

## ORIGINAL ARTICLES

### Effect of Pretreatments and Frying Time on Physical and Chemical Properties of Cottonseed Oil

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#### ABSTRACT

This study dealt with the evaluation of frying medium, namely, cottonseed oil used for frying of potato strips at heating temperature 180 °C. Analysis of frying oil was carried out every 2.5 hr (5 hr/4 days; total 20 hr). Physical and chemical properties; color index, refractive index, viscosity, free fatty acids, peroxide value, para-anisidin value, totox value, oxidative stability (Rancimat method) and total polar materials. Also, the absorbencies of the frying oil samples, measured at 430, 470, 480, 490 and 500 nm were used to evaluate the frying oil. It was found that cottonseed oil used for frying of potato strips (coated with mixture of carboxy methyl cellulose 1% and guar gum 0.5%) exhibited good stability as well as good physical and chemical properties in comparison with control samples.

**Key words:** cottonseed oil, frying, oxidative stability, coating, hydrocolloids, total polar materials.

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#### Introduction

Deep frying is a very popular practice in the food industry due to its convenience and enhancement of fried food flavor. Frying oil, used continuously or repeatedly at high temperatures, is subject to a series of degradation reactions and the formation of decomposition compounds. These decomposition compounds have a negative effect on flavor and nutritional value of the fried foods. Much concern is taken into consideration during deep fat frying, it includes keeping the good quality of fried food by prior treating the food with different treatments; and to prevent the increase in the formation of oxidation products to keep the frying oil in good condition so that the oil meets with the standard safety levels (Xu, 1999).

The quality of fried foods depends not only on the type of foods and frying conditions, but also on the oil used for frying. Thus, the selection of stable frying oils of good quality is of great importance to maintain a low deterioration during frying and consequently a high quality of the fried foods (Stevenson *et al.*, 1984). The oil must be able to withstand high temperatures and have high enough stability to be reusable. Furthermore, the oil needs to maintain a high oxidative stability during the shelf life of the product. Different types of oils can be used for frying. The chemical composition of frying oil and its physical properties has an influence both on the frying process and on the stability characteristic of oil against oxidation and decomposition. Therefore, the importance of the correct selection of the oil for frying is one of the most considerable issues (Rossi *et al.*, 2007).

Cottonseed oil could be a superior choice to meet the above requirements. One reason is that cottonseed oil enhances the flavor of foods cooked in it. It is well established that cottonseed oil produces the most flavorful potato chips on the market. Another reason is that it is not necessary to hydrogenate cottonseed oil to increase its stability. Components of the food (proteins, sugars, food lipids and moisture) being fried also contribute to the heterogeneity of the degradation products found in used frying oils (Melton *et al.*, 1994).

During the frying process via a series of complex physical and chemical reactions, oils are subjected to thermal oxidation, polymerization, and hydrolysis. These reactions lead to a decrease in tocopherols and total phenols (TP), an increase in the peroxide value (PV) and formation of decomposition products with high molecular weights such as polar compounds and polymeric triacylglycerols. Formation of polar compounds is strongly related with the primary and secondary oxidation that takes place during frying. An established quality index for frying oils indicates ~ 24 % polar compounds as a limit for rejection or replenishment of the cooking oil due to negative effects on the quality of frying oil and the flavor and nutritional value of the fried food. Some of these compounds may also be harmful to human health (Karakaya and Simsek 2011).

During frying the oil rapidly changes from a light yellow to an orange brown color. This is the combined result of oxidation, polymerization and other chemical changes which also result in an increase in viscosity of the frying oil (Medeni, 2003).

Coating of French fried potato strips can protect the frying oil from deterioration and in the same time keep the quality of the fried product (García, 2004 & Pedreschi and Zuniga 2009). Frying medium selection is more important in verifying the success of the frying process. Cottonseed oil is distinguished by having low polyunsaturated fatty acid content particularly linolenic acid level of 2% which is recommended (Daniel *et al.*, 2005).

In a previous work the optimum condition of frying coated potato strips was achieved (Ali *et al.*, 2012), it was advisable in present work to follow the alternation occurring in cottonseed oil during frying. The study of physical and chemical changes in the oil include total polar materials, oxidative stability, free fatty acid, peroxide value, para-anisidin, fatty acid composition. Moreover, colour index, refractive index and viscosity, shear stress as well as calculated tottox value and cox value. The alterations were studied at frying 180 °C for 20 hr.

## Material and Methods

### Materials:

Commercial potatoes was purchased from local market (The initial moisture content of potatoes was in the range of 75–82% in wet basis). Cottonseed oil free from synthetic antioxidants was supplied by Sila Oil Company (Fayoum Egypt).

Carboxy Methyl Cellulose (CMC) and Guar Gum (GG) were purchased from Loba Chemie.

### Methods

#### Preparation of potato strips:

Potato tubers were washed, hand-peeled and cut with a manual operated potato-cutting device into an 8 x 8 x 60 mm strips, then rinsed in tap water.

Potato strips were divided into two portions for each treatment. The first portion was not-blanching, while the second portion was blanching in 0.5% aqueous solution of calcium chloride at 85°C for 5 min.

Blanched potato strips were immersed in a mixture of aqueous solution of 1% carboxy methyl cellulose (CMC) and 0.5% guar gum (GG) hydrocolloids at room temperature for two minutes.

Blanched and hydrocolloids immersed potato strips were heated in microwave oven (Gold Star, 220-50 Hz power level and 980 W), which operated at 50% of the original power level for 4 min (Ali *et al.*, 2012).

Cottonseed oil (2.0 L) was placed in a 2-L capacity bench-top deep-fat fryer (Philips Comfort, Germany) and heated to 180 °C. Potato strips were fried in 20-g batches at constant frying temperature. The batches were fried for 30-min intervals for 2.5 h subsequently heating of the frying medium for 2.5 hr/day for 4 consecutive days without replenishing. The total time of frying and heating was 5 hr/day. At the end of each step 25 g of the oil was filtered into a screw-cap vial and stored in the dark at 4 °C until analyzed (Tyagi and Vasishtha 1996).

### Analytical methods:

Usually, more than two methods are required when using chemical analysis, for frying fat deterioration, because no single group of compounds has been identified as a key indicator of oxidative degradation of frying fats. During frying, the oil samples were analyzed for the following parameters: color index (CI), measured with a spectrophotometer Shimadzu Model UV 240 (Shimadzu, Japan) from 400 to 550 nm (Mordret *et al.*, 1985) and Refractive index was determined according to the method AOCS 1998, using Abbe refractometer (NYRL-3-Leica Mark, Leica Inc. Bauffalo, NY, USA).

Primary oxidation was measured by peroxide value method (PV) (AOCS 1998). Secondary products were measured by para-anisidine value (p-AV) according to Official and Tentative methods of the AOCS (1998). The total oxidation was calculated as follows:

$$\text{total oxidation} = 2\text{PV} + \text{p-AV}.$$

Total polar materials levels (TPM) were determined by column chromatography according to the AOCS official method 1998.

The susceptibility of all oil samples to oxidation was studied by using the Rancimat apparatus. The test was performed on an automated Metrohm Rancimat model 679 at 110±0.1°C and an air flow of 20 L/hr to determine the induction period (IP) of the oils (Aparicio *et al.*, 1999).

Determination of Fatty acids patterns of CSO before and after 20 h frying and heating was determined by GLC, the oil was converted into methyl esters via transesterification with 5 % hydrogen chloride gas in methanol (Chrisite, 1973) and transesterification reaction was monitored with the help of TLC. Fatty acids

methyl esters were analyzed using gas liquid chromatography on a Hewlett Packard Model 6890 chromatograph equipped under the same conditions in our previous work (Abdel-Razek *et al.*, 2011)

Calculated oxidizability (Cox) value: The Cox value of the oil samples was calculated by the percentage of unsaturated C18 fatty acids, applying the formula proposed by Fatemi and Hammond (1980): Cox value =  $(1 [18:1\%] + 10.3 [18:2\%] + 21.6 [18:3]) / 100$ .

Absorbance test procedure: In order to follow the changes that took place in the oil as the number of frying increased; its absorbance spectrum was measured with a spectrophotometer Shimadzu Model UV 240 (Shimadzu, Japan). The absorbance of the oil was measured at room temp after each frying. The wavelengths used were 430, 470, 480, 490 and 500 nm (Karakaya and Simsek 2011).

## Results and Discussion

During frying, various chemical processes such as oxidation, hydrolysis, polymerization and fission take place. These processes lead to the production of numerous decomposition products. Typical routes of deterioration of frying fats and oils and a list of methods for evaluation of oil deterioration have been described by (Fritsch 1981). Peroxides, which are the primary products of oxidation are extremely unstable under frying conditions and decompose to give secondary oxidation products. Peroxide values of CSO used for frying coated and uncoated potatoes strips in comparison with the control sample (zero time) are recorded in Table 1. It could be observed that there is no marked differences in PV between CSO used for frying coated and uncoated potatoes strips. Accordingly, PV was not proved to be a useful test for frying oils (Jackson, 1981).

P-Anisidine value (p-AV) is the measure of secondary oxidation products and can be used to follow the changes in frying CSO. The results (Table 1) show that p-AV increased more rapidly in CSO used for frying uncoated potatoes strips than CSO used for frying coated ones.

Totox value was calculated for CSO used for frying uncoated and coated potato strips at 180 °C for 20 hr (Table 1). It could be seen that the values for CSO used for frying of uncoated potatoes were higher than those for CSO used for frying coated potatoes.

Free fatty acid (FFA) content is considered as an appropriate measure for the decomposition of frying oil. The development of FFA arises partly from hydrolysis but FFA is also an end product of oxidation. Recommended upper limit of FFA is between 1% and 2% (calculated as oleic acid). The results of FFA determination during frying (Table 1) show that there was no significant difference between CSO used for frying uncoated and coated potato strips and it was below the limit value. Furthermore, because the determination of FFA by titration does not distinguish between FFA formed from hydrolysis, and FFA formed by oxidation, the increase in FFA may be a poor indicator of frying fat deterioration (Fritsch, 1981).

Fatty acid compositions of CSO at zero time, and CSO used in frying of uncoated and coated potato strips at 180°C (20 hr) are presented in Table (2). The main fatty acids in the CSO were oleic, linoleic and palmitic acids. The lowest saturated fatty acid content (SFA) was observed in CSO used for frying coated potato strips (31.1%). The lowest monounsaturated (MUFA) and polyunsaturated fatty acids (PUFA) were observed in oil used for frying uncoated potato strips (18.0% and 44.0%). From the results in Table 2, the PUFA/SFA ratio and Cox value were greater for the zero time, followed by CSO used for frying coated potato strips and CSO used for frying uncoated potato strips. It was noted that there was a little decrease in the content of C18:3 for coated CSO than in zero time. This decrease in unsaturation content could be attributed to the destruction of the double bonds by oxidation, scission, and polymerization (Tyagi and Vasishtha 1996). It is known that, the amounts and types of the fatty acids present in oil contribute to its functional properties. Table 2 shows decrease in C18:1 and C18:2 content of CSO used in frying uncoated potato strips which means more deterioration of the oil. It was also observed that C18:3 disappeared from CSO used for frying uncoated potato strips, whereas it slightly decreased in CSO used for frying coated potato strips.

Oxidative stability is an important property of edible oils in food science. It is represented by the time in which an oil sample resists oxidation and it can be used to indicate when the oil reaches an oxidation level inadequate for human consumption or even for its utilization in frying processes. This time, called induction period (IP), has been determined by heating the sample to a constant temperature (Gonzaga *et al.*, 2007). The Rancimat assay enables continuous monitoring of the oxidation process. The susceptibility of CSO used for frying uncoated and coated potato strips for oxidation, was determined by measuring the IP by the Rancimat assay. From Table 1 it can be seen that the IP of fresh CSO sample (zero time) was 22.03 hr which decreased by increasing time of frying and heating process to reach 0.13 hr and 0.14 hr for frying uncoated and coated potato strips respectively for 20 hr.

No marked differences in refractive index (RI) of CSO used for frying potato strips (coated and uncoated, or with no potato strips) for 20 hr at 180 °C (Table 1). RI of CSO ranged from 1.4680 to 1.4688 and from 1.4670 to 1.4682 in case of frying uncoated and coated potato strips respectively.

The Changes in color index (CI) of CSO used for frying coated and uncoated potato strips is illustrated in Table 1. The results showed that the CI of CSO oil used for frying was 59.07 at the beginning of frying (zero

time) increased to its maximum value of 150.63 and 94.02 in case of frying uncoated and coated potato strips, respectively, as frying time increased. The increase in CI means darker color of the oil and this may be caused by the starched components in potatoes. The darkness of the frying oil may be also due to Maillard reaction from the interactions of the ingredients and food nutrients, such as sugar and amino acids or may be the result of oxidative reaction (Medeni, 2003).

**Table 1:** Physical and chemical properties of cottonseed oil during frying of uncoated and coated potato strips at 180 °C for 20 hr.

Time (hr)	Treatment	Refractive Index	Color Index	Share Stress	Acidity	Peroxide Value	P-An Value	Totox Value	Oxidative Stability
0.0	CSO	1.4670	59.07	20.6	0.17	2.20	8.60	13.00	22.03
2.5	Uncoated	1.4680	58.13	22.3	0.12	1.92	44.33	47.53	1.10
	Coated	1.4670	58.44	23.6	0.20	1.80	44.31	47.91	1.16
5.0	Uncoated	1.4680	57.94	23.2	0.15	1.75	78.17	81.67	0.77
	Coated	1.4671	52.82	24.6	0.22	1.50	76.66	79.66	1.01
7.5	Uncoated	1.4680	73.74	25.4	0.21	1.80	94.95	98.59	0.57
	Coated	1.4673	56.8	26.2	0.23	1.50	80.38	83.38	0.60
10.0	Uncoated	1.4680	87.98	27.4	0.23	1.82	111.26	114.90	0.46
	Coated	1.4675	58.76	27.2	0.25	1.40	104.72	107.52	0.49
12.5	Uncoated	1.4680	95.64	29.9	0.25	1.92	115.16	119.00	0.40
	Coated	1.4679	65.14	28.4	0.25	1.30	114.02	116.62	0.43
15.0	Uncoated	1.4683	118.94	32.6	0.25	2.00	124.75	128.75	0.37
	Coated	1.4680	77.3	31.3	0.27	1.70	119.48	124.08	0.24
17.5	Uncoated	1.4685	146.49	37.1	0.30	2.16	129.04	133.36	0.17
	Coated	1.4680	81.4	32	0.27	2.30	128.64	132.04	0.13
20.0	Uncoated	1.4688	150.63	39.3	0.30	2.42	135.23	140.07	0.13
	Coated	1.4682	94.62	34.8	0.31	2.30	129.79	134.39	0.14

**Table 2:** Fatty acid composition of cottonseed oil at zero time and after 20 hr frying of coated and uncoated potato strips.

Treatment	Fatty acid composition													
	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	SFA	MUFA	PUFA	PUFA/SFA	Cox value
Zero-time (control)	0.1	25	0.8	3.3	19.2	50.4	0.4	0.4	0.4	28.8	20.4	50.8	1.76	5.46
After 20 hr frying of: Uncoated potato strips	0.4	32	-	5.6	18	44	-	-	-	38	18	44	1.16	4.71
Coated potato strips	0.3	27.4	-	3.4	20	48.7	0.2	-	-	31.1	20	48.9	1.57	5.25

The absorbance values of each oil sample measured at 430, 470, 480, 490 and 500 nm, increased markedly during frying (Figure 1 a & b) and were all correlated with frying time. The increase in absorbance indicate the changes that took place in the intensity of the color of CSO specially used for frying uncoated potato strips more than CSO resulted from frying of coated samples (Figure 1). As frying time increased there was a darkening of the oil, owing mainly to particles of food that caramelized and released soluble compounds into the oil (Vijayan *et al.*, 1996).

Measurement of total polar materials (TPM) is useful in estimating heat abuse in frying oils. Evaluating total polar materials has been characterized as one of the best indicators of heated oil quality (Blumenthal 1991). TPM includes all non triacylglycerols such as free fatty acids, mono- and diacylglycerols, glycerol, and polymers (Tan and Man 1999). Formation of polar materials, which indicates oil deterioration, is strongly related with the primary and secondary oxidation that takes place during frying. When the amounts of total polar material (TPM) reach 24% levels, oil is considered to be thermally degraded and should be replaced with fresh oil. TPM formed during deep fat frying processes are given in Figure 2. The amount of TPM in CSO increased with the time reaching 23.9 after 15 hr in case of uncoated, whereas in case of coated the TPM reached 24 at 17.5 hr. From the results in Table 1 and Figure 1 it was observed that a strong correlation between spectrophotometric absorbance readings and TPM (Xu, 2000 and Hamed *et al.*, 2011).

In deep fat-frying operations, the viscosity of the oil changes considerably with increasing time and temperature. Viscosity of an oil is strongly affected by its degradation products, increasing as a result of formation of dimmers, trimers, polymers, epoxides, alcohols and hydrocarbons (Stevenson *et al.*, 1984). Figure 3 shows the viscosity of CSO used for frying potato strips (uncoated and coated) for 20 hr at 180 °C. The results indicated that the viscosity of CSO used for frying uncoated potato strips was higher and increased more rapidly by increasing number of frying treatments. This has been attributed to polymerization and the concomitant formation of high-molecular-weight compounds via carbon-to-carbon and/ or carbon-to-oxygen-to-carbon bridges between fatty acids (Lin *et al.*, 1998; Jacobson 1991; Blumenthal 1991). The tendency of viscosity to increase during frying of the oil has been found to correlate well with formation of polymers (Gloria and Aguilera 1998). Shear stress was increased with frying time but the values were higher in case of frying uncoated potato strips.

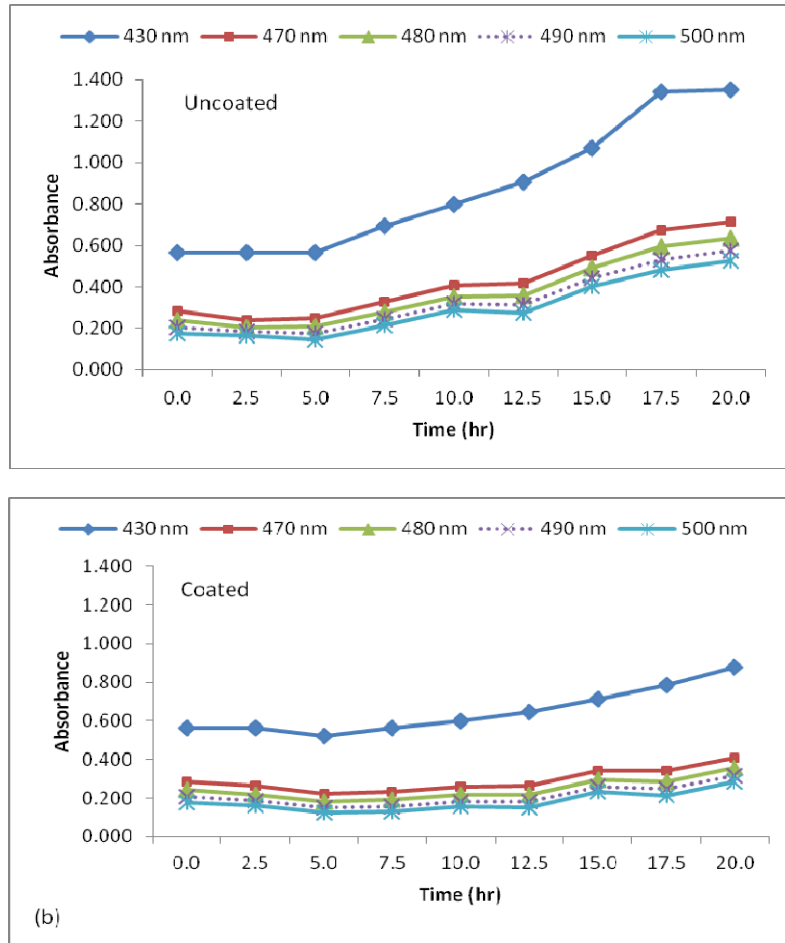


Fig. 1: Changes in absorbencies during frying of uncoated (a) and coated (b) potato strips.

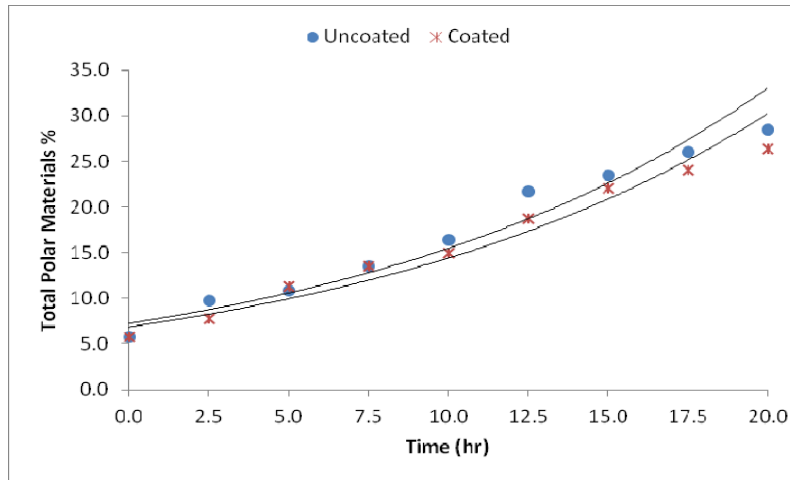
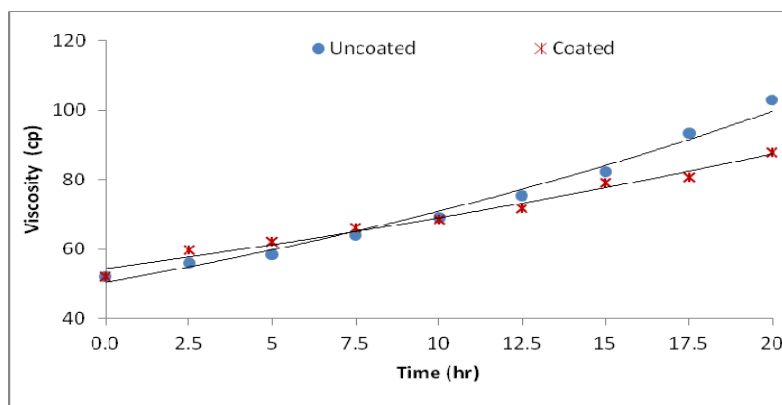


Fig. 2: Comparison of total polar materials, between CSO used in frying of coated and uncoated French fried potato strips.



**Fig. 3:** Comparison of viscosity, between CSO used for frying of coated and uncoated French fried potato strips.

#### Conclusions:

The correlation between the oxidative stability of the frying medium and other control parameters of fats (viscosity, shear stress, color index, totox value, TPM and absorption at wave lengths 430, 470, 480, 490 and 500 nm) during frying and heat treatment at 180 °C was affirmed. Coating of potato strips can protect the frying oil from deterioration to a certain extent and in the same time keep the quality of the fried product. Therefore, the oil did not exceed the risk levels of undesirable compounds. Thus, by virtue of using pretreatment of potato strips, oil uptake during frying was avoided and oil consumption is fairly economic without any replenishing.

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