Effects of Combining Antioxidants on the Oxidative Stability of Refined, Bleached and Deodorized Palm Olein during Continuous Deep Frying of Potato Chips

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Authors’ contributions

This work was carried out in collaboration among all authors. Author MAM designed the study, managed the literature searches, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors HAH, RSF and AAN managed the supervision and the analyses of the study. All authors read and approved the final manuscript.

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ABSTRACT

In this study, the effect of a novel antioxidants composite system based on a synergetic composite between Tertiary butyl hydroquinone (TBHQ), Ascorbyl palmitate, citric acid, and Dimethicone have been evaluated against the classical common antioxidant system based on TBHQ at the highest permitted dose of 200 ppm during successive deep-frying cycles. Also, the shelf life of fried food and its sensory performance and oil absorption content of fried food were comparatively studied. The novel antioxidant composite system is a synergetic blend of an artificial antioxidant, TBHQ and
vitamin C palmitate (Ascorbyl palmitate) as natural identical antioxidants, an effective sequestrant which is Citric acid and poly dimethyl siloxane as an anti-foaming system to obtain the highest oxidative stability impact during deep frying. The frying processes were carried at 180 °C for sliced potato chips for 8 successive frying cycles. Sensory evaluation of the fried potato has been conducted under accelerated storage conditions to determine the effect of the oil oxidative stability on the shelf life of fried food. The oxidative degradation of the oil was evaluated by measuring different oxidation and degradation parameters for their respective peroxide value (PV), free fatty acid (FFA %), the content of conjugated dienes, P-anisidine value, (p-A.V), induction period (IP), and Lovibond color. The (%) of oil absorption in the potato chips was also measured. The sensory evaluation has been done for fried foods to evaluate the crunchiness and likability of obtained french fries. Results revealed that the jump in primary & secondary oxidation parameters as PV and p-A.V of palm olein after 8 successive frying cycles was very limited for the antioxidant composite system I by only 1.842 ± 0.1 meq O2/kg in PV and by 6.2315 ± 0.45 for p-A.V. Same for FFA, the jump was limited for the antioxidant composite system I for only 0.084+/-.0.005 as well. However, the final PV, FFA after the 8 frying cycles are still within the Codex and local Egyptian regulation limits the edible oil human usage. Same for other quality parameters like color jump was limited to 3.4 Red jumps on Lovi bond scale for composite I. Study proofed that palm olein fortified with 650 ppm of the antioxidant composite (I) consists of TBHQ, Ascorbyl palmitate, citric acid, and polydimethylsiloxane at the specified synergistic ratios gives outstanding stability to refined Palm olein during the successive deep frying up to 8 successive frying cycles. It also achieved less oil absorption for french fries by about 3.5% less than the same oil fortified with 200 ppm TBHQ, which is the highest permitted dose of this strong antioxidant. (P≤0.05). Furthermore, sensory evaluation of the fried potatoes has been improved with the novel antioxidant system compared to the classical TBHQ system.

**Keywords:** Deep frying-antioxidant-sensory attributes-Oxidative stability; color index - paraanisidine antifoam.

### 1. INTRODUCTION

Quality, sensory performance, and shelf-life stability are the main criterion for developing, producing, and marketing any food products. There is high consumer demand for products that maintain a fresh appearance and good sensory attributes for the food as long as the product is valid on the shelf. Furthermore, increasing the shelf life of the product may hamper food manufacturing costs for producers and accordingly food prices for the end consumer. Fried food products are highly susceptible to losing freshness during shelf life. This is attributed to the high oil content which makes it more susceptible to lipid oxidation.

Different authors studied the impact of frequent frying cycles on the quality and healthy characteristics of multiple used oils showed. Studies results showed the level of degradation in the physicochemical and antioxidant properties of the vegetable cooking oil after repetitive use of frying [1]. Other studies were done of the repeated re-use of the different vegetable oils types for consecutive deep frying of potato chips showed that hard oils (like palm olein and palm oil) should be preferred to soft oils (like Sunflower, Canola, soybean oil) for deep frying of Irish potato chips [2].

The effect of the type of food used in multiple frying processes like Meat, fries, and fishes has been studied using three different types of frying oil brands in some African countries which oil compositions are Peanut 1 & Peanut 2 and Sunflower. The studies showed a remarkable increase after frying off the chemical properties reflecting the deterioration and oxidation stability parameters of oils including, acid value, peroxide value, and total polar components, and reached a level depending on the product to be fried and type of oil used [3].

The quality and oxidative stability of the frying medium can alter the acceptance of the fried product [4-6]. The lipid deterioration of frying oils is highly dependent on the chemical composition of the oil. Vegetable oils that are of high content of poly-unsaturation, are more subjected to oxidative deterioration, compared to that of a high content of oleic and saturated fatty acids, such as palm olein. The oxidative deterioration of frying oils, that are absorbed by food, can alter the functionality, the sensory nutritive value of fried food. It can even alter the safety of food...
[4,7-11]. The oxidative products resulting from lipid oxidation, especially reactive oxygen species are associated with cell damage, resulting in severe complications including cardiovascular diseases and cancer. In several cross-sectional studies, fried foods have been correlated to various cardiovascular risk factors [9]. Furthermore, the sensory attributed is one of the important quality factors of fried food that are highly sensitive to the quality and suitability of the frying oil. The degradation products formed in the frying oil interfere with the taste and flavor of fried food resulting in off-flavor. Consequently, these changes reduce consumer acceptance of the final product. In this regard, a wide range of antioxidants, either synthetic or natural, are added to fats, oils, and foods containing fats to inhibit the development of off-flavor arising from the oxidation of unsaturated fatty acids [5,12-17,8].

The effects of antioxidants on the changes in quality characteristics of refined, bleached, and deodorized (RBD) palm olein during deep-fat frying (at 180°C) of potato chips for 3.5 h/d for seven consecutive days in five antioxidant systems have been studied [18].

In this study, a novel antioxidant composite has been evaluated during deep frying of fresh potato chips. The composite is a synergistic blend of synthetic and vitamin-based antioxidants, with effective chelators, with the optimum ratios, to obtain the highest oxidative stability during frying. Refined, bleached, and deodorized (RBD) palm olein was used in this study because of its major commercial role in deep-fat frying. The primary objective of this study was to assess the frying performance of RBD palm olein treated with the prepared composite in comparison with the most commonly used antioxidant, TBHQ. A secondary objective was to study the oxidative stability and organoleptic quality of the fried potato chips produced in these systems under accelerated storage conditions for 30 days. The study intended to determine the effect of oil oxidative stability on the shelf life of fried food reflected through its organoleptic quality.

2. MATERIALS AND METHODS

2.1 Oil Medium

Fresh Refined, bleached, deodorized (RBD) palm olein (IV56) (Wilmar International Ltd.)

2.2 Antioxidants

Tertiary butyl hydroquinone (TBHQ) (DuPont), Ascorbyl palmitate (DuPont).

2.3 Sequestrant

Citric acid (DuPont)

2.4 Antifoam

Polydimethylsiloxane (Dimethicone / E900) (Wacker Silicones).

All chemicals and solvents used were of analytical grade. Fresh potatoes were peeled and sliced using a mechanical slicer. They were kept submerged in water at room temperature. They were then slightly dried out with tissue paper before weighing into a 600 g batch for frying.

2.5 Sample Preparation

Composite antioxidant was prepared by dissolving citric acid (50 ppm), Ascorbyl palmitate (50 ppm), TBHQ (200 ppm), Dimethicone/E900 (7 ppm) in mono propylene glycol. The composite was allowed to stir for 20 min until obtaining a homogenous mixture. Frying experiments were carried out in two systems that contained: RBD palm olein with novel antioxidant (System I); and RBD palm olein with TBHQ (System II). The temperature of RBD palm olein was brought up to 60°C, then 200 ppm of TBHQ and 650 ppm of the novel antioxidant composite was added to each system, respectively. The oil was stirred for 10 min to ensure the dissolution of antioxidant systems.

2.6 Deep Fat Frying (DFF) Experiments

Frying experiments were conducted in two replicates on each system. Samples were subjected to deep-frying under the same conditions. A deep fat fryer with a capacity of 18 liters was used in the experiment. The fryer was filled with frying oil and the temperature was set at 180°C throughout the trial. Oil samples were not replenished at any time during the experiment to achieve the maximum deterioration possible. Each oil sample was used for the DFF of 8 successive batches of potato chips (600 grams each). At the end of the frying, the fryer was switched off and the temperature was allowed to drop to 60°C. Oil samples for
analysis were collected in amber bottles at 60°C for further analysis. Analysis of oil was carried out immediately after the frying experiment and completed within 4 weeks. All Chips samples were kept for sensory assessment.

2.7 Analysis of Oil

The official AOCS methods were employed for determinations of free fatty acid (FFA %), and Peroxide value (PV), Anisidine value (AV), and a conjugated diene (%) [15]. The AV and conjugated dienes were measured using UV/Vis spectrophotometer Cary 60 UV-Vis, Agilent Technology, Canada at 350 and 233 nm, respectively. Oil color was measured in a 5.25 inch. a cell in a Lovibond® Tintometer PFX8800, UK. The accelerated Oxidative Stability of Oils (OSI) was performed by determining the induction period (IP) of oil samples using a Metrohm Rancimat Model 679 (Metrohm Herisau, Switzerland). The experiment was carried out at 120°C.

2.8 Oil and Moisture Content in Fried Potato Chips

The fat and moisture (%) in potato chips was determined using a Near-Infrared Transmission (NIT) analyzer (Infra-Lab, NDC, UK). Samples were first ground for 60 seconds in a domestic food grinder to obtain small particles. The samples were then loaded into an elongated sample cell of 18 mm path length, packed, and measured in the instrument. Samples were measured in duplicates.

2.9 Sensory Analyses of Fried Potato Chips

The sensory analysis was used to assess the organoleptic quality of the chips. The Fried potato chips were packed in laminated polythene bags and stored at (40°C) for storage analysis. Samples were assigned codes to eliminate bias. During storage analysis, bags were sampled at 1-week intervals for 4 weeks. Thirty panelists from the laboratory staff were selected to evaluate the sensory attributes of stored samples based on a five-point hedonic scale. Panelists were required to evaluate the overall acceptability of each sample using a numerical scale of 1 to 5 (1= not acceptable, 5 = extremely good). The panelist was also asked to state which sample they preferred the most if they could distinguish any difference (overall preference). This overall preference meant that they had to take into account any flavor of rancidity and undesirable taste [13,19,20,21].

2.10 Statistical Analysis

All data are presented as the mean +/- standard deviation (SD). Statistical analysis of all data was performed using 1-way ANOVA (StatView) whereas p values < 0.05 were considered statistically significant.

3. RESULTS AND DISCUSSION

3.1 Changes in Primary Oxidation Products

Evaluating the oxidative stability of frying oils includes measuring the primary and secondary breakdown products [15]. FFA content is a measure of the acidic components in the oil, which contributes to the development of off-flavors and off-odors in the fried product [15,22]. At the end of the frying period, FFA contents were 0.0842% and 0.1155 for System I (composite containing oil), and System II (TBHQ containing system), respectively. (both results are within the Codex regulatory limit for usage of oil in human consumption applications ). The composite system showed better FFA%, however, the difference was not significant (P>0.05). On the other hand, there was a significant improvement (P<0.05) between both systems in terms of peroxide value (see Table 1).

Final PV results after multiple frying cycles were 2.24 meq O2/ kg for antioxidant composite I and were 5.298 meq O2/ kg for composite II (both results are within the Codex regulatory limit for usage of oil in human consumption applications).

3.2 Changes in Secondary Oxidation Products

The PV test is a good measurement for oxidative deterioration in frying oils. However, very rancid oils can have a reduced PV value, while having high values of anisidine (AV). Consequently, the anisidine value (AV) and totox value are used to show the overall oxidation state [15,23]. As it is shown in Table 1, there is a significant improvement in AV values obtained in the case of the composite system, compared to the TBHQ system. This indicates that the composite has a positive impact on both primary and secondary oxidative products. This was reflected in terms of the total Totox number, calculated as AV +2PV.
3.3 Changes in Color and Rancimat Test

The color of frying oil darkens during frying, as a result of oxidation and formation of browning pigments from the potato chips [25]. At the end of the frying period, the red (R) and yellow (Y) color units were measured for TBHQ and composite Systems. The results showed that the color difference was not significant (P>0.05). Augustin et al. stated that the darkening of palm olein could not be exclusively linked to the oxidative deterioration of the oil. Therefore, it is not accurate to evaluate frying oil quality by only monitoring the changes in color during frying [24].

A commonly used method for evaluating the oxidative stability of the oil is the measurement of the induction period (IP). IP reflects the time during which the oil can resist oxidation, due to the presence of naturally occurring antioxidants or added antioxidants. The IP was measured using rancimat test [5,15,23,26]. As it is clear in the table, System I, containing the synergetic composite, showed a significantly better induction period, reflecting the extended oxidative stability and shelf life of the composite containing frying oil.

3.4 Oil and Moisture Content in Fried Potato Chips

Frying oil tends to be absorbed into the food during the frying process. Oil absorption in fried food may be as high as 40-50% of the food weight, making them calorie-dense and may contribute to obesity [9,27]. Oil content is a very important parameter in potato chips. An option of making traditional potato chips healthier is by reducing the oil content in the chips. Several types of research have been dealing with reducing oil absorption in frying food using certain additives [28,29]. A Japanese patent showed a method to reduce oil absorption in fried food by mixing at least one kind of oil with chemically-modified starch [26]. The fried food portion produced by this method showed to have lower oil content and acceptable taste, texture, and appearance. In another study, Methylcellulose (MC) and hydroxypropylmethylcellulose (HPMC) were used for coating chips and dough discs to reduce oil uptake in deep-fat frying [30,31]. However, few types of research have related the use of antioxidants to limit the oil absorption in fried food. In a US patent, an additive comprising a bio phenol-based extract was incorporated into a frying oil composition for reducing oil adsorption into food fried. The bio-additive developed was formulated from various parts of the Rutaceae plant family. It proved to function as a natural fat antioxidant, oil absorption inhibitor with other health-promoting properties making the fried food less hazardous to health [30].

The oil and moisture (%) are represented in Table 2. Potato chips fried with the composite system (System I) has significantly lower fat (p<0.05) content compared to that fried with the TBHQ system (System II). This is considered an added value from both a consumer and market perspective. Lower oil content is desirable for nutritional reasons. Furthermore, it is favorable for the growing market trend toward healthier food snacks.

3.5 Sensory Evaluation of Fried Potato Chips

Sensory evaluation was employed to assess the effect of an antioxidant on the organoleptic quality of fried potato chips. Although somewhat subjective, sensory evaluation remains the ultimate measure of rancidity, as no combination of chemical or physical tests is currently capable of assessing the composite sensory attributes of food [17,10,8]. The sensory perception of the sensory panel members, in terms of overall acceptability and overall preference (%), to word the potato chips during accelerated storage is represented in Table 3.

The results showed that potato chips of the composite system have significantly (p<0.05) higher overall acceptability, compared to that of
the TBHQ system during the storage period. Also, it was clear that acceptability to the fried chips decreased regularly with increasing time of storage for both systems (Table 3). When panelists were asked to discriminate between the two systems for overall preference, they showed a preference for potato chips fried with system 1 (composite system). This was very pronounced from week 1 after storage and continued until the last day of storage (Table 3). When sensory analysis data were compared with chemical measurements of oxidation, it was clear that the results of sensory preference for potato chips over time agreed with changes in PV, AV, and rancimat test values for the oil systems. In other words, the panel did detect the presence of rancid notes. Consequently, it can be concluded that the flavor likability of fried food is affected by the performance and oxidative stability of frying oil. The presence of rancidity notes and correlation between oxidation parameters values and sensory panel data have been observed in other studies Kalra et al. concluded that the frying medium plays an important role in the shelf life of a fried product. In another study done by Jaswir et al. it was proved that lowering the rate of oxidation of oil during deep-fat frying, by adding a natural antioxidant, contributed to measured sensory acceptability of fried potato chips [19].

3.6 Comparing the Current Results to Previous and Recent Studies

1-By comparing the current results with the novel antioxidant system applied to the results of the study done by - Emelike et al. [1] that were conducted to investigate and monitor the physicochemical, degradation, and antioxidant

| Table 1. Physio-chemical characteristics of frying oils during DFF |
|---|---|---|---|---|---|
| **Initial value** | **Final value** | **Difference** |
| | | |
| FFA(%) | CDs(%) | FFA | CDs | FFA(%) | CDs(%) |
| System I | 0.04± 0.0 | 0.124± 0.093 | 0.18565 | 0.084 | 0.18565 |
| System II | 0.038±0.0 | 0.153±0.052 | 0.1945 | 0.115 | 0.1945 |
| Color (Red) | | Color (Red) | | Color(Red) | |
| IP(h) | 2.9±0.0 | 9.50±1.5 | 6.4± 0.1 | 18.49±0.5 | 3.4 | 8.99 |
| System I | 3±0.1 | 10.25±1 | 6.5±0.2 | 14.39±1.1 | 3.6 | 4.24 |

| Table 2. Oil absorption and moisture % of fried potato chips |
|---|---|---|
| **Moisture %** | **Oil absorption %** |
| System I | 1.355±0.08 | 35.91±0.15* |
| System II | 1.31±0.15 | 37.15±0.01* |

*Refers to significantly (P < 0.05) different between the mean values

| Table 3. Sensory scores for over all acceptance of fried potato chips stored under accelerated storage conditions |
|---|---|---|
| **Over all acceptability (1 to 5)** | **Over all preference (% of panelists)** |
| System I | System II | System I | System II |
| Week 1 | 4 b | 2.9 b | 71.8 | 20.5 |
| week 2 | 3.19 b | 2.5 b | 78.6 | 18.4 |
| week 3 | 2.8 b | 1.3 b | 83.3 | 16.6 |
| week 4 | 2.1 b | 1.1 b | 93.4 | 6.6 |

a 1=not acceptable, 5=extremely good. b Mean of single determination of 30 observations. Means within each column with the different subscripts are significantly (P < 0.05) different. b Numbers represent the percentage of panelists who expressed their preference for particular sample
properties of frying oils used by local fried food vendors in Nigeria that shows a quality deterioration of most of the multiple used frying oil oxidation parameters that exceed the Codex regulation limit like the free fatty acid, Saponification value, smoke point, However, the peroxide values and the moisture content were within the Codex limit after three weeks of collection. Also, there was a decrease in iodine values of the frying oils except for most of the oil samples. Also, the collected samples after multiple frying showed a decrease in total phenolic content except for one sample.

2-Same finding was observed with comparing current novel antioxidant system results with the results obtained by Omara et al. [2] who used Palm olein (same as a current study) as an example for hard oil and Sunflower oil as an example for soft oil His results showed that the free fatty acid jump for hard oil (palm olein) after 7 frying cycles in same oil to exceed the codex limit and after 6 times for soft oil (sunflower oil). The same happened for another primary oxidation parameter (PV) and secondary oxidation parameters (p-A.V). However, this deterioration and degradation of oil happened though these are brands of oil collected from the Kenyan market and all contain TBHQ and citric acid as a standard antioxidant system for all selected oil brands. However, the study did not refer to its quantization in each brand.

3-Non of the above studies addressed the two main quality performance and healthy criteria for any oil designed for deep frying/cooking applications which are the sensory performance of the fried foods as well as the oil absorption extent which impact the desired targeted crunchiness for any fried foods, while current study addressed these two main criteria.

4. CONCLUSION

The results of this study have shown that the addition of the novel composite antioxidants to RBD palm olein improves its oxidative stability and reduces the oil absorption qty in fried potato chips when used as a deep-fat frying oil. This can be attributed to the synergetic effect of the components of the composite that reduced the oxidative deterioration of oil during deep frying. The accelerated storage study of fried potato chips carried out at 40°C showed the synergetic composite had a positive impact on the organoleptic properties of fried chips. Thus, it can be concluded that the proposed composite can enhance oxidative stability for the commercial application of frying oils. Besides, it reduces the oil absorption for french fries by about 3.5 and increases the crunchiness and the sensory performance of the fried potatoes to the classical TBHQ system at the highest permitted dose of 200 ppm.

DATA AVAILABILITY

The numerical data used to support the findings of this study are available from the corresponding author upon request.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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