Quality Improvement of Used Fried *Silybum marianum* Oil by Treatment with Activated Charcoal and Magnesium Oxide

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Summary: The crude *Silybum marianum* oil was used for frying of potatofillets (French fries) for 4 consecutive days at a rate of 20 minutes per day. The quality constants such as peroxide value (POV), anisidine value (AV), iodine value (IV), free fatty acid (FFA) and color index as optical density (O.D at 420 nm) have been determined before and after frying. The results showed an increasing pattern in the values of the above quality parameters. The peroxide value increased from 5.03 to 19.41meq/ kg, AV from 1.34 to 16.4, FFA from 0.09 to 2.41 %, and color from 0.02 to 1.9. Fried *Silybum marianum* oil was mixed separately with 3 levels of MgO (4, 6, 8 % w/ w) and activated charcoal (2, 6, 10 % w/ w). For all the treatments, the average percent improvement of quality indices was statistically analyzed. Increasing levels of both activated carbon and MgO significantly affected ($P < 0.05$) the different quality parameters tested so far.

Introduction

Deep fat frying is a traditional food processing method used worldwide for cooking many foods. During the deep fat frying process, the oil is exposed continuously (or repeatedly) to elevated temperature in the presence of air, moisture and food. Under such conditions, oxidation, hydrolysis and thermal decomposition of frying oil may take place leading to the degradation of oil [1]. The degradation products formed by these reactions and polymerization of unsaturated fatty acids include both volatile and non-volatile compounds [2, 3]. Although most of the volatiles are lost through steam distillation during the frying process, some remain in the oil and may be consumed with the fried foods. Nonvolatile decomposition products are produced primarily by thermal oxidation and polymerization of unsaturated fatty acids. It has been reported [4] that polar compounds are of particular concern because they accumulate in the frying oil where they promote further degradation and may be absorbed by the fried food and enter the diet of the consumers. It has been observed [5] that fats rich in unsaturated fatty acids yield more polymers than those having low concentration of unsaturated fatty acids. Huge amounts of oils and fats are used for deep fat frying and the deep fat fried foods are the major items of human diet [6]. It is, therefore, absolutely essential to ascertain the extent to which frying oil can be used. One commonly used method of maintaining oil quality is to add fresh oil periodically. Another procedure involves filtering the oil on a daily or continuous basis. Filtering is useful in extending the cooking life of frying oil. Food particles, if not removed before next utilization, may burn and develop undesirable flavors and increase the rate of oil deterioration. The adsorbent materials improve oil quality by reducing the level of free fatty acids and color compounds [7]. Considerably less work has been published on procedures used to clean or purify fried oils in Pakistan. The efficiency of activated carbon and magnesium oxide to improve the quality of used frying oil has been investigated in this study. Since activated charcoal and magnesium oxide are efficient adsorbents, it could bound trace amounts of toxic compounds and as such could cause health problems. After the treatment, the adsorbent materials should be completely recovered.

Heat, light and presence of metals in fats and oils initiate oxidation of the constituent organic compounds. The oxidation products which include hydro peroxides and cyclic peroxides decompose to produce a variety of volatile compounds. The resultant products can cause undesirable flavors and odors in oil [8]. Free fatty acids are produced by the hydrolysis of fats in the presence of water and enzymes during storage. Lipid hydro-peroxides produced in the oil as mentioned earlier are very unstable and break down to alkoxy free radicals, which decompose, most likely by cleavage on either side of the carbon attached to an oxygen atom [9].

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Results and Discussion

Physical and chemical changes in the *Silybum marianum* oil used for frying French fries over a four days period was investigated. The results illustrated progressive deterioration of the oil. Control oil (day 0) without any frying showed the lowest values of POV, FFA, AV and color. The rate of oxidation as measured by POV increased from 5.3 to 19.4 meq/ kg and FFA from 0.1 to 2.4 % with the successive increase in frying time. Increasing trends in POV and FFA for *Silybum marianum* oil is shown in Figs 1 and 2. It has been investigated that polyunsaturated oils have reduced stability at elevated temperature and that their peroxide values are gradually increased [10, 11].

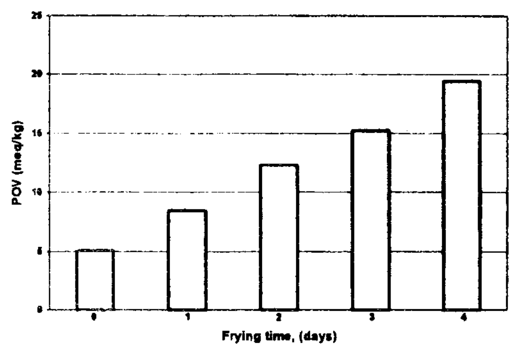

Fig. 1. Effect of deep fat frying on the peroxide value (POV) of *Silybum marianum* oil.

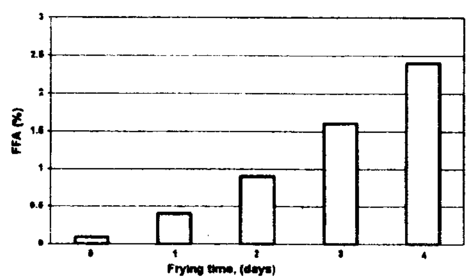

Fig. 2. Effect of deep fat frying on the free fatty acid value (FFA) of *Silybum marianum* oil.

The anisidine value measures the secondary breakdown products of peroxides and hydroperoxides, which are formed at increased rate during frying [9]. In this study, the anisidine value consistently increased from 1.34 to 16.41. Earlier findings showed that anisidine value, polymer contents, foam height and other quality parameters generally increase as long as frying period was advanced [12]. Fig. 3 shows the increasing trend in AV for *Silybum marianum* oil. The results regarding the influence of frying time on color of the oils, measured as O.D at 420 nm showed increased absorbance (from 0.22 to 2.36) with increasing frying time. Other investigators have also reported an increase in color during frying of oil and they suggested that measurement of oil color could not be used to monitor oil quality due to the possibility of interference of food components with oil during frying [13].

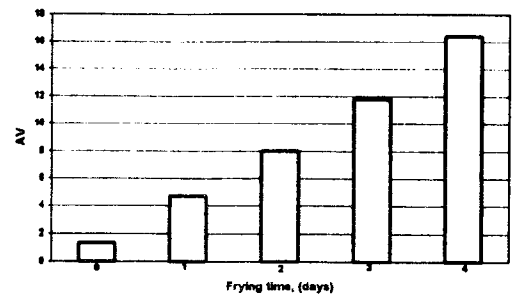

Fig. 3. Effect of deep fat frying on the anisidine value (AV) of *Silybum marianum* oil.

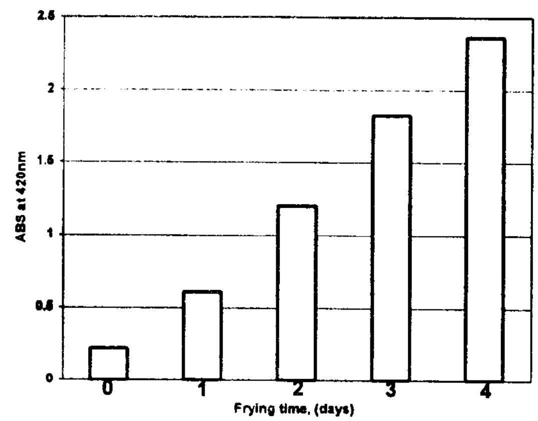

Fig. 4. Effect of deep fat frying on the color (O. D) of *Silybum marianum* oil.

The iodine value showed a decreasing trend with increasing frying time, primarily due to decrease in unsaturation during the frying process, resulting in the increased viscosity. The iodine value was 116.1 g/ 100 g in control samples, which decreased to 70.0 g/ 100 g after 4 days of frying. Fig. 5 shows a decreasing trend for the *Silybum marianum* oil. Similar trend has also been reported in sunflower, soybean, corn and crude rapeseed oils [14, 15].

Treatment of the oil with activated carbon and MgO was effective in reducing the FFA, POV, AV and photometric color. The results were expressed as % improvement and subjected to the analysis of variance procedure. The treatment levels were replicated thrice and the average % improvement calculated is shown in Tables-1 and 2. During the treatment, the increasing levels of both of activated carbon and MgO affected the FFA significantly ($P < 0.05$). The highest concentration of carbon (10 %) and MgO (6 %) resulted in 64.35 % and 55.7 % improvement, respectively in case of FFA, indicating that MgO is more effective than activated carbon. Conversely, activated carbon was effective in discoloration (56.2 %) of the used oil due to adsorptive characteristic of activated carbon, which removes impurities by occlusion.

Table-1. Effect of Magnesium Oxide Concentration on Quality Parameters of Fried *Silybum marianum* oil.

Amount of MgO in oil (w/ w)	Replication	FFA	POV	AV	Color
2 %	1	52.4	34.1	14.6	38.4
	2	53.7	34.6	14.2	37.7
	3	53.2	35.2	13.7	37.1
	Mean	53.1^c	34.6^c	14.2^c	37.7^c
4 %	1	58.4	38.2	16.3	39.2
	2	58.1	38.6	16.7	39.8
	3	59.3	39.1	15.4	38.8
	Mean	58.6^b	38.1^b	16.1^b	39.3^b
6 %	1	63.4	41.3	18.2	41.3
	2	64.2	41.5	17.6	42.5
	3	65.4	42.4	17.5	42.8
	Mean	64.3^a	41.7^a	17.8^a	42.2^a
Overall mean		58.7	38.3	16.0	39.7
CV		1.33	1.39	3.20	1.66
LSD		1.56	1.06	1.02	1.32

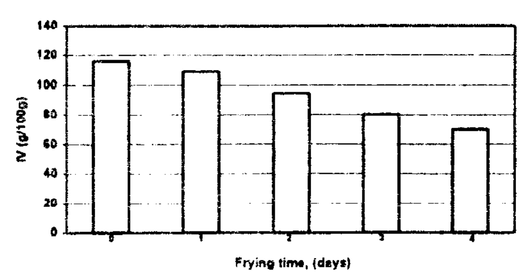

Fig. 5. Effect of deep fat frying on the iodine value (IV) of *Silybum marianum* oil.

To assess the effectiveness of the adsorbents on reducing the levels of peroxide and anisidine values, the overall percent improvement (mean of 9 values) was calculated. The MgO treated samples showed slightly better improvement for POV (41.3 %) and anisidine values (17.7 %), while in case of activated carbon samples the improvement in POV and AV was 32.8 % and 17.3 %, respectively. Different levels of treatment of activated carbon and MgO were statistically signifi-cant in improvement of oil quality by reducing POV and AV.

Table-2. Effect of Activated Charcoal Concentration on Quality Parameters of Fried *Silybum marianum* oil.

Amount of activated charcoal in oil (w/ w)	Replication	FFA	POV	AV	Color
2 %	1	43.2	21.6	13.9	47.7
	2	44.15	21.9	13.6	47.2
	3	43.7	22.3	14.1	48.1
	Mean	43.7^c	21.9^c	13.9^c	47.7^c
6 %	1	49.2	25.6	15.6	49.2
	2	48.9	25.1	15.7	50.4
	3	49.7	26.2	16.2	49.8
	Mean	49.3^b	25.6^b	15.8^b	49.8^b
10 %	1	55.1	32.4	17.3	55.6
	2	55.8	33.1	17.6	56.2
	3	56.2	32.8	17.1	56.7
	Mean	55.7^a	32.8^a	17.3^a	56.2^a
Overall mean		49.5	26.8	15.7	51.2
CV		0.99	1.60	1.77	1.05
LSD		0.98	0.85	0.55	1.07

Similar results were reported by previous workers [4-7] showing that commercially used shortening treatment with bleaching clay, charcoal, magnesium oxide celite and their mixtures effecti-vely reduced the quality indices *i.e.* dielectric constant, free fatty acid, color and total polar compounds in the fried oil. They further stated that a lower level of adsorbent and longer contact time might increase the yield values without diminishing the degradation products, while minimizing oil losses. The basic properties of adsorbents enable it to attract acids and polar colored compounds more effectively. Moreover tiny particle size of adsor-bents gives it a large surface area and may contri-bute to the remarkable adsorption. As such these adsorbents have high ability for FFA adsorption.

Results regarding selected fatty acid composition are presented in Table-3. Regarding the quality improvement in fatty acids by treating with MgO and charcoal, 30-45 % increase in the levels of linoleic and oleic acids was observed, while 30-40 % increase in the levels of palmatic and stearic acids was shown. Similar results were reported previously

Table-3. Effect of Frying and Adsorbents on Selected Fatty Acid Composition (%) in *Silybum marianum* oil.

Fatty Acid	Fresh	Fried	MgO treated	Improvement with MgO (%)	Charcoal treated	Improvement with Charcoal (%)
Palmatic	7.2	4.3	5.2	31.0	5.4	37.9
Stearic	2.0	1.0	1.3	30.0	1.4	40.0
Oleic	26.4	14.2	18.4	34.4	19.7	45.1
Linoleic	64.4	31.4	26.4	32.5	28.2	45.4

while working on quality improvement of used canola oil by treatment with activated carbon and silica [4]. Sensorically all fresh (0 day) chips had highly characteristic odour/ flavor. After 4 days of frying, chips were more intense in buttery odour/ flavor. For 0 and 4 days chips, there was no difference in sensory hardness, crispiness and color of the chips. The chips prepared in refurbished oil were rated as being different compared to fresh oil with regard to flavors, crispiness and color.

Experimental

Silybum marianum (Milk Thistle) seeds were collected from wildly grown plants in the periphery of Peshawar in the N.W.F. Province of Pakistan. From fully ripened, sound and healthy seeds the oil was extracted mechanically by cold pressing and filtered by ordinary filter paper. One kg potato fillets were fried in 2 L of oil for 20 min in conventional aluminum frying pane at 180 ^{0}C for 4 consecutive days. After each frying, oil was allowed to cool to room temperature for 18 hours and was again used for next frying. Samples of oil from each test frying were taken after each cooling cycle and analyzed for POV, FFA, and IV by standard procedure [16]. For POV, 1 g of oil sample was mixed with 25 ml of solvent mixture (glacial acetic acid and chloroform, 3: 2), shaken well and reacted with saturated potassium iodide for 1 min. The reaction was stopped by adding 25 ml of distilled water and titrated with standard $Na_2S_2O_3$ (0.01 N) using starch as indicator.

The free fatty acid value is the number of milligram of potassium hydroxide necessary to neutralize free acids in 1 g of sample. A known amount (5 g) of oil was weighed in a conical flask, 30 mL-neutralized ethanol along with a few drops of phenolphthalein indicator were added and the mixture heated on hot plate at 40 °C. The solution was titrated with NaOH until pink color was stable for at least 20 seconds. The FFA as % oleic acid contents was calculated.

For determination of iodine value 0.1 g of oil sample in a glass stoppered flask was taken and 10 ml of CCl_4 was added. Then 25 mL Wijis solution was added and the flask was kept under dark for 30 minutes. The stopper used was moistened with 10 % potassium iodide. Then 15 mL potassium iodide and 100 mL distilled water was added and the mixture was titrated with 0.01 N $Na_2S_2O_3$ using starch as indicator. Blank titration was also performed.

Anisidine value (AV) was determined with the method described by PORIM [17]. The method determines the amount of aldehyde (principally 2 alkenal) in oil and fats. Known amount of oil (1 g) was dissolved in *n*-hexane and made up to 25 mL. Absorbance (Ab) of the sample solution was taken at 350 nm wavelengths using the solvent (*n*-hexane) as blank. In the next step exactly 5 mL of the sample solution and 5 mL of hexane were mixed and 1 mL of *para*-anisidine reagent (0.25 % in acetic acid) was added and shaken well. After 10 minutes the absorbance of sample (As) of the mixture was recorded.

The color of oil (50 % *v/v* solution of oil in iso-octane) was measured as optical density at 420 nm using Shimadzu UV-Vis spectrophotometer model 160 by the method described by Mancini *et al.*, [7]. The fatty acid composition of oil was determined by employing the transesterification method using sodium methoxide as reported by Shehata *et al.*, [18]. About 100 g of untreated used oil were taken and treated with three levels (2, 6, 10% w/ w) of activated carbon and MgO (2, 4, 6 % w/ w) separately in a 250 mL bottle and agitated for 20 minutes in a shaking water bath. The oil samples were centrifuged at 3,000 rpm for 15 min and filtered through 2 layers of Whatman filter paper no. 1 under vacuum. The filtered oil was stored for analysis. The improvement in quality of oil was determined by standard formula:

$$\text{Improvement } \% = \frac{(\text{untreated used oil} - \text{treated used oil})}{(\text{Untreated used oil- unused fresh oil})} \times 100$$

Potato chips were prepared in fresh as well as in treated oil and subjected to trained panelists for evaluation of the products for color, odour and crispiness in individual booths. Statistical analysis of the data on % improvement was performed by analysis of variance, determining the co-efficient of variation (CV), which is the percentage of standard deviation to the mean [19].

Conclusions

From the results of this study, it could be concluded that deep fat frying increases the peroxide value, free fatty acid, color, and decreases the iodine value. Profound increase in anisidine value and a decreased iodine value are of special significance regarding the deterioration of oil. The quality of fried oil could be improved by the use of activated charcoal powder and MgO and can be reused for frying. Regarding the treatment, magnesium oxide was found better in improving the overall quality of oil, though activated charcoal was more effective to restore the amount of fatty acids in the oil.

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