3^{i}	102.3 ± 0.7^{j}	98.7 ± 0.3^{k}	97.1 ± 0.3^{i}	114.8 ± 0.9^{l}	103.6 ± 0.8^{m}
Colour "R" value	5.50 ± 0.16^{l}	5.50 ± 0.05^{l}	5.60 ± 0.05^{l}	5.50 ± 0.16l	6.60 ± 0.13^{o}	7.10 ± 0.05^{p}
Colour "Y" value	70 ± 0.4^{m}	69.1 ± 0.5^{m}	71.6 ± 0.4^{n}	70 ± 0.4^{m}	86.0 ± 0.4^{r}	90.2 ± 0.2^{s}

A: Oil from the fried product; B: Oil left behind in the fryer.

[C] Moisture content of the *papads* was 11.84%.

[D] Results are mean ± standard deviation of three different determinations.

[E] For each parameter, values of A, B and P 36 are compared for the individual items *papad* and fish fry and the ones with different superscripts are significantly different ($P = 0.05$) as measured by Duncan's multiple-comparison test.

Table 2
Quality of oil extracted from French fries having varying initial moisture contents and that of the corresponding fryer oil[C,D,E]

Parameter	Samples of French fries having initial percent moisture content of									
	76.70 ± 0.18			63.10 ± 0.87			52.03 ± 0.27		10.14 ± 0.41	
	P36	A	B	P36	A	B	P36	A	P36	A	B
% FFA	0.92 ± 0.01^{b}	1.16 ± 0.04^{a}	0.93 ± 0.06^{b}	0.92 ± 0.01^{a}	1.02 ± 0.05^{a}	0.97 ± 0.01^{a}	0.92 ± 0.01^{c}	1.11 ± 0.01^{a}	0.98 ± 0.02^{b}	0.92 ± 0.01^{c}	1.03 ± 0.04^{a}	1.21 ± 0.06^{b}
% CD	0.22 ± 0.02^{d}	0.32 ± 0.02^{c}	0.21 ± 0.01^{d}	0.22 ± 0.02^{c}	0.28 ± 0.02^{b}	0.24 ± 0.01^{c}	0.22 ± 0.02^{c}	0.27 ± 0.03^{c}	0.26 ± 0.02^{c}	0.22 ± 0.02^{e}	0.33 ± 0.02^{c}	0.40 ± 0.01^{d}
p-AV	22.71 ± 0.34^{f}	24.27 ± 0.34^{e}	25.12 ± 0.98^{e}	22.71 ± 0.34^{e}	23.18 ± 0.65^{d}	23.49 ± 0.55^{d}	22.71 ± 0.34^{e}	22.15 ± 0.25^{e}	25.47 ± 0.77^{f}	22.71 ± 0.34^{f}	13.39 ± 0.18^{g}	22.31 ± 0.85^{f}
TPM	18.62 ± 0.53^{g}	28.74 ± 0.29^{f}	20.75 ± 1.06^{g}	18.62 ± 0.53^{g}	27.08 ± 0.32^{e}	21.22 ± 0.95^{f}	18.62 ± 0.53^{h}	24.55 ± 0.12^{g}	20.14 ± 0.90^{h}	18.62 ± 0.53^{h}	23.14 ± 0.35^{g}	24.13 ± 1.18^{g}
Viscosity (cPs, 30 °C)	97.1 ± 0.3^{i}	20.7 ± 1.1^{h}	97.8 ± 0.5^{i}	97.1 ± 0.3^{i}	107.6 ± 1.3^{g}	100.9 ± 0.5^{h}	97.1 ± 0.3^{h}	102.6 ± 1.0^{i}	99.9 ± 0.6^{i}	97.1 ± 0.3^{j}	104.3 ± 0.6^{i}	98.5 ± 1.5^{i}
Colour "R" value	5.50 ± 0.16^{k}	6.00 ± 0.08^{j}	5.50 ± 0.09^{k}	5.50 ± 0.16^{j}	5.80 ± 0.05^{i}	5.50 ± 0.05^{j}	5.50 ± 0.16^{k}	5.60 ± 0.05^{k}	5.30 ± 0.08^{l}	5.50 ± 0.16^{m}	5.20 ± 0.05^{k}	5.80 ± 0.05^{l}
Colour "Y" value	70 ± 0.4^{m}	81.1 0.21	70.8 ± 0.2^{m}	70 ± 0.4^{m}	79.0 ± 0.8^{k}	72.0 ± 0.4^{l}	70 ± 0.4^{n}	76.3 ± 0.1^{m}	69.2 ± 0.9^{n}	70 ± 0.4^{o}	61.8 ± 0.2^{m}	72.8 ± 0.6^{n}

A: Oil from the fried product; B: Oil left behind in the fryer.
[C] P36 was used for frying.
[D] Results are mean ± standard deviation of three different determinations.
[E] For each parameter, values of A, B and P36 are compared for the individual items and the ones with different superscripts are significantly different ($P = 0.05$) as measured by Duncan's multiple-comparison test.

the sample holding cell along with the sample vial and the Lovibond Tintometer was maintained at 45 °C in a built-in temperature control system.

3. Results and discussion

A variety of deep fat-fried products with moisture content ranging between 10% and 75% were studied in the present investigation.

3.1. Frying oil P36

The heat-abused frying oil, P36, was evaluated for quality parameters (Table 1). The values clearly indicated the frying oil to be substantially heat damaged. During frying, a further deterioration in the quality of the frying oil was observed.

3.2. Papads and fish fry

Table 1 compares the quality of oil extracted from fried *papads* and fish fry to that left in the fryer, when P36 was used for frying. The quality of the lipid extracted from *papads* was not very substantially different from P36, as well as that left behind in the fryer. This could be due to shorter frying times of 7–8 s. *Papads* contains alkaline salts known as *papadkhar* in their formulation (Shurpalekar, Prabhakar, Venkatesh, Vibhakar, & Amla, 1972), which are known to degrade the oil by increasing alkaline contaminants. The results could be dramatic, if multiple frying cycles were continued.

The moisture content of the fish before frying was 74.52%. It was fried for 1 min and 20 s and the quality of the oil extracted and that left in the fryer is also shown in Table 1. The values of the evaluated parameters were higher in the oil extracted from fish fry as compared to that of the oil left in the fryer.

3.3. French fries

Table 2 shows the quality of the lipid extracted from French fries that were prepared from potatoes with initial moisture contents of 72.7%, 63.1%, 52.03% and 10.14%. The corresponding frying times were 270, 250, 225 and 50 s. A notable fact is that the quality of the oil left in the fryer was less deteriorated compared to that of the product oil, when the potatoes used for frying had moisture content of 72.7%, 63.1% and 52.03%. The lipid extracted from the product was inferior to that of the oil used for frying. A reverse situation was seen when potatoes having a lower moisture content of 10.14% was used. The frying time was directly correlated to the moisture content, with products having higher moisture content requiring longer frying times.

Polar oxidized lipid compounds, free fatty acids, and conjugated dienoic acids formed during the use of frying oil are selectively adsorbed on the surface of the product undergoing frying, the water molecules being directly

involved in ensuring adsorption. During frying, the escaping moisture throws back only triacylglycerols from the frying food components into the medium of frying which becomes heat-damaged at a later stage. Thus, the lipid of a fried product is comparatively more embedded with the oxidized and other polar components compared to the frying oil. It is the moisture of a product that forms the link between the oxidized compounds of heat-damaged frying oil and the constituents such as starch and protein of a fried product. There are reports of fried products taking up more of the oxidized fat from the frying oil by selective sorption (Pokorny, 1980). However, in this selective sorption, moisture plays a major role. Narayan and Kummerow (1963), while studying the factors influencing formation of complexes between oxidized lipids and proteins in model experiments found that the "binding" of proteins to oxidized lipids resulted only in the presence of water. In the dry state, no reaction was observed. It is also reported that lipids and proteins do not form complexes unless the fat or fatty acids are oxidized. The present study asserts the role of moisture in the preferential adsorption of oxidized lipids from the frying oil in the normal practice of preparing various deep-fat fried products.

4. Conclusions

The present investigation on a few products fried in heat-abused palm oil indicated the significance of moisture content of a product in determining the quality of the lipid picked up by the product from the frying oil. When the moisture content of the product was high (>50%), the quality of its lipid was found to be inferior to that of the frying oil. At lower moisture levels (<12%), the trend reversed, as seen from the analysis of *papads* and French fries with low initial moisture content.

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