Changes in Vegetable Oil Used for Commercial Frying: A Case Study from Rawalpindi, Pakistan

[1]ANWAAR AHMED*, [2]NISAR AHMED MALIK, [3]MUHAMMAD ATIF RANDHAWA, [4]SAEED AKHTAR, [1]ASIF AHMAD, [5]HAJRA AHMED AND [5]SYED SHAHZAD SHAH
[1]*Department of Food Technology, PMAS-Arid Agriculture University, Rawalpindi 46300, Pakistan.*
[2]*Senior Medical Officer, Cantonment Hospital, Rawalpindi 46300, Pakistan.*
[3] *National Institute of Food Science and Technology, University of Agriculture, Faisalabad 38040, Pakistan.*
[4] *Department of Food Science and Technology, Bahauddin Zakariya, University Multan, Pakistan.*
[5]*Department of Home and Health Sciences, Allama Iqbal Open University, Islamabad*
anwaarft@hotmail.com*

(Received on 7th July 2011, accepted in revised form 2nd May 2012)

Summary: The objective of present study was to evaluate the vegetable oils used for commercial frying of chicken and samosa, an indigenous fried product of Pakistan. Physiochemical analysis of the excessively used vegetable oils showed that refractive index and specific gravity was affected non significantly as a result of frying operation. However, acid value, saponification value, peroxide value, free fatty acids and total polar compounds were significantly lower ($p<0.05$) in the oil used before frying as compared to the values recorded after frying operation. The oils, before and after frying of samosa and chicken exhibited the iodine values in the range of 87.9±0.07- 120.5±11 and 86.5±1.03-118.4±10.45, respectively. Stearic acid, palmitic acid and oleic acid content were found to be lower in oils before frying than after frying in both the products, however, linoleic acid and linolenic acid indicated higher values in oil before frying than after frying. Total polar compounds (TPC) were shown to be significantly lower in oil before frying than after frying of samosa and chicken. TPC increased from 2.3±0.25 to 32.2.9±0.83 and 2.30±0.30 to 29.18±0.96, respectively in oils used for samosa and chicken. The higher values of TPC might be due to excessive number of frying and use of low quality oil. The study concluded that the changes in the chemical profile of excessively used oil were severe enough to cause several health hazards and rendered oils unfit for human consumption.

Key Words: Vegetable Oil, Deep Frying, Total Polar Compounds, Lipid Profile, Samosa, Chicken.

Introduction

Fats and oils had been one of the important constituents of our food since prehistoric times as a source of heat and light. The largest supply of vegetable oils comes from the seeds of soybean, cotton, peanut, and the oil-bearing trees of palm, coconut, and olive. Lipids in food exhibit unique physical and chemical properties. The chemical properties of oil are important with relation to their functional properties in many foods [1].

Frying is a process of cooking, involving the direct transfer of heat from hot oil to cold food. It imparts unique properties in processed foods and makes them more delicious and appetizing. During this process, frying oil undergoes several physico-chemical changes that deteriorate the quality of food and makes the food unfit for edible purposes [2, 3]. Deterioration of frying oils is in general followed by changes in free fatty acid (FFA) level, color of the oil or an increase in polarity of the oil [4-6]. The vegetable oils are highly susceptible to oxidation but the chemistry of vegetable oils and fats at frying temperature is more complex than just thermal oxidation or auto-oxidation [7, 8].

The negative aspect of frying may be ascribed through hydrolysis of fats into free fatty acids and mono and diglycerides. The fatty acids can oxidize to hydroperoxides, conjugated dienoic acids, epoxides, hydroxides and ketones. These compounds may undergo fission into small fragments or may remain in the triglyceride molecule and cross-link with each other, leading to dimeric and higher polymeric triglycerides [9]. The positive affect of frying in food is that it gives a distinctive flavor to fried products; some flavors are common to all fried foods and some are additional and specific for particular products, e.g. French fries [10, 11]. The color of the fried product often differs substantially from that of the original food material. The most important reactions are non-enzymatic browning reactions occurring between reducing sugars and free

*To whom all correspondence should be addressed.

amino acids, called Millard reactions. Colorless premelanoidins are a group of intermediary products with very low nutritional value. They are rapidly polymerized into macromolecular deep brown melanoidins, which are completely unavailable for human nutrition [12]. Severl studies indicated that products generated through oxidation of oil can be carcinogenic. Some volatile oxidation products produced at high temperature, exposure to UV radiation and in oxidative conditions were found to be mutagenic during frying [13-15].

Due to public health concerns, there is a strong demand to trim down the oil content of fried foods [16-18]. Conventional edible oils due to continuous deep frying causes many physical and chemical changes in oils like thermal oxidation, hydrolytic rancidity, color darkening, increased viscosity, decreased smoking point, higher polar compounds etc. that make the fried food product unsafe for human consumption. Albeit, frying of oils is of commercial and economic importance and may provide considerable savings to the food processors [19] however, the safety of the repeatedly used oils remains a fundamental concern since hypercholesterolemia, hypertension, mutagenesis, heart attacks, obesity and diabetes are the critical maladies resulting from the consumption of such oils. The objective of the current study was to evaluate the changes in vegetables oils as a result of excessive commercial frying.

Results and Discussions

Physical Evaluation

The mean values for refractive index and specific gravity of oil before and after frying of samosa and chicken have been given in Table-1. It is evident from the statistical results that no significant effect was observed on refractive index and specific gravity of oil. The slight non significant increase in specific gravity can be attributed to oxidation and polymerization reactions that make the oil denser resulting in increase in specific gravity.

Chemical Evaluation

The mean values regarding chemical parameters of oil have been presented in Table-1. The acid value was found to be significantly lower in oil before frying (1.40±0.10 and 1.1±0.09 meq/L) than after frying (4.63±0.30 and 5.0±0.11 meq/L) of samosa and chicken, respectively. It is evident from the results that variation in product regarding acid value remained non significant while highly significant effect was observed on acid value of oil due to difference in condition of frying. Frying temperature and time are the most significant factors that bring about changes in acid value of the product. Asap and Augustin [20] studied the effect of temperature and time for the deep frying of fried products and found that acid value increased which is the indication of deterioration of oil.

The data for saponification value of oil manifested non significant difference between products. The results for saponification value was found to be significantly lower in oil before frying than after frying of samosa and chicken. The saponification value of oil was found to be higher in samosa than chicken with no significant difference.

The results regarding peroxide value (POV) of oil has presented that the variation in products significantly affected peroxide value of oil (Table-1). It is manifested that POV was found to be significantly lower in oil before frying (3.2±0.25 and 2.9±0.19 meq/g) than after frying (15.21±0.20 and 18.92±0.88 meq/g) of samosa and chicken, respectively. This study substantiate the previous finding of several researchers who described the effect of deep fat frying on oxidative parameters of sunflower oil [21].

The analysis for iodine value of oil before and after frying of samosa and chicken manifested highly significant effect of frying on iodine value of oil while the differences in products were found to be non-significant. The iodine value decreased from 120.5±11.0 to 87.9±0.07 after frying of samosa and it decreased accordingly during the frying of chicken from 118.4±10.45 to 86.51±1.03 (Table-1).

The mean values for free fatty acids (FFA) of oil before and after frying of samosa and chicken revealed that FFA was found to be significantly lower in oil before frying (0.26±0.11 and 0.30±0.05%) than after frying (2.9±0.11 and 3.07±0.64%) in the oil used for frying of samosa and chicken. Some researcher proposed the FFA value of 0.03-0.8 % in fresh refined oils [22]. The increase in FFAs could be attributed to hydrolysis of fats particularly the polyunsaturated mono and diglycerides. Higher is the FFA higher will be the rancidity of oil which may cause many qualitative defects in oils.

The total polar compounds (TPC) were found to be significantly lower in oil before frying than after frying of samosa and chicken (Table-1). In the oil used for samosa, TPC increased from 2.30±0.25 to 32.20±0.83 whereas for chicken it increased from 2.30±0.30 to 29.18±0.96. It is evident from the results for TPC that there was a significant increase in TPC after frying operation of food products. The oil which was used for samosa frying generated more TPC than the oil used for chicken frying. The present results are well supported by the findings of other researchers [23, 24] who stated that the oils deteriorated faster at frying temperature due to the formation of polar compounds. Generally the oils with a higher level of unsaturated fatty acids produce more polar compounds compared to the more saturated ones. Frying of food may be problematic due to lengthy oil exposure to extreme conditions and the lack of adequate oil replenishment and discarding. TPC is one of the most reliable criteria for discarding frying oil after a certain number of fryings following a standard of 27% as recommended by HACCP.

Lipid Profile Analysis

The mean values for palmitic acid content (PA), stearic acid content (SA), oleic acid (OA), linoleic acid and linolenic acid content of oil before and after frying of samosa and chicken have been given in Table-1. It is evident from the results that highly significant effect was observed on palmitic acid contents of oil due to change in the products and condition. A significant increase in PA after frying was observed that was higher in chicken frying as compared to samosa frying. The proportion of palmitic acid in all oils increased significantly and is strongly correlated with hours of deep frying as indicated by previous researchers [25].

The highly significant effect of frying was observed on stearic acid contents due to differences in the condition however variation in product was found to be non-significant. It was observed during present studies that chicken produced more SA than samosas in the oil. Asap and Augustin [26] reported that unsaturated fatty acids are more susceptible than saturated ones to oxygen attack during thermal oxidation and this can result in the increase in level of saturated fatty acids due to hydrolysis and polymerization.

The content of OA in oil before and after frying of samosa and chicken represented that all the variables exerted significant effect on oleic acid contents of oil used for frying of different products. It was observed during present studies that chicken produced more oleic acid contents (26.4±1.04) than samosas (18.5±0.53) in the oil (Table-1). The results showed that oleic acid contents of oil changed little after the process of frying. In the process of hydrolysis, oxidation and polymerization, all fatty acid contents changed accordingly.

It is manifested from the results given in Table-1 that highly significant effect was observed on linoleic acid contents of oil due to differences in the condition and products. It is evident from linoleic acid contents that there was a decrease in linoleic acid contents after frying in oil. It was also observed during present studies that the oil in which chicken was fried contained more linoleic acid than the oil used for samosas. It might be due to the difference in the fried products. Similarly, highly significant effect was observed on linolenic acid contents of oil due to differences in the condition and product. It is evident from results that there was a decrease in linolenic acid contents after frying in oil. It was observed during present research that the oil used in chicken exhibited more linolenic acid contents than the oil used in frying of samosa. It might be due to the differences in the composition of fried products. Because different vegetables and condiments used in samosa preparation, might have negative impact on the quality of oil in the course of deep frying. Warner and Mounts [27] reported that higher level of poly-unsaturated fatty acids makes the oil more prone to degradation at elevated temperatures during deep-frying. This decreasing trend in linoleic acid contents of oils after deep and repeated frying give rise to many health hazards as it is an essential fatty acid that performs different metabolic functions in body. Further research needs to be continued on the role of dietary fat in human nutrition and its health impact [28].

Table-1: Changes in quality of oil on deep frying of Samosa and Chicken

Paramètre	Samosa		Chicken	
	Before Frying	After Frying	Before Frying	After Frying
Refractive index	$1.5±0.20^{a}$	$1.5±0.20^{a}$	$1.5±0.10^{a}$	$1.5±0.10^{a}$
Specific gravity	$0.92±0.11^{a}$	$0.96±0.24^{a}$	$0.89±0.07^{a}$	$0.91±0.09^{a}$
Acid Value (meq/L)	$1.4±0.10^{b}$	$4.6±0.30^{a}$	$1.1±0.09^{b}$	$5.0±0.11^{a}$
Saponification Value	$169.0±10.50^{b}$	$243.5±19.52^{a}$	$159.2±9.81^{b}$	$249.8±10.20^{a}$
Peroxide Value (meq/g)	$3.2±0.25^{b}$	$15.2±0.20^{a}$	$2.9±0.19^{b}$	$18.9±0.88^{a}$
Iodine value	$120.5±11.00^{a}$	$87.9±0.07^{b}$	$118.4±10.45^{a}$	$86.5±1.03^{b}$
Free Fatty acid (%)	$0.26±0.11^{b}$	$2.9±0.11^{a}$	$0.3±0.05^{b}$	$3.0±0.64^{a}$
Total polar compound (%)	$2.3±0.25^{b}$	$32.2±0.83^{a}$	$2.3±0.30^{b}$	$29.1±0.96^{a}$
Palmitic Acid	$5.3±0.11^{b}$	$13.7±0.99^{a}$	$6.7±0.80^{b}$	$13.8±0.95^{a}$
Stearic Acid	$2.8±0.20^{b}$	$3.7±0.50^{a}$	$2.8±0.50^{b}$	$3.7±0.66^{a}$
Oleic Acid	$16.9±0.22^{a}$	$18.5±0.53^{b}$	$24.6±0.25^{b}$	$26.4±1.04^{a}$
Linoleic acid	$36.4±0.90^{a}$	$33.1±1.03^{b}$	$41.8±1.15^{a}$	$39.1±1.05^{b}$
Linolenic acid	$3.4±0.20^{a}$	$2.4±0.11^{b}$	$4.1±0.11^{a}$	$3.2±0.29^{b}$

Means sharing the same letters in the rows are not significantly different ($P<0.05$). Values are the means ±SD of three replicates ($n=3$)

Experimental

Material

The vegetable oils used for the frying of chicken and samosa were collected before and after frying from different locations in the cantonment area of Rawalpindi, Pakistan. The oil samples were collected at the two stages i.e. at the start when fresh oil was used and at last frying when the oil was considered to be discarded by the producer. The number of frying was also counted and the samples were taken in three replications. The oil samples were taken in air tight amber colored glass bottles, brought to laboratory immediately and stored in refrigerator at 4 ºC for various physicochemical parameters**.**

Physico-Chemical Analysis

The refractive index was measured directly from Abbe's Refractrometer according to the standard procedure [29]. The specific gravity of the oil samples was estimated by using Pycnometer at standard temperature of 25°C [29]. American oil Chemist Society methods were used for the determination of acid value (Method Cd 3a-63), peroxide value (Method Cd 8-53), iodine value (Method Cd 1-25) and saponification value (Method Cd 3-25).

Free fatty acids and total polar compounds (TPC) were calculated following the procedure of AOAC (2000) [29]. To measure TPC, the frying fats were separated by column chromatography on silica gel into nonpolar and polar components. The polar components were determined indirectly by subtracting concentration of nonpolar components. Polar components were calculated by the following expression:

$$\text{Polar Components (\%)} = (E - A) \times 100/E$$

where

A= non polar fraction (g)
E= sample in 20 mL aliquot (g)

Lipid Profile Determination by GC-FID

Samples were prepared according to the procedure of Ashraf and Gillani [30]. For analysis a Hewlett-Packard Gas Chromatographic System (Model 6890) equipped with split/splitless injection system and flame ionization detector was used. A fused capillary column DB-Wax (30 m x 0.25 mm id, 0.25 µm) was used for separation of fatty acids methyl esters. Injector temperature was 250 °C and 1 µL sample was injected with a split ratio of 1:50 and the detector temperature was 280 °C. The carrier gas was hydrogen with a head pressure 53 kPa constant pressure (36 cm/sec at 50 °C). The following oven program was used: 50 °C, 1 min, 25 °C/min to 200 °C, 3 °C/min to 230 °C, 18 min. The detector gases were hydrogen: 40 mL/min; air: 450 mL/min; helium make-up gas: 30 mL/min.

Statistical Analysis

Data obtained from physico-chemical analysis were analyzed statistically using analysis of variance and Duncan's Multiple Range test by following the methods described by Steel *et al* [31]. The level of significance was defined at $p<0.05$. Each experiment was repeated at least thrice and the values are reported as means.

Conclusion

Fried foods contribute a significant proportion of the total fat consumed by the Pakistani People. Fried foods are popular due to their taste, distinctive flavor, aroma and crunchy texture. During the present study, samosa produced more changes/degradation than chicken in the frying oils. Use of different vegetables and condiments in samosa preparation, might have imparted negative impact on the quality of oil in the course of deep frying. Excessive frying and use of low quality oil resulted in enhanced TPC values beyond permissible limits.

Acknowledgements

The authors are grateful to the National Institute of Food Science and Technology, University of Agriculture, Faisalabad-Pakistan, for providing facilities to carry out a part of the research project.

References

1. W. W. Nawar, Lipids. In: Fennema OR (ed.) Food Chemistry 3rd Ed Marcel Dekker, New York, p. 225 (2006).
2. J. Pokorny and Z. Reblova. *Food Technology and Biotechnology*, **37**, 139 (1999).
3. C. Dobarganes, G. Márquez-Ruiz and J. Velasco. *European Journal of Lipid Science and Technology*, **102**, 521 (2000).
4. A. J. Paradis and W. W. Nawar. *Journal of Food Science*, **46**, 449 (1981).
5. Y. A. Tan, S. H. Ong, K. G. Berger, H. H. Oon and B. L. Cyr Poh. *Journal of American Oil Chemists Society*, **62**, 999 (l985).

6. S. Melten, S. Jafar, D. Skyes and M. K. Trigiano. *Journal of American Oil Chemists Society*, **71**, 1301 (1994).
7. C. Gertz, S. Klostermann and S. P. Kochhar. *European Journal of Lipid Science and Technology*, **102**, 543 (2000).
8. C. Susana, M. Ricardo, S. Artur, P. P. O. Beatriz, A. P. José. *Food and Chemical Toxicology*, **48**, 2972 (2010).
9. A. Iftikhar. *Pakistan Journal of Food Science*, **9**, 29 (1999).
10. S. Chang, R. J. Peterson and C. T. Ho. *Journal of American Oil Chemists Society*, **55**, 718 (1978).
11. R. K. Wagner and W. Grosch. *Journal of American Oil Chemists Society*, **75**, 1385 (1998).
12. A. N. Califano and A. Calvel. *Journal of Food Processing and Preservation*, **12**, 1 (1988).
13. G. Marquez-Ruiz and M. C. Dobarganes. Nutritional and physiological effects of used frying fats. In: Erickson M. D. (ed.), Deep Frying: Chemistry, Nutrition and Practical Applications, 2nd Ed, Champaign, IL: AOCS press. p. 160 (1996).
14. A. Zeb, S. Khan, I. Khan and M. Imran. *Journal of the Chemical Society of Pakistan*, **30**, 790 (2008).
15. G. Hageman, R. Kikken, F. Ten Hoor and J. Kleinjans. *Mutation Research*, **204**, 593 (1988).
16. H. Esterbauer. *American Journal of Clinical Nutrition*, **57**, 779S (1993).
17. R. G. Moreira and M. A. Barrufet. *Journal of Food Engineering*, **35**, 1 (1999).
18. H. Ni and A. K. Datta. *Food and Bioproducts Processing*, **77**, 194 (1999).
19. J. Meriem, Bo, N. Consolate and J. Tang. *Food Research International*, **40**, 341 (2007).
20. T. Asap and M. A. Augustin. *Journal of the Science of Food and Agriculture*, **37**, 1045 (1986).
21. F.K Bangash and H. Khattak Maianum. *Journal of the Chemical Society of Pakistan*, **28**, 121 (2006).
22. T. Mehmood, A. Ahmad A. Ahmed and N. Khalid, *Journal of the Chemical Society of Pakistan*, **34** (2012) IN PRESS.
23. G. R. Takeoka, G. H. Full and L. T. Dao. *Journal of Agricultural and Food Chemistry*, **45**, 3244 (1997).
24. B. Geeta, Z. Weibiao, J. B. Philip, L. Hui-Ling and N. Fung-Leng. *Food Chemistry*, **121**, 338, (2010).
25. X. Q. Xu, V. H. Tran, M. Palmer, White and P. Salisbury. *Journal of American Oil Chemists Society*, **76**, 1091 (1999).
26. T. Asap and M. A. Augustin. *Journal of American Oil Chemist Society*, **63**, 1169 (1986).
27. K. Warner and T. L. Mounts. *Journal of American Oil Chemists Society*, **70**, 983 (1993).
28. M. Asif. *The Pharma Research Journal*, **4**, 16 (2010).
29. AOAC. Official Methods of Analysis, *The Association of the Official Analytical Chemists*. Arlington, USA. (2000).
30. F. Ashraf and S.R Gillani. *Journal of the Chemical Society of Pakistan*, **29**, 343 (2007).
31. R. G. D. Steel, J. H. Torrie and D. A. Dicky., Principles and procedures of statistics: A Biometrical Approach. 3rd edn. McGraw Hill Book Co. Inc., New York (1997).