Water Contamination Impacts on Biodiesel Antioxidants and Storage Stability

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ABSTRACT: Biodiesel (fatty acid methyl esters) can oxidize in storage to form acids and gums that negatively impact engine performance and durability. Antioxidant additives are used to increase biodiesel storage stability, and previous studies that evaluated the effectiveness of antioxidants demonstrated that more polar antioxidants tend to be the most effective (provide the largest improvement in stability per unit of antioxidant added). However, polar antioxidants have significant water solubility, and diesel fuel storage tanks are commonly contaminated with water (forming a layer of water under the fuel). This study investigates whether nonpolar antioxidants, which are less effective in dry environments, might be more effective under wet conditions simulating real-world storage. Biodiesel blends treated with polar and nonpolar antioxidants were subjected to accelerated aging using the ASTM D4625 protocol (storage at 43 °C, open to air, for up to 24 weeks) both with and without added water. Fuels treated with polar/higher-effectiveness compounds and stored in contact with water (simulating water in a storage tank) or high humidity showed accelerated loss of stability compared to dry storage. The same fuel treated with a nonpolar antioxidant and stored in the same conditions did not exhibit accelerated stability loss and thus had higher storage stability over the long term despite treatment with an initially less effective additive. Analysis of the fuels during aging showed that this loss of stability was not due to oxidation but rather extraction of the polar antioxidant into the water layer. Antioxidant additives that are incompatible with wet or humid storage conditions were found to cause faster-than-anticipated loss of stability, which was preventable with use of nonpolar additives.
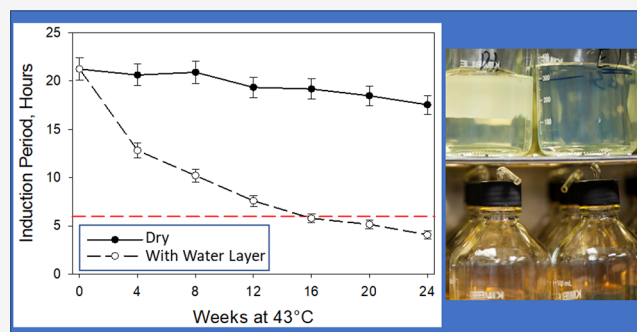
INTRODUCTION

Biodiesel—a mixture of mono-alkyl esters of long-chain fatty acids—is a renewable fuel used in compression-ignition engines and burners, produced via catalytic transesterification of fats and oils with an alcohol.[1] The most common form of biodiesel currently in use is fatty acid methyl ester (FAME).[2] In the United States, common feedstocks for making biodiesel include soy oil, distillers corn oil, canola oil, waste cooking oil, and animal fats.[3] In 2020, biodiesel consumption in the United States was 6.8 billion liters,[4] while global production was 43 billion liters.[5] Life cycle greenhouse gas emission reductions for neat biodiesel (B100) relative to petroleum diesel range from 40 to 86% depending on feedstock and assumptions regarding land use change.[6]

B100 is required to meet various quality metrics in ASTM standard specification D6751[7] (or EN 14214). Biodiesel blended with petroleum diesel at up to 20 volume percent is approved by many engine original equipment manufacturers if it conforms to the requirements of ASTM D7467.[8] One key metric of these quality specifications for biodiesel and biodiesel blends is resistance to oxidation in storage, referred to as oxidation stability.[7–11] The FAMEs that comprise biodiesel retain the polyunsaturated carbon chains present in the parent fats and oils used in their production (such as methyl linoleate

and methyl linolenate) and therefore have similar tendency to autoxidize when exposed to air and heat over time.[1,12,13] The di- and tri-unsaturated chains contain relatively weak bis-allylic carbon−hydrogen bonds that are susceptible to H-abstraction by free radicals, producing a radical that can react with dissolved oxygen (O_2). The peroxyl radical that is formed can abstract hydrogen from a bis-allylic site internally or from another polyunsaturated ester molecule, forming hydroperoxides and additional radicals in a chain reaction, or react with an ester radical to form peroxy-linked dimers. The peroxides formed are unstable and undergo a unimolecular reaction, cleaving the compound adjacent to the double bond. This produces lower molecular weight radicals that subsequently react to form acids, aldehydes, ketones, and other species.[14] These undergo reactions to form oligomeric and polymeric products.[15,16] Oxidative degradation, if left un-

Table 1. Stabilization Factors and Relative Effectiveness Rankings of Common Biodiesel Antioxidants in B100[28−33]

| Reference | Stabilization Factor | | | | | | Effectiveness Ranking[a] |
| | *Increasing Polarity* ← | | | | | | |
	PA	PG	TBHQ	BHA	BHT	α-Tocopherol	
[29]	--	14.8	12.3	11.6	4.9	3.9	PG > TBHQ > BHA > BHT > Toc
[30]	2.5	2.3	2.4	1.7	1.6	1.0	PA > TBHQ > PG > BHA > BHT > Toc
[31]	2.4	2.1	1.6	1.0	1.0	--	PA > PG > TBHQ > BHT= BHA
	2.7	2.0	3.3	1.0	1.7	--	TBHQ > PA > PG > BHT > BHA
	4.5	3.8	4.3	1.8	1.8	--	PA > TBHQ > PG > BHT = BHA
	3.4	3.5	3.2	2.1	1.8	--	PG = PA > TBHQ > BHA > BHT
	4.0	4.1	4.2	1.9	1.7	--	TBHQ = PG > PA > BHA > BHT
[32]	104.1	--	18.8	15.2	14.8	--	PA >> TBHQ > BHA > BHT
[28]	4.3	4.4	5.7	2.4	2.4	--	TBHQ > PG > PA > BHT= BHA
[33]	12.4	7.2	2.7	4.6	3.2	--	PA > PG > TBHQ > BHA > BHT
[33]	9.0	8.6	19.0	3.2	3.5	--	TBHQ > PA > PG > BHT > BHA

[a]Pyrogallol (PA), propyl gallate (PG), *tert*-butyl hydroquinone (TBHQ), butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), α-tocopherol (Toc).

Table 2. Water Solubilities and Octanol−Water Partition Coefficients (P_{ow}) of Biodiesel Antioxidants[43]

	PA	PG	TBHQ	BHA	BHT	α-tocopherol
water solubility, g/L	625	3.5	∼2	insoluble[a]	insoluble	insoluble
log P_{ow}	1.0	1.8	2.9	3.2	5.1	12.2

[a]Practically insoluble <0.01 g/L.

checked, can lead to deleterious impacts on fuel quality—such as the formation of gums and acids—ultimately impacting engine performance and durability.[13] Total acid number (TAN) is also controlled in biodiesel and biodiesel blend quality specifications because, in part, of the potential for oxidative degradation.

Surveys of fuel quality have shown that U.S. B100 biodiesel as produced meets the oxidation stability quality metric of Rancimat induction period (IP) ≥ 3 h,[17,18] which is intended to ensure an IP ≥ 6 h for blends in petroleum diesel up to B20.[10] However, B20 biodiesel blends sampled from retail and end-user tanks show a significant failure rate (5 to 15%) for oxidation stability.[19−21] It is unclear if this is caused by oxidative degradation during handling and blending in the fuel distribution system or other factors.

The stability of B100 and its blends with hydrocarbon fuels can be enhanced with the use of antioxidant additives that act as radical scavengers, shutting down oxidation.[11,21−24] Naturally occurring antioxidants such as α-tocopherol have been found to be less effective than synthetic antioxidants.[22,24,25] Antioxidant effectiveness is a rating of the increase in IP per unit of compound added; higher effectiveness means that a lower dose rate is required to reach a target IP value.[25] There have been numerous studies on the response of biodiesel and biodiesel blends' IPs to common antioxidants.[22−27] Synthetic antioxidants studied for use in biodiesel have largely been hindered phenols and can be broadly categorized into polar and nonpolar, with the more polar (and hence less hydrocarbon-soluble) antioxidants being the most effective in B100.[28]

Table 1 provides a synopsis of several studies on the performance of common phenolic antioxidants in B100 biodiesel. The data provided in this table are by no means exhaustive; however, each of these studies compared these antioxidants at the same concentration of 1000 mg/kg using Rancimat IP to measure stability, and thus they are of comparable evaluations and rankings. A useful metric for comparing the effectiveness of antioxidants in fuels is the stabilization factor, defined as the ratio of the IP with an antioxidant added to the IP without additization.[25,26] Notably, the effectiveness and stabilization factors are not constant from one study to another as absolute values are effected by the stability level of the base fuel sample (without an added antioxidant).

Table 2 provides the water solubilities and octanol−water partition coefficients (log P_{ow}) of the antioxidant compounds in Table 1 to highlight their relative polarities. As shown in Table 1, the more polar phenolic antioxidants such as pyrogallol (PA), propyl gallate (PG), and *tert*-butyl hydroquinone (TBHQ) tend to be more effective in FAMEs than less polar/more hydrocarbon-soluble antioxidants such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), and α-tocopherol (Toc).[11,24,25]

Assessments of antioxidant effectiveness using measurement of IP or other highly accelerated tests are useful in understanding how to best stabilize fuel for storage and handling. However, these studies have focused on limited

conditions and time frames. Environmental factors such as contamination from water or oxidizing metals or stability in real-world storage scenarios require longer test protocols, often on the order of months or even years.[32,34−38] Water is nearly unavoidable in fuel transportation and storage, forming a water layer at the bottom of fuel storage tanks, and is therefore a very likely contaminant for diesel and biodiesel blends to encounter.[39] Although water is not known to contribute directly to the overall free radical mechanism of FAME oxidation,[40,41] water may be capable of extracting polar antioxidants, rendering them ineffective. One prior study evaluated the effect of water on oxidation in storage for a biodiesel that had not been stabilized with antioxidants.[42] The authors observed no impact of water on oxidation. This study investigates whether nonpolar antioxidants, which are less effective in dry environments, might be more effective under wet conditions simulating real-world storage—testing the hypothesis that highly polar antioxidants are extracted into the water layer where they no longer protect the fuel from oxidation.

■ EXPERIMENTAL SECTION

Test Methods. Rancimat IP for biodiesel blends was measured by method EN 15751, which is commonly referred to as the Rancimat test or oil stability index.[44] In this evaluation, the fuel is stressed by heating to 110 °C with air flowing through the liquid substrate providing high temperature and excess oxygen to accelerate oxidation. As the polyunsaturated FAMEs oxidize, they form peroxides, which in turn break down to form volatile carboxylic acids.[45,46] The resultant acids are swept along with the flow of air into a small container of water with constant monitoring of conductivity. A curve of conductivity over time is evaluated, and the inflection point provides a measure of the fuel's induction period (IP) in hours.[47] A minimum induction period has been included in specifications to ensure adequate stability and quality during storage and use—designated as oxidation stability in ASTM D6751 (3 h minimum for B100), ASTM D7467 (6 h minimum for B20), and EN 14214 (6 h minimum for B100).

Hydrocarbon diesel fuels produced in a petroleum refinery do not contain polyunsaturated hydrocarbon chains, and therefore Rancimat IP is not a meaningful stability metric for these fuels. ASTM method D7545 (Rapid Small Scale Oxidation Test or RSSOT) was used to monitor oxidation of B0 (petroleum diesel used for preparing B20 blends). In this method, the fuel is heated in a pressure vessel to 140 °C under 700 kPa of oxygen. The pressure is monitored over time until a breakpoint (rapid oxygen consumption) is reached, defining the IP for this test. The B0 was treated with BHT to a RSSOT IP value of ~2 h.

Acid number was measured by ASTM D664 Method B, a potentiometric titration. The water content was measured by the Karl Fisher titration method, ASTM D6304. Peroxides were measured by potentiometric titration based on a modified AOCS Cd 8b-90 method. EN15751, ASTM D7545, ASTM D664, and ASTM D6304 are standardized methods with measurement precision that has been established in interlaboratory studies. For the modified AOCS Cd 8b-90 peroxide method, repeatability was measured by performing 10 replicate tests on samples having a range of peroxide contents. Method repeatability is tabulated in the Supporting Information (SI) and was used to place 95% confidence interval error bars on the charts of results. Note that the acid number and peroxide methods were used to measure these species in both the fuel and water layers.

A gas chromatography with mass spectrometry (GC−MS) method was developed to monitor changes in antioxidant concentrations in the fuels during storage. Method details are reported in the SI. PA was not analyzed due to inability to detect the low concentrations of less than 10 ppm added to reach IP of ~12 h (discussed below). The instrument was calibrated using BHT and TBHQ dissolved in

heptane and B0 containing a 2,4-dimethylphenol internal standard. The resulting linear calibration had an R^2 > 0.995. The limit of detection for TBHQ was estimated to be 10 ppm.

Fuels and Aging Procedure. A commercially available distilled soy B100 and petroleum refinery hydrocarbon diesel (B0) were used to prepare a baseline 20% biodiesel blend (B20). Distilled biodiesel was used to ensure that little to no natural antioxidants would be present that could confound the study results, and the fatty acid makeup and properties of this material are provided in the SI. Properties of the petroleum diesel are also shown in the SI. The B20 was divided into three separate samples for additization. The first sample was additized with a more polar/highly effective antioxidant PA (pyrogallol or benzene-1,2,3-triol, Sigma Aldrich). The second sample was additized with a less polar/less effective BHT (butylated hydroxy toluene or 2,6-di-*tert*-butyl-4-methylphenol, Sigma Aldrich). The third was treated with TBHQ (*tert*-butylhydroquinone or 2-(1,1-dimethylethyl)-1,4-benzenediol, Sigma Aldrich), a polar antioxidant with effectiveness expected to be between PA and BHT in B100. All three B20s were additized to roughly the same initial IP, nominally 10 to12 h. Note that a specific concentration of these compounds was not targeted, but rather a common IP value to create ideally equal stabilities varied only by antioxidant chemistry. Antioxidant concentrations and initial IP values are shown in Table 3. Note that TBHQ has been shown to be significantly more effective than BHT in B100 but to have similar effectiveness in biodiesel blends, as observed here.[32]

Table 3. Antioxidant Concentrations and IPs of Lab-Prepared B20 Samples

antioxidant	ppm	initial IP
PA, highly polar	7	12.2
BHT, nonpolar	120	10.0
TBHQ, moderately polar	125	11.0

These three laboratory-prepared samples were then subdivided into three separate aliquots for storage stability assessments. The first aliquot was stored in a 500 mL vented glass jar holding 400 mL of fuel in an oven at 43 °C per ASTM D4625 (dry). The second was stored in an identical jar at the same temperature with an added water bottom (50 mL water + 400 mL fuel) to simulate water contamination (wet). This sample was held in a humidity chamber to maintain water saturation. The humidity chamber was used to age the water-contaminated samples to ensure that the fuel remained saturated and to prevent evaporation of the water layer into the very dry local ambient air during accelerated storage. Humidity was maintained using a saturated solution of potassium sulfate placed in the bottom of the chamber, which produces a relative humidity of 92% at 28 °C. The third aliquot was also stored in the humidity chamber but without added water, allowing for water absorption from the atmosphere (humid). A B0 control (no biodiesel) was tested alongside the B20s in each of the three storage scenarios. Replicate results for storage in both dry and wet environments for IP, peroxide, TAN, and water content are shown in the SI and show excellent repeatability, providing high confidence that the relatively large effects observed in this work are significant. A picture of a set of sample jars is provided in Figure 1.

Lab-prepared samples were aged for 24 weeks in these three accelerated storage conditions (simulating 2 years for the D4625 standard method—the dry scenario) with regular monitoring for signs of oxidation. IP, acid number, peroxide concentration, and water content were measured at regular intervals. Aging was terminated if an acid number > 0.3 mg KOH/g was reached, indicating failure of the acid number limit in quality standards. The total insoluble material was measured at the end of the test period following the protocol of ASTM D4625 modified with glass fiber filters.

As a final sample set, four nominally B20 blends were collected in the field as part of a previously published study.[21] Properties of these fuels are reported in the SI. In that study, samples were collected from
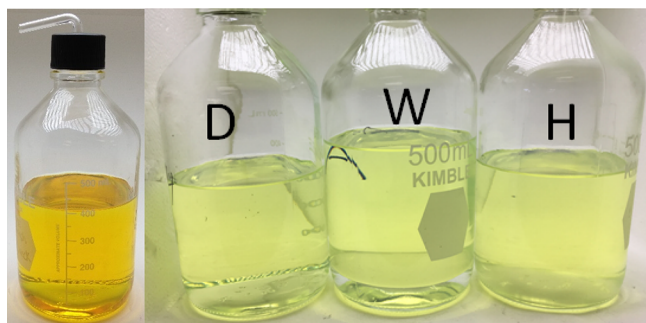
Figure 1. D4625 sample jar (left) and sample jars held in three storage scenarios (right): D, accelerated dry storage in an oven; W, accelerated wet storage in humid air with added water bottom; and H, accelerated storage in humid air without added water—note visible haze from water absorption into the fuel.

across the United States and evaluated for storage stability. Two samples with Rancimat IP < 10 h were selected along with two samples with IP > 20 h, resulting in lower-stability and higher-stability samples. These were stored for 24 weeks both in a test oven at 43 °C per ASTM D4625 accelerated stability (nominally 4× accelerated oxidation; 1 week to 1 month) and in a controlled humidity chamber at the same temperature with a water layer added to the fuels (50 mL of water added to 400 mL of fuel). A biocide additive was added to 18 MΩ deionized water prior to blending to prevent microbial growth from contributing to changes during storage.

■ RESULTS

A lab-prepared B20 sample was used to evaluate the hypothesis that water could impact stability indirectly by impacting antioxidants. The distilled B100 used for this blend had an initial IP of 0.7 h, confirming that this had little or no added antioxidants present that might interfere with this experiment. The baseline acid number was 0.15 mg KOH/g, well below the maximum value allowed in D6751 for B100 of 0.5 mg KOH/g. The resultant B20 prepared from this blendstock had a baseline IP of 3 h before addition of antioxidants. Antioxidants were initially added to small samples of this B20 at varied concentration in a scoping study to determine the appropriate concentrations to achieve the desired starting IP of approximately 10 h. Table 3 provides the antioxidant concentrations added and initial IPs of the three lab-prepared samples. After treatment with antioxidants, samples were subjected to accelerated aging and monitored at regular intervals for changes in IP and signs of oxidation (increase in peroxide and acid content). The B0 used to blend the B20 was treated with BHT and demonstrated minimal decline in stability over 24 weeks and a small but measurable negative impact of water on RSSOT (ASTM D7545) IP (see the SI).

Water Impact with a Highly Polar Antioxidant (Pyrogallol). IP was found to decrease quickly for B20 treated with PA both when stored with a water bottom and in a humid environment compared to dry storage (Figure 2A). This contrasts with dry storage where the IP decreased much more slowly. After 2 weeks of storage in contact with water, the PA-treated samples fell below 6 h IP. The rate of change in IP slowed after this initial rapid decline, and the IP remained nearly constant until after 10 weeks, when IP decay accelerated. By 15 and 16 weeks, respectively, the IP of the humid and wet samples went down to essentially zero. At 8 to 12 weeks, peroxides began to increase and ultimately achieved quite high values (Figure 2B) and the acid number eventually increased to above the limit of 0.3 mg KOH/g (Figure 2C), at which point the samples were removed for filtration of
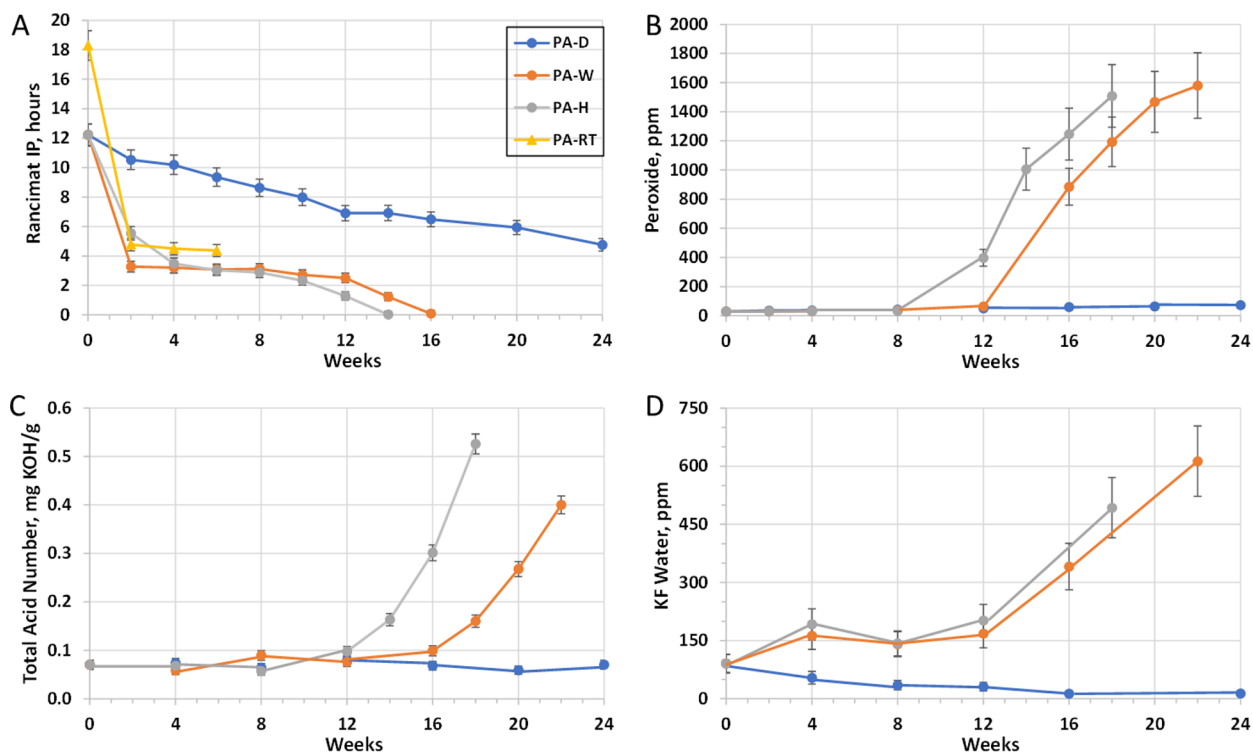

Figure 2. (A−D) Oxidation stability results for B20 samples treated with PA stored in multiple scenarios: accelerated (43 °C) dry storage (PA-D), accelerated storage in humidity with a water bottom (PA-W), accelerated storage in humidity without added water (PA-H), and room temperature in a nitrogen-purged sealed container with added water bottom (PA-RT). Error bars are test method repeatability.
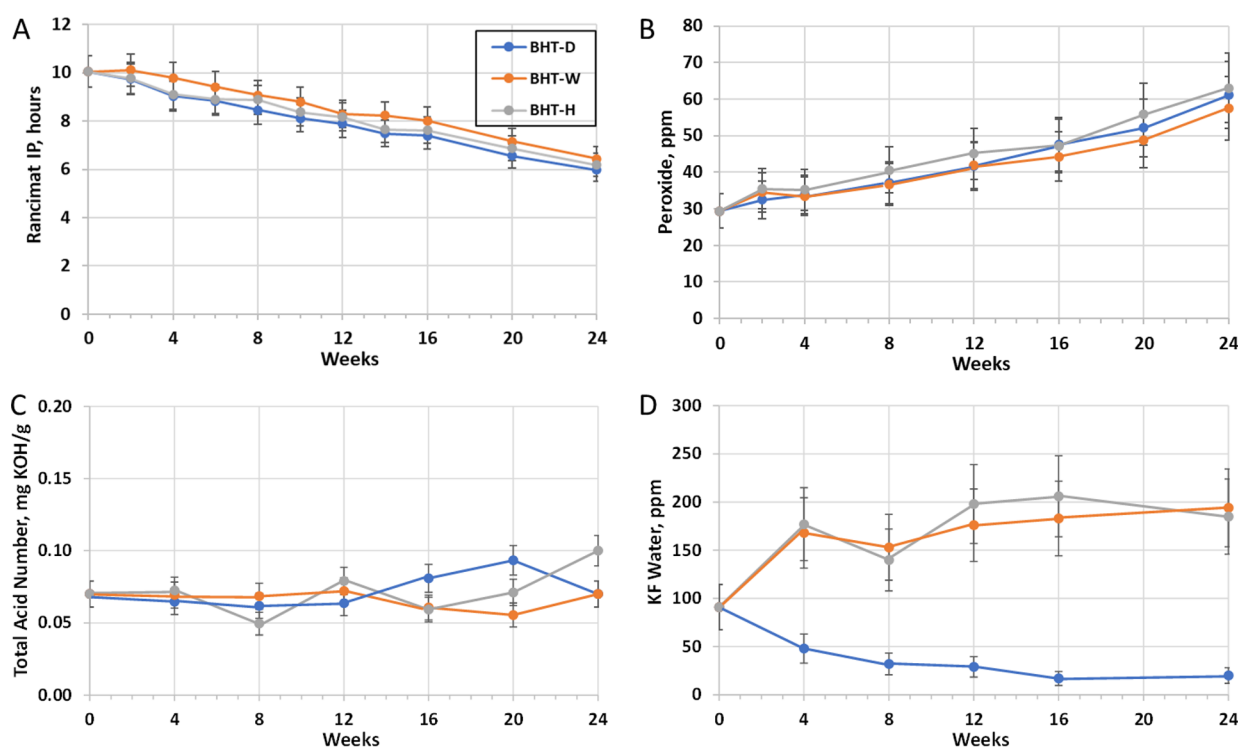
Figure 3. (A−D) Oxidation stability results for B20 samples treated with BHT stored in multiple scenarios: accelerated (43 °C) dry storage (BHT-D), accelerated storage in humidity with a water bottom (BHT-W), and accelerated storage in humidity without added water (BHT-H). Error bars are test method repeatability.

insoluble material. The total insoluble material was measured at 125 mg/100 mL (75 filterable/50 adherent) for the wet storage sample (PA-W) after 22 weeks of accelerated storage. In the case of the humid storage sample (PA_H), this was 205 mg/100 mL (5 filterable/200 adherent) after 18 weeks of storage. These extremely high acid and insoluble levels render these fuels no longer usable in diesel engines. The dry storage sample did not produce any measurable insoluble material at the end of 24 weeks. In addition, the acid and peroxide concentrations remained low for the dry storage sample, indicating that oxidation did not occur for the fuel stored in this scenario; IP was reduced as the antioxidant was consumed.

The dissolved water concentration was nearly identical for both wet and humid storage until after the onset of oxidation (Figure 2D), indicating that the humid storage fuel had absorbed water from the environment to the point of saturation. A visible haze from free water was noted for this sample during sampling intervals, further indicating water saturation. As expected, the dry storage sample lost water from evaporation at the test temperature. The wet and humid samples showed a large increase in water content after the production of peroxides, which was due to either water produced by oxidation or the fuel developing the ability to dissolve water from the production of polar oxygenated species.

Interestingly, the sample stored with a water layer (PA-W) accumulated peroxides and acids more slowly than the sample stored in a humid environment without a water layer (PA-H). Analysis of the water layer for PA-W at the end of the 24 week experiment showed a peroxide content of 180 ppm and an acid content of 2.2 mg KOH/g. The water layer extracted these water-soluble oxidation products, making it appear that the

water layer sample oxidized more slowly when in fact PA-W and PA-H likely oxidized at very similar rates.

A possible explanation for the observed initial rapid decrease in IP for wet and humid storage with PA-treated B20 is that the antioxidant was being extracted by the water layer. The concentration of PA required to reach the desired IP was too low to confidently measure with the GC−MS method; therefore, an additional experiment was conducted to explore the possibility of extraction. Another sample was prepared and treated with PA at 10 ppm. This was then exposed to a water bottom and placed in a closed, nitrogen-purged jar (preventing contact with air) and held at room temperature protected from light for 6 weeks. This room-temperature sample is shown in Figure 2A as PA-RT. The IP of this sample decreased to below 6 h within 2 weeks without added heat or access to oxygen and then remained constant. This initial rapid loss in IP was not due to oxidation as it was stored at room temperature and not exposed to oxygen. Therefore, this was likely due to extraction of the polar antioxidant into the water layer.

Water Impact with a Nonpolar Antioxidant (Butylated Hydroxy Toluene). In contrast to the B20 treated with PA, the samples treated with BHT did not show a negative impact on IP when exposed to water or humidity (Figure 3A). IP slowly declined at the same rate for wet and dry samples, while peroxides slowly increased but never exceeded 70 ppm (Figure 3B, versus values well over 1000 ppm for the wet and humid PA-treated samples). There was minimal acid (Figure 3C) and insoluble formation, and peroxide and acid levels in the water layer of BHT-W were very low. Figure 4 shows the results of GC analysis of the fuel for BHT concentration. BHT levels slowly decreased as it was consumed by oxidation, in line with the slow decline in IP shown in Figure 3. BHT is insoluble in water and is clearly not extracted into the water
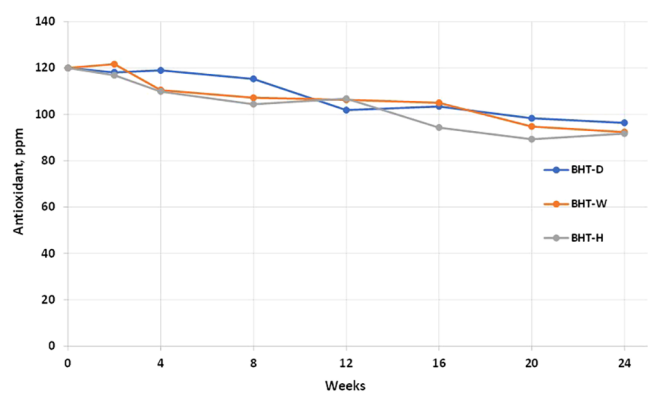
Figure 4. Concentration of BHT in B20 samples during storage at 43 °C in dry (D), wet (W), and humid (H) conditions.

layer, providing identical performance in wet and dry environments.

Water Impact with a Moderately Polar Antioxidant (*tert*-Butyl Hydroquinone). The IP values of samples treated with TBHQ are provided in Figure 5A. The TBHQ-treated samples exposed to water showed an initial decline in IP relative to the dry case followed by a fairly constant value beyond 10 weeks. These fuels did not produce a high concentration of peroxides (Figure 5B), acids (Figure 5C), or insolubles after 24 weeks of storage. The fuel maintained some oxidation reserve, preventing degradation of fuel properties. The amount of water absorbed by the B20 samples both with a water bottom and in a humid environment reached a maximum of ~200 ppm. In the case of the humid samples, free water was visible as haze, indicating that this was the saturation point of the fuel (as was also observed for the PA- and BHT-treated B20 samples). Peroxide and acid levels in the

water layer for TBHQ-W were at low levels, very similar to what was observed for BHT-W. As noted with the PA-treated sample, the TBHQ-treated B20 experienced extraction of the moderately polar antioxidant to the water phase, as shown in Figure 6. TBHQ was reduced to nearly half of the initial
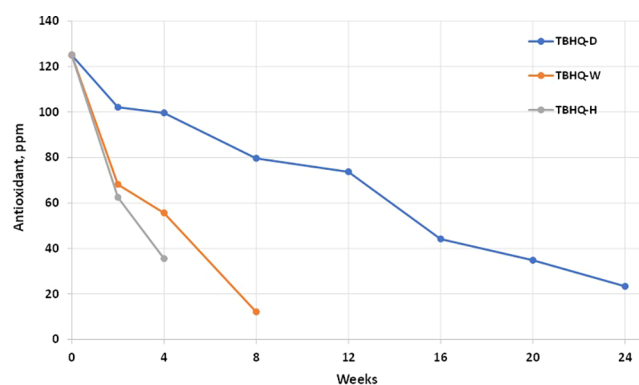

Figure 6. Concentrations of TBHQ in B20 samples during storage at 43 °C in dry (D), wet (W), and humid (H) conditions. The method limit of detection is 10 ppm.

concentration within 2 weeks when in contact with water or humidity (Figure 6). The antioxidant was reduced to below detection (<10 ppm) after 8 weeks. Given the observed stability (minimal formation of oxidation products) even after extraction of most of the antioxidants, TBHQ levels below 10 ppm can apparently impart significant resistance to oxidation.

Another notable feature of the TBHQ results is the much more rapid consumption of TBHQ relative to BHT for dry storage. BHT levels were just below 100 ppm at 24 weeks, while the TBHQ concentration had dropped to near 20 ppm.
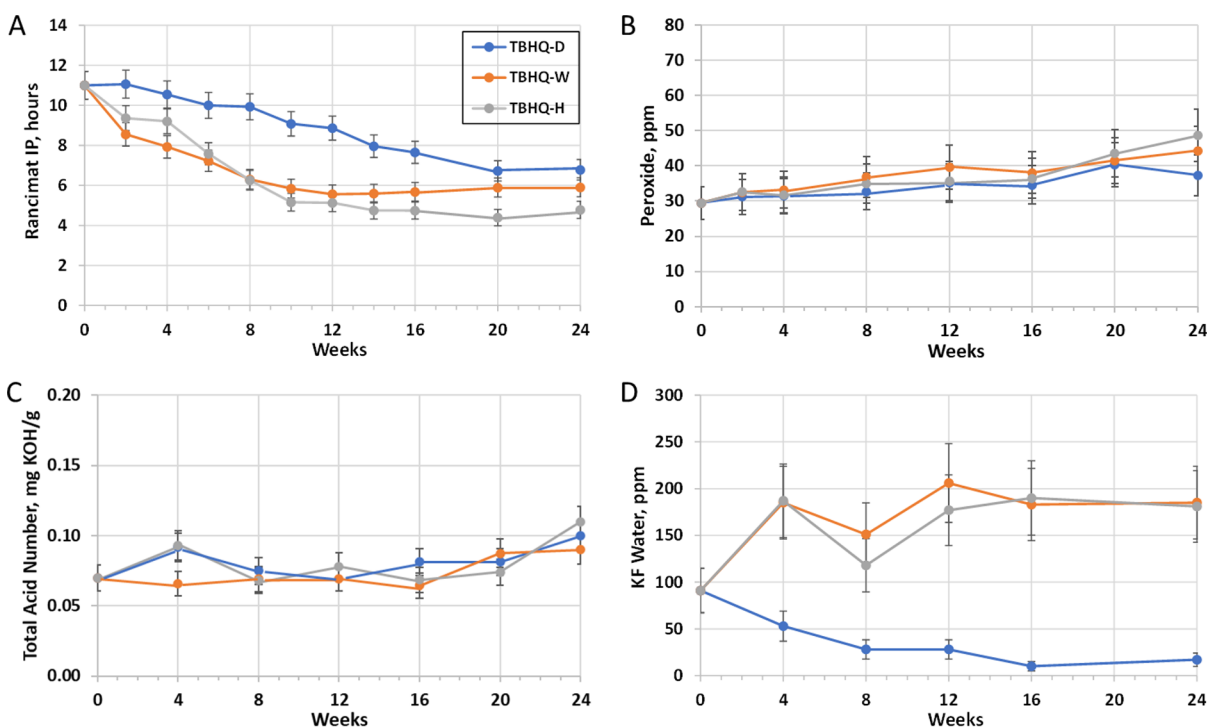

Figure 5. (A−D) Oxidation stability results for B20 samples treated with TBHQ stored in multiple scenarios: accelerated (43 °C) dry storage (TBHQ-D), accelerated storage in humidity with a water bottom (TBHQ-W), and accelerated storage in humidity without added water (TBHQ-H). Error bars are test method repeatability.
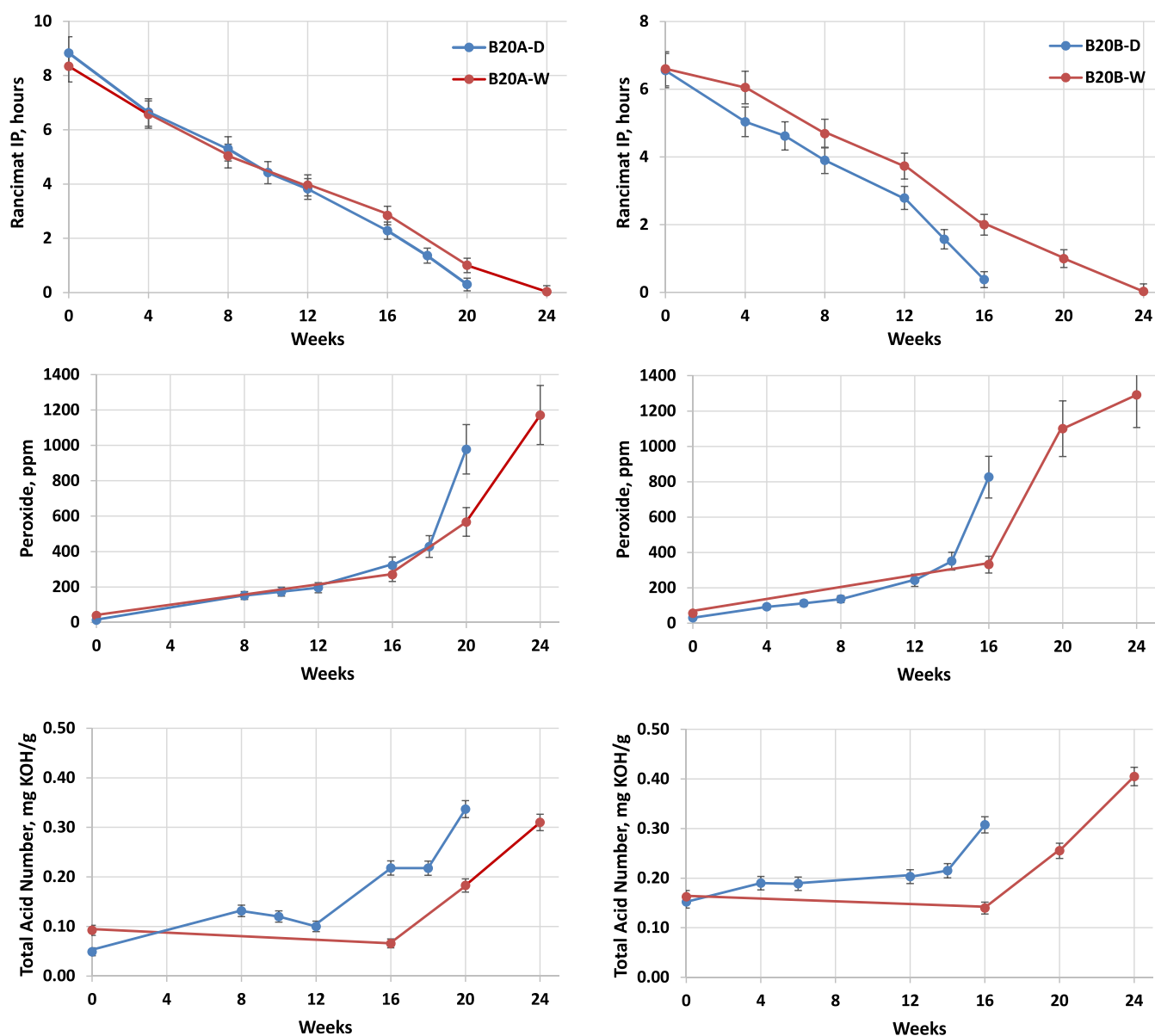
Figure 7. Oxidation stability results for lower-stability (IP < 10) B20 field samples stored in a test oven at 43 °C (D) compared to storage with added water bottom in a humidity chamber at 43 °C (W). Error bars are EN15751 method repeatability.

Water Effect on Field Sample Stability. To provide a more practical perspective on the effect of water on the storage stability of B20, samples obtained from retail station and fleet storage tanks as part of a previous study were evaluated. For these samples, we have no knowledge of the biodiesel source or feedstock, nor of antioxidant blending. Properties measured for these four samples are reported in the SI, including validation that the samples contained nominally 20 vol % biodiesel. The IP values measured during accelerated aging for the four field samples are presented in Figures 7 and 8. Two samples with lower stability (<10 h initial IP), A and B (Figure 7), showed similar storage stability in the dry case and for exposure to water. Sample A took 20 weeks to reach essentially 0 IP, a high peroxide level, and exceed the acid number limit of 0.3 mg KOH/g in the dry case (0.33 mg KOH/g at 20 weeks) but took 4 weeks longer (4 months simulated) to reach this limit in the wet case—possibly because of extraction of acids into the water layer. Sample B was only stored for 16 weeks in dry storage as it reached 0.31 mg KOH/g acid number and

high peroxide content at that time, but it took an additional 8 weeks (8 months simulated) to reach this limit in the wet case. For the wet case, Sample B had an acid number of 0.14 mg KOH/g at 16 weeks, reaching a value of 0.40 mg KOH/g at 24 weeks—as observed for Sample A, this may have been because of extraction of acids into the water layer.

The two higher-stability samples (>20 h initial IP), C and D, demonstrated vastly different behaviors (Figure 8). With these two samples, the IP in the wet storage case was reduced compared to the dry case by the first sampling interval (4 weeks) and continued to decline. The dry samples showed very little change in IP over the course of 24 weeks, while the introduction of water had a large negative impact. Because of the initially very high stability of samples C and D, the IP never reached zero over the 24 week experiment. Thus, these samples did not show exponential growth in peroxide content nor high acid numbers.

The results strongly suggest that samples A and B were prepared with a nonpolar antioxidant that was not extracted
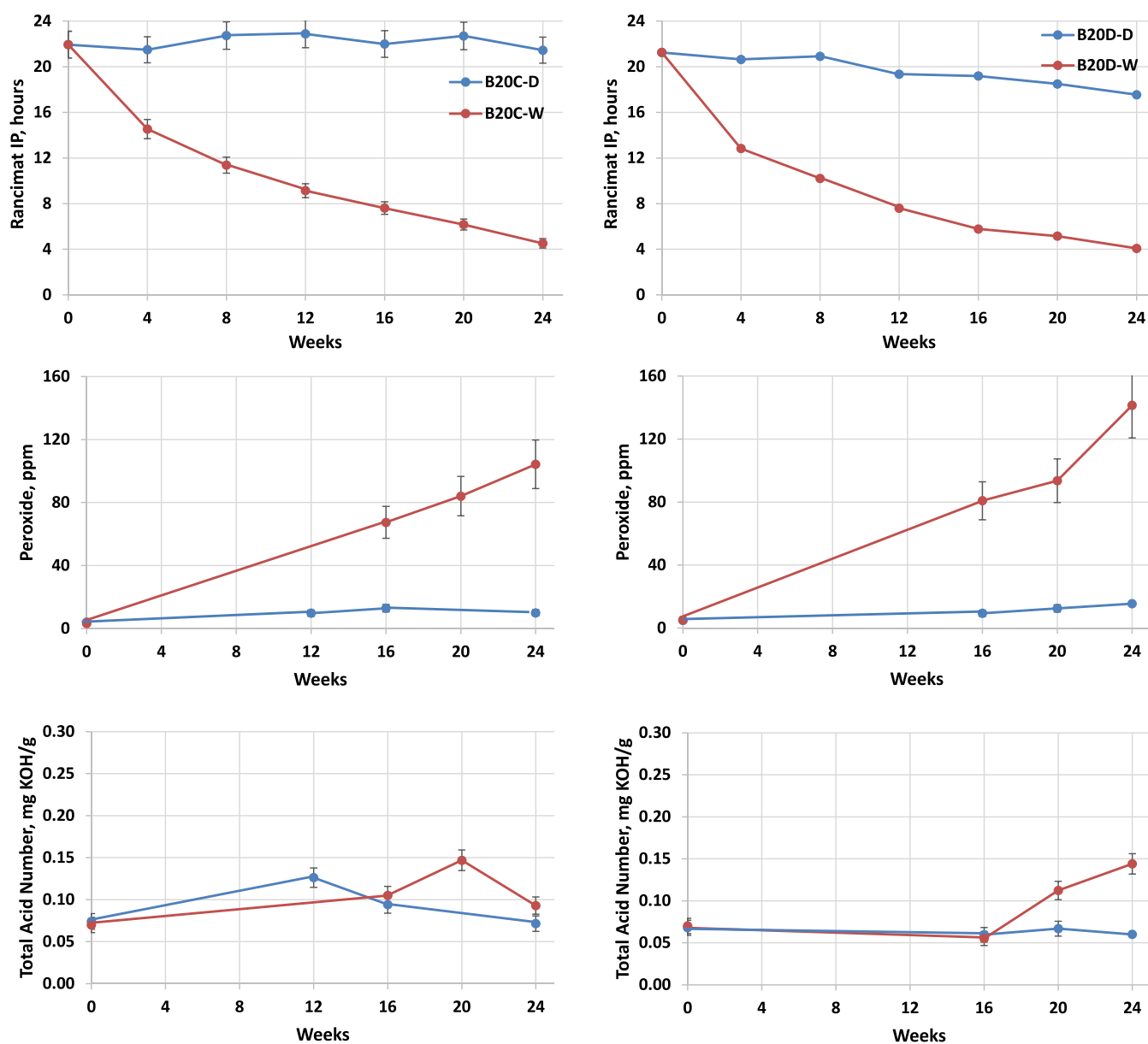
Figure 8. Oxidation stability results for higher-stability (IP > 20) B20 field samples stored in a test oven at 43 °C (D) compared to storage with added water bottom in a humidity chamber at 43 °C (W). Error bars are EN15751 method repeatability.

into the water layer—consistent with their relatively low initial stability while high stability. Samples C and D may have been prepared with a more polar antioxidant that produced their high initial Rancimat IP, but that was extracted upon exposure to water. Because the decrease in IP for samples C and D was not as rapid as observed for the laboratory B20 prepared with PA (Figure 2), the antioxidant used may have been moderately polar and similar to TBHQ.

■ DISCUSSION AND CONCLUSIONS

Water is the most common contaminant in diesel fuel storage and distribution systems.[39] Surveys of biodiesel blend quality for samples from throughout the United States have reported similar concentrations of water to those observed in this study, with many fuels between 100 and 200 ppm.[19] The levels of dissolved water reached in the wet and humid cases reported here are not out of the ordinary in fuel distribution systems, indicating that water-saturated fuel can commonly be

encountered in the marketplace. Water does not appear to directly influence the rate of biodiesel oxidation;[40,41] it is neither directly negative nor positive in an obvious way.[41] However, contact with water can influence oxidation reserve by impacting antioxidants. Samples treated with a polar/highly effective antioxidant showed reduced oxidation reserve within 2 weeks. The use of nonpolar antioxidants, although less effective in bench-scale B100 tests, would be protective against premature IP loss from downstream water contamination.

This study has demonstrated that simple analysis of antioxidant effectiveness in accelerated bench tests may not translate to effectiveness in real-world storage. The response of a biodiesel blend to an antioxidant like TBHQ can be quite different than expectations based on B100 testing alone. The compound BHT—largely regarded as a poorly effective additive for biodiesel in terms of stabilization factor—had advantages with regard to storage stability for biodiesel blends as its response is considerably higher in a blend than one

would expect from measurements on B100, and it demonstrates resistance to water contamination. This feature of highly effective but highly polar antioxidants may account for the observation that biodiesel blend samples collected from retail and fleet tanks can have significantly lower stability than anticipated, even failing the minimum stability requirement in fuel standards.[19−21] Future research on biodiesel additives should focus on impacts in blended fuels and how these additives may behave when in contact with downstream contamination in the longer term. Given a study showing synergistic effects for secondary antioxidants added with BHT,[48] research on antioxidant formulations providing protection under both wet and dry conditions should also be a priority.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.2c03911.

> Composition and properties of soy biodiesel used to prepare laboratory blended fuels; properties of petroleum diesel used to prepare laboratory blended fuels; stability of petroleum diesel over D4625 aging; properties of B20 blends obtained from retail station and fleet tanks; method repeatability; details of gas chromatography method for determination of antioxidant concentration; results of replicate D4625 (dry oven) aging of B20 sample A (field sample); results of replicate D4625 aging modified to have a water layer and performed in a humidity chamber for B20 sample D (field sample) (PDF)

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Notes

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