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ORIGINAL PAPER

The Effect of Natural and Synthetic Antioxidants on the Oxidative Stability of Biodiesel

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Abstract A significant problem associated with the commercial acceptance of biodiesel is poor oxidative stability. This study investigates the effectiveness of various natural and synthetic antioxidants [α-tocopherol (α-T), butylated hydroxyanisole (BHA), butyl-4-methylphenol (BHT), *tert*-butylhydroquinone (TBHQ), 2, 5-di-*tert*-butyl-hydroquinone (DTBHQ), ionol BF200 (IB), propylgallate (PG), and pyrogallol (PY)] to improve the oxidative stability of soybean oil (SBO-), cottonseed oil (CSO-), poultry fat (PF-), and yellow grease (YG-) based biodiesel at the varying concentrations between 250 and 1,000 ppm. Results indicate that different types of biodiesel have different natural levels of oxidative stability, indicating that natural antioxidants play a significant role in determining oxidative stability. Moreover, PG, PY, TBHQ, BHA, BHT, DTBHQ, and IB can enhance the oxidative stability for these different types of biodiesel. Antioxidant activity increased with increasing concentration. The induction period of SBO-, CSO-, YG-, and distilled SBO-based biodiesel could be improved significantly with PY, PG and TBHQ, while PY, BHA, and BHT show the best results for PF-based biodiesel. This indicates that the effect of each antioxidant on biodiesel differs depending on different feedstock. Moreover, the effect of antioxidants on B20 and B100 was similar; suggesting that improving the oxidative stability of biodiesel can effectively increase that of biodiesel blends. The oxidative stability of untreated SBO-based biodiesel decreased with the increasing indoor and outdoor storage time, while the induction period values with adding TBHQ to SBO-based biodiesel remained constant for up to 9 months.

Keywords Biodiesel · Biobased products

Introduction

Augmenting petroleum-derived fuels with renewable fuels has gained widespread attention in the past few years. One such renewable fuel is biodiesel, which is defined as the mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, according to ASTM D 6751-07 [1]. Biodiesel offers numerous environmental, economic and energy security benefits, and production capacity has grown considerably in the past 2–3 years, especially in Europe and the USA. Annual biodiesel production in the USA was only 2 million gallons in 2000, increasing to 25, 75 and 250 million gallons in 2004, 2005 and 2006, respectively [2]. Currently, methanol is predominantly used in the transesterification process for biodiesel production [3]. The presence of high levels of unsaturated fatty acid methyl esters (FAME) makes biodiesel very susceptible to oxidation as compared to petroleum diesel [4]. Oxidative processes bring about increased viscosity as a result of condensation reactions involving double bonds, also leading to the formation of insolubles, which can potentially plug fuel filters and injection systems [5]. The increased acidity and increased peroxide value as a result of oxidation reactions can also cause the corrosion of fuel system components, hardening of rubber components, and fusion of moving components [5, 6]. ASTM D6751-07 includes an oxidation stability standard of a 3 h minimum induction period (IP) as measured using the Rancimat test (EN14112) [1]. The European Committee for

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standardization adopted a 6 h minimum IP as the specification [7]. A survey of retail biodiesel samples performed in 2004 indicated that only 4 out of 27 B100 samples met the oxidative stability standard of 3 h and over 85% had an IP less than 2 h [8]. In a 2006 survey report, the range of induction periods in 10 samples was 0.43–4.26 h, and only 3 out of 10 B100 samples met the standard [9]. Our survey [10] of B20, B10, and B5 samples from retail stations also found that over 50% had an IP less than 6 h, the proposed ASTM oxidative stability for B6–B20.

Factors which influence the oxidative stability of biodiesel include fatty acid composition, natural antioxidant content, the level of total glycerin, and the conditions of fuel storage such as temperature, exposure to light and air, and tank material of construction [8, 11, 12]. Previous studies have found that antioxidants can be effective in increasing the stability of biodiesel [4, 11, 13, 14]. However, these effects have not been fully elucidated and results have been inconclusive or conflicting. Sendzikiene et al. [11] found that butylated hydroxyanisole (BHA) and butyl-4-hydroxytoluene (BHT) have nearly the same effect on the oxidative stability of rapeseed oil-, and tallow-based biodiesel, and the optimal level of synthetic antioxidants was determined to be 400 ppm. Mittelbach et al. [15] reported that pyrogallol (PY), propylgallate (PG), and *tert*-butylhydroquinone (TBHQ) could significantly improve the stability of biodiesel obtained from rapeseed oil, used frying oil, and beef tallow, whereas BHT was not very effective. Moreover, Domingos et al. [4] found that BHT had the highest effectiveness for refined soybean oil-based biodiesel, while BHA displayed little effectiveness.

In this study, eight antioxidants (namely α-tocopherol (α-T), BHA, BHT, TBHQ, 2, 5-di-*tert*-butyl-hydroquinone (DTBHQ), ionol BF200 (IB), PG, and PY) were evaluated for their potential to reduce the degree of oxidation of various biodiesels under various storage conditions. Each antioxidant was added at concentrations from 250 to 1,000 ppm to biodiesel derived from soybean oil (SBO), cottonseed oil (CSO), poultry fat (PF), and yellow grease (YG). Moreover, the effect of antioxidants on distilled SBO (DSBO)-based biodiesel, and 20% SBO-based biodiesel blends (B20) were investigated, in comparison to unblended B100.

The major feedstock for biodiesel production is rapeseed oil in Europe, while soybean oil is the major feedstock in the USA. Biodiesel made from soybean oil has a significantly higher content of methyl linoleate (C18:2) and methyl linolenate (C18:3) than that made from rapeseed oil, and therefore soy-based biodiesel demonstrates noticeably poorer oxidative stability [16]. Moreover, in a stability study of biodiesel and biodiesel blends [17], long-term storage of biodiesel was recognized as an important issue. Although the BIOSTAB project conducted in Europe focused on the long-term stability of rapeseed-based biodiesel at room temperature, and outside ambient temperature for up to 24 months [18], few studies have evaluated soy-based biodiesel. Therefore, the long-term stability of soy-based biodiesel with or without synthetic/natural antioxidants was investigated.

Experimental

Materials

Fresh SBO-, CSO-, PF-, and YG-based biodiesel, were obtained directly from Biodiesel Industries (Denton, TX, USA). Certification #2 ultra low sulfur diesel (ULSD) was obtained from Haltermann Products (Channelview, TX, USA). Distilled SBO (DSBO)-based biodiesel was obtained by vacuum distillation at 132–138 °C from SBO-based biodiesel. The blends were made on a volume basis and stored in glass bottles at room temperature. Biodiesel was used as B100 or in a blend with petroleum diesel. A blend of 20% biodiesel with 80% ULSD, by volume, is termed: “B20” [19].

The α-tocopherol (α-T), butylated hydroxyanisole (BHA, 98.5%), butyl-4-methylphenol (BHT), 2, 5-di-*tert*-butyl-hydroquinone (DTBHQ, 99%), propylgallate (PG), *tert*-butylhydroquinone (TBHQ, 97%), and pyrogallol (PY, 99%) were purchased from Sigma–Aldrich Inc. (St Louis, MO, USA). Ionol BF200 (IB) was obtained from Degussa Sant Celoni (Barcelona, Spain). Up to 1,000 ppm of antioxidants was found to dissolve in the biodiesel samples.

Analysis

Composition

The fatty acid composition of each biodiesel was determined using a Perkin–Elmer Clarus 500 GC-MS with a split automatic injector, and a Rtx-WAX (Restek, Bellefonte, PA, USA) column (length: 60 m; ID: 0.25 mm, coating: 0.25 μm). Details of the procedure have been described elsewhere [20].

Oxidative Stability

Oxidative stability of biodiesel with and without the addition of antioxidant was determined according to the Rancimat method using a Metrohm 743 Rancimat instrument (Herisau, Switzerland). The Rancimat test is the specified standard method for oxidative stability testing for biodiesel in accordance with EN14112 [7]. The IP was determined by the measurement of a sudden increase of conductivity upon the formation of volatile acids. Samples of 3 g (B100) or 7.5 g (B20) were analyzed at a heating block temperature of 110 °C and constant airflow of 10 L/h. To evaluate the reliability of the method employed, one group of the tests was carried out in triplicate (Fig. 1), the absolute difference between two independent single test results did not exceed the repeatability limit of EN14112 method.

Kinematic Viscosity and Acid Number

The viscosity of biodiesel at 40 °C was determined following ASTM D 445 using a Rheotek AKV8000 automated kinematic viscometer (Poulten Selfe & Lee Ltd., Essex, England). Acid number of biodiesel was determined according to ASTM D 664 using a Brinkman/Metrohm 809 Titrando (Westbury, NY, USA). The acid number is the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample to a specified end point.

Free Glycerin and Total Glycerin

Free glycerin and total glycerin were determined according to ASTM D 6584 [21] with a Perkin Elmer Clarus 500 GC equipped with a flame ionization detector (GC-FID). A PE-5HT column (15 m in length, with a 0.32 mm internal diameter, and a 0.1 µm film thickness) was used. The column was held at 50 °C for 1 min and then ramped to 180 °C at 15 °C/min, 230 °C at 7 °C/min, and 380 °C at 30 °C/min, respectively. Finally, it was held at 380 °C for 10 min. Hydrogen (99.9999%, Cryogenic Gases, Detroit, MI, USA) was used as the carrier gas with a flow rate of 3 mL/min.

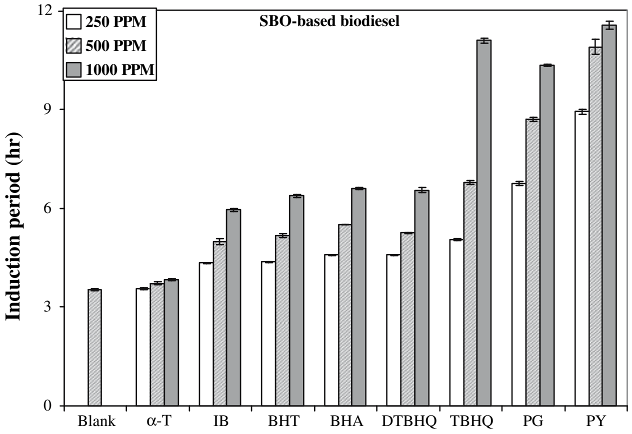

Fig. 1 Effects of concentration of α-T, IB, BHT, BHA, DTBHQ, TBHQ, PG, and PY on the induction period of soybean oil (*SBO*-) based biodiesel

Cloud Point, Pour Point, and Cloud Filter Plugging Point

The CP, PP, and CFPP measurements were done as per ASTM standards, D 2500-25 for CP [22], D 97-96a for PP [23], and D 6371-05 for CFPP [24]. A Lawler model DR-34H automated cold properties analyzer (Lawler Manufacturing Corporation, Edison, NJ, USA) was used to measure the cold flow properties.

Long-Term Storage Stability

SBO-based biodiesel with and without different antioxidants at a concentration of 1,000 ppm were stored in 3-gallon carbon-steel containers. The containers were not purged with nitrogen and were not airtight to allow sample contact with air. One set of samples was stored indoors (at room temperature, 23 °C); the others were stored outdoors (at Michigan ambient temperature from December, 2006 to September, 2007). The recorded ambient temperature value ranged between −13.1 and 27.4 °C (Table 1) according to national climatic data center. Samples of 100 mL were periodically taken for acid number, kinematic viscosity, and Rancimat induction period measurement.

Results and Discussion

Analysis of Biodiesel Samples

Physical property data on the five types of biodiesel samples are given in Table 2. On the whole, most of the values were within the limits given by ASTM D6751-07. Attention should be paid to the high acid number in YG-based biodiesel. SBO- and CSO-based biodiesel met the limit of a 3-h induction period; however, PF-, YG-, and DSBO-based biodiesel did not meet the oxidative stability specification. The IP of CSO-based biodiesel was the highest without added antioxidant among the five types of biodiesel.

The FAME compositions for the different biodiesel samples are shown in Table 3. For SBO-based biodiesel, methyl linoleate (C18:2) is the predominant FAME (48.7%); followed by methyl oleate (C18:1, 25.3%), and methyl palmitate (C16:0, 14.1%). As expected, the FAME compositions of DSBO-based biodiesel and SBO-based biodiesel are nearly identical. Similarly, for YG-based biodiesel, methyl linoleate is the predominant FAME (46.2%), followed by methyl oleate (31.43%), and methyl palmitate (16.1%). CSO-based biodiesel also was predominantly methyl linoleate (53%), but with methyl palmitate having the second greatest abundance (24.7%),

Table 1 Detroit average temperature (°F) from December 2006 to September 2007

Month	Dec. 2006	Jan. 2007	Feb. 2007	Mar. 2007	Apr. 2007	May 2007	Jun. 2007	Jul. 2007	Aug. 2007	Sep. 2007
Max (°C)	4.7	0.2	−4.3	8.4	12.4	21.6	26.7	27.4	26.9	23.9
Min (°C)	−2.2	−7.4	−13.1	−2.5	1.2	8.1	12.2	12.7	15.2	11
Ave (°C)	1.2	−3.7	−8.7	2.9	6.8	14.8	19.4	20.1	21	17.4

Table 2 Physical properties of SBO-, DSBO-, CSO-, PF-, YG-based biodiesel, and ULSD

	ASTM method	ASTM specification[a]	SBO	DSBO	CSO	PF	YG	ULSD
Viscosity, 40 °C (mm^2/s)	D 445	1.9–6.0	4.336	4.050	4.221	4.386	4.552	2.154
Acid number (mg KOH/g)	D 664	0.5 max	0.215	0.179	0.262	0.298	0.515	0.005
Free glycerin (mass %)	D 6584	0.020	0.006	0	0.001	0.001	0.000	–
Total glycerin (mass %)	D 6584	0.24	0.177	0	0.186	0.143	0.016	–
Cloud point (°C)	D 2500	Report	3	4	6	7	13	−25
Pour point (°C)	D 97		−3	0	0	3	0	−36
Cold filter plugging point (°C)	D 6371		−3	0	3	2	−3	−26
Oxidative stability induction period (h)	EN 14112	3 minimum	3.52	0.77	6.57	0.67	2.25	–

[a] Specification as given in Reference 1

followed by methyl oleate (18.5%). The FAME composition of PF-based biodiesel differed greatly from the vegetable oil-based biodiesel, where methyl oleate (36.6%) was the predominant FAME, followed by methyl linoleate (27%), and methyl palmitate (21.8%). For SBO-based biodiesel, total saturated FAME (19.2%) was lower than the values of CSO (28.2%) and PF (30.9%). These results are in good agreement with other reports [16, 25].

The oxidative stability of biodiesel in general depends on the FAME compositions as well as the presence of natural antioxidants in the feedstock. High levels of unsaturated fatty acids make the biodiesel more susceptible to oxidation and resultant shorter induction times [26, 27]. The CSO-based biodiesel has less unsaturated FAME than SBO-based biodiesel, and the IP is indeed higher for CSO-based biodiesel. Moreover, the natural antioxidants appear to remain in the distillation residue following distillation, which results in a lower IP in DSBO-based biodiesel than SBO-based biodiesel while having the same FAME composition [8, 28]. Previous studies have also shown that undistilled biodiesel is more stable when compared with distilled biodiesel [28, 29]. It is interesting to note that PF-based biodiesel has a lower unsaturated FAME content; however it exhibits poor oxidative stability, as compared to SBO-based biodiesel. This can be attributed to lower concentrations of naturally occurring antioxidants in PF-based biodiesel [11]. Similar results have shown that the vegetable oil-based biodiesel is more stable than animal fat-based biodiesel [11].

Table 3 Fatty acid methyl esters (FAME) composition of SBO-, DSBO-, CSO-, PF-, and YG-based biodiesel

FAME composition (wt) %					
FA	SBO	Distilled SBO	CSO	PF	YG
C14:0	0	0	0.76	1.04	0.14
C16:0	14.1	16.02	24.74	21.82	16.12
C16:1	0.7	0.56	0.37	3.71	0.02
C18:0	5.15	5.37	2.68	7.61	3.96
C18:1	25.29	26.51	18.45	36.59	31.43
C18:2	48.7	46.31	52.99	27.02	46.05
C18:3	6.08	5.23	0	1.78	2.28
∑SFA (%)	19.2	21.39	28.2	30.9	20.22
∑UFA (%)	80.8	78.61	71.8	69.1	79.78

Effect of Antioxidants on Oxidative Stability of SBO-, CSO-, PF-, and YG-Based Biodiesel

Figure 1 shows the IP of SBO-based biodiesel as a function of the concentration of added antioxidant. The antioxidants were added to the SBO-based biodiesel in a concentration range between 250 and 1,000 ppm. Generally, the IP of samples were observed to increasing with the increasing antioxidant concentration. PY was found to be the most effective antioxidant in terms of increasing IP over the range of 250–1,000 ppm, while α-T shows the smallest increase. PG was the second most effective antioxidant in the range of concentrations between 250 and 50 ppm, followed by TBHQ; however, TBHQ was more effective than PG at 1,000 ppm. The addition of BHA, BHT, DTBHQ, and IB was found to increase IP, and their effects are very close to each other with BHA exhibiting the highest IP increase at concentrations near 1,000 ppm.

Dunn [30] reported that PG, BHT, and BHA were most effective and α-T least effective in increasing oxidation onset temperature (OT) of soybean oil. In this study, PG, and PY were the most effective antioxidants with an IP > 6 h at 250 ppm and TBHQ improved the IP > 6 h at 500 ppm, while DTBHQ, BHT, and BHA increased IP > 6 h at 1,000 ppm. However, Ruger et al. [31] showed that TBHQ was the most effective for soy based biodiesel as measured by viscosity, while PG increased slightly and BHT and BHA show no improvement. Domingos et al. [4] showed that BHT displayed the highest effectiveness in the concentration range from 200 to 7,000 ppm in refined soybean oil based biodiesel, TBHQ displayed a greater stabilizing potential at 8,000 ppm, while BHA showed no noticeable increase from 2,000 to 8,000 ppm. It should be noted in their study, the original biodiesel had a very low IP (0.16 h), and different range of additive concentrations were utilized [4]. Therefore, different results on antioxidant may be due to differences in the feedstocks of biodiesel, and experimental protocols.

The effects of the concentration of eight antioxidants on the oxidative stability of CSO-, YG-, and PF-based biodiesel are shown in Figs. 2, 3, and 4, respectively. All antioxidants were found to increase the IP with increasing concentration.

For CSO-based biodiesel, TBHQ gave the highest IP increase at 250–1,000 ppm, followed by PY, PG, and DTBHQ (Fig. 2). It was noted that BHA and BHT had almost the same effectiveness with the CSO-based biodiesel. However, the addition of IB displayed no noticeable increase in oxidative stability at 250 and 500 ppm, and only a slight increase at 1,000 ppm. Compared to the SBO-based biodiesel, the effectiveness of antioxidants for CSO-based biodiesel was somewhat different, with TBHQ having the greatest effect on oxidative stability, reaching to 30.2 h at 1,000 ppm.

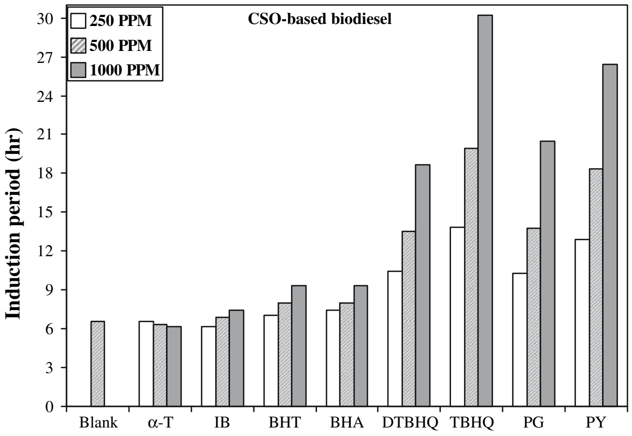

Fig. 2 Effects of concentration of α-T, IB, BHT, BHA, DTBHQ, TBHQ, PG, and PY on the induction period of cottonseed oil (*CSO-*) based biodiesel

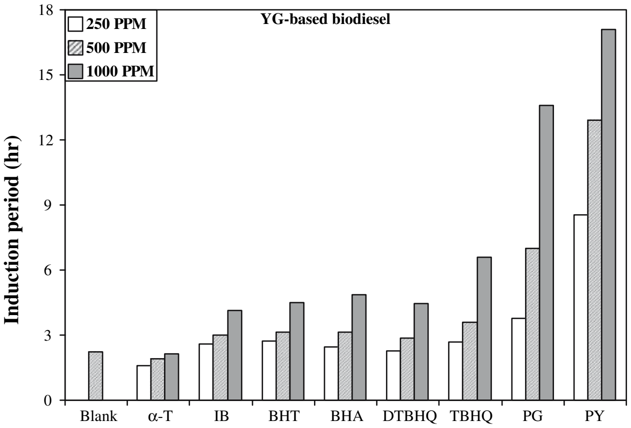

Fig. 3 Effects of concentration of α-T, IB, BHT, BHA, DTBHQ, TBHQ, PG, and PY on the induction period of yellow grease (*YG-*) based biodiesel

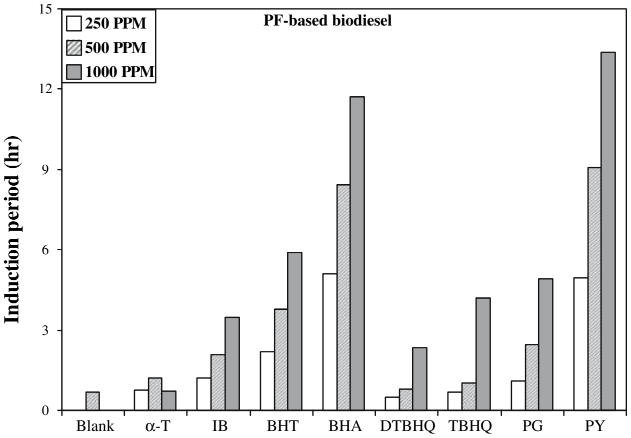

Fig. 4 Effects of concentration of α-T, IB, BHT, BHA, DTBHQ, TBHQ, PG, and PY on the induction period of poultry fat (*PF-*) based biodiesel

For the YG-based biodiesel (Fig. 3), the untreated sample did not reach the ASTM specification for B100 (2.25 vs. 3 h). The effectiveness of antioxidants on the IP of YG-based biodiesel is very similar to SBO-based biodiesel: PY produced the best improvement. PG was the second most effective antioxidant followed by TBHQ, BHA, BHT, DTBHQ, and IB. However, the addition of α-T had no or even negative effects. It was noted that only PY at 250 ppm can improve the IP > 6 h, as well as PG at 500 ppm and TBHQ at 1,000 ppm. The effect of PY, PG, TBHA, BHA, and BHT are consistent with a previous study with frying oil-based biodiesel [15]. Schober et al. [12] also showed that DTBHQ is a good additive for recycled cooking oil methyl ester stability.

For PF-based biodiesel (Fig. 4), the IP of untreated biodiesel was very low (0.67 h). PY was found to provide the greatest improvement, followed by BHA. BHT was the third most effective antioxidant, where the IP can meet the ASTM specification (>3 h) at 500 ppm while PG, TBHQ, and IB are effective only at 1,000 ppm. The addition of DTBHQ even at 1,000 ppm was ineffective in meeting ASTM specs. No noticeable increase in oxidative stability was observed by the addition of α-T. Raemy et al. [32] reported that PG can improve the oxidative stability of chicken fat. In this study, only PY and BHA at 500 ppm could improve the IP > 6 h.

Many antioxidants have been studied for their effects on biodiesel oxidative stability [4, 15, 31, 34], including PG, TBHQ, BHT, BHA, IB, and α-T. In this study, all of the test antioxidants except the natural antioxidant α-T had a measurable positive impact on the oxidative stability of all different types of biodiesel. The pattern of effectiveness for antioxidants on SBO-, CSO-and YG-based biodiesel is BHA–BHT < DTBHQ–TBHQ < PG–PY, with the exception of TBHQ having the most effect on the oxidative stability for CSO-based biodiesel. The different effects of antioxidants can be attributed to their molecular structures. These types of antioxidants have an aromatic ring with different functional groups at different position of the ring. The active hydroxyl group can provide protons that combine with oxidized free radicals, thus delaying the initiation of or slowing the rate of oxidation [13, 33]. Based on their electro-negativities (which is defined as the tendency of the hydroxyl group to attract a bonding pair of electrons), the antioxidants having an active hydroxyl groups (–OH) can be ranked as: BHA–BHT < DTBHQ–TBHQ < PG–PY. For vegetable oil based biodiesel, they were almost in accordance with the rank. However, the antioxidant action on PF-based biodiesel was different: the rank is TBHQ < BHT << PY–BHA. These suggest that the effect of antioxidants on biodiesel depend on the oil feedstock (Table 2). Mittelbach and Schober [15] showed that TBHQ produced the best results at 1,000 ppm for rapeseed oil based biodiesel; while PG and PY are the most effective followed by TBHQ, BHA, and BHT for used frying oil, and sunflower seed oil based biodiesel; and PY is the best for beef tallow oil based biodiesel. Surprisingly, α-T displayed no noticeable effectiveness in this study. Similar results were also observed elsewhere [33].

Effect of Antioxidant on Oxidative Stability of DSBO-Based Biodiesel

Figure 5 shows the IP of DSBO-based biodiesel as a function of the concentration of eight antioxidants. The DSBO-based biodiesel without antioxidant has a much lower oxidative stability (0.77 h) than un-distilled (3.52 h). With the distilled sample, TBHQ and BHA achieved the best result, followed by PY, and then by BHT, DTBHQ, PG, and IB having similar effects. The addition of α-T had the smallest increase on IP. It was noted that TBHQ and BHA at 500 ppm and PY at 1,000 ppm could improve the IP > 6 h. A similar study found that the effect of antioxidants to distilled sunflower seed oil was as following [15]: TBHQ > BHA–PG ~ PY > BHT. Liang et al. [13] has also demonstrated that TBHQ is more effective compared to BHT with distilled palm diesel. Although the distilled and un-distilled samples had almost the same FAME composition, they contained different levels of natural antioxidants, total glycerin content, and sterol glucosides [20]. One recent study has reported that relative antioxidant content, FAME compositions, and total glycerin content impacted the oxidative stability of biodiesel [27]. The different content of minor component is the likely explanation for the different effects of antioxidants on un-distilled and distilled biodiesel.

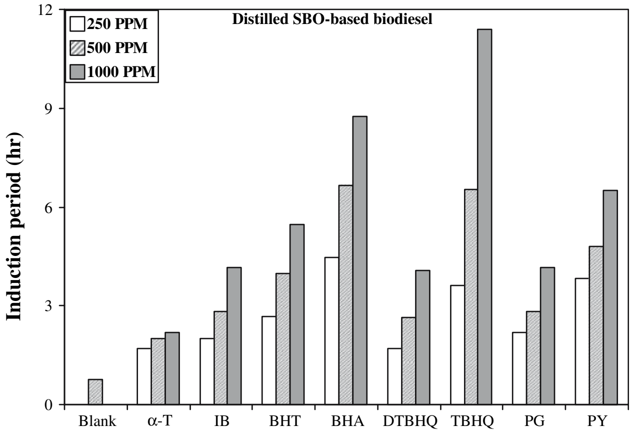

Fig. 5 Effects of Concentration of α-T, IB, BHT, BHA, DTBHQ, TBHQ, PG, and PY as a function of induction period of distilled SBO-based biodiesel

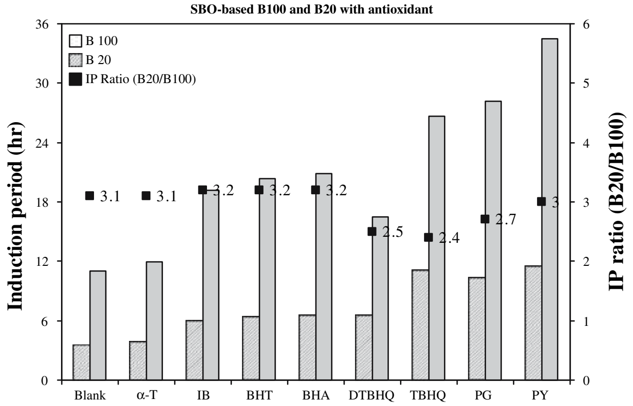

Fig. 6 Effects of antioxidants on the induction period of SBO-based B100 and B20

Effect of Antioxidant on Oxidative Stability of SBO-Based B100 and B20

In Fig. 6, the effect of eight types of antioxidants on the IP of both B20 and B100 soy-based biodiesel is shown. Antioxidant was added at a concentration of 200 ppm for the B20 and 1,000 ppm for the B100. The IP of untreated B20 is significantly higher than that of the B100. For B20 samples, the addition of PY resulted in the highest IP (34.49 h), followed by PG and TBHQ. BHA, BHT, DTBHQ, and IB had similar effects; whereas α-T was not effective. For B100, there is a similar observation on the effect of antioxidant. Moreover, the ratios of IP between B20 and B100 for different antioxidants were observed to be relatively constant (2.4–3.2). These results suggested that the effect of antioxidants on B20 and B100 was similar.

Long-Term Storage Stability of SBO-Based Biodiesel

To determine the effect of antioxidants on biodiesel oxidative stability under long-term storage conditions, the IP of SBO-based biodiesel during indoor and outdoor storage were measured as a function of time (Fig. 7a, b). For

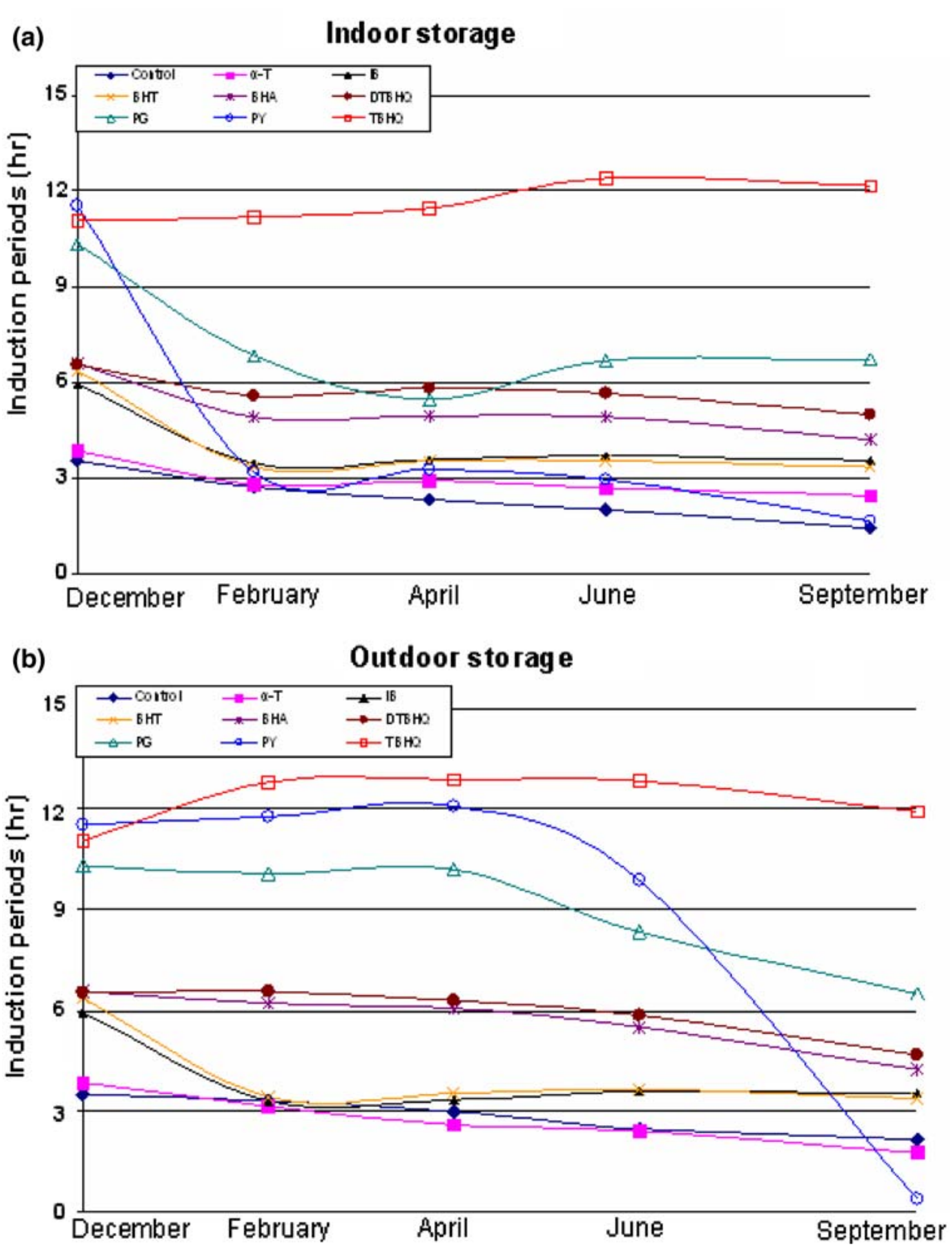

Fig. 7 Effects of antioxidants on the induction period of SBO-based biodiesel as a function of stored time: **a** indoor, and **b** outdoor

indoor storage, the fuel was stored at constant room temperature (23 °C), while for outdoor storage conditions of the Michigan ambient temperature from December, 2006 to September, 2007 prevailed (Table 1).

In Fig. 7a, the IP of untreated SBO-based biodiesel gradually and nearly linearly decreased by 59.6% (from 3.52 to 1.42 h) over the 9 month indoor storage conditions, while the initial IP by the addition of TBHQ was observed to be higher (11.08 h) and is very stable for up to 9 months. The initial value of IP of SBO-based biodiesel with DTBHQ, BHA, and α-T are 6.54, 6.59, and 3.84 h, respectively, and then gradually decreased by 23.7, 36.4, and 36.5% for up to 9 months. Moreover, the initial IP of biodiesel with PG, BHT, and IB were 10.32, 6.37, and 5.94 h, and decreased very rapidly by 33.7, 47.9, and 40.4% after two month of storage, respectively. After that, IP was slightly decreased for up to 9 months. However, the oxidative stability of biodiesel with PY was found to significantly decrease from 11.54 to 1.65 h after 9 months. Only TBHQ and PG could retain the IP to 6 h for up to 9-month indoors storage.

Under outside storage conditions, samples were exposed to a range of low and high temperature during the 9-month period. The oxidative stability of untreated SBO-based biodiesel decreased gradually by 38.8% (Fig. 7b). At the same time, adding TBHQ resulted in a stable IP for up to 9 months. The effect of BHT (decrease by 47.1%) and IB (decrease by 40.1%) under outdoor storage was very similar to indoors. However, the stability of biodiesel with DTBHQ, BHA, PY, PG, and α-T during the outdoor storage period is different with indoors: with a slow decrease in oxidative stability during the first 4-month period (winter time), and then rapid decrease after that (summer time). Those samples with added PY had a significant decrease from 9.89 to 0.4 h during the 6 to 9 month period. Clearly, the Michigan ambient temperature during the summer period significantly affected the effectiveness of antioxidants PY, PG, DTBHQ, and BHA. Notably, TBHQ and PG were able to maintain an IP of 6 hr for up to 9-months outdoor storage. Bondilli et al. [34] reported that TBHQ decreased by approximately 8% of its initial value, whereas PY did not show any significant variation under commercial storage conditions over 1 year.

Table 4 shows the acid number of SBO-based biodiesel with different antioxidants as function of storage time. It is an indicator for the stability of the fuel because the acid value may increase as the fuel is oxidized. The value of the acid number for untreated SBO-based biodiesel increased with time under both indoor and outdoor storage. Samples with antioxidants α-T, IB, BHT, BHA, DTBHQ, and TBHQ have slight increases in acid number. However, these values are within the specification (0.5 KOH mg/g). Interestingly, the initial values of acid number by adding of both PY and PG were observed to reach to 0.91 and 0.496 KOH mg/g, respectively, and they were not very stable during storage. Similar results were also observed in the European BIOSTAB project [18]. This can be attributed to poor solubility of PY and PG in biodiesel [30].

The viscosity of SBO-based biodiesel with different antioxidants as function of storage time was also measured (Table 5). Viscosity of biodiesel increases when the sample is oxidized to form the polymeric compounds. The values of viscosity for all of samples were found to slightly increase for up to 9 months. However, the limit value (6.0 mm^2/s) at 40 °C was not reached in any cases. These results suggested that the changes in acid number and viscosity may not correlate closely with the changes in oxidation stability of biodiesel [18].

Table 4 Acid number of SBO-based biodiesel with antioxidant as a function of storage time

Acid number (mg KOH/g)									
Antioxidant	Indoor					Outdoor			
	Control	2-mon	4-mon	6-mon	9-mon	2-mon	4-mon	6-mon	9-mon
Blank	0.176	0.217	0.245	0.27	0.296	0.214	0.233	0.242	0.282
α-T	0.224	0.217	0.238	0.245	0.245	0.205	0.225	0.239	0.263
IB	0.212	0.223	0.233	0.242	0.234	0.209	0.229	0.233	0.237
BHT	0.211	0.22	0.23	0.246	0.244	0.209	0.229	0.232	0.243
BHA	0.203	0.194	0.235	0.243	0.244	0.204	0.216	0.228	0.242
DTBHQ	0.212	0.208	0.244	0.256	0.256	0.212	0.23	0.247	0.29
TBHQ	0.212	0.222	0.234	0.245	0.229	0.212	0.222	0.231	0.227
PG	0.496	0.479	0.519	0.792	0.546	0.485	0.508	0.78	0.3
PY	0.914	0.743	0.478	0.445	0.373	0.988	0.797	0.373	0.511

Table 5 Kinematic viscosity of SBO-based biodiesel with antioxidant at 40 °C as a function of storage time

Kinematic viscosity (mm^2/s)

Antioxidant	Indoor					Outdoor			
	Control	2-mon	4-mon	6-mon	9-mon	2-mon	4-mon	6-mon	9-mon
Blank	4.321	4.291	4.326	4.364	4.419	4.292	4.299	4.319	4.329
α-T	4.381	4.35	4.353	4.373	4.396	4.339	4.352	4.384	4.423
IB	4.295	4.325	4.307	4.319	4.329	4.288	4.292	4.306	4.322
BHT	4.302	4.323	4.313	4.331	4.35	4.312	4.293	4.317	4.334
BHA	4.315	4.312	4.325	4.344	4.379	4.291	4.297	4.33	4.394
DTBHQ	4.298	4.3	4.304	4.311	4.314	4.303	4.3	4.307	4.309
TBHQ	4.321	4.306	4.303	4.316	4.318	4.288	4.299	4.315	4.317
PG	4.329	4.324	4.338	4.363	4.361	4.346	4.323	4.337	4.369
PY	4.292	4.348	4.32	4.344	4.377	4.332	4.295	4.301	4.337

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