

by tocopherols at high concentration has been discussed earlier (18,25). In the same way, BHT inhibited the production of *trans-trans* isomers. On the contrary, no hydroperoxide isomers were detected with hydroquinone and ascorbyl palmitate, with or without α -T.

The inhibitors of the prooxidant activity of α -T could act in two different ways:

- by chelating the prooxidant metals
- by regenerating α -T, thus reducing the concentration of chromanoxo radical which would be involved in the prooxidant activity.

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Effect of TBHQ on Quality Characteristics of RBD Olein During Frying

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The changes in quality characteristics of refined, bleached and deodorized palm olein (RBD olein) during heating with intermittent frying for 5 hr/day for weight consecutive days in three systems were compared. The systems were (i) RBD olein without antioxidant (system 1); (ii) RBD olein to which 200 ppm of tertiary butylhydroquinone (TBHQ) had been added prior to frying on the first day (system 2), and (iii) RBD olein which had TBHQ added to a level of 200 ppm at the start of each day. The addition of TBHQ reduced the level of polar components and polymers in the oil, decreased the rates of change in iodine value and dielectric constant and decreased the rate of oxidation of C18:2. The reduction in the rates of these undesirable changes was more pronounced when the TBHQ was added to the system on each day of frying than when there was a single addition of TBHQ prior to frying on the first day. The undesirable effect of adding TBHQ was that it darkened the oil.

The liquid fraction of palm olein is being used increasingly in frying operations. The changes in quality during frying are of importance, as frying oil is absorbed by the food being fried and forms an important constituent of the diet.

Oils undergo a complex series of changes and

reactions during frying (1,2). The physical and chemical changes occurring in oils under frying conditions have been studied (3-5). However, the rate of changes occurring during frying is affected by the frying conditions and the characteristics of the fat.

This study investigated the changes in oil quality characteristics of RBD olein during frying conditions. The effect of a single addition of TBHQ to the frying oil was compared with the effect of adding TBHQ on each day.

EXPERIMENTAL PROCEDURES

Materials. RBD olein was obtained from Lam Soon Oil and Soap Mfg. Sdn. Bhd.; TBHQ (97%) was from Aldrich Chemical Co. Inc., Milwaukee, Wisconsin. Potatoes were obtained from a local supermarket. They were cleaned, then sliced with a mechanical slicer. Potato slices (2 mm) were washed with water. Excess water was drained off before the pieces were fried.

Frying experiments. The conditions used were heating with intermittent frying for 5 hr/day for eight consecutive days. The systems were (i) RBD olein without antioxidant (system 1); (ii) RBD olein to which 200 ppm TBHQ had been added prior to frying on the first day (system 2); and (iii) RBD olein which had TBHQ added up to a level of 200 ppm at the start of each day

(system 3).

RBD olein (4 kg) was put into a Valentine industrial fryer. The temperature was brought up to 60 C, 200 ppm TBHQ was then added in systems 2 and 3 and the oil was stirred for 10 min to ensure dissolution of TBHQ. In the case of system 1, the oil also was held for 10 min at 60 C, although no TBHQ was added. The temperature was then raised to 180 C. Frying started 15 min after the temperature had reached 180 C. A batch of 100 g potato chips was fried for 4 min at every 30-min interval for a period of 5 hr per day for eight consecutive days. At the end of each 5-hr frying period, the lid was put on the fryer and the oil allowed to cool overnight. In system 3, an additional 190 ppm TBHQ was added so that the level of TBHQ in the frying oil at the beginning of each frying day was 200 ppm. It was assumed that the rate of loss of TBHQ during a frying day and the standing period overnight were the same throughout the eight days.

Oil samples for analysis (110 g) were removed from the fryers at the end of every two days. These were kept in a cold room (4 C) until they were analyzed.

Analysis of TBHQ. The method used for extraction and determination of TBHQ in the oil was based on those of Page (6) and Kirleis and Stine (7). A HPLC 1084 LC Hewlett Packard Series fitted with a UV detector set at 292 nm was used. The column, 200 mm × 4.6 mm i.d., Hypersil ODS C-18 (10 μm) was used. Recovery studies were carried out by spiking oil samples with a known amount of TBHQ.

Analysis of oils. The AOCS Official Methods (8) were used for the determinations of peroxide value, Lovibond color and smoke point. IUPAC methods (9) were used for assessment of iodine, p-anisidine and acid values and UV absorbances at 232 and 268 nm. Oil color was also determined spectrophotometrically (10). The percentage of polar components was determined by column chromatography (11). Polymer content, which was defined as the weight of that portion of the oil which remained insoluble in methanol at room temperature after methanolysis, was analyzed according to the method of Peled et al. (3). The dielectric constant was measured with a Foodoil Sensor Model NI-20. The instrument was calibrated with a standard zero which was provided with the instrument.

The fatty acid composition of the oil was determined by gas chromatography after preparation of fatty acid methyl esters (12,13). The results are expressed as the peak area ratios of linoleate (C18:2) relative to palmitate (C16:0). This represents the ratio of the glyceride-bound fatty acids.

RESULTS AND DISCUSSION

Characteristics of RBD olein used in frying experiments. The RBD olein used in this study was of good quality, as indicated by its initial low peroxide value of 0.8 meq/kg and p-anisidine value of 1.0. The iodine value was 57.2, while the acid value was 0.12 mg KOH/g oil. The fresh oil had the following composition: C16:0 (40.2%), C18:0 (4.1%), C18:1 (43.3%), C18:2 (10.6%) and others (1.8%). The smoke point was 218 C, and the oil had a bland odor and flavor.

Analysis of TBHQ in oils. Recovery studies showed that the recovery of TBHQ from the oil was 96%. The

standard error in duplicate analysis was 0.50 ppm.

Analysis of oils showed that the level of TBHQ in the oil at the beginning of days 2 and 3 was 10 ppm, indicating that 95% of TBHQ was lost during a frying day and standby period overnight. Loss of TBHQ during frying can be the result of a variety of factors, including steam volatilization of TBHQ, thermal decomposition of TBHQ, and absorption of TBHQ by the food fried.

Changes in RBD olein systems during frying. The changes in quality parameters of oil after heating and frying for 5 hr per day for eight days are given in Table 1. A range of parameters was used because no one parameter can depict frying life accurately. Although the more reliable indicators have been considered to be dielectric constant (where only one type of product and oil is used) and total polar components, the other parameters were evaluated also, because various authors have used them in assessing frying life of oils (1,14).

Polar components and dielectric constant. The addition of TBHQ to the oil reduced the level of polar components and decreased the rate of change in dielectric constant of RBD olein used for eight days of frying. The effect of addition of TBHQ on each day of frying (system 3) was greater than that caused by the single addition of TBHQ (system 2). However, the oils in all three systems had reached the end of their useful frying life by the end of day 4. Billek et al. (11) suggested that a frying fat should be discarded when the percentage of total polar components in the oil reached 27%. Fritsch et al. (15) suggest that changes in dielectric constant of oils are a good measure of oil deterioration during frying.

Iodine value and C18:2/C16:0 ratio. The change in iodine value after eight days of frying was 10.5, 9.9 and 8.6 units for systems 1, 2 and 3, respectively. The corresponding C18:2/C16:0 ratios were 0.095, 0.099 and 0.123 for systems 1, 2 and 3, on day eight of frying. These results showed that the overall rate of oxidation of unsaturated fatty acids and that of C18:2 was reduced in the presence of TBHQ and that consistent addition of TBHQ at the start of each day had a greater effect than a single addition.

Polymers and oil color. The polymers content of the oil was reduced in the presence of TBHQ. The polymers content in system 3 after eight days of frying was 0.52 times that in system 1. The reduced polymers content in system 3 may be attributed to the effect of TBHQ and its breakdown products on the oxidation of oil. Phenolic antioxidants, like TBHQ, have been reported to be particularly effective against polymerization. For example, they have been found to inhibit polymerization of vulcanized rubber (16).

Both the bathochromic shift and Lovibond color measurements showed that added TBHQ caused the oil to darken at a more rapid rate than oil without the antioxidant. Luckadoo and Sherwin (17) also found that TBHQ-treated oils discolored during high temperature exposure. The influence of phenolic antioxidants on darkening is known. In the presence of heat and metals, phenolic antioxidants form colored compounds (18). Polymers also contribute to color. However, in these systems, where the rate of polymer formation is highest

EFFECT OF TBHQ ON FRYING OIL

TABLE 1

Changes in Characteristics of RBD Olein during Heating and Frying^a

Quality Parameter	System 1	System 2	System 3
Polar Components (%)			
Day 0	5.5	5.5	5.4
2	19.1	18.1	17.3
4	29.9	29.5	27.7
6	39.8	39.4	34.5
8	47.4	45.4	41.3
Dielectric Constant			
Day 0	1.36	1.36	1.38
2	3.26	3.13	3.08
4	5.00	4.82	4.65
6	6.64	6.47	5.89
8	7.80	7.46	7.05
Iodine Value			
Day 0	57.2	57.2	57.2
2	53.9	54.5	55.0
4	51.3	51.6	52.0
6	48.6	49.5	50.5
8	46.7	47.3	48.6
C18:2/C16:0 Ratio^b			
Day 0	0.262	0.262	0.262
2	0.212	0.217	0.217
4	0.158	0.167	0.172
6	0.124	0.128	0.145
8	0.095	0.099	0.123
Polymers (%)			
Day 0	0	0	0
2	0.48	0.33	0.35
4	1.75	1.47	1.17
6	2.95	2.87	1.81
8	4.95	4.01	2.55

in system 1, it can be deduced that the effect of added TBHQ on color development is greater than that due to polymer formation.

UV absorbances and acid value. The $E_{1\text{cm}}^{1\%}$ at 232 nm of the oil after eight days of frying was lower in system 3 than in system 1 or 2. The lower UV absorbance at 232 nm may be related to the corresponding lower polymers content in system 3. UV absorbance at 232 nm measures conjugated dienes, and the formation of polymers generally is believed to require the presence of conjugated dienes (19). The $E_{1\text{cm}}^{1\%}$ at 268 nm, which is an indicator of the degree of secondary oxidation, increases when TBHQ is added to the oil. It is not understood why this is so because TBHQ retards the rate of deterioration of oil.

The acid value of oils with added TBHQ was also higher than that of system 1. The increase in acid value during frying is due mainly to hydrolysis of the oils, although oxidative pathways can also result in the production of acids. TBHQ functions as an antioxidant, and it is expected that it will not have an influence on the rate of hydrolysis of triglycerides.

The results of the study show that the addition of TBHQ on each frying day retards the rate of oxidation of the oil. The effect probably is due to the combined effect

Quality Parameter	System 1	System 2	System 3
Bathochromic Shift (nm for which $E_{1\text{cm}}^{1\%} = 1$)			
Day 0	316	316	316
2	339	340	342
4	353	356	369
6	369	373	392
8	383	391	416
Lovibond Color^c			
Day 0	0.5R, 3.0Y	0.5R, 3.0Y	0.5R, 3.0Y
2	1.6R, 13.0Y	1.5R, 11.0Y	1.9R, 20.0Y
4	2.0R, 20.0Y	2.0R, 20.0Y	4.5R, 45.0Y
6	3.6R, 36.0Y	4.5R, 45.0Y	10.0R, >80 Y
8	7.4R, 70.0Y	7.6R, 70.0Y	19.0R, >80 Y
$E_{1\text{cm}}^{1\%}$ at 232 and 268 nm			
Day 0	1.87, 0.39	1.87, 0.39	1.97, 0.39
2	8.49, 1.91	7.89, 2.06	7.83, 2.11
4	11.71, 1.96	11.23, 2.10	10.23, 2.27
6	12.51, 2.17	12.58, 2.35	11.13, 2.68
8	13.17, 2.65	13.02, 2.69	11.46, 3.23
Acid Value (mg KOH/g oil)			
Day 0	0.10	0.10	0.10
2	0.35	0.72	0.71
4	1.42	1.40	1.50
6	2.22	2.12	2.41
8	2.95	3.00	3.33

^aThe average standard error of analysis carried out in duplicate is 0.2% for percentage polar components, 0.05 units for dielectric constant, 0.5 units for iodine value, 0.003 for C18:2/C16:0 ratio, 0.20% for percentage of polymers, 0.20 and 0.05 absorbance units for $E_{1\text{cm}}^{1\%}$ at 232 and 268 nm, respectively, and 0.20 mg KOH/g oil for acid value. The differences in bathochromic shift and Lovibond color measurements in two experiments were less than 3 nm and 1.0 R, respectively.

^bRatio of glyceride fatty acids.

^cMeasurements in a 1-in. cell.

of TBHQ itself and its breakdown products. It has been shown that there are at least four breakdown products of TBHQ which have antioxidant effects (20,21).

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✿ Changes in Volatile Constituents of Bell Peppers Immediately and 30 Minutes After Stir Frying

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Bell peppers (*Capsicum annuum* var. *grossum*. Sendt) were stir fried for two min, and their volatile constituents were analyzed immediately and 30 min after stir frying. Autoxidation of unsaturated fatty acids in stir frying and aging is the main cause of changes in volatile compounds.

Traditionally, Chinese foods are cooked quickly and eaten immediately; at the moment when it is just cooked, the food has the best flavor, color and texture. However, Chinese foods available commercially should maintain their initial quality for a minimum storage period of at least six mo to one yr.

A very common technique in Chinese cooking is stir frying. By this method, a small amount of vegetable oil is put into a wok and is heated to a very high temperature. Shallots, garlic or other seasonings are added to produce aroma and flavor, and other foods are added, cooked and stirred last. The function of oil in stir frying is not clear; the authors feel it has the following functions: (i) producing aroma; (ii) serving as a heating medium, and (iii) dehydration. Foods are flavorful after stir frying in oil; however, they are easily oxidized. Lipid oxidation is accelerated in stir frying and causes an undesirable aroma. Therefore, more basic information is needed before Chinese foods can be commercialized and have extended shelf lives.

The formation of a number of aroma compounds can be traced to lipid oxidation at the various stages of food processing. Lipid oxidation can be caused by enzymic oxidation reactions or by thermal decomposition. The enzymic oxidation formation of aldehydes, ketones, alcohols and oxoacids on disruption of plant tissues is an important biosynthetic pathway by which fruit and vegetable volatiles are formed (1-3). The autoxidation of fatty acids and their esters at elevated temperature also has been studied (4-7).

Volatile constituents of bell peppers (*Capsicum*

annuum var. *grossum*. Sendt) have been studied thoroughly (3,8). In the present work, changes in volatile constituents in both stir fried bell peppers and the oil in which they were cooked were studied.

EXPERIMENTAL

Stir frying. A Chinese wok 36 cm in diameter was used. The wok was dried by heating, then 150 ml soybean oil was added and heated to 125 C. Bell peppers (1200 g; strips ca. 5 cm × 12 cm) were added and stir fried for 2 min. No cover was used. The stir fried bell peppers were removed to a dish immediately after frying.

Measurement of temperature. In order to determine the internal temperature of the samples, a thermocouple wire was inserted into the bell pepper strip or put into the oil. Bell peppers boiled in water for five min also were monitored, for comparison. All samples were transferred to dishes to cool after five min heating. Values obtained were from the average of three measurements.

Sample preparation. Stir fried bell peppers with the fried oil as described above and 600 ml distilled water were extracted for 2 hr in a Likens-Nickerson apparatus (9). Glass-distilled pentane and diethyl ether (1:1) were used as extracting solvents, and n-decane (E. Merck, Darmstadt, Federal Republic of Germany.) was added as an internal standard. The volatile extracts were dried with anhydrous Na₂SO₄ and concentrated to a minimum volume by using a spinning band distillation apparatus (Kontes Co., Vineland, New Jersey). The aged sample was obtained by putting the stir fried bell pepper in a dish at room temperature.

Gas chromatography. Gas chromatography was conducted using a Shimadzu GC-8APF equipped with a flame ionization detector. Two 50 m × 0.2 mm fused silica columns coated with Carbowax-20M and OV-1 (Chrompack International, B.V., Middleburg, The Netherlands) respectively, were used. The oven temperature was programmed from 50 to 200 C at 2 C/min and then held at 200 C for 55 min. The injector and detector temperatures were 250 C. The carrier gas was hydrogen at a flow

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