

✦ Efficacy of the Antioxidants BHA and BHT in Palm Olein During Heating and Frying

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ABSTRACT

The effectiveness of butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) in retarding the deterioration of RBD palm olein during static heating (180 C) and frying operations was assessed by determining the peroxide, anisidine, acid and iodine values; absorbances at 232 and 268 nm; and the fatty acid composition of the oil. During static heating of the oil, BHA was found to be a more effective antioxidant than BHT whereas, during intermittent frying of potato chips, both the antioxidants were relatively ineffective in retarding the deterioration of the oil. The loss of BHT from the oil during static heating exceeded that of BHA. On the other hand, when potato chips were fried in the oil periodically, a higher loss of BHA was observed.

INTRODUCTION

Deep-fat frying is extensively used both at home and on a commercial scale to enhance the organoleptic properties of foods. A myriad of chemical changes occur both in the frying medium and the product fried. These affect the quality of the oil and the food product. Repeated use of frying oils results in the development of undesirable chemicals that have been believed to pose a health hazard. Oils and fats manufacturers often treat the refined oils with antioxidants with the hope of retarding the undesirable changes during storage and frying operations and possibly lengthening the shelf-life of the fried product. It is believed that the antioxidants protect the fat from oxidation during the time the oil is exposed to high temperatures (1).

There appears to be limited information on the effectiveness of antioxidants in retarding the deterioration of oils during frying, although a number of studies have been carried out on antioxidant efficacies during storage (2, 3). The importance of using actual frying conditions to study antioxidant effectiveness cannot be overstated, as extrapolation of data on the action of antioxidants from storage to frying conditions may be misleading (4).

Refined, bleached and deodorized (RBD) palm olein was used in this study because of its major commercial role in deep-fat frying. The study entailed an evaluation of the effectiveness of butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA), during static heating at 180 C and during the intermittent frying of potato chips. The loss of antioxidants from RBD olein during frying and heating operations was also monitored in view of the importance of maintaining the desired level of the antioxidant in fryers during industrial operations.

The various oxidation, fission, hydrolytic, dehydration and polymerization reactions occurring during a deep-fat frying process coupled with the escape of steam volatiles from the oil make it difficult to judge oil deterioration by a single analytical test. In the past, a combination of the conventional methods has been used to assess deterioration of oil quality during frying (5). More recently, newer methods, like the estimation of remaining triglycerides in the used oil, have been developed to assess the gross deterioration in quality of the frying fats (6, 7).

EXPERIMENTAL PROCEDURES

Sample Preparation

Refined, bleached and deodorized palm olein was procured

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from a local refinery. The antioxidants, BHA and BHT were of laboratory grade obtained through Sigma Chemical Company, Saint Louis, MO. The oil samples were subjected to three different treatments, viz., oil containing BHA, BHT and a control with no antioxidant added. All the oil samples were brought to 180 C in the same manner in a Hamilton DeLuxe deep-fat fryer with an aluminum liner. Each antioxidant, at a level of 200 ppm, was added directly to the oil which was stirred with a motor-driven glass stirrer for 30 min at 60 C to effect complete dissolution of the antioxidants. The temperature of the oil was then raised to 180 C without stirring.

In order to assess the significance of the frying operation in oil deterioration and antioxidant loss, the experiment was conducted in two stages. The first experiment involved static heating of the oil at 180 C, while the second included heating to the same temperature with intermittent frying.

Heating Experiment

In this experiment the oil was maintained at 180 C for 4 hr/day on two consecutive days. At hourly intervals during heating, a 10-mL oil sample was withdrawn for the estimation of antioxidant concentration. At the end of each day, a 100-mL sample was taken for chemical assessment of the oil quality, and the remaining oil was allowed to cool overnight at room temperature.

Frying Experiment

The layout of the frying experiment was similar to that of the heating experiment, except that at hourly intervals a batch of 400 g of potato chips (French fries) was fried for a 10-min period. The potato chips (5.0 × 0.7 × 0.7 cm) were prepared from potatoes procured from a local market. The potatoes were peeled and chipped on the day of use and were kept submerged in distilled water until needed. After draining off excess water, the potato chips were placed in a perforated aluminum basket and lowered slowly into the heated oil. The temperature of the oil prior to each frying was 180 C but during frying it ranged between 125 and 130 C.

The volume of the oil was not replenished to the original volume after any of the heating and frying operations.

Analysis of BHA and BHT

The level of BHA and BHT in the oil samples was determined on a Pye-Unicam series 204 gas chromatograph (GC) fitted with flame ionization detectors. The procedure of Hartman and Rose (8) was adopted. The glass column was 1.5 m × 4 mm id, packed with 10% SE 30 on 100–200 mesh Diatomite C AW-DMCS. The first two inches of the column were packed with silanized glass wool. The temperature of the column was 160 C and that of the injector and detector was 250 C. The flow rates were 50 mL/min, 55 mL/min and 500 mL/min for carrier gas nitrogen, hydrogen and air, respectively. The solutions for GC analysis contained 0.1 g oil/mL ethyl acetate (Merck, Darmstadt, West Germany) and 11.95 ppm methyl undecanoate (Sigma Chemical Company, Saint Louis, MO) as internal standard. A 5- μ L sample of the solution was injected into the gas chromatograph. The concentration of antioxidant was calculated using the equation:

$$\text{ppm}_{\text{AO}} = (\text{ppm}_{\text{IS}} \times \text{peak area}_{\text{AO}}) / (\text{K} \times \text{peak area}_{\text{IS}} \times \text{oil, g/mL})$$

where AO is the antioxidant, IS is the internal standard and K is a factor given by:

$$\text{K} = (\text{peak area}_{\text{AO}} \times \text{ppm}_{\text{IS}}) / (\text{peak area}_{\text{IS}} \times \text{ppm}_{\text{AO}})$$

The factor K was determined using known concentrations of the internal standard (11.95 ppm) and the antioxidants, BHA and BHT (analytical grade, Supelco Inc., Bellefonte, PA). Typically, between 10 and 20 ppm antioxidant concentrations were used for the determination of the K factor. The value of this factor was checked at the beginning of each day's analysis as variations in K may result from prolonged use of the column, minor changes in the operating parameters of the GC and fluctuations in the sensitivity of the detector. K values for BHA and BHT ranged between 0.74 and 0.94, and 1.15 and 1.20, respectively. However, the variation in K values was insignificant during the course of analyses carried out in a single day. The standard solutions of BHA and BHT were freshly prepared for the determination of the K factor as antioxidant solutions were found to decompose on storage.

Analysis of the Oils

AOCS Official Methods (9) were used for the determination of peroxide and iodine values. The absorbances at 232 and 268 nm, anisidine and acid values were obtained using IUPAC methods (10). The fatty acid composition of the oil was determined by gas chromatography using operating conditions as reported before (11).

RESULTS AND DISCUSSION

Comparison of Oil Quality During Heating and Intermittent Frying

The changes in quality characteristics of the RBD palm olein during static heating and intermittent frying of potato chips are given in Table I. The oils receiving the same treatment experienced a greater degree of deterioration during intermittent frying of potato chips than during static heating at 180 C. The extent of oil deterioration was better reflected in the changes in acid value, C18:2/C16:0 ratio and absorbance at 232 nm. The peroxide, anisidine and iodine values also provided supporting evidence for the extent of oil deterioration, although the changes in these values were not as apparent as those in the abovementioned parameters. The changes in absorbance at 268 nm are discussed later.

Peroxide, Anisidine and Iodine Values

The low peroxide values of the oils during heating and frying arise because peroxides tend to decompose at 180 C (12). Nevertheless, the peroxide value may be taken as a rough measurement of the instability of the oil. The possibility of peroxide formation during the cooling period between sampling of the hot oil and executing of the peroxide test cannot be discounted. The peroxide values measured here, however, do correlate with the greater loss of stability in oils used for intermittent frying.

Hydroperoxides, the product of primary oxidation, react to form secondary products of which aldehydic components are measured by the anisidine test. This test has an enhanced sensitivity for unsaturated aldehydes, particularly

TABLE I

Analytical Data on RBD Palm Olein in Heating (H) and Frying (F) Experiments^a

Treatment	Peroxide value (meq/kg)	Anisidine value	Iodine value	Acid value	E _{1 cm} ^{1%} ^b		C18:2 C16:0
					232 nm	268 nm	
No antioxidant (H)							
Initial	2.6	0.9	56.6	0.27	1.98	0.35	0.308
Day 1	2.1	43.3	56.6	0.33	3.88	2.30	0.291
Day 2	1.5	55.2	55.1	0.40	5.12	3.04	0.282
No antioxidant (F) ^c							
Initial	2.0	1.0	58.4	0.32	1.84	0.33	0.303
Day 1	6.2	46.9	57.1	0.40	4.11	1.94	0.284
Day 2	4.3	66.6	56.3	0.51	5.58	2.18	0.274
BHA (H)							
Initial	2.1	1.0	57.8	0.25	1.84	0.30	0.306
Day 1	2.0	33.2	57.3	0.28	3.13	1.84	0.295
Day 2	1.2	36.9	57.3	0.30	3.82	2.42	0.289
BHA (F)							
Initial	2.9	0.9	57.7	0.26	1.88	0.32	0.310
Day 1	5.2	45.3	56.3	0.36	3.96	1.94	0.289
Day 2	4.0	66.1	55.7	0.48	5.86	2.42	0.271
BHT (H)							
Initial	2.2	1.3	56.8	0.29	2.13	0.35	0.303
Day 1	2.2	42.5	56.8	0.33	4.24	2.45	0.288
Day 2	1.5	54.1	55.9	0.39	5.29	3.18	0.280
BHT (F) ^c							
Initial	2.4	1.3	58.7	0.30	1.85	0.34	0.302
Day 1	5.2	46.7	58.3	0.39	4.05	1.95	0.285
Day 2	5.0	67.2	57.0	0.50	5.78	2.40	0.265

^aAverage of triplicate determinations.

^bNot corrected for triglyceride absorption.

^cRBD palm olein from a second can.

2,4-dienals (13), but does not measure the ketonic secondary products of oxidation. It is noteworthy that there is a marked increase in anisidine value on the first day of heating and intermittent frying followed by a comparatively smaller change on the second day. Similar large increases in aldehydic oxidation products have also been reported during the initial stages of heating of cottonseed oil (14). The higher final anisidine value during frying suggests that steam produced during the frying of food does not necessarily remove the anisidine reactive compounds. However, the anisidine test may not be an effective measure of the frying oil quality under these conditions as changes in anisidine values were not proportional to deterioration in frying oil quality.

The small, though observable, differences in iodine value of the oils used in heating and frying experiments are indicative of the increased rate of oxidation during frying. A significant change in iodine value will only be observed when there is excessive deterioration of the oil. The differences in initial iodine values of the samples were due to sampling error as the stearin-rich palm olein fraction tends to settle during storage. Hence, higher iodine values were obtained for the oil samples withdrawn from the top of the can.

Absorbances at 232 and 268 nm

Unlike the peroxide value, the absorbance at 232 nm which also measures the degree of primary oxidation shows a trend of increasing diene content with progress in heating and frying times. These differences arise mainly because hydroperoxides are thermally destroyed at the temperatures of heating and frying. Although not obvious from these results, it has been suggested that smaller increases in diene content are expected in later stages of frying when an equilibrium between the rate of formation of conjugated dienes and the rate of formation of polymers is attained (14). It is now generally accepted that thermal polymerization requires the presence of a conjugated double bond in one of the fatty acids (4).

The increase in absorbance at 268 nm are not commensurate with the anisidine values. A more steady increase in absorbance at 268 nm was observed in complete contrast to the very large increase in the anisidine value on the first day. Furthermore, the absolute value for absorbances at 268 nm were lower in frying than in heating experiments. The apparent discrepancy between these values measuring secondary oxidation can be understood based on the fact that absorbance at 268 nm is a measure of particularly the diethylenic ketones, whereas ketones are not monitored in the anisidine test (13). The relative rates of formation of ketonic and aldehyde oxidation products coupled with the possibility of volatilization of these products may further contribute to the observed differences between the anisidine value and absorbance at 268 nm.

Acid Value and Fatty Acid Composition

There is a significant difference in acid values of the oil in the heating and frying experiments. In the heating experiment where no water is added to the oil, the increase in acid value may be due to the reaction of glycerides with water formed during the other deterioration reactions of the oil (14, 15). The higher acidity in oils of frying experiments is expected since water present in the potato chips provides for an increased rate of hydrolysis with resultant increase in the formation of free fatty acids. The possibility of part of this acidity arising from the presence of component carboxylic groups in polymeric products of heating and frying cannot be excluded (12, 14). The acid value of the oil determined in these experiments may not

be quantitatively related to the acidic products formed during oil deterioration as free fatty acids may be lost through volatilization at the high temperatures of heating and frying. Loss of acidic products may also occur due to the neutralization effect of food being fried.

The fresh oils used in these series of experiments had the following fatty acid composition: C16:0 (38.5%), C18:0 (4.4%), C18:1 (43.5%), C18:2 (11.8%), others (1.8%), which was found to change during heating and frying experiments. A marked decrease in C18:2/C16:0 ratio was observed during intermittent frying, which was consistent with increased deterioration in oil quality under these conditions.

The greater degree of oil deterioration occurring during frying may be explained, in part, by the interaction of food components with the oil. It is also likely that water present in the potato chips accelerated the thermal oxidation and hydrolytic cleavage of the oil (14, 16), although other studies conflict with the suggestion that a small amount of water promotes oil deterioration. Instead, it has been suggested that steam produced during frying can exert an antioxidant effect (17). Another factor contributing to the increased deterioration in oil quality during frying experiments may be the increase in effective surface area of the oil caused by agitation of the oil during frying.

Effectiveness of Antioxidants

In heating experiments, the rate of deterioration of RBD olein treated with BHA is less than that for oil treated with BHT, as indicated by the smaller changes in quality characteristics for BHA-treated oil (Table I). This observation that BHA compared with BHT affords more protection to RBD palm olein during static heating at 180 C differs from the order of effectiveness of these two antioxidants observed in RBD palm olein stored at 60 C (18). The reversal in the order of effectiveness of BHA and BHT could be related to the exposure of the oil to differing conditions that may alter the action of these antioxidants (4).

During frying, it is observed that BHA and BHT added at a level of 200 ppm are relatively ineffective in retarding oil deterioration. This is apparent from the similarity of the changes in quality characteristics of frying oils without antioxidants, with BHA, and BHT (Table I). In contrast to this observation, tertiary butylhydroquinone was found to impart stability to RBD palm olein used for the frying of banana chips (19).

The observations that BHA and BHT do not protect the oil from deterioration during frying are contradictory to the prescribed use of these antioxidants for delaying the onset of rancidity in oils during deep-fat frying (1). The beneficial effects on the deep-fried food due to the carry-through of antioxidants does, however, still warrant the use of these antioxidants. Although the stability of the potato chips was not tested in these experiments, it has been shown earlier that the addition of tertiary butylhydroquinone to the frying bath improved the stability of deep-fried banana chips (19).

The major implication of this comparative study of antioxidants is the necessity to assess antioxidant effectiveness under conditions for which their use is intended.

Antioxidant Loss

The results in Table II show that loss of antioxidants in frying experiments is greater than in the corresponding heating experiments. The availability of additional pathways for antioxidant loss during combined heating and frying is responsible for the observed results. Loss of antioxidants from heated oils may be attributed to the

TABLE II

Changes in the Concentration (ppm) of BHT and BHA in RBD Palm Olein During Heating and Frying Experiments^a

Time (hr)	BHT		BHA	
	Heating	Frying	Heating	Frying
Day 1-0 ^b	181	190	191	187
1	155	164	175	160
2	126	138	153	135
3	112	106	133	104
4	101	91	121	78
Day 2-0 ^b	94	63	108	50
1	83	55	101	36
2	72	45	95	26
3	63	37	85	c
4	57	27	81	c

^aAverage of duplicate determinations. Errors less than 10%.

^bTime at which temperature reached 180 C.

^c<20 ppm.

volatilization of the antioxidant through evaporation, decomposition (20, 21) and the scavenging reactions of the antioxidants. In frying experiments, additional loss of antioxidant occurs through steam distillation resulting from the introduction of water present in the food, absorption and interaction of the antioxidant with the food. A recent study on antioxidants in soy oil (20) showed that the percentage losses of BHA and BHT from the oil during simultaneous steam distillation and heating at 180 C exceeded losses during static heating at 180 C. Although the author (20) had suggested that steam distillation did not significantly increase the rate of antioxidant loss, interpolation of his data revealed that at the end of 4 hr, the percentage losses of antioxidants were at least 10% higher in the case of combined heating and steam distillation than during exposure to heat alone. A comparison of the results on antioxidant-treated soy oil (20) and RBD palm olein indicated that antioxidant losses were greater in soy oil. The higher rate of antioxidant loss in soy oil may be related to the more unsaturated nature of this oil, which renders it more susceptible to deterioration and subsequently provides a higher concentration of reactive species for the scavenging of the antioxidants.

BHA versus BHT Loss

During static heating of palm olein, the loss of BHT exceeded that of BHA whereas, during intermittent frying of potato chips, BHA loss exceeded that of BHT.

The observed higher rate of BHT loss from RBD palm olein during static heating is in agreement with the order of antioxidant loss from soy oil (20). The relatively higher rate of BHT loss may be explained by the interplay of the relative importance of losses through evaporation, decomposition and scavenging reactions. It is not possible to ascribe the extent to which each of these routes are responsible for antioxidant loss. However, it may be useful to reflect on the factors contributing to the rates of antioxidant loss. The relative rates of evaporative losses of BHA and BHT are dependent, among other factors, on the latent heat of evaporation. The lower latent heat of evaporation for BHT (14 kcal/mol) compared to 16 kcal/mol for BHA (22) would indicate a faster rate of evaporation for BHT at the same temperature. However, a reverse order of relative antioxidant loss through decomposition might be expected because the more hindered molecular structure of BHT retards its destruction by higher temperatures (23). On the other hand, the other avenue for antioxidant loss through

scavenging reactions may possibly partly account for the observed order of greater BHT loss during heating, since the greater degree of deterioration in BHT-treated oil (Table I) would provide a larger amount of reactive species for combination with the phenolic antioxidant.

The observation that BHA loss is greater than that of BHT during frying may be understood in terms of the better adsorption of BHA to the food fried. It has been shown that foods fried in BHA-treated oils had a longer shelf-life span due to better carry-through effect of this antioxidant (24). This implies that a greater amount of BHA is transferred to the fried product, thereby diminishing the concentration of BHA in the oil. Although the steam volatility of BHT is greater than that of BHA, BHT loss during frying is less because the carry-through effect of BHT is not as great as that of BHA (24).

This study has shown that there is a rapid loss of antioxidants from RBD palm olein during heating and frying, and that BHA and BHT are relatively ineffective antioxidants under frying conditions. The carry-through effect of BHA in imparting a greater stability to the fried food product merits further investigations with regard to the specific food product fried in palm olein.

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