Effect of Deep Fat Frying on Physico-Chemical Properties of *Silybum Marianum* and Sunflower Seed Oils

F. K. BANGASH AND H. KHATTAK
Institute of Chemical Sciences
University of Peshawar, Peshawar25120, Pakistan.

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Summary: The crude *Silybum marianum* oil and sunflower oil were used for repeated deep fat frying of potato-fillet (French fries) for 5 consecutive days @ 20 minutes per day at 180 – 190°C and then allowed to cool for 18 hours at 25C^0. The test oils were evaluated for physical and chemical deterioration. The quality indices peroxide value (POV), anisidine value (AV), iodine value (IV), free fatty acid (FFA) and color (O.D at 420nm) of the samples were measured. It was found that all the quality parameters significantly increased as frying time was advanced, while the reverse trends regarding IV was observed in all the test oil. The highest average POV (38.1meq/kg), FFA (15.9 %) and AV (9) were observed in *Silybum marianum* oil while IV (97.1g/100g) in sunflower oil. The maximum change in color (discoloration) was observed in sunflower oil.

Introduction

Deep fat frying is a traditional and long used method of cooking and is popular throughout the world for preparation and manufacture of many foods. This method is commonly used in traditional catering restaurants, fast food chains and in industrial frying operations such as potato chips, instant noodles [1]. During the deep fat frying process the oil is exposed continuously or repeatedly to elevated temperatures in the presence of air, moisture and food. Under such conditions oxidation, hydrolysis and thermal decomposition of fried oil may take place. The degradation products formed by these reactions and polymerization of unsaturated fatty acids include both volatile and non-volatile compounds [2, 3]. Biochemical and oxidative changes occurs in fatty food materials caused by lipase enzymes, during storage at elevated temperatures [4, 5]. The free radicals formed by fatty acids react with oxygen to generate peroxides that enter into a multitude of reactions, producing numerous products, such as aldehydes, ketones, acids, esters and polymerized fat [6]. The extent of reaction depends on the frying temperature, aeration, type of fried oil or fat and the food that is being fried [7]. As the reaction proceeds, the degradation of frying oil becomes intense and effects the functional, sensoric and nutritional qualities of frying oil as well as that of food prepared in the degraded frying oil. The type of food being fried and its interaction with oil has been reported to contribute to the deterioration of frying oil [8].

Comparative evaluation of the oils commonly consumed in Pakistan, for their quality changes during frying process, has not been studied. It is important to prevent oxidation of edible fats and oils and of food that contain oils to maintain their quality and safety. Heat, light and metals in the fats and oils can initiate oxidation of fats and oils. The quality and stability of the fats/oils used for frying are of great concern to food technologists, nutritionists and consumers [9]. They have pointed out that the changes occur in the fried fat may adversely effect the flavor and nutritional value of the oil as well as the food fried. The objective of this study was to evaluate the comparative frying performance of a non-conventional oil, *Silybum marianum* oil (SMO) with a conventional oil such as sunflower oil (SFO).

Results and Discussion

The results show an increase in all the measured parameters with increased frying time. The extent of oxidation of the samples as measured by POV increased from 16.17 meq/kg to 81.4 meq/kg for SMO and from 18.6 meq/kg to 85.5 meq/kg for SFO during the frying. It is clear from the Fig. 1 that more increase in POV take place for SMO than for SFO. The FFA increased from 17.9% to 29.4 % for SMO and 8.21% to 23.2% for SFO with the successive increase in frying time and it is clear from the Fig. 2 that more increased in FFA value take place for SFO than SMO. It has been suggested that

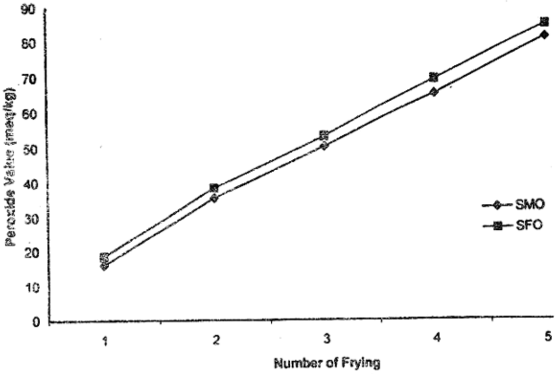

Fig. 1. Peroxide value as a function of frying for SMO and SFO.

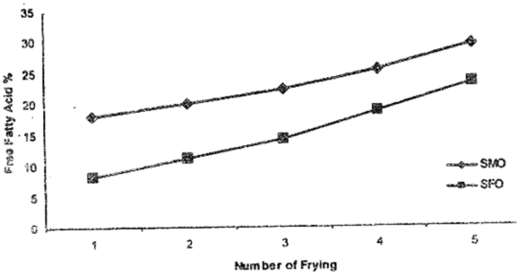

Fig. 2. Free fatty acid as a function of frying for SMO and SFO.

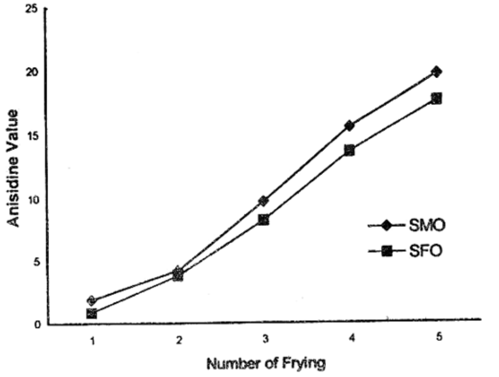

Fig. 3. Anisidine value as a function of frying for SMO and SFO.

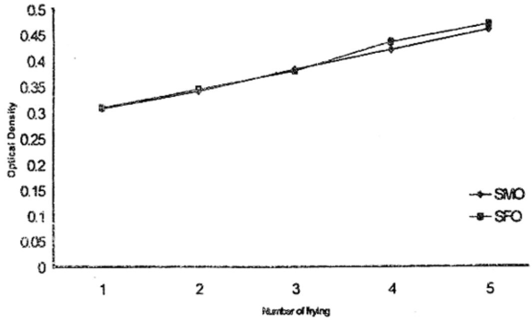

Fig. 4. Optical density as a function of frying for SMO and SFO.

production of FFA was the best predictor of fats deterioration during frying and the presence of FFA could be used to monitor the extent of oil abused [10]. Anisidine value measures the secondary breakdown products of peroxides and hydro-peroxides, which are formed at rapid rate during frying process [11], and was generally higher in *Silybum marianum* than the sunflower oil. Anisidine values in this study increased from 1.89 to 19.63 for SMO and 0.87 to 17.58 for SFO. Fig. 3 shows the increasing trend in AV for both the oils. Some workers [1] showed that polymer contents, foam height and other quality parameters generally increase as the frying period was advanced. Other investigators have reported [12], that poly-unsaturated oils have reduced stability at elevated temperatures and their peroxide value increase gradually. The results regarding the influence of frying time on color of the oils measured as OD at 420 nm show increased absorbance with increasing frying time. The value of OD increased from 0.31 to 0.4612 for SMO and from 0.3113 to 0.4721 for SFO. Fig. 4 indicates that more color change take place for SFO than SMO. The increase in color during frying of oils has also been reported by other investigators [3] and stated that measurement of oil colour could not be used to monitor oil quality due to the possibility of interference of food components with oil during frying. The iodine value (IV) decreased with increase of frying time, primarily due to decrease in un-saturation during the frying process, which also result in the increase of oil's viscosity. The iodine values for the controlled samples are 108.5 g/100g and 116.07 g/100g for SMO and SFO respectively, which decreased to 80.1 g/100g for SMO and 81.3 g/100g for SFO after the 4th day of frying. Fig. 5 shows a decreasing trend for both the oils. Similar trend has also been reported in sunflower, soybean, corn and crude rape seed oils [13]. Steven and co-workers [14] found that on deep-frying of triolein, polymer formation exceeded 20%.

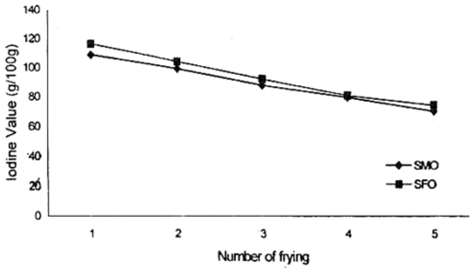

Fig. 5: Iodine value as a function of frying for SMO and SFO.

They also observed increase in the free fatty acid, total acid value and para-anisidine value indicating that thermal oxidation and degradation of triolein had occurred. The present study has similar findings as that of Neill *et al* [15] related to the effect of elevated temperature on oil. They reported that the repeated use of frying oils effect the flavors and color of oils.

Bangash *et al* [16] studying the effect of the storage stability of red palm oil with radiation concluded that the quality parameters FFA, POV, AV were higher in the irradiated samples than in the controlled while the reverse trend was noted in the case of iodine value, color and β-carotene.

Experimental

Silybum marianum (Milk Thistle) seeds were collected from wildly grown plants in the periphery of Peshawar in N.W.F.P Pakistan, while the sunflower seeds were purchased from Agriculture Research Institute Tarnab, Peshawar. Fully ripened, sound and healthy seeds were ground with electric grinder. Extraction of oils from the seeds were carried out in Soxhlet apparatus using purified hexane as the solvent. Potatoes were washed, peeled and cut into 3 mm thick fillets (French Fries) by mechanical cutter, washed with water to remove starch and fried in aluminum frying pan. Approximately 500 g fillets were fried in one liter of each oil for 20 minutes (5 minutes heating and 15 minutes frying) for five consecutive days. After each frying, oils were allowed to cool to $25C^0$ for 18 hours and again used for next frying. Samples of each test-fried oil were taken after each cooling cycle. The peroxide value (POV), Free Fatty acid (FFA) as % oleic acid and iodine value were measured according to the method of AOCS [17]. For determination of peroxide value (meq/kg) samples were mixed with mixture of glacial acetic acid and chloroform (2:3) reacted with saturated potassium iodide, and titrated with standard $Na_2S_2O_3$. For measuring free fattly acids, samples of oil/fat were neutralized with ethanol, using phenolphthalein indicator, and titrated with NaOH. The iodine value (g/100g) determines the degree of unsaturation was found by mixing the samples with CCl_4, Wijis solution, potassium iodide and distilled water, and titrated with 0.01 N $Na_2S_2O_3$ using starch as indicator. Color was measured as absorbance of 50% (v/v) solution (sample/isooctane) and determined spectrophotometerically at 420 nm [9]. The unsaturated aldehydes contained in the oil were determined as the anisidine value [18]. The samples were dissolved in *n*-Hexane and the absorbance of the sample solution was taken at 350 nm. Hexane and para-anisidine regent (0.25% in acetic acid) were added to the sample solution, absorbance of the mixture was again recorded and AV was calculalated.

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Nomenclature:

β	=	Beta
SMO	=	*Silybum marianum* Oil
SFO	=	Sunflower Oil
POV	=	Peroxide Value
FFA	=	Free Fatty Acids
AV	=	Anisidine Value
IV	=	Iodine Value
OD	=	Optical Density
NIFA	=	Nuclear Institute for Food & Agri-culture
PORIM	=	Palm Oil Research Institute of Malaysia
meq	=	milli equivalent
ppm	=	parts per million

References

1. I. Ahmad, *Pak. J. Food Science,* **9,** 24 (1999).
2. T. Ahmad, S. Atta and A. Sattar, *Proceeding 2nd All Pakistan Science Conference.,* (1993).

3. T. Ahmad, A. Sattar, S. A. Nagra and M. A. Sheikh, *Pak. J. Pharmacy Punjab University,* 9(2), 51 (1996)
4. J. L. Sebedio, A. Bonpunt and J. Prevost, *J. Agri, Food Chem.*, **38**, 869 (1990).
5. J. L. Sebedio, A. Grandgriard and Y. Maikky, *JOACS.*, **68**, 299 (1991).
6. B. J. F. Hudson, *Evaluation of Oxidative Rancidity Techniques In Rancidity in Foods.* Eds. J. C. Allen. R. J. Hamilton. Applied Science Publishers, London, 14 (1983).
7. S. S. Chang, R. J. Peterson and H. O. Chi-Tang, *JOACS.*, **55**, 718 (1978)
8. S. G. Stevenson, V. Jenser and M. Eskin, *JOACS.*, **61**, 1102 (1984).
9. F. J. Mancini, L. M. Smith, R. H. Creveling and H. F. Sheikh, *JOACS.*, **63**, 1453 (1986).
10. S. G. Stevenson, V. Jenser and M. Eskin, *J. Can. Inst. Food Sci. Tech.*, **18**, 187 (1984).
11. M. J. Werman and I. Neeman, *JOACS.*, **63**, 352 (1986)
12. A. A. K. Wahale, *Some compositional, quality and consumption aspects of palm oil in UAE.* Paper presented at palm oil familiarization program (POFP), Kuala Lumpur, Malaysia, (1997).
13. Y. H. Chu, and S. Luo, *JOACS.*, **71**, 897 (1994)
14. L. H. Steven, M. R. Myers and W. E. Artz, *JOACS.*, **71**, 1239 (1994)
15. J. M. McNeill, Y. Kakuda and B. J. Kamel, JOACS., **63**, 1564 (1986)
16. F. K. Bangash, T. Ahmed, S. Atta and A. Zeb, *J. Chin. Chem. Soc.*, **51**, 991 (2004).
17. *AOAC. Official and Tentative Methods*, 3rd ed. Method Cd. 8 (1972).
18. *PORIM Test Methods*, Palm Oil Research Institute of Malaysia. In Methods of Test for Palm Oil and Palm Oil Products. PORIM's, Publication, Kula Lumpur, Malaysia, Section 2.4, 1 (1993).