Oxidative Stability and Storage Behavior of Fatty Acid Methyl Esters Derived from Used Palm Oil

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ABSTRACT: Fatty acid alkyl esters, especially FAME, are the most commonly used liquid biofuel. Because biofuels are expected to be important alternative renewable energy sources in the near future, more studies on their stability against oxidation need to be addressed. Biofuel derived from vegetable oils is well researched, currently with more attention focused on the reuse of waste oil sources than on pure vegetable oil for such production. A method to convert used palm oil, i.e., used frying oil, and residual oil of spent bleaching earths (SPE) to their respective methyl esters has been established by the Malaysian Palm Oil Board. These methyl esters can be used as diesel substitute. However, the methyl esters obtained from used frying oil have a low induction period (3.42 h). In Europe, any methyl esters must have an induction period of at least 6 h in Rancimat stability to be usable as biodiesel, as required by European Biodiesel Standard (EN 14214). To meet this requirement, the used frying oil methyl esters (UFOME) obtained can be treated with different types of antioxidants, either synthetic or natural, at different treatment levels, such as vitamin E, 3-*tert*-butyl-4-hydroxyanisole (BHA), 2,6-di-*tert*-butyl-4-methyl-phenol (BHT), 2,5-di-*tert*-butyl hydroquinone (TBHQ), and *n*-propyl gallate (PG), to investigate their oxidative stability and storage behavior. The order of increasing antioxidant effectiveness with respect to the oxidative stability of UFOME is: vitamin E < BHT < TBHQ < BHA < PG. Because methyl esters derived from residual oil of SBE have an induction period of 14.6 h, their treatment with antioxidants is unnecessary.

Paper no. J11219 in *JAOCS 83*, 947–952 (November 2006).

KEY WORDS: Antioxidants, induction period, oxidative stability, Rancimat test, residual oil, spent bleaching earths, stabilization factor, storage stability, used frying oil methyl esters, used palm oil.

Opinions regarding renewable fuels have become more favorable owing to the increase in environmental awareness by global industrial communities and society in general. A search for biodegradable, environmentally acceptable fuels has commenced for the sake of maintaining a more sustainable environment for future generations.

The world's vast demand for renewable liquid biofuel is a scenario that leads to the search for new sources of such products. Although vegetable oil is abundantly available and has been a major resource for the production of biofuel, other inexpensive resources such as spent, used, or waste vegetable oils and animal fats can also be considered owing to the benefits that their recycling would provide (1). However, these oils normally are inferior in their physical properties, especially oxidative stability, because of the severe conditions to which they have been subjected.

Fatty acid alkyl esters, especially FAME, are the most commonly used liquid biofuel or biodiesel. Biodiesel based on vegetable oils has advantages over petroleum diesel, but it also possesses some drawbacks such as poor oxidative stability (2). In line with the European Standardization Programme for biodiesel, oxidative stability of biodiesel for application as an automotive diesel fuel must have a minimum induction period of 6 h *via* Rancimat test at 110°C (proposed EN 14112) (3). Thus, any fuel potentially eligible for use as biodiesel must fulfill the current requirement and specification.

The Malaysian Palm Oil Board (MPOB) has established methods to convert used palm oil (i.e., used frying oil, mainly as palm olein) and residual oil (mainly as crude palm oil) extracted from spent bleaching earths (SBE) to their respective FAME (4). The suitability of methyl esters derived from used palm oil, especially used palm olein-based frying oil, as biofuel is not promising and poses uncertainty because the feedstocks exhibit inferior oxidative stability. Thus, it is essential to study the FAME with added antioxidants to investigate their oxidative stability. The study of appropriate additives for biofuel or biodiesel is necessary. The stability evaluation of biodiesel from sources such as sunflower oil methyl esters (5,6), soybean oil methyl esters (7,8), rapeseed oil methyl esters (9), palm oil methyl esters (10), tallow fats methyl esters and used frying oil methyl esters (5,6, 11) has been carried out using antioxidants such as TBHQ, propyl gallate (PG), pyrogallol (PY), BHA, 2,6-di-*tert*-butyl-4-methyl-phenol (BHT), and α-tocopherol as oxidation retardant. Some of these antioxidants, especially PY and PG, showed beneficial effects on biodiesel oxidative stability.

In this paper, the influence and effectiveness of a series of commercial natural (vitamin E) and synthetic antioxidants (BHA, BHT, TBHQ, PG) on the oxidative stability of FAME derived from used frying oil are described. The goal of the study is to find the most effective antioxidant for biodiesel feedstock derived from used frying oil and to determine the minimum antioxidant concentration at which the oxidative stability can be maintained to meet the specification at a longer storage time.

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EXPERIMENTAL PROCEDURES

Materials. Samples of FAME were prepared *via* transesterification of used frying oil and residual oil recovered from SBE. Used frying oil was collected from local Malaysian fast food restaurants whereas SBE were collected from local palm oil refineries. The SBE was extracted for its residual oils in a Soxhlet extractor by hexane until hexane exiting the extractor was colorless. All solvents used were of analytical grades purchased commercially. The catalyst, i.e., sulfonated ion exchange catalyst (RH resin), was purchased from Chemitreat (M) Sdn. Bhd., and sodium hydroxide was obtained commercially. The preparation of FAME using a sulfonated ion exchange resin *via* esterification and sodium hydroxide *via* transesterification was discussed elsewhere (12).

The antioxidants [vitamin E (α-tocopherol), BHA, BHT, TBHQ and PG] were purchased from Sigma-Aldrich. The samples of biofuel were supplemented with 100, 250, 500, 750, and 1000 ppm of each antioxidant, respectively, and the corresponding induction periods were measured immediately (week zero) with the Rancimat instrument. The samples with antioxidants were kept in the dark at room temperature in sample bottles with sealed lids, and the Rancimat measurement was conducted every week for a period of 5 wk (week 1 to week 5). This storage condition illustrated the behavior and influence of antioxidants in the initial stage of storage, which demonstrated a drastic change in induction periods.

Apparatus. The Model 743 Rancimat (Metrohm AG, Herisau, Switzerland) was used for the measurement of oxidative stability. Biofuel samples of 3 g, held in heating blocks at 110°C, were analyzed under constant airflow of 10 L/h. All determinations of induction period were performed in duplicate and the mean values reported. The effectiveness of all antioxidants is expressed by a stabilization factor F, where $F = \mathrm{IP}_x/\mathrm{IP}_o$, IP_x = the induction period of sample in the presence of antioxidant, and IP_o = the induction period of sample without antioxidant.

RESULTS AND DISCUSSION

FAME derived from used palm oil were characterized for their fuel properties as shown in Table 1. Whereas used (palm olein-based) frying oil methyl esters (UFOME) exhibit very poor oxidative stability, crude palm oil-based methyl esters from residual oil of SBE have adequate oxidative stability, 14.6 h (14), and conform to the Europe Biodiesel Specification. The two palm oils used in this study originate from different palm oil fractions. UFOME was found to have a higher degree of unsaturation, which causes a lower induction period, than used palm oil. The lower induction period of UFOME further accounts for the severe oxidation degradation and deterioration (4) of the oil and its natural antioxidants (carotene and vitamin E) during heating of the frying oil. The FFA and PV of UFOME are 0.2% and 13.6 mequiv/kg, respectively, thus also accounting for the low oxidative stability. To make UFOME competitive and able to meet the European Biodiesel Specification, treatment with antioxidants to enhance the oxidative stability is essential.

The influences of the antioxidants (vitamin E, BHA, BHT, TBHQ, and PG) on the storage stability of UFOME for 5 wk are shown in Figure 1. Generally, the induction periods of UFOME increase with the increase of antioxidant concentration. The ability of these antioxidants to enhance the oxidative stability of UFOME depends on the antioxidant characteristics and dosage added. Above 100 ppm, all antioxidants could increase the induction periods of UFOME to significant levels at zero storage. However, the induction periods decrease rapidly over storage for 5 wk in the dark at room temperature as indicated by a decrease of 10–20% (vitamin E), 8–15% (BHT), 22–35% (TBHQ), 7–10% (BHA), and 3–15% (PG) (Table 2). Nevertheless, the induction periods still remained above 6 h at 500 ppm and above (for vitamin E, BHT, TBHQ) and at 250 ppm and above (for BHA and PG) after a significant decrease over 5 wk. Thus, an antioxidant concen-

TABLE 1
Fuel Properties of FAME Derived from Used Palm Oil

Properties	UFOME[a]	SBE residual oil methyl esters[a]	Fresh palm oil methyl esters[b]
Density @ 25°C (kg/L)	0.8863	0.9051	0.8700
Viscosity @ 40°C (cSt) ASTM D 445	4.4	3.7	4.5
Sulfur content (wt%) IP 242	0.04	0.04	0.04
Pour point (°C) ASTM D 97	15.0	16.0	16.0
Flash point (°C) ASTM D 93	192	172	174
Gross heat of combustion (kJ/kg) ASTM D 240	37,365	38,080	40,135
Oxidative stability (h) EN 14112	3.42	14.59	23.33

[a] Results shown are only for these particular batches. UFOME, used frying oil methyl esters; SBE, spent bleaching earths; IP 242, Institute of Petroleum Test Method 242.
[b] Source: Choo *et al.* (13).

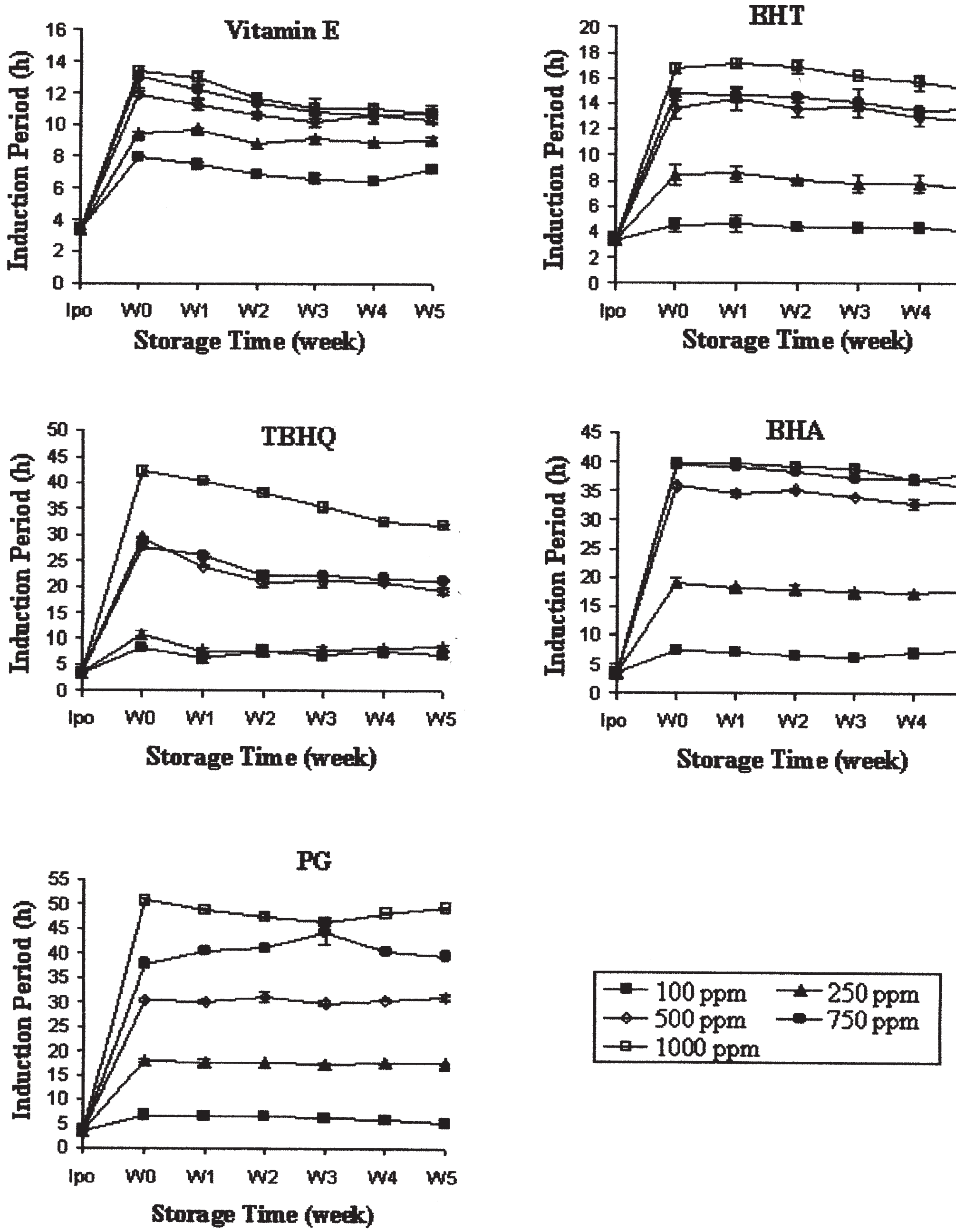


FIG. 1. Storage behavior of used frying oil methyl esters (UFOME) influenced by vitamin E, 2,6-di-*tert*-butyl-4-methyl-phenol (BHT), TBHQ, BHA, and propyl gallate (PG) at 100 (■), 250 (▲), 500 (◇), 750 (●), and 1000 (□) ppm. Storage conditions: room temperature, amber bottle, sealed tight. Storage time: 5 wk. Error bars represent SD ($n = 2$).

tration of ≥500 ppm is sufficient to meet the oxidation stability specification for a longer storage time.

The influences and the effectiveness of vitamin E, BHA, BHT, TBHQ and PG on the oxidative stability of UFOME are clearly illustrated in Figure 2. PG gave the highest induction periods at higher concentrations (500–1000 ppm) followed by TBHQ, BHT, BHA, and vitamin E. At lower concentrations (100–250 ppm), the effectiveness of antioxidants to enhance the induction periods was not in the same order. In most cases, PG, BHA, and TBHQ were the most effective antioxidants as clearly reflected in their higher F values (Table 2) compared with other antioxidants. As a result, they are promising antioxidants to use to enhance the oxidative stability of UFOME.

The order of antioxidants affording increasing of oxidative stability for UFOME at 500–1000 ppm is: vitamin E < BHT < TBHQ < BHA < PG. All antioxidants (except for PG at 250 ppm) tested at concentrations of 100–250 ppm are insufficient to impart good oxidative stability to UFOME, thus they could not fulfill the biodiesel requirement. The induction periods

TABLE 2
Percentage Decrease of Induction Periods[a] (IP) and *F* Values of UFOME with Vitamin E, BHT, TBHQ, BHA, and PG at Various Concentrations Under Storage for 5 wk at Room Temperature[a]

Antioxidant	IP decrease (%)	*F*	Antioxidant	IP decrease (%)	*F*
Vitamin E			BHT		
100 ppm	17	2.33	100 ppm	15	1.32
250 ppm	10	2.75	250 ppm	15	2.48
500 ppm	14	3.48	500 ppm	12	3.99
750 ppm	18	3.81	750 ppm	8	4.30
1000 ppm	20	3.91	1000 ppm	12	4.90
TBHQ			BHA		
100 ppm	22	2.39	100 ppm	16	2.14
250 ppm	29	3.16	250 ppm	10	5.56
500 ppm	35	8.58	500 ppm	9	10.47
750 ppm	22	8.11	750 ppm	10	11.50
1000 ppm	25	12.30	1000 ppm	7	11.60
PG					
100 ppm	20	1.95			
250 ppm	3	5.25			
500 ppm	4	8.87			
750 ppm	15	11.06			
1000 ppm	9	14.82			

[a] IP, mean of two replicate analyses; Percentage IP decrease = $100(IP_{max} - IP_{min})/IP_{max}$.
[b] $F = IP_x/IP_o$; IP_x = IP of UFOME in the presence of each antioxidant at week zero; IP_o = initial IP of UFOME = 3.42. For other abbreviation see Table 1.

improve linearly for vitamin E, BHA, and BHT at concentrations from 500 to 1000 ppm. These antioxidants have almost no effect on the induction periods of UFOME after reaching their maximal performances at 500 ppm.

The structures of vitamin E, BHA, BHT, TBHQ and PG are shown in Scheme 1. All of them have an aromatic ring with at least two different functional groups substituted at the *ortho*, *meta*, and *para* positions of the ring. The antioxidative properties of these antioxidants against UFOME can be predicted by their chemical structures. Based on their electronegativities, the antioxidants having active hydroxyl groups (–OH) can be ranked as: BHA = BHT < TBHQ < PG. During the oxidation of UFOME in the presence of oxygen, the reactant will inevitably release the reactive by-products called "free radicals." The active hydroxyl group in the antioxidants tested can provide protons (H) that combine with the oxidized free radicals released, thus decelerating the rate of oxidation when UFOME is used as biofuel.

BHA and BHT have only one hydroxyl group with different substituents, i.e., –OMe and –Me connected to the *para* position of the ring, respectively. Because the –OMe group in BHA is an electron-withdrawing group (15) owing to the ability of carbanium (Me) to withdraw sufficient electron density from the oxygen donor having unshared pairs of electrons (Scheme 2), the aromaticity of the six-membered ring becomes more polarized and more electrons are delocalized near the carbon adjacent to the –OMe group. As a result, the hydroxyl group becomes more likely to be oxidized into a quinone structure (16). Hence, the release of more protons to eliminate the excess of free radicals is more favorable compared with the hydroxyl group in BHT. In BHT the methyl group ($-CH_3$) connected to the aromatic ring is an electron-donating group, and it tends to donate an electron to the aromatic ring. This phenomenon deters the formation of quinone structures and the release of its protons to combine with oxidized free radicals. Thus, BHT is less efficient as an antioxidant than BHA. Surprisingly, vitamin E is the least effective compared with the other antioxidants in this study, though it appears to be different in its structure. That is, at the *para* po-

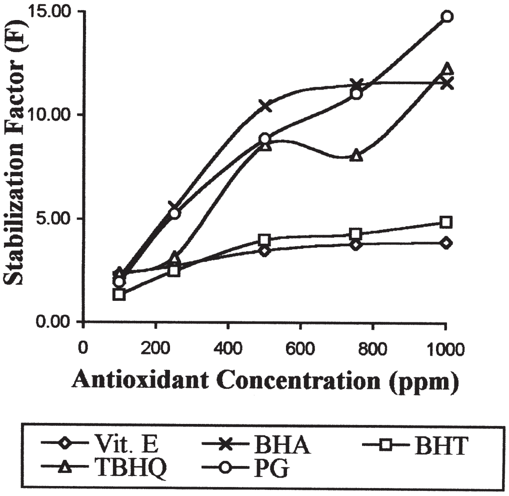
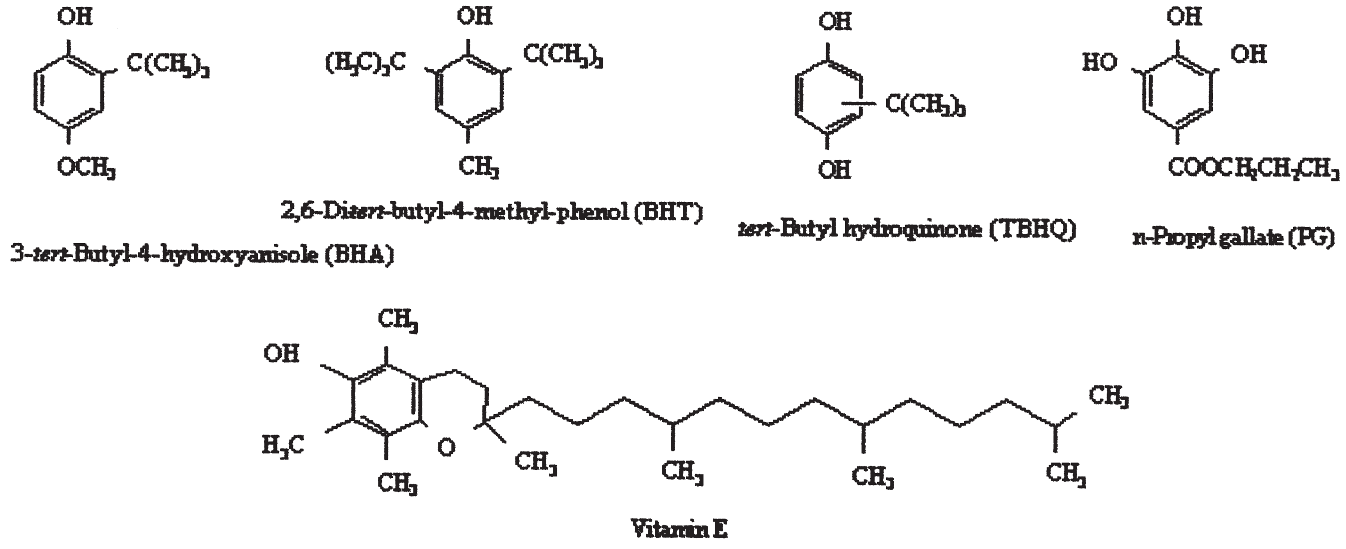


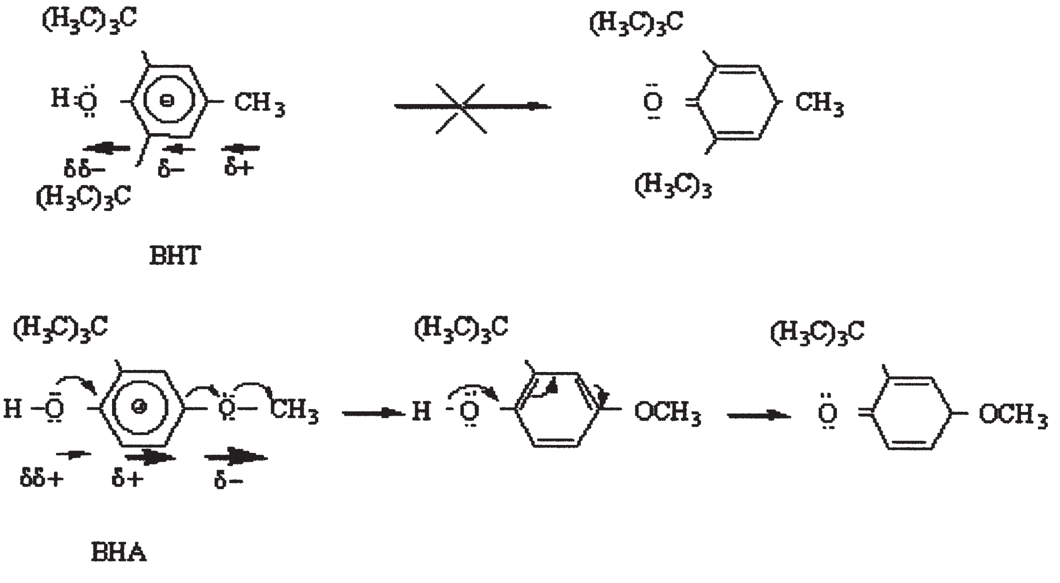
FIG. 2. The effectiveness and influence of vitamin E (◇), BHT (□), TBHQ (△), BHA (×), and PG (○) on the oxidative stability of UFOME as reflected by the stabilization factor (*F*) values at various antioxidant concentrations. *F* values were tabulated in Table 2. For abbreviation see Figure 1.



SCHEME 1

sition is an electron-withdrawing group (–OR), which has very weak field strength. Moreover, its *ortho* and *meta* positions are connected to three similar electron-donating groups (–CH_3) that restrict its release of protons.

The antioxidants BHA, TBHQ, and PG have electron-withdrawing groups at the *para* position of the aromatic ring whereas BHT has an electron-donating group. In order of decreasing strength, the electron-withdrawing properties of BHA, TBHQ, and PG are: COOR (PG) > OR (BHA) > OH (TBHQ). A greater number of active hydroxyl groups in these antioxidants, in the order of PG > TBHQ = BHA, could compensate for the polarization effect of the aromatic ring by favoring the release of more protons to initiate the formation of a quinone structure. PG, which has three hydroxyl groups, has a carboxyl group at the *para* position of the aromatic ring. The carboxyl moiety contains a propyl group, which is a relatively strong electron-donating group compared with a methyl group. It has some deactivating effect on the carboxyl's ability to withdraw electrons from oxygen atoms having lone pairs of electrons. However, the electron density in the aromatic ring is not weakened, as in the case of BHA and TBHQ, because PG has three active electron-donating hydroxyl groups. Thus, the tendency of PG in its quinone oxidative state to release the greatest number of protons is the most favorable, thereby PG performs most effectively to prevent the auto-oxidation of UFOME. TBHQ is less effective than BHA



SCHEME 2

because its hydroxyl group at the *para* position is a weaker electron-withdrawing group than the –OMe group of BHA connected at the same position.

ACKNOWLEDGMENT

The authors wish to thank the Director-General of MPOB for permission to publish this paper.

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[Received August 30, 2005; accepted August 16, 2006]