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Synergistic Effects of Antioxidants on the Oxidative Stability of Soybean Oil- and Poultry Fat-Based Biodiesel

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Abstract Biodiesel is an alternative fuel composed of saturated and unsaturated methyl ester fatty acids that is very prone to oxidation attack. Exposure to air, heat, light, and metallic contaminants can lead to autoxidation, and the degradation of fuel properties such as kinematic viscosity and total acid number. This study examines the effectiveness of blends of primary antioxidants from combinations of butylated hydroxyanisole (BHA), propyl gallate (PG), pyrogallol (PY) and *tert*-butyl hydroquinone (TBHQ) to increase oxidative stability. Results indicate that binary antioxidant formulations: TBHQ:BHA, TBHQ:PG and TBHQ:PY were most effective at 2:1, 1:1, 2:1 weight ratio, respectively in both distilled soybean oil- (DSBO) and distilled poultry fat- (DPF) based biodiesel. Antioxidant activity increased as the loadings were increased. The synergisms of the antioxidant pairs were different with different biodiesel types, suggesting a dependence on the fatty acid methyl ester (FAME) composition. The best synergistic effect was observed with the TBHQ:BHA blends while the best stabilization factors (SF) were achieved by using the TBHQ:PY blends. Quantification of antioxidant content in stored biodiesel with TBHQ:PY blend demonstrates that the main factor of synergy is the regeneration of PY by TBHQ.

Keywords Biodiesel · Biobased products · Autoxidation · Lipid chemistry · Lipid analysis

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Introduction

Biodiesel, which is derived from vegetable oils or animal fats [1, 2] through transesterification to produce mono-alkyl esters, exhibits fuel properties comparable with conventional petroleum diesel [3–5]. Biodiesel provides enhanced lubricity properties and produces low exhaust emissions, such as particulate matter, polycyclic aromatic hydrocarbons, sulfur dioxide and smoke [6, 7]. However, significant problems associated with the commercial acceptance of biodiesel include increase nitrogen oxides emissions, poor cold flow properties and oxidative stability.

Lipid autoxidation reactions have been investigated extensively [8–11]. Through the resultant transesterification of lipid materials, biodiesel exhibits the same fatty acid profile as the source oil or fat. Since many vegetable oils and animal fats possess significant amounts of unsaturated fatty acids (UFA), oxidative stability is of concern, especially under long periods in storage conditions above ambient temperatures, with exposure to air and/or light, and/or in the presence of some contaminants [12]. The main fatty acid methyl esters (FAMEs) in biodiesel are saturated C16, and saturated and unsaturated C18; C18 contain one double bond for oleic acid (C18:1), two for linoleic acid (C18:2), and three for linolenic acid (C18:3). Relative oxidation rates were found to increase as the degree of saturation increased [13]. The polyunsaturated fatty acid chains contain a higher total number of reactive bis-allylic sites than the monounsaturated ones, and hence are more prone to oxidation. Also, dimerization and oligomerization can occur from peroxides, formed from the reactions of radicals through oxidation, reacting with other fatty acids. Fang and McCormick [14] reported that dimerization of the peroxides is not the sole mechanism for

molecular weight growth and formation of deposits in biodiesel, but all possible mechanisms involve peroxide formation at the initiation reaction of oxidation. This stresses the importance of minimizing peroxide formation in biodiesel manufacturing and handling, hence the need for antioxidants.

Inhibition of oxidation through the use of antioxidants has been observed to increase the induction period (IP) of biodiesel to varying degrees [15–17]. Tang et al. [18] studied the effectiveness of eight antioxidants: alpha-tocopherol (α-T), butylated hydroxyanisol (BHA), butyl-4-hydroxytoluene (BHT), tert-butyl hydroxyquinone (TBHQ), 2, 5-di-tert-butyl-hydroquinone (DTBHQ), propyl gallate (PG), pyrogallol (PY) and a commercial antioxidant, Ionol BF in short- and long-term storage. The naturally occurring antioxidant, α-T, was found not to be an effective antioxidant, only slightly increasing the IP of the biodiesel. The study indicated that the synthetic antioxidants were more effective in increasing the IP of biodiesel, and biodiesel from different feedstocks showed different IP improvement. BHA, TBHQ, PG and PY resulted in the best IP improvement at different concentrations; however, long term storage revealed that PG and PY rapidly lost effectiveness with time while TBHQ was stable throughout as much as 9 months of storage.

Cooperative effects (synergy) of antioxidants in fats and oils are documented in several studies [19–24]. Miranova et al. [19] reported that mixtures of α-T and myricetin produced a synergistic effect during the autoxidation of triglycerols of sunflower oil, where the best interaction was achieved using equal molar ratios of the antioxidants at concentrations lower than 0.001 M. Kinetic analysis demonstrated that α-T regenerates myricetin during autoxidation. A study conducted by Becker et al. [20] showed that binary combinations of four antioxidants (α-T, astaxanthin, quercetin and rutin) revealed factors that may affect the synergism and antagonism of antioxidant blends: structural organization of the lipid; solubility, polarity and the hydrophilic nature of the antioxidants. A transfer of hydrogen from BHT regenerated BHA resulting in higher antioxidant activity than the components used singly in soybean oil, lard and methyl oleate [21]. Niki et al. [22] demonstrated synergism between α-T and ascorbic acid in methyl linoleate; it was observed that ascorbic acid donates hydrogen to regenerate α-T. Antioxidants (BHT, alkylated phenol/dithiophosphoric acid ester/diphenylamine and zinc diamyl dithiocarbamate) and anti-wear additives combinations were also reported to have synergistic effects in vegetable oil-based lubricants based on the FA profile (especially on the polyunsaturation) and the effectiveness of the inhibitors [23, 24].

Although a few studies [15–18] reveal that antioxidants improve the oxidative stability of biodiesel, and reports have been made about the synergism of antioxidants in edible oils and fats [19–22] and in lubricating oils [23, 24], the synergy of synthetic antioxidants in biodiesel has not been fully elucidated. The objectives of this paper are: (a) to investigate the synergistic effects of synthetic antioxidants: BHA, PG, PY and TBHQ in binary formulations on biodiesel; (b) to correlate the degree of unsaturation to the antioxidant activity; and (c) to develop a mechanistic understanding of the synergistic effect.

Experimental Procedures

Materials

Soybean oil (SBO) based-biodiesel was obtained from NextDiesel (Adrian, MI, USA) and poultry fat (PF) based-biodiesel was obtained from Biodiesel Industries (Denton, TX, USA). Distilled soybean oil (DSBO) and distilled poultry fat (DPF) biodiesels were produced at 185 °C and 4.7 mbar using a Koehler (Bohemia, NY, USA) K80200 vacuum distillation apparatus to minimize the effects of minor components, naturally occurring antioxidants, as well as other volatile contaminants on the oxidative stability of the biodiesel.

The synthetic antioxidants: BHA (98.5%), PG (≥98%), PY (99%) and TBHQ (97%) were acquired from Sigma-Aldrich Inc. (St. Louis, MO, USA). The chemical structures of antioxidants are shown in Fig. 1. Four commercial antioxidants (A, B, C and D) were obtained from their respective producers.
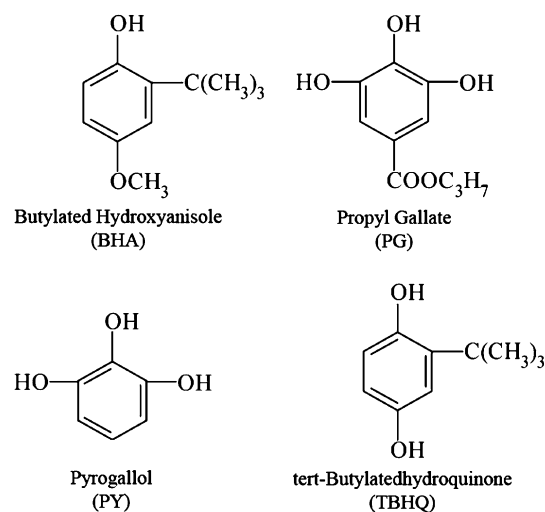
Fig. 1 Chemical structures of antioxidants: BHA, PG, PY and TBHQ

Methods

Sample Preparation

The different binary blends were prepared by mixing different solid phase antioxidants at weight ratios of 1:0, 0:1, 1:1, 2:1, 1:2, 3:1 and 1:3. The antioxidant blends, with a total loading of 1,000 ppm, were added to DSBO-B100 and DPF-B100 and mixed thoroughly. The effects of loading (1,000, 500, 250, 200, 150, 100, and 50 ppm) for selected blends were also investigated. Extra care was taken to avoid contamination and degradation of the antioxidants used. Freshly distilled samples without any additives were used as the control for DSBO and DPF.

Composition

The FAME composition of the original and the distilled biodiesel was determined using a Perkin-Elmer (Bellefonte, PA, USA) Clarus 500 GC–MS with a split automatic injector and an Rtx-WAX column (60 m length, 0.25 mm ID and 0.25 µm coating). Detailed analysis procedures have been described elsewhere [25].

The determination of the amount of natural antioxidant was done with the use of a Perkin-Elmer Clarus 500 GC with a flame ionization detector (FID). The unit has an automatic unit micro liter sampler and was fitted with a PE-5HT column (15 m length, 0.32 mm ID and 0.1 µm film thickness) with the following program: initial temperature at 50 °C held for 1 min and then ramped by (a) 15 °C/min to 180 °C, (b) 7 °C/min to 230 °C, and (c) 30 °C/min to the final temperature of 380 °C where it was held for 10 min. The system used hydrogen gas (99.9999%, Cryogenic Gases, Detroit, MI) flowing at 3 mL/min as the carrier gas. Details of the procedure have been described elsewhere [26].

Oxidative Stability

The oxidative stability of B100 biodiesel samples was determined using a Metrohm 743 Rancimat (Herisau, Switzerland) per the EN14112 method. In this test, a 10 L/h stream of dry air is bubbled into 3 g (B100) samples maintained at 110 °C, volatile oxidation products such as

carboxylic acids, mainly formic acids [27], are carried through the detector chamber containing deionized water. The change in conductivity is measured and recorded every 36 s (0.01 h). The increase in conductivity is measured as a function of time until maximal change which reflects the IP.

TAN and Kinematic Viscosity

TAN is expressed as the milligrams of KOH per gram of sample required to reach the equivalence point. TAN values were determined based on the ASTM D664 method using a Brinkman Metrohm 809 Titrando instrument (Westbury, NY, USA). The kinematic viscosity of biodiesel was determined by measuring the time for a volume of liquid to flow under gravity through a calibrated capillary viscometer at 40 °C as per ASTM D445, utilizing the Rheotek AKV8000 automated kinematic viscometer (Poulten Selfe & Lee Ltd., Essex, England).

Tests results were reported as mean of triplicate runs with values (errors are within ± 5%) compliant with the repeatability limits of their respective standard method.

Results and Discussion

Oxidation and Analysis of Biodiesel

The biodiesel was vacuum distilled to eliminate effects on the oxidative stability by impurities such as trace metals. The trace Cu and Fe levels within the distilled biodiesel were determined using a Perkin-Elmer Optima 2100 DV optical emission spectrometer (Restek, Bellefonte, PA, USA) and were found to be in the range of 0.0001 and 0.001 ppm, respectively. Oxidation of the samples using the Rancimat at 110 °C with the addition of 0.01 and 0.02% citric acid metal chelator indicated a negligible effect of metals in the oxidation.

Table 1 summarizes the IP, TAN and viscosity results for the distilled and undistilled biodiesel along with the limit values in the biodiesel standard. FAME compositions, total SFA and UFA, and natural AO content of the biodiesel are shown in Table 2. FAME compositions of SBO and DSBO had no significant differences and the SBO

Table 1 Specifications related to the quality in biodiesel standards

Specification	Methods	Unit	ASTM D6751-08	EN 14214	Biodiesel samples			
					SBO	DSBO	PF	DPF
Oxidative stability (IP)	EN 14112	h	3 min	6 min	2.68	0.17	0.52	0.93
Linolenic acid content (C18:3)	EN 14103	% m/m	–	12 max	7.5	7.2	1.4	1.4
Total acid number (TAN)	ASTM D664, EN 14104	mg KOH/g	0.500 max	0.500 max	0.525	0.309	0.550	0.360
Kinematic viscosity (v)	ASTM D445, ISO 3104/3105	mm^2/s	1.9–6.0	3.5–5.0	4.14	3.99	4.32	4.29

Table 2 Fatty acid methyl ester (FAME) composition and the physical properties of SBO-, DSBO-, PF- and DPF-based biodiesel samples

FAME composition (wt) %										Natural AO (ppm)
FA	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	$\sum$SFA	$\sum$UFA	
SBO	0	10.2	0	4.3	22.6	55.5	7.5	14.5	85.5	167
DSBO	0	12.4	0	4.1	22.1	54.2	7.2	16.5	83.5	40
PF	1	20.1	3.1	7.3	40.1	27	1.4	28.4	71.6	–
DPF	1.6	25.9	4.1	6.1	36	25	1.4	33.6	66.4	–

FAME profile is in agreement with other studies [28, 29]. On the other hand, distillation of PF to DPF resulted in a decrease in the total UFA profile from 71.6 to 66.4% which is mainly due to C18:1 and C18:2. Consequently, the total SFA composition rose because of C16:0. This instance may be attributed to mild oxidation during the distillation process causing the unsaturated component of DPF to drop.

A study of the kinetics of lipid autoxidation reported that relative oxidation rates of UFA are as follows: C18:3 > C18:2 $\gg$ C18:1 [13]. In general, the higher the degree of unsaturation, especially the polyunsaturation, the higher the rate of oxidation with the total amount of C18:3 and C18:2 for SBO (63%) much higher than PF (28.4%), the IP for SBO should be expected to be much lower than the IP of PF. However, in this case it is the opposite, with the IP of SBO (2.68 h) being much higher than that of PF (0.52 h). This is likely due to the amount of natural antioxidants present in the biodiesel, as indicated by previous studies [12, 19] which have concluded that the oxidative stability of biodiesel depends on the FAME compositions as well as other factors such as natural antioxidant content. SBO was found to contain 167 ppm of natural antioxidant while none could be detected in PF. This finding confirms the higher oxidative stability observed for vegetable oil-based biodiesel than animal fat-based biodiesel [16]. In addition, this finding suggests that the amount of natural antioxidant plays a major role in determining the oxidative stability of biodiesel.

Upon distillation, the biodiesel minor components (sterols, glycerides and natural antioxidant) were greatly reduced. The natural antioxidant content in SBO dropped from 167 to 40 ppm, while the IP decreased from 2.68 to 0.17 h, on the other hand, the IP of DPF (0.93 h) was higher than the IP of PF (0.52 h). Even though there is a concern on the validity of an IP below 1 h, this reproducible observation may be a result of the decrease of the total UFA, removal of the some oxidation products, volatile impurities and polymeric materials in the vacuum distillation. Likewise, the reduction of TAN, conforming to ASTM D6751-08 and EN 14214, and viscosity values support this conclusion.

The IP for all the biodiesel samples and the TAN value for the undistilled biodiesel samples did not meet the ASTM D6751-08 and EN 14214 specifications suggesting that the biodiesel samples under study were already significantly oxidized. The results also suggest that the viscosity is not greatly affected by the level of oxidation; consequently, it is not a good indicator of the level of oxidation.
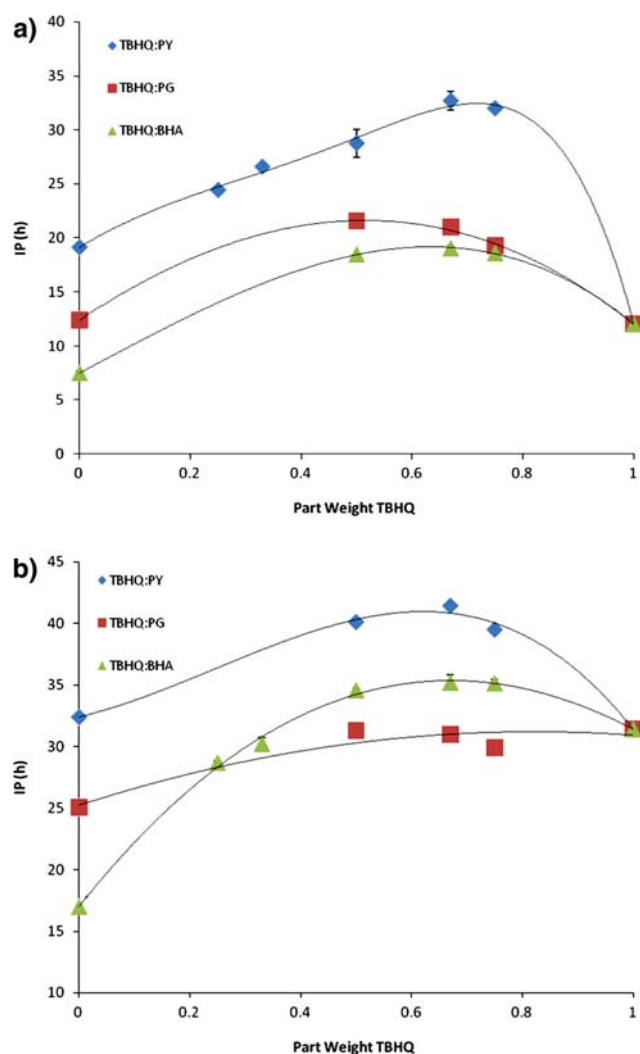
Antioxidant Blending

The effects of blending ratios of TBHQ: BHA, PG and PY on the IP of B100 are shown in Fig. 2. The highest IP (32.79 h) was achieved by using a 2:1 weight ratio (667 ppm TBHQ, 333 ppm PY) in DSBO. Similarly, the highest IP (43.49 h) was obtained by using this same antioxidant binary formulation in DPF. As a general observation, using any blend ratio of TBHQ:BHA, TBHQ:PG and TBHQ:PY in DSBO and DPF resulted in an improved IP greater than when using the individual antioxidants by themselves at the same loading, regardless of type of biodiesel.

The effects of the different antioxidant blends on the pertinent parameters relating to oxidative stability (IP, TAN, viscosity and stabilization factor (SF) which expresses the antioxidant effectiveness by the IP ratio of inhibited and uninhibited oxidation [19]) are presented in Table 3. The most effective antioxidant is PY, followed by PG, TBHQ and finally BHA during oxidation of DSBO and DPF at 110 °C is in good agreement with previous studies [18, 30]. The antioxidant effectiveness (based on SF) in both DSBO and DPF is highest with PY (individual or in binary formulation). The SF is expressed as:

$$SF = {IP_1}/{IP_0} \qquad (1)$$

where IP_1 is the IP with inhibitor while IP_0 is the IP of the control sample without antioxidant.

Similar to the previous study [18], biodiesel with PG or PY loading produced increased TAN values (Table 3). The highest TAN values 0.521 and 0.433 mgKOH/g with 1:1 TBHQ:PG in DSBO and DPF, respectively, were observed. On the other hand, there was very little difference in viscosity, as the increase in viscosity is linked more to secondary degradation products.

Fig. 2 The resultant IP values of using binary antioxidant blends at 1,000 ppm loading: **a** in DSBO, and **b** in DPF

According to Miranova et al. [19], inhibition of oxidation can be expressed using two kinetic characteristics: the effectiveness and the strength of the inhibitor. The effectiveness of the inhibitor represents the possibility of blocking the propagation phase through interaction with the peroxyl radicals, which is responsible for the duration to reach the IP. The strength gives the possibility of antioxidant moieties participating in other side reactions which may change the oxidation rate during the course of IP. For our study, we focus on the effectiveness of the inhibitor systems, expressed as Eq. 1 above.

The resulting improvement in IP (considering the stability reported in our previous study [18]) and the SF are in the order of PY > PG > TBHQ > BHA in DSBO and DPF (Table 3). In DPF, the SF for TBHQ and PG are similar and close to the SF for PY. This is quite different from the SFs in DSBO. In general PY (individual or in blends) have highest SF in both DSBO and DPF.

Antioxidant Synergy

Inhibitors sometimes can reinforce each other, synergistically. The percent synergism (%SYN) is calculated on the basis of the IPs observed as follows [8]:

$$\% \, \mathrm{SYN} = \frac{(\mathrm{IP_{mix}} - \mathrm{IP_0}) - [(\mathrm{IP_1} - \mathrm{IP_0}) + (\mathrm{IP_2} - \mathrm{IP_0})]}{[(\mathrm{IP_1} - \mathrm{IP_0}) + (\mathrm{IP_2} - \mathrm{IP_0})]} \times 100\%$$

(2)

where $\mathrm{IP_{mix}}$, $\mathrm{IP_0}$, $\mathrm{IP_1}$ and $\mathrm{IP_2}$ are the induction periods of the samples containing the mixture of inhibitors, of the control sample, and of the samples containing the individual antioxidants. A positive value defines a synergistic effect between the implicated antioxidants, while a negative value corresponds to an antagonistic effect.

The IP using the same antioxidants is much higher in DPF than in DSBO. Sharma et al. [23] concluded that antioxidants increased their response in oils with a lower amount of polyunsaturation which was the case for the degree of polyunsaturation of DPF versus DSBO. Similarly, all IP improvement using antioxidant blends in DPF were greater than in DSBO. In our study, all binary blending of the different antioxidants produced higher IP compared to the sum of IPs of each antioxidant component in DSBO (Table 3), hence a positive %SYN value. However, in DPF only the 2:1 TBHQ:BHA weight ratio produced a positive synergy (13.36%), while 1:1 TBHQ:PG and 2:1 TBHQ:PY resulted in antagonism (−13.76 and −3.93%, respectively), this contradicts the significant IP results above. Although there was observed negative synergy, the huge IP increase in DPF is still noteworthy. Details of this phenomenon may be linked to the high level of oxidation of the parent PF-based biodiesel. On the other hand, it was reported that the effectiveness of antioxidants depends on the nature biodiesel feedstock [18], thus, for this study we note the synergy of antioxidants is also feedstock dependent.

Based on the previous studies [19–24] on antioxidant synergy and this investigation, we propose two schemes of interaction: (a) hydrogen donation of the more active antioxidant to regenerate the other antioxidant and (b) formation of heterodimer from the moieties of the antioxidant during autoxidation. Figure 3a and b show the two proposed schemes that are assumed to work simultaneously within the system to arrive at total synergistic effect.

Antioxidant Regeneration

Primary antioxidants act as radical scavengers to inhibit oxidation [15–18, 23]. Hydrogen is abstracted from the active hydroxyl (–OH) groups and then donated to the free

Table 3 Inhibited oxidation parameters of DSBO- and DPF-based biodiesel samples

Biodiesel	Antioxidant	Concentration		Ratio		IP (h)	TAN (mg KOH/g)	Viscosity, 40 °C (mm²/s)	SF	%SYN
		ppm	M × 10⁻⁴	Weight	Molar					
DSBO	TBHQ	500	3.5			6.85			40.29	
	TBHQ	667	4.6			8.73			51.35	
	BHA	333	2.1			4.00			23.53	
	PG	500	2.7			10.46			61.53	
	PG	1,000	5.4			14.34	0.546		84.35	
	PY	333	3			15.82			93.06	
	PY	1,000	9			19.34	0.611		113.76	
	TBHQ: BHA	1,000	6.7	2:1	2:1	19.51	0.342	4.03	114.77	56.09
	TBHQ:PG	1,000	6.2	1:1	1:1	21.55	0.521	4.02	126.76	25.99
	TBHQ: PY	1,000	7.6	2:1	1:1	32.69	0.431	4.02	192.29	34.32
DPF	TBHQ	500	3.5			17.43			18.74	
	TBHQ	667	4.6			21.05			22.63	
	BHA	333	2.1			11.05			11.88	
	PG	500	2.7			19.52			20.99	
	PG	1,000	5.4			28.31	0.569		30.44	
	PY	333	3			25.11			27	
	PY	1,000	9			34.15	0.494		36.72	
	TBHQ: BHA	1,000	6.7	2:1	2:1	35.21	0.406	4.33	37.86	(13.36)
	TBHQ:PG	1,000	6.2	1:1	1:1	31.19	0.433	4.31	33.54	(−13.76)
	TBHQ: PY	1,000	7.6	2:1	1:1	43.49	0.371	4.30	46.76	(−3.93)

radical to inhibit the rate of oxidation. The resulting antioxidant is a stable radical that can react with other fatty acid free radicals and further contribute to oxidation inhibition. In the same manner, when antioxidants are present in combinations, one antioxidant can become a hydrogen donor for the other, thus regeneration takes place, as in BHA and BHT [21]. Through this mechanism, the donor is consumed while the hydrogen acceptor antioxidant propagates its oxidation inhibition.

In Fig. 3a, the proposed mechanism is the regeneration of PY in the TBHQ:PY blends. PY, being the more effective antioxidant, readily donates its hydrogen from its hydroxyl group to fatty acid free radicals creating an antioxidant radical in the process. TBHQ then transfers hydrogen to the antioxidant radical to regenerate it back to PY. In the process, TBHQ was converted to a radical that can form stable products with other free radicals, this together with the interaction and regeneration of PY represents an effective synergistic effect between the two antioxidants. Antioxidant quantification using GC-FID from a 3 month storage study of DSBO with 2:1 TBHQ:PY indicated that the consumption of TBHQ is greater than the consumption of PY, with the total amount of PY close to its original value (values not shown here). The results support the assumption for the regeneration of PY by TBHQ.
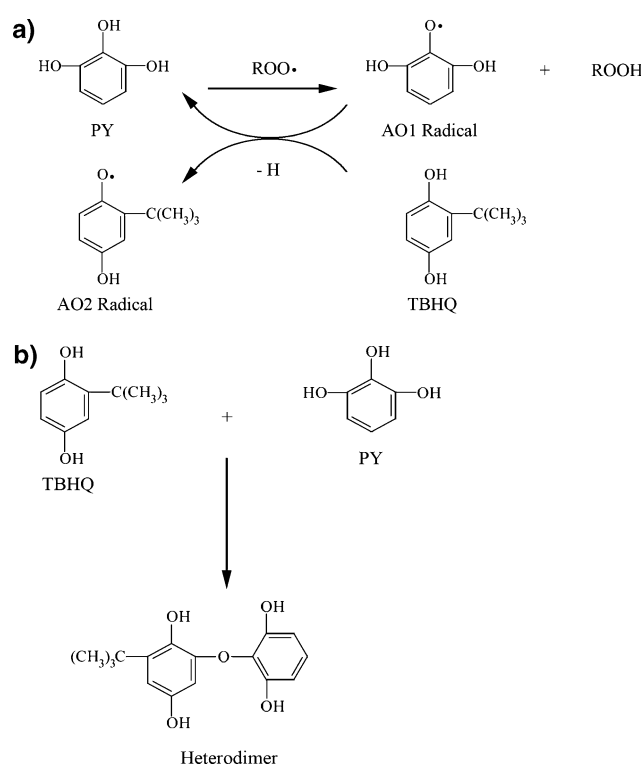
Fig. 3 Proposed mechanisms for the synergistic interaction between TBHQ and PY: **a** antioxidant regeneration and **b** antioxidant heterodimer formation

Heterodimer Antioxidant

Primary antioxidants degrade to form different species/ moieties that participate in the reaction during the autoxidation of fats and oils. Kikugawa et al. [31] reviewed the study of degradation effects in the mechanism of action of primary antioxidants, properties of degradation products and the role of synergists (antioxidant class) in regenerating primary antioxidants. Degradation under autoxidation of fats and oils in thermal oxidation, active oxygen method and UV/Vis irradiation were carried out, formations of moieties and antioxidant dimers were observed in primary antioxidants. TBHQ yielded derivative products that retain antioxidant properties, some even have higher activity than TBHQ based on different substrates [32]. Degradation of PG resulted in the formation of species that retained antioxidant properties, a similar analogy can be used in the case of PY.

Antioxidant mixtures initiated the formation of heterodimers from the degradation products of the primary antioxidants. Based on previous studies [33, 34], mixtures of BHA and BHT produced heterodimers of comparable activity to that of BHT. Likewise, BHT and PG produced two heterodimers composed of two phenols each, the products were found to be better antioxidants in SBO. Cuvelier et al. [35] established the relationship between structure and the activity of these phenolic antioxidants. Combinations of two phenols were found to increase efficiency as compared to lone phenols. From our results of antioxidant blending, the best combination was achieved by using TBHQ:PY, and it can be inferred that the degradation product moieties of both the primary antioxidants are effective antioxidants as well. In Fig. 3b, the dimerization of these moieties produced new antioxidant species that contain two phenols which in effect are better antioxidants than the parent antioxidants. The synergism is a result of the effect of increase in activity of these resultant heterodimers coupled with the effectiveness of the original antioxidants. Proper detection/quantification of such antioxidant moieties/heterodimers within the biodiesel sample system is still under study.

Effect of Antioxidant Concentration

An increase in the IP was observed as antioxidant loading was increased in both DSBO and DPF. In Fig. 4a, a nearly linear increase in IP was observed up to 500 ppm, and leveling off from 500 to 1,000 ppm. The leveling observation may be attributed to the possible saturation of biodiesel with the antioxidant blend. Another possibility may be related to the dissolution of the solid-phase antioxidants, as reported by Dunn [36] for both PY and PG. Interestingly, for DPF a more linear concentration effect and
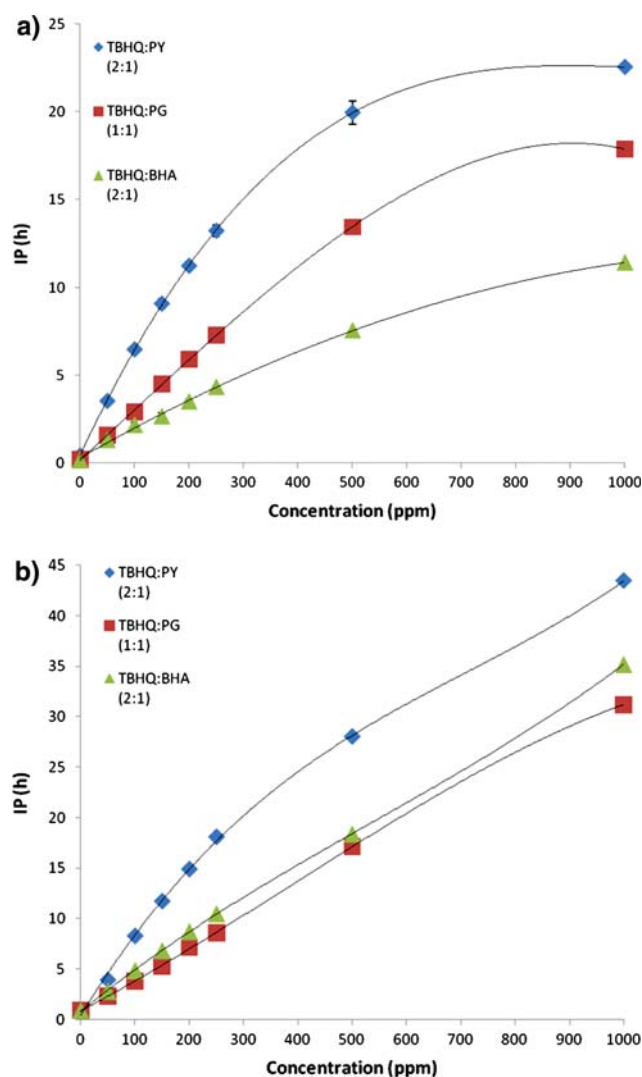

Fig. 4 The IP values at varying antioxidant blend loadings of 2:1 TBHQ:BHA, 1:1 TBHQ:PG and 2:1 TBHQ:PY in **a** DSBO and **b** DPF

greater magnitude were observed (Fig. 4b), this shows the increased effect of the antioxidants at lower polyunsaturation to a point of maximized efficiency without saturation.

Compared with the four commercial antioxidants (A, B, C and D) at equal loading of 200 ppm (active ingredient content), the IP with a 2:1 TBHQ:PY formulation in both DSBO and DPF was much higher (Fig. 5). Similarly, all binary formulation in Table 3 produced better IP values as compared to the commercial antioxidants.

Conclusion

The following conclusions can be drawn from the study of binary antioxidant blending in DSBO and DPF:
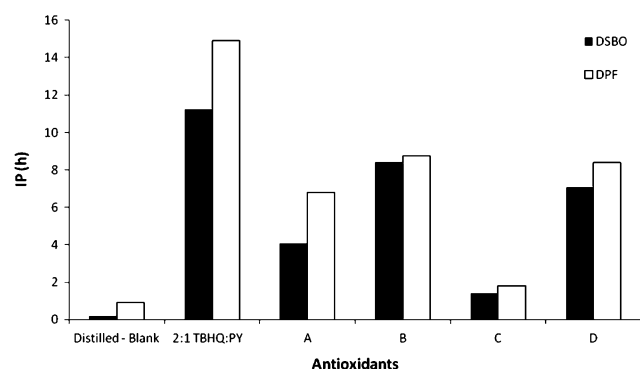
Fig. 5 Comparison of the IP values of DSBO- and DPF-based biodiesel utilizing 2:1 TBHQ: PY and four commercial antioxidants (A, B, C and D) at 200 ppm total loading

1. The different types of biodiesel have different levels of oxidative stability based on their FAME composition and more predominantly, their natural antioxidant level. The effect of the degree of oxidation undergone by the fuel must also be considered.

2. BHA, PG, PY and TBHQ produced higher IP improvement in biodiesel feedstock with lower amount of polyunsaturation, hence a dependence on feedstock. Likewise, the synergies of the antioxidants were also different depending on the biodiesel feedstock.

3. The best synergy was produced by the 2:1 TBHQ:BHA blend while the best improvement in IP was achieved by using the 2:1 TBHQ:PY blend. Considering %SYN and SF, these two formulations are good choices for long term storage.

4. Quantification of antioxidant content in stored biodiesel demonstrates that TBHQ regenerates the PY. This is the dominating factor behind the synergistic effect of the TBHQ:PY blend.

5. Antioxidants behave similarly in fats and oils, and in biodiesel. The IP improvement was feedstock dependent taking emphasis on the degree of polyunsaturation, more importantly synergistic effect can also be observed in biodiesel.

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