Tertiary-Butyl Hydroquinone Treatment for Crude Palm Oils

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ABSTRACT

Bleachability of crude palm oil was studied with respect to oxidation state of the oil at time of bleach, amount of bleaching clay needed, and the effects of an antioxidant treatment with tert-butylhydroquinone (TBHQ) on oxidation reactions. These studies confirm the adverse effects of oxidation on bleachability of palm oil and the effectiveness of TBHQ in preserving bleachability. Citric acid was shown to benefit only old oxidized oils. TBHQ was effective in the laboratory and at a full-scale plant experiment in retarding onset and rate of oxidation reactions.

INTRODUCTION

The work reported here relates specifically to bleachability of crude palm oil in response to oxidation and tert-butylhydroquinone (TBHQ) treatment. Fresh crude palm oil is deep red in color and contains over 700 ppm β-carotene. Crude palm oil is normally shipped and stored at elevated temperatures which increases the oxidation hazards. If the free fatty acid content is high in the oil, the oil can pick up iron during processing, storage or shipping. Iron is an effective oxidation catalyst. Several papers have been published on effects of iron content on oxidation rates and effects of oxidation on bleachability. Bek-Nielsen (1) studied the effects of iron content in palm oil on oxidation rate, expressed as Totox value, where Totox = 2(peroxide value) + anisidine value. Yeoh (2) studied the effects of iron content in palm oil on oxidation rates expressed as peroxide values, extinction values at 223 nm and 269 nm, and the disappearance of β-carotene. Bek-Nielsen and Krishnan (3) studied the effects of an antioxidant treatment in palm oil on peroxide values and on bleachability (% color removed). Fraser and Frankl (4) studied colors of palm oils at various stages of processing.

The objective of this study was to measure the effects of TBHQ treatment on rates of oxidation as measured by Totox values and by disappearance of β-carotene and effects on bleachability of crude palm oil as determined by a direct bleach test (DBT). The study is reported in three experiments: experiment 1 covers effects of oxidation and TBHQ treatment on bleachability; experiment 2 covers effects of TBHQ and citric acid combination on rate of oxidation; and experiment 3 covers TBHQ treatment of crude palm olein at full scale.

EXPERIMENT 1: OXIDATION AND EFFECTS ON BLEACHABILITY

Crude palm oil (Table I, oil type A) was treated with 150 ppm TBHQ (dissolved in ethanol) and stored for 10 weeks at 43 C. Peroxide values (PV), anisidine values (AV), and β-carotene content were determined at intervals of two weeks. Totox values were calculated from: Totox = 2PV + AV. At the end of each interval, a portion of the oil was bleached at 150 C for 1 hr with 5% AOCS activated bleaching earth—a DBT (5).

After the final week, the oil was divided into six parts: two parts bleached with 3% earth, two with 5% earth, and two with 7% earth. Each part was bleached for 1 hr at 150 C. Untreated oil was stored, then bleached in the same manner as the TBHQ-treated oil. Lovibond red values were measured with a 5.25-in. cell.

Residual Lovibond red values were regressed against Totox values and against β-carotene content in ppm. The regressions fit quadratic models: $R^2 = .83$ and $R^2 = .88$ for Totox and β-carotene content, respectively (N = 12).

Results

During storage, Totox values increased and β-carotene disappeared for both treated and untreated samples, but in the treated samples, the rates of change in the responses were reduced.

Figure 1 is a plot of the regression equations and shows that as Totox values increase, the ability to reach low red colors decreases under otherwise constant bleaching conditions. β-Carotene content decreases on storage, but it is presumed to oxidize to a form which is more difficult to bleach.

Figure 2 is the Lovibond red values of bleached oils plotted against time for TBHQ-treated oil and the control. The treated oil plot shows the expected induction period with essentially no slope up to about eight weeks before

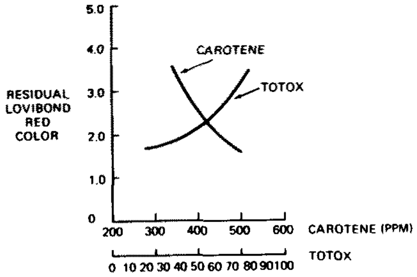

FIG. 1. Residual Lovibond red color after bleach: 5% clay, 150 C, 1 hr, (AOCS activated bleaching earth); n=12.

TABLE I

Properties of Experimental Palm Oils

Type	Type palm oil	Peroxide value (meq/kg)	Carotene content (ppm)	Anisidine value	Iron (ppm)	Copper (ppm)
A	Whole crude palm oil	2.68	711	1.579	10	<1
B	Alkali-refined crude palm oil	3.51	410	4.09	7	<1
C	Old oxidized crude palm oil	5.30	509	6.43	11	<1

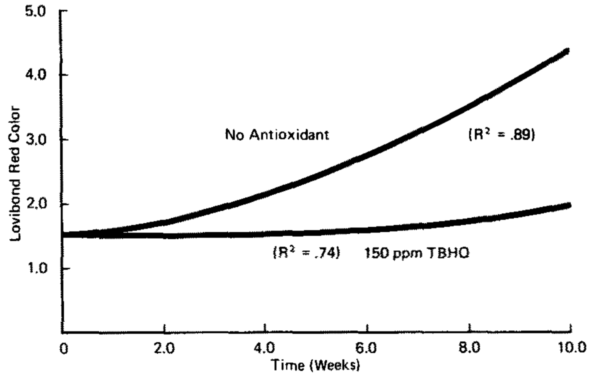

FIG. 2. Bleachability of crude palm oil across time: 5% clay, 1 hr, 150 C, n=12.

Lovibond red colors (after bleach) were affected. Lovibond red colors of bleached, untreated oil showed adverse effects of oxidation in the second week.

Figure 3 is the Lovibond red values plotted against quantity of clay used during bleach after tenth week for the TBHQ-treated oil and control. The curves show that less clay was needed to achieve the same color level for treated oil than for control; or if same clay level were used for both oils, lower red color values resulted in the TBHQ-treated oils.

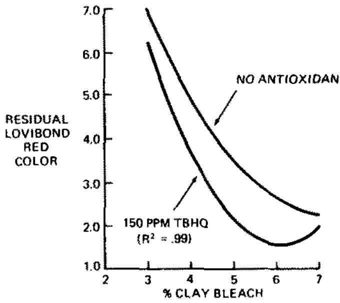

FIG. 3. Residual Lovibond red color after bleach of oil stored with and without TBHQ (n=12).

EXPERIMENT 2: EFFECTS OF TBHQ AND CITRIC ACID ON OXIDATION RATE

The palm oils used in this experiment are described in Table I: fresh crude palm oil (A), alkali-refined palm oil (B), and old crude palm oil (C). The oils were treated with combinations of TBHQ and citric acid (dissolved in ethanol) in a central composite design (Table II). The treated and untreated samples were stored in the dark at 52 C and β-carotene was measured periodically. Oil type B was included to test the effects of alkali refining. Oil type C was included to test whether the antioxidant treatment is beneficial if oxidation is extensive prior to treatment.

TABLE II

Central Composite Design for Response Surfaces

TBHQ (ppm)	Citric acid (ppm)
0	0
100	0
200	0
0	300
100	300
200	300
0	600
100	600
200	600

The raw data was submitted to stepwise regression relating to β-carotene content to TBHQ and citric acid content for each type of oil. The regression equations were entered on a plotter for response surfaces.

Results and Discussion

Figure 4 is the plot of β-carotene in fresh crude palm oil (A) with respect to various treatment levels of TBHQ and citric acid at termination of the experiment. The plot shows the large beneficial effects of TBHQ and little effect from citric acid.

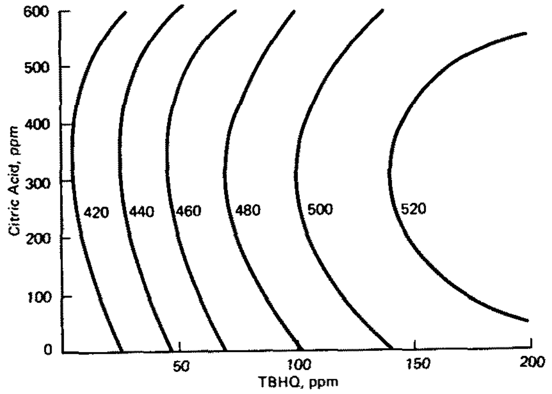

FIG. 4. β-Carotene content (ppm) in whole crude palm oil. Multiple R² = .98. Storage, 90 days at 52 C (n=36).

Figure 5 is the plot of β-carotene content in alkali-refined palm oil (B) against levels of TBHQ and citric acid treatment at termination of the experiment. Similarly to Figure 4, the plot shows the beneficial effect of TBHQ and little effect from citric acid. A comparison of Figures 4 and 5 shows the greater disappearance rates of β-carotene from alkali-refined oil.

Figure 6 is the response surface for old oxidized crude palm oil (C) and the plot shows a benefit from both TBHQ and citric acid with an optimum at about 100 ppm TBHQ and 300 ppm citric acid.

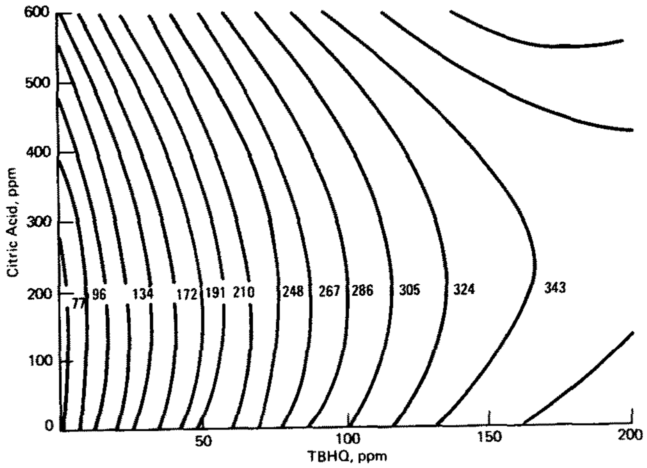

FIG. 5. β-Carotene content (ppm) in alkali-refined crude palm oil. Multiple R² = .90. Storage, 90 days at 52 C (n=36).

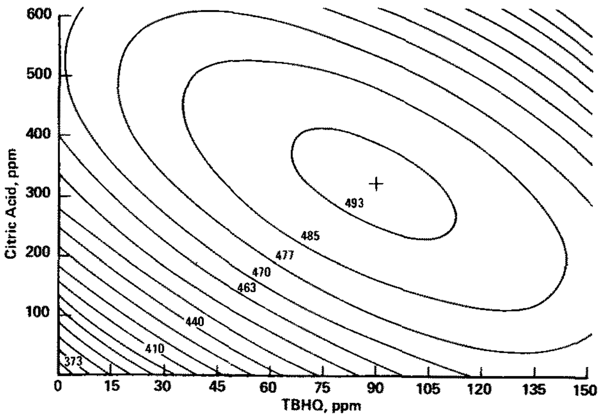

FIG. 6. β-Carotene content (ppm) in old oxidized crude palm oil. Multiple R^2 = .91. Storage, 50 days at 52 C (n=6).

TABLE III

Bulk Oil Description

1. Quantity: 1,300,000 lb
2. Type oil: Crude palm olein
3. Age: Unknown at time of treatment
4. Properties:
   Fe content (ppm) = 14.88
   Anisidine value = 10.95
   Carotene (ppm) = 530
   E233 = 3.793
   E269 = 0.784
   Free fatty acid = 3.574
   Fe content (ppm) = 6.5
5. Storage conditions:
   Dark storage
   Temperature = 38 C
   Air in head space
   Continuous side stirred

EXPERIMENT 3: FULL-SCALE PLANT EXPERIMENT WITH PALM OLEIN

A bulk quantity of palm olein was made available at a refinery for this experiment and the description of the oil is in Table III. An ethanol solution of 11% TBHQ and 36.5% citric acid was added directly to the bulk oil in a storage tank for a target level of 110 ppm TBHQ and 365 ppm citric acid. A sample of untreated oil was saved for a laboratory control and a sample of treated oil was taken for a laboratory control after the bulk stored oil was shown to be homogeneous by TBHQ assays. The bulk stored oil and laboratory controls were stored in the dark at 38 C and assayed weekly for peroxide values and β-carotene content.

Results and Discussion

Figure 7 shows the rates of disappearance of β-carotene from the stored oils. Figure 8 shows the rate of formation of peroxides in the negative control, whereas the bulk stored oil and positive control assays for peroxides remained essentially unchanged over the course of the experiment.

Although an ethanol solution was used in this experiment to facilitate treatment of bulk oil in storage, the usual commercial practice would be a continuous addition of a stock solution of TBHQ and citric acid by metering pump while transferring bulk oil to storage. The stock solution could be made using a variety of safe solvents, including propylene glycol.

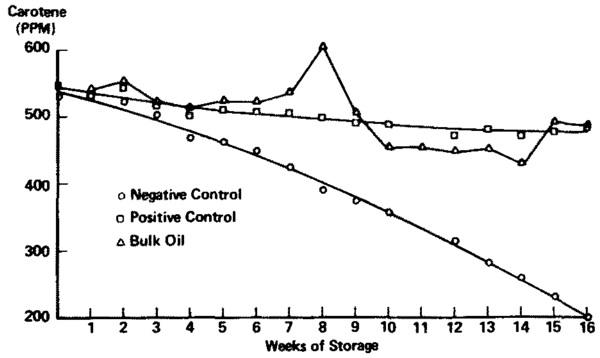

FIG. 7. β-Carotene content (ppm) in bulk stored palm olein (dark storage at 38 C).

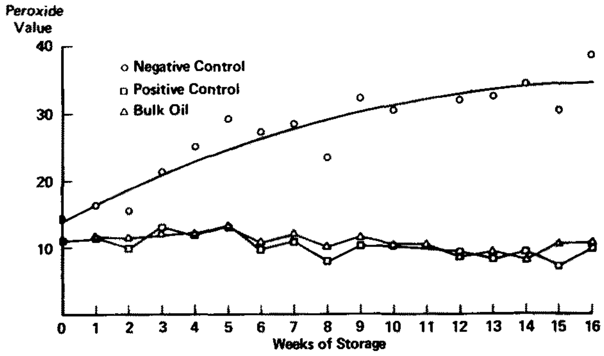

FIG. 8. Peroxide values in bulk stored palm olein (dark storage at 38 C).

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