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Long-term storage stability of biodiesel and biodiesel blends

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ABSTRACT

Longer-term storage stability of biodiesel and blends was studied in experiments simulating up to one year for 100% biodiesel (B100) and three years for blends. Aging was simulated by holding samples at 43 °C to accelerate oxidation (ASTM D4625). Biodiesels were treated with antioxidants before and after aging, with continued aging after antioxidant treatment. Treating aged biodiesel was effective at restoring stability; however, antioxidant effectiveness was decreased relative to fresh biodiesel. Blends were prepared at B5 (5 vol.%) and B20 (20 vol.%) with biodiesel having either 3- or 6-hour Rancimat induction time and low or high polyunsaturated ester content with two diesels produced from hydrocracked or hydrotreated feedstocks. All B5s were stable for the entire storage time regardless of B100 induction time. B20s were unstable if prepared from high polyunsaturated ester biodiesel with a 3-hour induction time. Base diesel stability had considerable effect on blend stability. All but the lowest-stability B20s remained within specification, indicating that long-term storage of biodiesel blends is possible if the biodiesel has high oxidative stability and storage conditions are clean. Induction time decreases indicated loss of stability (consumption of antioxidant) prior to blend degradation; therefore, induction time monitoring is recommended for predicting quality changes during storage.

1. Introduction

Biodiesel is a renewable fuel blending component derived from lipid feedstocks such as vegetable oils and animal fats. Triacylglycerols are converted to mono-alkyl esters via transesterification with methanol to produce a material that has properties more closely resembling those of diesel fuel than the lipid feedstock. Much like the vegetable oils and animal fats from which biodiesel is derived, the presence of unsaturated components leads to susceptibility to oxidative degradation. This oxidative susceptibility is beneficial from an environmental perspective, as it renders the fuel biodegradable; however, this is a concern from a fuel quality standpoint, as quality can degrade during storage and handling.

The storage stability of biodiesel was first studied by du Plessis et al. in 1985, who monitored the production of acids, peroxides, and aldehydes, as well as increase in viscosity and decline in Rancimat induction time over a period of 90 days [1]. They found that exposure to heat and air greatly accelerated degradation of biodiesel, but when stored at 20 °C in closed containers or stored after the addition of an antioxidant, the biodiesel remained stable. Further research on the stability of biodiesel for 180 days of storage showed that exposure to metals also increased the rate of degradation, and that exposure to higher temperatures in pro-oxidizing conditions accelerated loss of stability [2]. Bondioli et al. assessed the applicability of accelerated test methods designed for evaluating storage stability (ASTM International [ASTM] D4625) and oxidative stability (ASTM D2274) of petroleum diesel to biodiesel. In conjunction with measuring filterable and adherent insoluble product formation over 24 weeks of storage at 43 °C, they monitored production of acids, peroxides, aldehydes, and polymers, and increase in viscosity as well as decline in Rancimat induction time [3]. Despite detecting evidence of oxidation by an increase in peroxides, acids, and polymers, they did not detect the production of significant amounts of insoluble products. The formation of insoluble products in accelerated tests was found to be less predictive of biodiesel stability than Rancimat induction time. In addition to analyzing biodiesel stability using accelerated test methods, the stability of biodiesel at ambient conditions was studied for 12 months [4]. Without exposure to air, samples exhibited a decline in Rancimat induction time but little change in peroxide values or viscosity. One sample was exposed to temperature cycling by leaving it outdoors and exposed to air by shaking the container once per week. This sample showed considerable degradation. Antioxidant additives were found to improve the storage stability of biodiesel; however, the effectiveness of these additives is influenced by the amount of double bonds, and thus the reactivity, of the biodiesel samples [5,6]. Although storage conditions strongly influence the stability of biodiesel, production and purification can play a large role in long-term stability. Serrano et al. have shown a significant increase in biodiesel stability by adding citric acid to water used to purify biodiesel after esterification, possibly due to chelation of low concentration metals [6,7].

More fundamental work shows that the stability of biodiesel is strongly influenced by the makeup of unsaturated esters. Polyunsaturated esters are much more susceptible to oxidation than saturated or

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monounsaturated esters [8–10]. For example, the relative rates of degradation for methyl linoleate (C18:2) and methyl linolenate (C18:3) compared to methyl oleate (C18:1) are 41 and 98, respectively [9]. This is due to the fact that the double bonds in the fatty acid esters are present in methylene-interrupted configuration rather than conjugated structures. The bis-allylic hydrogen in these structures is susceptible to abstraction by free radicals, which renders the molecule reactive with elemental oxygen. Peroxyl radicals formed from reaction with oxygen abstract hydrogen from the bis-allylic site of other polyunsaturated esters, forming hydroperoxides and additional radical esters that propagate a chain reaction, or react with an ester radical to form peroxy-linked dimers. The peroxides formed are relatively unstable and react intramolecularly, cleaving the compound adjacent to the double bond into lower molecular weight radicals that then form acids, aldehydes, ketones, alcohols, olefins, and alkanes [10]. These species, in turn, undergo reactions to form oligomeric and polymeric products [11]. The degradation of hydroperoxides is catalyzed by trace metals. These products of oxidation reactions degrade quality due to increased acidity, viscosity, and insoluble components [12].

The oxidation mechanism of polyunsaturated fatty acid esters can be thought of as having three phases, which are represented graphically in Fig. 1 [13]. Phase 1 is the induction period or lag phase, in which oxygen consumption occurs slowly. Antioxidant compounds are depleted during this phase, but the chemical composition of the fuel is not yet significantly impacted. Free radicals form, but they react primarily with antioxidants (if present) rather than the biodiesel itself. The length of time the fuel will remain in this phase is governed by the amount of reactive species present and antioxidant concentration, as well as environmental factors such as oxygen availability and heat. Phase 2 is the exponential phase or phase of peroxidation, in which oxygen consumption and peroxide formation increase rapidly. The antioxidant has been consumed by this point and the reaction of oxygen with the fuel substrate is taking place. Finally, in Phase 3, the rate of peroxide degradation exceeds the rate of peroxide formation. During this phase, there is an exponential increase in the production of acids and other degradation products, and the fuel quality is heavily impacted.

Predicting the amount of time biodiesel will remain in the lag phase, and thus its storage stability, is a complex endeavor. Measuring the total molar concentration of double bonds present in a B100 (such as with iodine value) provides an indication of stability; however, this is not adequate to characterize reactivity given that monounsaturated esters may be present in high quantity, as in the case of a rapeseed-derived biodiesel, but are much less reactive than even low concentrations of polyunsaturated esters [14]. There is a much stronger correlation between the induction time of biodiesel and the amount of bis-allylic sites present than with the overall number of double bonds present [15]. However, oxidative stability is complicated by the fact that it is influenced not only by the makeup of the esters, but also by the presence of natural or synthetic antioxidants, dissolved metals, contact with oxygen, heat, and other factors. Metals levels that are below detection in common analytical procedures are still capable of initiating oxidation [9], and it is impossible to avoid exposure to metals from storage tanks and piping. The same metals that initiate oxidation catalyze peroxide decomposition to form secondary oxidation products [2]. Natural and added antioxidants inhibit oxidation. These are radical scavengers that readily donate hydrogen atoms to radicals, generating stable products and terminating the chain reaction mechanism of oxidation. The dissolved oxygen concentration also affects oxidation, as contact with oxygen is necessary for degradation to occur [16].

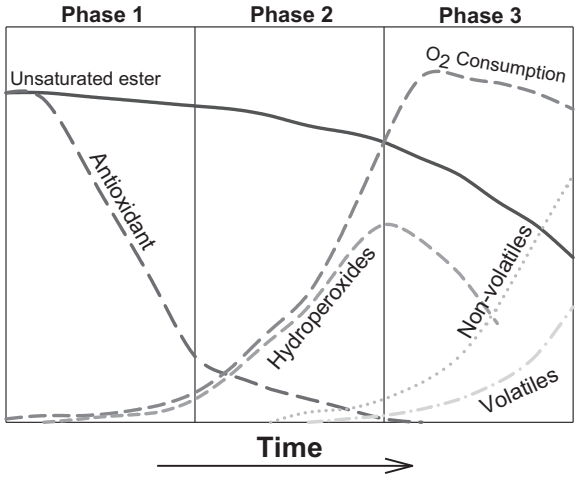

Fig. 1. Graphical representation of the phases of oxidation of polyunsaturated fatty acid esters. Graphic modified from [13], page 236.

Given these factors that promote and prevent oxidation, predicting the stability of a biodiesel in storage is a multifaceted problem [17–19]. To deal with this complexity, one of the key concepts is that of oxidation reserve. Qualitatively, oxidation reserve is the ratio of factors that prevent oxidation to factors that promote oxidation, as shown in the following proportionality:

$$\textbf{oxidation reserve} \propto \frac{\textbf{antioxidant concentration}}{\textbf{Radical Initiator Concentration} + \textbf{Bisallylic Site Concentration} + \textbf{oxygen}}.$$

To ensure adequate oxidation reserve during storage, transportation, and use, exposure to metals, oxygen, and other oxidizing conditions must be limited to the greatest extent possible and adequate antioxidant must be added to extend the induction time.

Biodiesel specifications include oxidation stability requirements, which are meant to ensure adequate stability during typical fuel consumption timeframes of 6 months, given proper storage and handling techniques. These stability requirements are intended to provide a stable blendstock for preparing biodiesel blends, as biodiesel is generally used in a mixture with petroleum diesel up to a 20 vol.% (vol%) blend (B20). The ASTM specification for B100 and D6751, requires a minimum value for Rancimat induction time of 3 h as well as a maximum acid value of 0.5 mg KOH/g [20]. The European specification, EN 14214, requires a Rancimat induction time of at least 6 h, an acid value below 0.5 mg KOH/g, as well as a limit in the amount of linolenic acid methyl ester (C18:3) of 12 wt.% (wt%) and a limit of an iodine value below 120 to ensure low concentration of reactive esters [21]. The Rancimat induction time stability test is essentially a measure of the oxidation reserve in the presence of excess oxygen. In this test, air is bubbled through a sample held at 110 °C and then through deionized water. The water conductivity is monitored and shows a sharp increase when volatile oxidation products are formed. The time required for this to occur is reported as the Rancimat induction time.

Biodiesel blends tend to have improved stability over B100; however, the blend stability is dominated by the biodiesel stability [22,23]. Similar to B100, the stability of blends is highly influenced by storage temperature. A recent study demonstrated that biodiesel blends stored in polyethylene fuel tanks were stable for 380 days when held at 23 °C, but production of peroxides and acids was detected when the fuel was stored for 56 days at 80 °C [24]. When blended with diesel fuel, polymeric materials formed in oxidized biodiesel may be insoluble in the hydrocarbon matrix and form insolubles that could not be measured in the B100 [3]. Antioxidant additives have been found to be effective at stabilizing biodiesel blends [25]. Similar to B100, blend specifications include limitations for oxidation stability measured as Rancimat induction time and acid value to ensure fuel quality during use and handling [26].

Longer-term storage of biodiesel for low-use applications of diesel fuel, such as back-up generators, will require higher oxidation reserve than is necessary for typical use to ensure that the fuel remains stable. The ASTM specifications for B100 and biodiesel blends include guidance for stability monitoring when fuel is stored for greater than 6 months

[20,26]. In the case of petroleum diesel fuel, guidance is offered for storage times greater than 12 months [27]. It is recommended that acid value and particulate matter be measured regularly to ensure the fuel has not degraded prior to use. The instability of biodiesel compared to petroleum diesel leads to many questions and concerns about storing fuel that may contain even low concentrations of biodiesel. This study seeks to determine if biodiesel blends can be stored for longer periods of time—as long as three years—and if so what the necessary fuel properties to ensure adequate oxidation reserve and thus stability during storage may be.

2. Experimental

2.1. Methods of analysis

The storage stability of both biodiesel and blends was monitored following ASTM method D4625 for middle distillate storage stability. The storage conditions for this method are as follows: 400 mL of sample is placed in a 500 mL glass bottle, the lid of the sample container is vented with a glass tube to allow for evaporation, and samples are held in an oven at 43 °C to accelerate aging and tested at regular intervals for filterable and adherent insoluble impurities formed by oxidative degradation. One week of storage under these conditions is considered equivalent to one month of actual underground storage at 21 °C [28]. Measurements were also taken of the peroxide value, acid value, and Rancimat induction time to monitor additional indicators of oxidation, both primary and secondary oxidation products, as well as oxidation reserve.

Peroxide value was determined by iodometric titration following American Oil Chemists Society (AOCS) Cd 8b-90, modified for potentiometric endpoint detection, using a Metrohm 809 Titrando automatic titrator with platinum electrode. Acid value was measured following ASTM D664, Method B, for biodiesel and blends using the same automatic titrator as for peroxide value with pH sensing electrode. Rancimat induction time was measured following EN 15751 using a Metrohm 873 Biodiesel Rancimat and 18 M Ω resistivity water. Fatty acid methyl ester (FAME) profiles of the biodiesel samples were measured by gas chromatography with flame ionization detection (GC-FID) using an Agilent 7890A GC. Samples were diluted into heptane with methyl tridecenoate (NuCheck Prep, Elysian, Minn.) added as an internal standard. Compound separation was achieved with a Varian Select FAME column (100 m × 0.25 mm, 0.25 μm d_f). The initial oven temperature was set at 140 °C, with a 5-min hold, then ramped at 3 °C/min to 190 °C, with a 10-min hold; the second ramp was 4 °C/min to 210 °C, with a 5 min hold; and the final ramp was at 4 °C/min, to 240 °C, with a 4-min hold. The FID temperature was 250 °C. Concentrations of individual FAMEs were determined from a five-point calibration curve generated using a standard FAME solution (NuCheck Prep, Elysian, Minn., Cat # GLC-744).

2.2. Fuel samples

Samples of biodiesel were obtained from commercial suppliers. Properties of the biodiesel samples are provided in Table 1. Metallic elements were measured in the biodiesel samples by ASTM D7111. The results of this analysis are provided in the Supporting Information (SI) Table SI-1. Biodiesels A and B were obtained after unknown antioxidants were added by the manufacturers to stabilize the samples. Biodiesels C and D were obtained prior to the addition of antioxidants. The oxidation stability of Biodiesels C and D was below the ASTM D6751 specification limit of 3 h [20]; however, the peroxide and acid values of these samples were low, indicating that the low oxidation reserve was not due to oxidation but due to a lack of antioxidants. All other biodiesel properties were within ASTM D6751 limits with the exception of flash point for Sample A. The FAME profiles of these samples are provided in Table 2. Included in Table 2 are the calculated bis-allylic position equivalents (BAPE) for each biodiesel. The BAPE is calculated from the percent of polyunsaturated FAME present in the sample weighted by the number of bis-allylic sites present in the ester molecules. This value provides an indication of the oxidative reactivity of a biodiesel, as bis-allylic positions are the most susceptible to oxidation [15].

$$\mathbf{BAPE} = \%\boldsymbol{C18{:}2} + \mathbf{2}\,\boldsymbol{x}\,\%\boldsymbol{C18{:}3}$$

Antioxidants used to stabilize the biodiesel samples were tertiarybutylhydroquinone (TBHQ) and butylated hydroxytoluene (BHT) purchased from Sigma Aldrich. Antioxidant solutions were prepared by adding individual compounds to a small quantity of biodiesel to a point of near saturation and percent antioxidant was determined by weight. Antioxidant solutions were then added to biodiesel samples by volume to the desired part-per-million (ppm) concentration.

The petroleum diesel fuels used for blending with the B100s in this study were obtained from two different refineries. Both samples are ASTM D975-compliant No. 2 ultra-low sulfur "B0" diesels. The samples are differentiated by their manufacturing processes. One is from a

Table 1
Properties of biodiesel samples.

Property	Test method	Units	D6751 limits	B100 A	B100 B	B100 C	B100 D
Acid value	ASTM D664	mg KOH/g	0.50 max	0.27	0.25	0.13	0.25
Peroxide value	AOCS Cd 8b-90	mmol O_2/kg	–	12.2	2.5	7.2	0.4
Cold soak filtration test	ASTM D7501	Seconds	360 max	88	78	66	91
Oxidation stability	EN 15751	Hours	3 min	4.8	8.4	0.6	1.3
Cu strip corrosion	ASTM D130	Rating	3 max	1A	1A	1A	1A
Cloud point	ASTM D2500	°C	Report	0.5	9.6	−0.5	6.4
Cetane number	ASTM D613		47 min	47.1	57.8	55.3	61.8
Water and sediment	ASTM D2709	vol.%	0.050 max	0.01	0.01	<0.005	<0.005
Viscosity (40 °C)	ASTM D445	cSt	1.9–6.0	4.0	4.6	4.0	4.4
Flash point	ASTM D93	°C	130 min	116	138	176	171
Carbon residue	ASTM D4530	wt.%	0.050 max	0.007	0.007	0.020	0.007
Sulfur	ASTM D5453	ppm	15 max	2.8	11.3	0.5	8.3
Free glycerin	ASTM D6584	wt.%	0.020 max	0.006	0.008	0.005	0.009
Total glycerin		wt.%	0.240 max	0.103	0.120	0.007	0.075
Phosphorus	ASTM D4951	ppm	10 max	<5	<5	<5	<5
Calcium	ASTM D7111	ppm	5 max	<0.1	<0.1	<0.1	<0.1
Potassium		ppm	5 max	1.8	1.7	1.7	1.6
Magnesium		ppm	5 max	<0.1	<0.1	<0.1	<0.1
Sodium		ppm	5 max	<1.0	<1.0	<1.0	<1.0
Sulfated ash	ASTM D874	wt.%	0.020 max	<0.001	<0.001	<0.001	<0.001

Table 2
Fatty acid methyl ester (FAME) profiles of biodiesel samples.

FAME	B100 A	B100 B	B100 C	B100 D
C14:0	<0.2	1.5	<0.2	1.2
C16:0	12.4	21.9	11.2	17.4
C16:1	<0.2	3.2	<0.2	3.2
C17:0	<0.2	<0.2	<0.2	0.6
C18:0	3.8	12.3	4.5	9.0
C18:1	24.2	41.9	22.3	33.2
C18:2	50.3	17.9	53.7	26.3
C18:3	7.3	1.1	7.7	1.5
C20:0	0.3	0.2	<0.2	<0.2
C20:1	0.3	<0.2	<0.2	0.3
BAPE	65	20	69	29

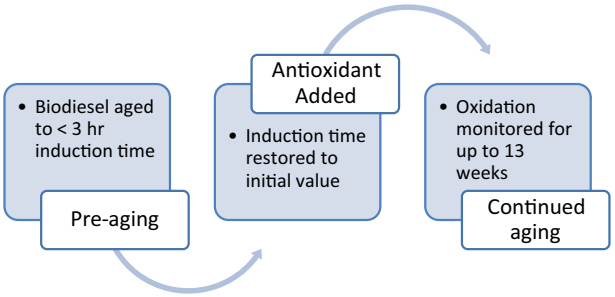

Fig. 2. Biodiesel pre-aging experiment. Biodiesel was aged to fail the induction time specification prior to adding an antioxidant, after which aging was continued for up to 13 weeks.

refinery where the diesel was produced by a (relatively more severe) hydrocracking process, while the second is from a refinery using a (relatively less severe) hydrotreating process. In addition to the type of fuel processing employed, the hydrocarbon compositions of the samples can also be influenced by the types of crude oil processed at these refineries, which are different. This information was provided by the supplier. The composition and select properties of these two samples are provided in Table 3. Metallic elements were measured in the diesel samples by ASTM D7111. The results of this analysis are provided in the SI in Table SI-2. Although oxidation stability is not required as part of the D975 diesel fuel specification, oxidative stability was measured for each distillate fuel by ASTM D2274. The results of this test provided in Table 3 indicate that the hydrotreated diesel had lower oxidative stability than the hydrocracked diesel. The hydrotreated sample was found to produce 5.1 mg of insoluble material per 100 mL of fuel compared to only 1.2 mg/100 mL for the hydrocracked diesel.

Biodiesel blends were prepared with each diesel fuel at both 5% (B5) and 20% (B20) by volume. Blend concentrations were verified by ASTM method D7371.

2.3. Fuel aging experiments

Biodiesels A and B were divided into multiple aliquots. A portion of each fresh biodiesel was purged and blanketed with nitrogen and sealed to preserve for later use. Separate aliquots of both A and B were aged under D4625 conditions until they reached induction times of less than 3 h. This initial aging was conducted to reduce the oxidation reserve of the samples and provide "pre-aged" samples for experimentation. An illustration of the experimental steps is shown in Fig. 2. Once the samples were aged to below 3-hour Rancimat induction time, antioxidants were added at a concentration sufficient to restore the induction time to that of the fresh biodiesel. This step was taken to determine if the oxidation reserve could be restored after samples had entered Phase 2 of the oxidation mechanism. Separate aliquots of Biodiesel A were treated with TBHQ and BHT, while Biodiesel B was only treated with TBHQ. The fresh biodiesels that were stored under nitrogen were then treated with the same concentration of antioxidant in order to compare the effects of treating both oxidized and non-oxidized biodiesel. These pre-aged/treated and fresh/treated samples were then placed back into the test oven to continue to oxidize under the D4625 conditions. The treated samples were aged for up to 13 weeks to simulate 1 year of B100 storage. The fresh biodiesel was aged for the same time period without added antioxidant to provide a baseline for stability. One additional sample of Biodiesel A was prepared by blending 50 mL of pre-aged biodiesel with 350 mL of fresh biodiesel to evaluate the impact of stabilizing oxidized biodiesel by dilution.

Biodiesels C and D were received with induction times below the 3-hour specification limit, and therefore had very little oxidation reserve upon receipt. These samples were aged under D4625 conditions until induction times were measured as <0.1 h in order to examine the impact of aging biodiesel to well below the specification limit and well into Phase 2 of the oxidation mechanism prior to addition of antioxidants. After aging, the samples were treated with TBHQ at a concentration sufficient to reach induction times of at least 3 h and then oxidized further to monitor the impacts of pre-aging. In conjunction with oxidizing the pre-aged samples, fresh samples were treated with TBHQ to an induction time of at least 3 h and aged to monitor the differences between oxidizing pre-aged and fresh samples. Both the fresh/treated and pre-aged/treated samples were aged for up to 16 weeks in D4625 conditions to observe the effects of aging beyond 1 year of storage.

Biodiesel blend storage stability was studied with blends prepared from Biodiesels C and D. These biodiesels were selected for blending experiments because they were not treated with antioxidants by the manufacturers, which allowed for control of the antioxidant concentration. Only fresh biodiesels were used for blending experiments. Biodiesels C and D were treated with TBHQ with concentrations sufficient to reach induction times of 3 h and 6 h, and both stability levels were used to prepare blends with each diesel fuel. B5 and B20 blends were aged under D4625 conditions for 39 weeks to simulate 3 years of quiescent storage.

Table 3
Properties of diesel fuels.

Property	Test method	Units	Hydrocracked no. 2 diesel	Hydrotreated no. 2 diesel
Aromatics	ASTM D1319	%	38.0	30.6
Olefins		%	3.8	3.4
Saturates		%	58.2	66.0
Total aromatics	ASTM D5186	%	29.6	26.5
Mono aromatics		%	26.9	20.4
Poly aromatics		%	2.6	6.1
Carbon	ASTM D5291	%	86.89	86.54
Hydrogen		%	13.06	13.27
Sulfur	ASTM D5453	ppm	2.9	6.5
Accelerated stability	ASTM D2274	mg/100 mL	1.2	5.1
Cloud point	ASTM D2500	°C	−21.5	−10.5
T90	ASTM D86	°C	322	319

3. Results and discussion

3.1. B100

Biodiesels A and B were pre-aged to reduce the oxidation reserve (and enter Phase 2 of the oxidation mechanism) prior to addition of antioxidants. This step was taken to assess the possibility of restoring the oxidation reserve after it has been reduced to a point at which a biodiesel no longer passes the minimum Rancimat induction time. Biodiesel A reached an induction time of less than 3 h after 5 weeks of accelerated aging (5 months simulated storage). An aliquot of this pre-aged biodiesel was treated with TBHQ at a concentration sufficient to obtain an induction time approximately equal to the fresh (as received) biodiesel, and an additional aliquot was treated with BHT in the same manner. A

mixture of fresh and pre-aged biodiesel was prepared by blending 12.5 vol.% pre-aged biodiesel into the fresh sample (50-mL aged fuel per 400-mL fuel sample). These pre-aged/treated samples were further aged for 9 weeks, at which point induction times were 1 h or less and the test was terminated. The fresh sample was also aged for 9 weeks without added antioxidants to provide a baseline for the sample stability. Aliquots of the fresh biodiesel were treated with the same concentrations of antioxidants and aged for the same length of time to compare the effects of adding antioxidants before and after oxidation.

Rancimat induction times of the various samples of Biodiesel A are shown in Fig. 3A. The pre-aged biodiesel reached an induction time nearly equivalent to the fresh sample (approximately 5 h) with the addition of 200 ppm (1.2 mmol/kg) TBHQ or 500 ppm (2.3 mmol/kg) BHT. The pre-aged/fresh mixed sample had an equivalent induction time to the pre-aged/treated samples. Addition of the same concentrations of antioxidants to the fresh biodiesel resulted in induction times of 9.2 h with TBHQ and 7.5 h with BHT. There is a linear decline in the induction time of both the fresh and pre-aged/treated biodiesels ($R^2 > 0.9$), and the slope of induction time decay is nearly equivalent (approximately −0.5 h/week). The fresh/treated samples both remained above the 3-hour specification limit after 9 weeks of aging; however, there is a large difference between the aging rates in the two antioxidants added to the fresh samples. The BHT-treated fresh sample exhibits a linear decay in induction time ($R^2 = 0.97$) and has a slope of −0.5 h/week, while the TBHQ-treated sample shows very little decay that is within the precision of the measurement. Higher antioxidant effectiveness of TBHQ compared to BHT has been observed in previous studies of biodiesel stability [5,19,25,29,30] and is also observed in Fig. 3. The reason for this difference in effectiveness can be explained by structural differences in these compounds. TBHQ contains two hydroxyl groups while BHT contains only one. This second hydroxyl group provides an additional site for capturing free radicals, thus increasing the effectiveness of TBHQ as an antioxidant relative to BHT [29,30].

Peroxide values of the Biodiesel A samples are shown in Fig. 3B. The peroxide value of the fresh sample increases at a steady rate of approximately 2.5 mmol O_2/kg/week at first, and then there is a sharp increase in the slope of peroxide formation to 8.8 mmol O_2/kg/week after 4 weeks of accelerated aging, once the Rancimat induction time has fallen below 3 h. Similarly, the pre-aged sample treated with TBHQ maintains a nearly constant peroxide concentration for the first 4 weeks of continued aging (weeks 5 through 9), and then shows a sharp increase in slope to 10.6 mmol O_2/kg/week after falling below a 3-hour induction time. In contrast to the TBHQ-treated sample, the pre-aged sample treated with BHT has a linear increase in peroxides ($R^2 = 0.99$) throughout the aging period with a slope of 5.3 mmol O_2/kg/week, but the net change in peroxide is approximately equivalent to the TBHQ-treated sample. The mixture of pre-aged and fresh biodiesel also shows a linear increase in peroxide ($R^2 = 0.96$), but with a sharper slope of 8.9 mmol O_2/kg/week, resulting in nearly equivalent peroxide value to the other pre-aged samples at the end of the 14 weeks despite its lower initial value at 5 weeks. The fresh sample treated with BHT has a linear increase in peroxides ($R^2 = 0.96$) with a slope of 2.8 mmol O_2/kg/week, resulting in a final peroxide value at 9 weeks of aging equivalent to that of the fresh sample at 5 weeks, which is consistent with the Rancimat induction time decay observed for this sample. The fresh biodiesel treated with TBHQ is the only sample to show no net increase in peroxides over 9 weeks of aging.

Despite the peroxide production observed, only one sample had an acid value above the maximum value of 0.5 mg KOH/g set by the D6751 specification. This sample was the pre-aged sample treated with TBHQ, which had an acid value of 0.58 mg KOH/g after 9 weeks of aging. None of the B100 samples produced insoluble material that could be measured by ASTM D4625 filtration. The fact that sediment was not detected may be due to the polar nature of the compounds formed, which remain soluble in the FAME matrix, but can become insoluble when blended with less polar media [3,11].

Biodiesel B was received with an induction time of 8.4 h and had a much lower BAPE value and much higher storage stability than Biodiesel A. This sample required 26 weeks of accelerated aging (2 years of simulated storage) to reach an induction time below 3 h. Only TBHQ was used as an antioxidant for this biodiesel. The addition of 200 ppm TBHQ was sufficient to restore the pre-aged sample induction time to the original value. This same concentration of antioxidant resulted in an induction time of 17.7 h for the fresh sample. Aging was carried out for 13 weeks for the fresh, fresh/treated, and pre-aged/treated samples. Induction time results of the samples of Biodiesel B are shown in Fig. 4A. Fresh Biodiesel B treated with TBHQ shows no net loss in induction time

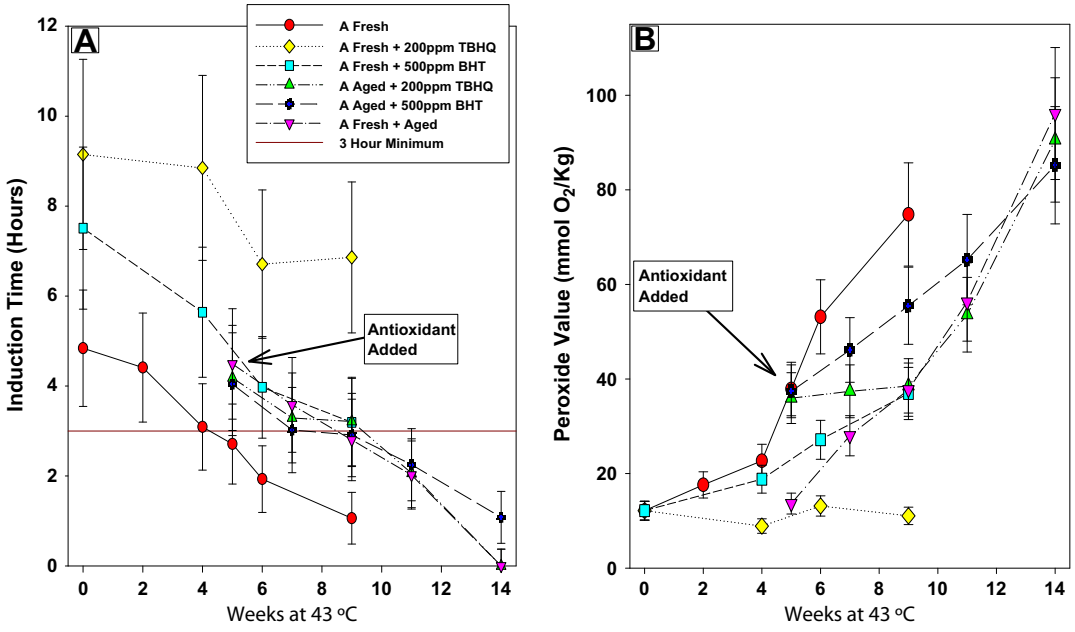

Fig. 3. Induction times (Chart A) and peroxide values (Chart B) of Biodiesel A during aging. Induction time error bars are calculated from the published reproducibility of EN 15751 [31]. Peroxide value error bars are the in-house repeatability determined from the 95% confidence interval of a minimum of 10 replicates of representative samples.

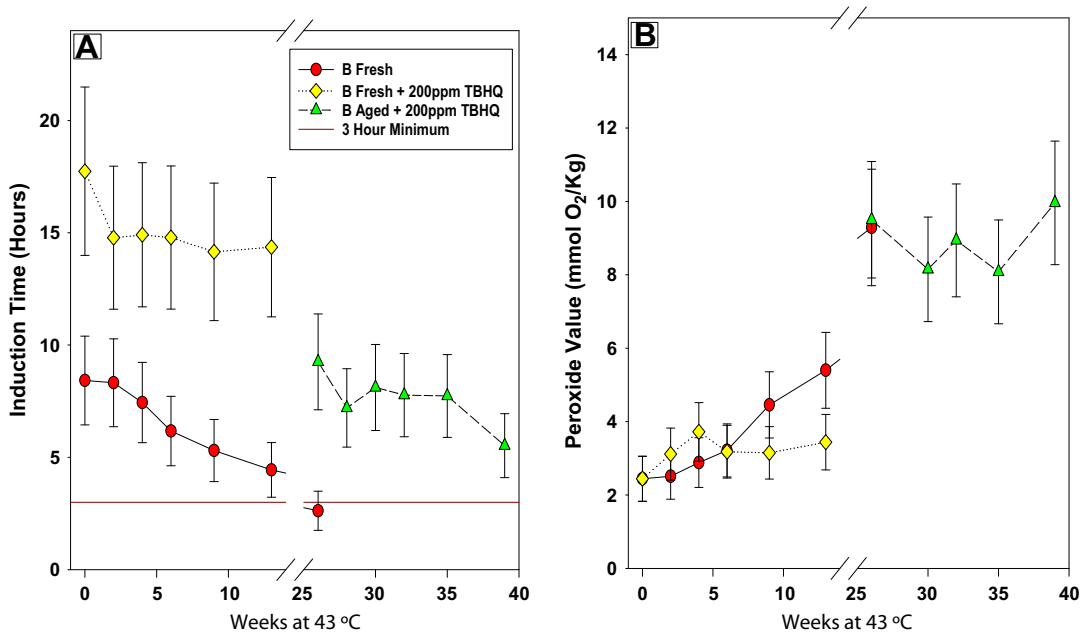

Fig. 4. Induction times (Chart A) and peroxide values (Chart B) of Biodiesel B during aging. Induction time error bars are calculated from the published reproducibility of EN 15751. Peroxide value error bars are the in-house repeatability determined from the 95% confidence interval of a minimum of 10 replicates of representative samples.

over 13 weeks. The pre-aged/treated sample's induction time decayed to 5.5 h after an additional 13 weeks of aging. Peroxide values of the Biodiesel B samples are shown in Fig. 4B. Note that the maximum peroxide level attained was an order of magnitude lower than observed for Biodiesel A. The pre-aged/treated sample did not produce any additional peroxide after an additional 13 weeks of accelerated aging. None of the Biodiesel B samples showed an increase in acid value, and no insoluble material was measured in any of the samples. Despite reaching an induction time of less than 3 h, the pre-aged sample did not enter Phase 2 of the oxidation mechanism, and therefore rapid peroxide production was not observed.

Both biodiesels A and B were treated with unknown antioxidants by the manufacturer. Biodiesel A had sufficient oxidation reserve to remain in Phase 1 of the oxidation mechanism for 9 weeks when 200 ppm of TBHQ was added to the fresh sample; however, the total concentration of antioxidant or what compounds were used to treat the sample is unknown. A similar situation is observed with Biodiesel B, which was received with sufficient oxidation reserve to remain in Phase 1 for 26 weeks. To further explore the necessary concentration of antioxidant to provide adequate oxidation reserve, experiments were preformed with Biodiesels C and D, which were not treated with antioxidants by the manufacturer.

With Biodiesels A and B, the goal of experiments was to age samples to just failing Rancimat induction time prior to addition of antioxidants; however, C and D were below the specification minimum when they were received. As previously noted, this low induction time was not the result of oxidation, but an indication of a lack of added antioxidants. Aging studies were conducted with these biodiesels that sought to explore the impact of aging biodiesel well below the specification limit. Both C and D were aged at 43 °C to an induction time of <0.1 h and then treated with TBHQ to approximately 3-hour induction time. The fresh samples were treated with TBHQ to 3 h induction time as well for comparison. Both biodiesels took 3 weeks of accelerated aging to reach an induction time of <0.1 h. In the case of Biodiesel C, the fresh sample required 300 ppm (1.8 mmol/kg) of TBHQ to reach the 3-hour induction time, while the aged sample required 1000 ppm (6.0 mmol/kg). Fresh and aged Biodiesel D required 100 ppm (0.6 mmol/kg) and 1300 ppm (7.9 mmol/kg) of TBHQ, respectively, to reach the same induction time. The pre-aged/treated and fresh/treated samples were aged for up to 16 weeks and monitored for induction time decay and peroxide value increase. The acid values of these samples were measured before and after aging.

Rancimat induction times of Biodiesels C and D are shown in Fig. 5A. Biodiesel C shows similar results to Biodiesel A, with the pre-aged/treated sample linearly losing stability at the same rate as the fresh/treated sample of similar induction time (approximately −0.25 h/week). In the case of Biodiesel D, there is a large discrepancy between the fresh/treated sample and the aged/treated sample. The fresh/treated Biodiesel D loses stability rapidly while the aged/treated sample remains stable for 16 weeks of aging. This result appears counterintuitive, given that the fresh/treated sample is considerably less stable than the aged/treated sample; however, the cause of this is likely the low concentration of antioxidant in the fresh/treated sample. Biodiesel D required only 100 ppm of TBHQ to reach an induction time of 3 h, and this did not provide adequate oxidation reserve for storage. However, the pre-aged sample required 1300 ppm of TBHQ to reach 3 h, which provided adequate oxidation reserve for 16 weeks. The results show that while a minimum requirement for induction time may ensure a minimum level of stability, it does not correlate with nor predict the amount of time a biodiesel can be stored before going out of specification.

Despite the similar rate of decline in induction period for Biodiesel C fresh/treated and pre-aged/treated, the acid values of these two samples presented in Fig. 6 were considerably different. At the end of 16 weeks of aging, the acid value of the fresh/treated sample was 0.30 mg KOH/g, while the pre-aged/treated sample was 0.55 mg KOH/g. Biodiesel D fresh/treated and pre-aged/treated also showed considerably different acid values. By 12 weeks of aging, the fresh/treated sample reached 0.67 mg KOH/g while the pre-aged/treated sample reached 0.50 mg KOH/g at 16 weeks of aging. The differences in acid values can be explained by the differences in peroxide values of these samples, as shown in Fig. 5B. Biodiesel C pre-aged/treated reached a peroxide value of 52 mmol O_2/kg prior to the addition of TBHQ. The peroxide value of this sample remained consistent until 14 weeks of aging, at which point the value increased rapidly to a final value of 143 mmol O_2/kg. Similarly, the fresh/treated sample maintained a consistent peroxide value until 12 weeks of aging at which point there was a sharp increase; however, the final peroxide value reached was 108 mmol O_2/kg. The larger peroxide value of the pre-aged sample indicates that the sample was

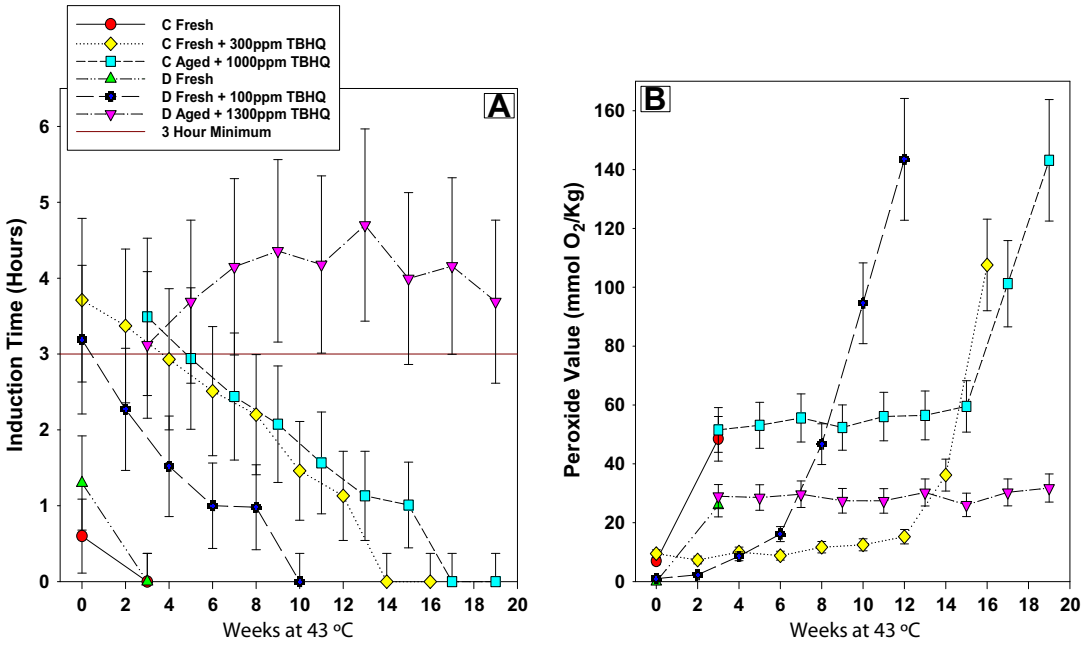

Fig. 5. Induction times (Chart A) and peroxide values (Chart B) of Biodiesels C and D during aging. Induction time error bars are calculated from the published reproducibility of EN 15751. Peroxide value error bars are the in-house repeatability determined from the 95% confidence interval of a minimum of 10 replicates of representative samples.

further into Phase 2 of the oxidation mechanism, which is also reflected in the higher acid value of this sample after 16 weeks of storage. Despite the very similar induction periods of these two samples the peroxide values and acid values indicate that the pre-aged/treated sample was more severely oxidized than the fresh/treated sample.

Biodiesel D did not show a similar aging rate with regard to induction time decay, likely due to the low antioxidant treat rate in the fresh/treated sample. The fresh/treated Biodiesel D aged rapidly, while the aged/treated sample maintained consistent induction period as well as peroxide value throughout the 16 weeks. The acid value of this sample also did not significantly increase during aging; however, this value was 0.46 mg KOH/g when TBHQ was added and therefore was very close to failing specification. These results indicate that a sample very near the specification maximum for acid value can be sufficiently stabilized with antioxidant to have a large oxidation reserve, but the concentration necessary will be fairly high.

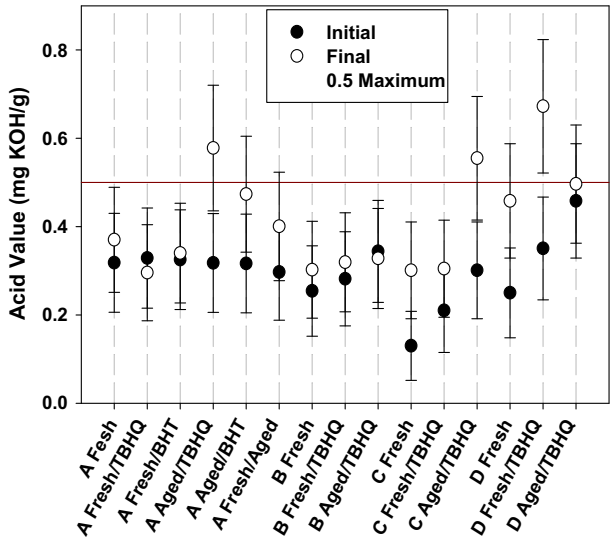

Fig. 6. Acid values of biodiesels before and after aging at 43 °C. Error bars are calculated from the published reproducibility of ASTM D664.

Storage stability of biodiesel—the amount of time it remains in Phase 1 of the oxidation mechanism—is influenced by physical and chemical properties as well as the environment in which it is stored. There is a clear difference in the oxidative stability between biodiesels A and B, likely due to the vast difference in BAPE values, and likely due to antioxidants added prior to receipt of these samples. When biodiesel has been allowed to enter Phase 2 of the oxidation mechanism and peroxide formation becomes exponential, it may be possible to add additional antioxidants to restore the oxidation reserve and return to Phase 1, as demonstrated with pre-aged Biodiesel D. However, the concentration necessary to restore stability will be much greater than what was required when the biodiesel was in Phase 1. Antioxidants will provide much greater oxidation reserve if they are added prior to the onset of exponential oxidation, before the fuel has entered Phase 2 of the oxidation mechanism. The results observed with Biodiesel D show that addition of insufficient antioxidant during Phase 1 can result in rapid degradation of B100, even if the added concentration resulted in a 3-hour induction time.

3.2. Biodiesel blends

Blends were prepared using Biodiesels C and D, which had been treated with TBHQ to B100 induction times of 3 and 6 h, respectively. Each biodiesel was blended to B5 and B20 with each diesel fuel. Biodiesel C required 300 ppm (1.8 mmol/kg) TBHQ to reach an induction time of 3 h and 600 ppm (3.6 mmol/kg) to reach 6 h. Biodiesel D required 100 ppm (0.6 mmol/kg) to reach 3 h and 400 ppm (2.4 mmol/kg) to reach 6 h. Blends were held at 43 °C for 39 weeks to simulate 3 years of quiescent, underground storage. The peroxide value of each blend was monitored biweekly throughout the experiment. At 17 weeks, the Rancimat induction time of the blends was tracked, as no change in peroxide value had been detected.

Induction times of the B5 blends are shown in Fig. 7. The blends are divided into two groups of four by diesel fuel: hydrocracked in Fig. 7A and hydrotreated in Fig. 7B. Each group of four blends is divided by Biodiesel C or D with an initial B100 induction time of 3 or 6 h. All of the B5 blends have an initial induction time greater than 12 h. At 39 weeks of aging, none of the B5 blends is below the 6-hour minimum induction time specified by ASTM D7467 for B6 to B20 blends. Although the blends

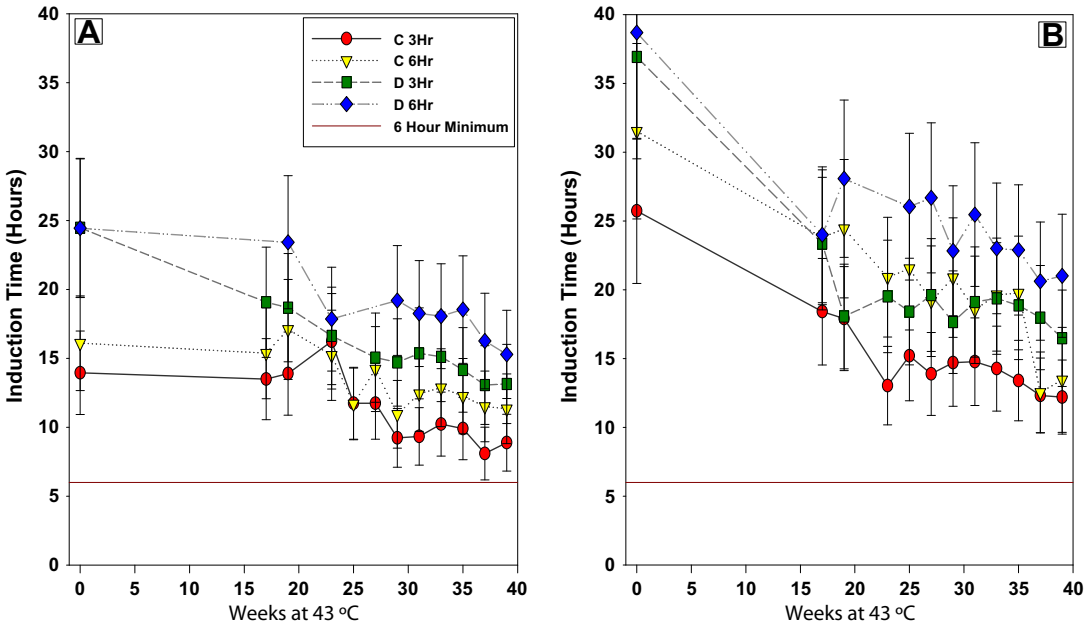

Fig. 7. Induction times of B5 blends. A: Hydrocracked diesel blends and B: Hydrotreated diesel blends. Error bars are calculated from the published reproducibility of EN 15751.

tested here are blended at B5, which is considered equivalent to diesel fuel according to ASTM D975 [27], there is no oxidative stability specification for diesel fuel, therefore the results are compared to the blend specification.

B20 blend induction times are shown in Fig. 8. The initial induction times of the B20 blends are lower than those of the B5 blends; however, these are again at 12 h or greater. All but two of the B20 blends remain above the 6-hour minimum induction time by 39 weeks of aging. The two blends that fail induction time were prepared with Biodiesel C, which had an initial B100 induction time of 3 h. There is a notable difference between these two blends, as the blend prepared with hydrotreated diesel reaches an induction time of <0.1 h at 39 weeks, while the hydrocracked blend is below 6 h by 23 weeks but maintains a consistent induction time of approximately 4 h for the remainder of the 39 weeks. Table 3 includes the oxidative stability of the two diesel fuels measured by ASTM D2274. Under accelerated oxidative conditions, the hydrocracked diesel produced 1.2 mg/100 mL of insoluble material, while the less stable hydrotreated diesel produced 5.1 mg/100 mL. The reason for this difference has not been determined, as the olefinic content of the diesels shown in Table 3 is very similar, and the metallic elements (Table SI-2) that could contribute to oxidative degradation are either below the method detection limit or are present in nearly the same quantities in the two samples.

The acid values of all of the blends did not increase for the entire 39 weeks with the exception of the B20 blend prepared with Biodiesel C, 3-hour and hydrotreated diesel. This blend reached an acid value of 0.3 mg KOH/g by the end of the test interval, which is the maximum value set by ASTM D7467. Similarly, the peroxide value of this sample was the only one to increase significantly during the test. At 29 weeks of aging, a notable increase in peroxide value was detected and this

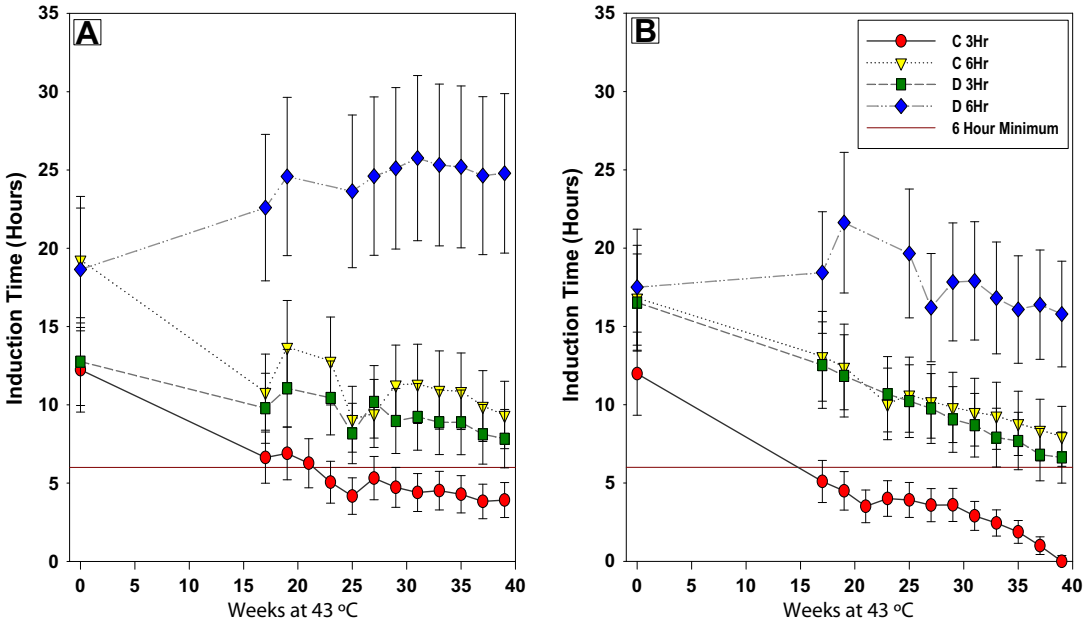

Fig. 8. Induction times of B20 blends. A: Hydrocracked diesel blends and B: Hydrotreated diesel blends. Error bars are calculated from the published reproducibility of EN 15751.

continued rapidly, reaching a value of 112 mmol O_2/kg by 39 weeks. All other B20 blend peroxide values remained below 5 mmol O_2/kg, and all B5 blend peroxide values remained below 2 mmol O_2/kg.

All blends were tested for filterable and adherent insolubles initially and then biweekly starting at week 35. None of the blends produced sediment that could be confidently measured by ASTM D4625. It is important to note that the precision of D4625-04(09), the current version at this time, is such that the reproducibility of the method is larger than the test result at any value below 4 mg/100 mL, at which point the reproducibility is equal to the test value ($R = 2.20\sqrt{X}$) [28]. For all blends, no values greater than 4 mg/100 mL were measured in this study, and therefore no statistically significant changes in total insolubles were measured. In order to further assess polymeric content the viscosity of the lowest stability blend, the B20 prepared with Biodiesel C, 3 h and hydrotreated diesel, was measured by ASTM D445 at 40 °C. The initial value for this blend was 3.047 cSt, and the final value was 3.235 cSt. For comparison, the B20 blend prepared with Biodiesel C with a 6-hour induction time, and hydrotreated diesel had an initial viscosity of 3.040 cSt, while the final value was 3.044 cSt. There is a clear increase in the viscosity of the lowest-stability B20, but this remained well below the specified maximum of 4.1 cSt in ASTM D7467. Despite this increase in viscosity, gravimetric analysis was not sensitive enough to detect any insoluble polymer formation in the sample. It is possible that the observed change in viscosity is due to the production of soluble polymeric material.

The biodiesel blend oxidation reserve is much higher than that of B100. Storage of B5 blends for a simulated 3 years did not result in any observable oxidation, even with Biodiesel D treated with 100-ppm TBHQ, which degraded rapidly as a B100. All of these fuels remained in Phase 1 of the oxidation mechanism for the entire storage time. The B20 blends were not as stable as the B5 blends, but stability was still much greater than with B100. The B20 blends prepared from biodiesels with 6-hour B100 induction times were stable after 3 years of simulated storage. Blends prepared with low BAPE biodiesel having 6-hour induction time resulted in the highest stability.

All of the B5 and B20 blends exhibited induction time decay without observable peroxide formation. Fig. 9 shows a comparison of the peroxide values for the least stable B20s compared to the induction time during aging. These samples were prepared with Biodiesel C, 3-hour initial induction time and both hydrocracked and hydrotreated diesels. With both blends, the induction time falls to below the 6-hour limit, but the peroxide value increase is only detected once the blend with hydrotreated diesel reaches an induction time of approximately 3 h. These results indicate that monitoring Rancimat induction time decay can indicate loss of blend oxidation reserve (consumption of antioxidant) before other changes in the fuel can be measured. Note that acid value was found to increase only in the blend with an increase in peroxide value; therefore, acid production was only detected after loss of Rancimat induction time.

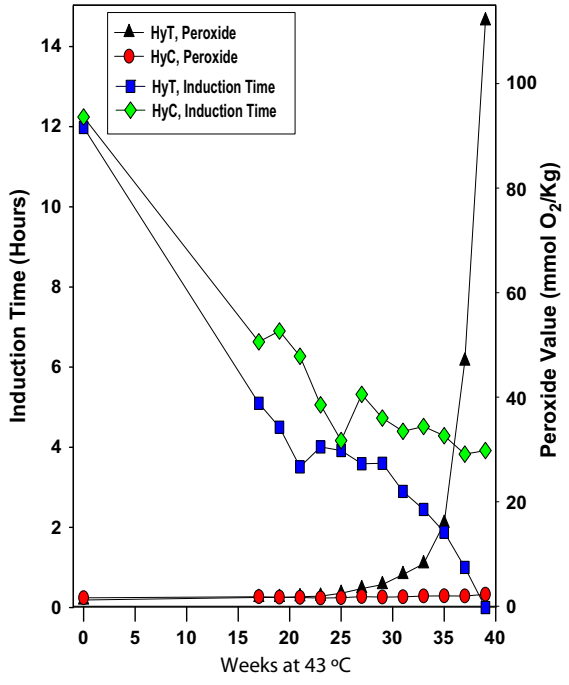

Fig. 9. Comparison of induction time decay and peroxide value increase for B20 blends prepared with Biodiesel C, 3-hour induction time with hydrocracked (HyC) diesel and hydrotreated (HyT) diesel.

4. Conclusions

The results of these storage experiments must be interpreted with caution. It should be noted that oxygen exposure, contamination from metals and other radical initiators, water exposure, light exposure, and heat could all contribute to degradation of fuel quality. The conditions used for aging samples in this experiment are more representative of clean, well-maintained, underground, quiescent storage and do not necessarily apply to all fuel storage situations. However, these results are intriguing in that they suggest that it is possible to store biodiesel blends over the long term. Further research would be advantageous to determine how degradation caused by exposure to water and heat could be mitigated with additives or fuel properties. In the case of underground storage and limited oxidizing conditions, the addition of antioxidants and use of biodiesel with at least a 6-hour induction time and all other properties conforming to ASTM D6751 will be sufficient to store fuel for longer than 6 months and up to several years. The use of a lower BAPE biodiesel is also advantageous, as evidenced by the fact that blends with Biodiesel D even with a 3-hour B100 induction time did not oxidize by 39 weeks of accelerated aging.

When storing fuel in the long term, a monitoring program is recommended by fuel specifications. Regularly measuring acid and insoluble material formation during storage is already recommended in the ASTM D6751 and D7467 appendixes, but these results suggest that including Rancimat induction time as part of a monitoring program would provide an earlier indication of fuel degradation. Tracking acids and insoluble material, as is now recommended, provides an indication of when the fuel is in Phase 2 or has entered Phase 3 of the oxidation mechanism, and may already be problematic by the time these compounds have formed. Tracking induction time decay during storage can indicate changes prior to when the fuel enters Phase 2 of the oxidation mechanism (has consumed antioxidants) and before it has produced acids or insoluble materials that could cause operational problems.

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Appendix A. Supplementary data

Additional data are provided. This information is available free of charge via the Internet at http://www.sciencedirect.com. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuproc.2014.07.045.

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