Re-Additization of Commercial Biodiesel Blends During Long-Term Storage

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Abstract

Commercial biodiesel blends were aged at 43°C while monitoring stability. The oxidation stability—or oxidation reserve expressed as Rancimat induction period (IP)—gradually decreased from its initial value. At a predetermined IP threshold, an antioxidant was used to restore IP to the ASTM D7467 specification minimum of 6 hours, referred to as re-additization. At lower IP values, the amount of antioxidant required increased significantly, and the effectiveness tended to be reduced. Once IP fell to essentially zero, the acid content increased to above the allowable limit and insoluble material was also detected. Storage life was increased relative to the as-received fuels as evidenced by longer time to produce acids. Experience in the field may vary based on storage conditions; however, these results indicate re-additization can significantly increase storage life of biodiesel blends when used with regular monitoring of IP and acid number. An assessment of the storage stability of the as-received fuels showed that the initial IP did not predict storage behavior, although fuels above the specification minimum remained stable for greater than 12 weeks accelerated aging (1 year simulated).

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Keywords: Renewable Fuel; Biodiesel; Oxidation Stability; Storage Stability; Antioxidant

1. Introduction

Biodiesel is a renewable compression-ignition fuel blendstock derived from fats and oils [1,2]. The triglycerides that compose the oils are converted to alkyl esters via transesterification with an alcohol, most often methanol, yielding fatty acid methyl esters (FAMEs) [3]. This product retains the fatty acid carbon chains of the triglycerides, which tend to be a combination of saturated and unsaturated chains [4]. Unsaturated carbon chains, particularly polyunsaturated chains, are susceptible to oxidation under mild conditions when exposed to air over time (autoxidation) [5,6]. If oxidation occurs to a large enough degree, it can lead to deleterious changes in fuel properties, such as the production of acids and insoluble polymers [7,8,9]. This is of concern for fuel storage, given that acids can cause corrosion of storage tanks and engine fuel systems, [10,11] and insoluble materials can cause filter blocking and injector fouling [12].

The ability of a fuel to resist changes in physico-chemical properties caused by interaction with the environment is known as its storage stability [9]. The length of time biodiesels and blends with hydrocarbon diesel can be stored before problematic changes occur (storage life or shelf life) is largely dependent on its rate of oxidation, which depends on many factors that are related to both fuel properties and storage conditions [13,14]. The most reactive sites in the fatty acid structure are adjacent to two unsaturated carbons, known as bis-allylic positions; therefore, the concentration of polyunsaturated esters has a large influence on stability [15,16]. Antioxidant additives slow the process of oxidation by interrupting the free radical mechanism, increasing storage life [9,17-24]. Sustained exposure to heat, air, light, or oxidizing metals accelerates oxidation and reduces storage life [9,13,17,22,25-27]. The overall stability can

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be thought of qualitatively as the oxidation reserve, the proportionality of factors that prevent oxidation to those that promote it [28].

$$\textbf{Oxidation Reserve} \propto \frac{\textbf{Antioxidant Concentration}}{\textbf{Radical Initiator Concentration} + \textbf{Bisallylic Site Concentration}}$$

The inherent oxidation reserve of biodiesel and biodiesel blends is assessed by test method EN 15751 (commonly known as the Rancimat test, or oxidation stability index) in which a sample is exposed to heat and air to accelerate oxidation and generate degradation products. An induction period (IP) is reached once the sample has broken down to form volatile acids, expressed in hours (hr). The higher the IP value, the greater the resistance to oxidation or the greater the inherent oxidation reserve. Oxidation stability measured by this test is specified in US specifications ASTM D6751 for biodiesel at a minimum of 3 hr and in ASTM D7467 for B6 – B20 blends at a minimum of 6 hr. These limits have been established to ensure biodiesel blends have sufficient stability to prevent problematic changes during normal storage for up to 6 months [29].

The majority of diesel fuel is consumed relatively soon after production, but some low-use applications require longer-term storage, i.e., longer than one year. Storing diesel fuel for longer than one year requires additional considerations to ensure adequate fuel quality at the time of use, including high initial oxidation reserve and monitoring for signs of degradation during storage [30]. Long-term storage of biodiesel and its blends raises some concerns given differences in oxidation stability relative to hydrocarbon diesel. Although chemical or physical property limits that indicate the end of storage life of biodiesel have not been well defined, a limit on the acid number (also called total acid number) is included in the ASTM specifications. ASTM D6751 limits the acid number of pure biodiesel to a maximum of 0.5 mg KOH/g, and

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ASTM D7467 limits B6 – B20 blends with hydrocarbon diesel to 0.3 mg KOH/g. These limits are included to ensure free fatty acids have been removed during production; however, it is recommended that the acid number be monitored for increases during long-term storage to detect evidence of oxidation [2,29]. An acid number increase to above the specification limit as a result of oxidation indicates that a fuel is no longer fit for use. For example, Bouilly and coworkers studied injector failure when operating on oxidized B20s [12]. Although they found that acid number did not correlate well with injector failure time, their results showed that failures occurred after the acid number had increased above 0.3 mg KOH/g and IP had fallen below 3 hr. In another study, biodiesel blends stored in vehicle fuel tanks in a hot climate were shown to be equivalent to a hydrocarbon diesel when the acid number remained below the limit of 0.3 mg KOH/g and IP remained above 3 hr; high-pressure fuel pumps showed no signs of abnormal wear and filters showed no signs of deposits when operating on the stored fuel [31]. A practical limit for defining the storage life of biodiesel and blends would therefore be the acid number limit included in the specifications.

Studies on the long-term storage of pure biodiesel have demonstrated 6 months to one year prior to out-of-specification acid number with adequate initial oxidation reserve [13,14,20,26,32]. Tang and coworkers found that with the use of antioxidants soybean-based biodiesel could be stored up to 30 months prior to detecting high acid number [33]. Biodiesels having low oxidation reserve can become problematic in much shorter timeframes, within 4 months [8], but the use of antioxidants has been shown to be effective at stabilizing low IP samples and increasing storage life [21,22,34]. Re-additization—adding antioxidants after detecting a decrease in IP—was studied by Christensen and coworkers and shown to be effective at increasing B100 biodiesel storage life [28].

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Pure biodiesel is not typically stored for long periods as it is primarily used as a blend with hydrocarbon diesel. Blending biodiesel with hydrocarbon diesel tends to improve its stability significantly [35]. The stability of a blend is largely influenced by the stability of the biodiesel and blend concentration [36]. Studies of biodiesel blend storage stability have used accelerated testing, given the longer storage lives encountered with primarily hydrocarbon fuels, following ASTM method D4625 for storage stability of middle distillate fuels [8,28]. In this test, the fuel is kept in vented glass jars in an oven at a constant temperature of 43°C ± 1°C. This test method states that at this temperature, the rate of oxidation is accelerated roughly by a factor of four compared to storage at a constant ambient temperature of 21°C, which the method describes as normal ambient conditions. One week of this test being approximately equivalent to one month in "typical" storage conditions [37]. This method was developed to evaluate potential storage stability of diesel fuels prior to the advent of ultra-low sulfur diesel or biodiesel. Currently, this fourfold acceleration in aging has not been verified with modern fuels. Additionally, given the large influence of environmental factors that vary depending on the storage scenario, such as heat, air exposure, fuel tank materials, and contamination, storage life may vary considerably in the field compared to a laboratory test. However, this test method provides a consistent basis for evaluating the storage stability of diesel-range fuels. The results from this test – 1 week accelerated simulating 1 month – will be referred to as potential storage life.

Accelerated tests have shown that blends prepared with biodiesel having an initial IP ≥ 3 hr result in B5 and B20 blends with sufficient stability for storage lives greater than 12 weeks (a simulated year of storage), but blends prepared with low-IP biodiesel had high acid number within 6 weeks (simulated 6 months) [8]. Blends prepared with biodiesel having an IP of 6 hr

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resulted in B5 and B20 blends that still met the IP minimum for blends by the end of 36 weeks of accelerated aging, simulating storage stability of greater than 3 years [28]. Yang and coworkers studied storage of B20 blends at 15°C and 40°C in which blends prepared with biodiesel having IP > 5 hr remained below the acid number limit after 300 days of storage at both temperatures, indicating the storage lives of these fuels were longer than the time studied [38].

Previous studies on biodiesel and blend stability have shown promising results for long-term storage with lab-prepared blends. It has been demonstrated that high oxidation reserve indicates longer storage lives, potentially allowing for blends to be stored for multiple years without problematic changes to fuel properties. Here we report on the long-term storage stability of commercial biodiesel blends collected from across the United States. During storage, the potential for stabilization via re-additization is explored with addition of an antioxidant at pre-determined IP thresholds followed by continued aging.

2. Experimental

2.1. Biodiesel Blends

Twelve nominally 20% biodiesel blends (B20s) were collected from 12 different states, and one sample was prepared in the lab using a distilled B100 and a biodiesel-free hydrocarbon diesel (B0). Blends were tested for ASTM specification D7467 properties; these results are provided in Table 1. The test methods listed in Table 1 were followed as written except for peroxide number; ASTM D3703 was modified for endpoint detection by potentiometry in place of colorimetric titration. Properties of the distilled B100 and B0 were reported previously [31] and are provided in the supporting information in Table S1. Sample A did not meet the minimum

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value for oxidation stability. This sample met the specification for acid number, indicating the fuel had not yet degraded, so was included in storage stability experiments.

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Table 1: B20 Blend Properties

			Nashville, TN	Charlotte, NC	San Antonio, TX	Denver, CO	Jefferson City, MO	Riviera Beach, FL	Phoenix, AZ	Lexington, KY	Hood River, OR	Hamel, IL	Philadelphia, PA	Oakland, CA	In-house blend
Property	Units	ASTM Method	A	B	C	D	E	F	G	H	I	J	K	L	M
Biodiesel content	vol%	D7371	20.2	20.4	17.1	22.0	19.4	22.0	20.7	20.1	20.1	15.3	20.3	19.0	20.4
Rancimat IP	hr	EN 15751	2.3	18.2	21.4	8.8	14.6	21.3	32.0	6.6	26.4	19.8	17.9	21.9	7.9
Acid number	mg KOH/g	D664	0.14	0.05	0.02	0.05	0.09	0.07	0.06	0.15	0.04	0.06	0.06	0.07	0.02
Peroxide number	ppm	D3703	96.3	2.0	11.3	13.6	8.0	4.9	2.3	30.6	1.4	3.4	10.5	4.1	15.6
Viscosity at 40°C	cSt	D445	2.746	2.810	2.958	2.985	2.166	2.802	2.813	2.703	2.849	2.879	2.648	3.063	2.846
Flash point	°C	D93	63	63	46	72	55	62	71	47	71	77	64	73	--
Cloud point	°C	D5773	-10.0	-10.7	-8.0	-11.9	-18.7	-9.9	-6.0	-9.3	-11.0	-14.3	-10.6	-13.8	-9.3
Sulfur	ppm	D5453	6.9	4.8	5.1	8.1	3.9	6.8	6.6	6.6	5	4.7	7.1	1.3	--
Distillation, T90	°C	D86	335.5	335.1	332.3	335.2	331.1	335.8	336.9	336.3	334.6	328.4	334.3	320.9	--
Carbon residue	wt%	D524	0.11	0.06	0.06	0.07	0.08	0.07	0.07	0.08	0.08	0.07	0.11	0.05	--
Aromatics	vol%	D1319	33.1	39.2	35.1	40.0	35.3	32.5	46.3	39.5	35.1	39.1	51.5	14.7	--
Olefins	vol%	D1319	1.7	1.6	1.2	2.3	1.0	1.1	1.3	0.7	1.3	1.4	1	0.2	--
Saturates	vol%	D1319	65.2	59.2	63.7	57.7	63.7	66.4	52.4	59.8	63.6	59.5	47.5	85.1	--
Ash	wt%	D482	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	--
Water and sediment	vol%	D2709	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	--
Water	ppm	D6304	119	182	115	77	65	155	72	186	135	64	130	80	49
Copper strip corrosion	Rating	D130	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a	--

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FAME profiles of biodiesels in the blends were determined using heart-cutting two-dimensional (2D) gas chromatography (GC) using the GC parameters described by McCurry and Wang [39]. Samples were prepared according to method EN 14103 for determination of ester content of biodiesel. The samples were injected onto an Agilent 7890A GC equipped with a Deans Switch microfluidic valve. A non-polar column (DB-5; 15 m x 0.25 mm ID x 0.1 μm) was used for initial separation, and FAMEs were transferred to a polar column (HP-INNOWax 30 m x 0.25 mm ID x 0.5 μm) using the Deans Switch for separation from hydrocarbons. FAMEs were then quantified using the procedure of EN 14103. FAME profiles are provided in Table 2 along with the calculated bis-allylic position equivalents (BAPE). This value indicates the number of positions on the polyunsaturated FAME molecules, which are susceptible to oxidation, providing a relative measure of reactivity [40]:

$$\mathrm{BAPE} = \%\mathrm{C18{:}2} + 2 \times \%\mathrm{C18{:}3}$$

Table 2: FAME profiles of biodiesel from B20 samples determined by 2D GC

FAME, wt%	A	B	C	D	E	F	G	H	I	J	K	L	M
C14:0	ND	ND	ND	ND	ND	0.7	1.3	0.4	0.5	0.5	ND	ND	ND
C16:0	13.3	10.8	10.4	11.2	10.8	16.2	17.9	12.9	12.3	13.5	12.0	12.6	11.6
C16:1	0.8	ND	ND	ND	ND	1.0	1.3	0.5	0.6	0.6	0.3	0.3	ND
C17:0	ND	ND	ND	ND	ND	0.3	0.6	ND	0.2	ND	ND	ND	ND
C18:0	4.8	4.3	4.6	4.4	4.1	7.5	10.8	5.7	5.2	6.3	4.9	2.8	4.4
C18:1	27.6	23.0	27.4	25.8	22.0	34.2	34.4	27.0	42.1	28.7	27.6	32.8	23.7
C18:2	47.5	54.1	50.2	50.9	55.2	36.4	29.5	47.5	34.7	44.5	48.2	49.6	53.1
C18:3	5.9	7.8	7.5	7.6	7.9	3.8	4.3	5.9	4.5	5.9	7.0	1.9	7.1
BAPE	59	70	65	66	71	44	38	59	44	56	62	53	67

ND = not detected

To place the BAPE values in context, a typical soy-derived biodiesel would have a BAPE of approximately 60 to 75, a canola-derived biodiesel would have a BAPE between 30 and 40, and a pure tallow-derived biodiesel would typically have a BAPE below 10 [41].

2.2. Storage Stability and Re-additization

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Each as-received B20 was subdivided into three separate 400 mL aliquots that were held in vented 500-mL glass jars in an oven at 43°C, per ASTM method D4625 to assess middle distillate storage stability. Sample D was tested in duplicate (six jars). Samples were tested monthly by EN 15751 to track changes in IP. When IP reached < 4 hr, one jar was removed from the oven and re-additized with butylated hydroxytoluene (BHT, purchased from Sigma Aldrich), to a concentration sufficient to raise the IP to > 6 hr – bringing the sample back within D7467 specification. The second jar was re-additized upon reaching an IP of < 2 hr and the third at < 0.5 hr, ultimately generating three separate samples for each B20. A flow chart describing the re-additization experiments is provided in Figure 1. After addition of BHT, aging was continued with monitoring of IP, acid number, peroxide number, and BHT concentration. Concentration of BHT was determined by GC-mass spectrometry following an in-house developed method, details of which are provided in the supporting information. The end of storage life was defined as the point at which an acid number ≥ 0.3 mg KOH/g was detected. At the termination of aging total filterable and adherent insolubles were measured following the procedure of D4625.

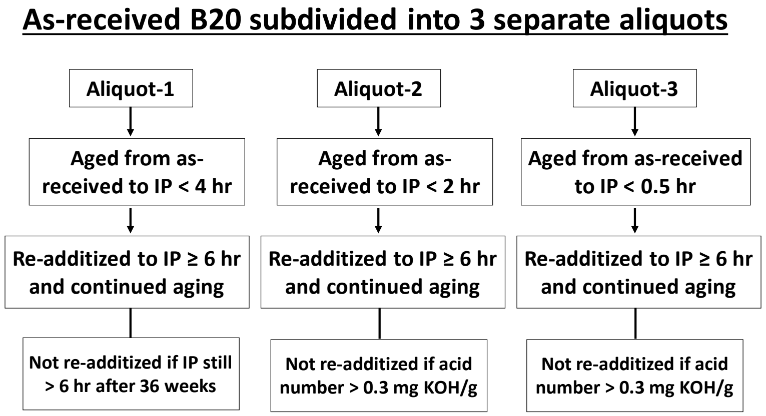

Figure 1: Description of re-additization experiments

3. Results and Discussion

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3.1 As-received B20s

IP values and acid numbers measured throughout accelerated aging of the as-received fuels are shown in Figure 2. Blends that initially met the ASTM D7467 specification minimum IP of ≥ 6 hr had potential storage lives of one year, and much longer for blends with higher initial IP values. By 12 weeks, two of the samples were below the 6 hr IP specification, but were at or above 3 hr and below the maximum acid number of 0.3 mg KOH/g, which was found in previous research to indicate adequate oxidation reserve for immediate use in an engine [12,31]. Sample A, having an initial IP below the minimum at 2.3 hr, had no measurable IP by 4 weeks of accelerated aging. At this time, the sample showed high acid number, peroxides, and insolubles (discussed in more detail below). It is likely that within 4 months this out of specification fuel could become problematic.

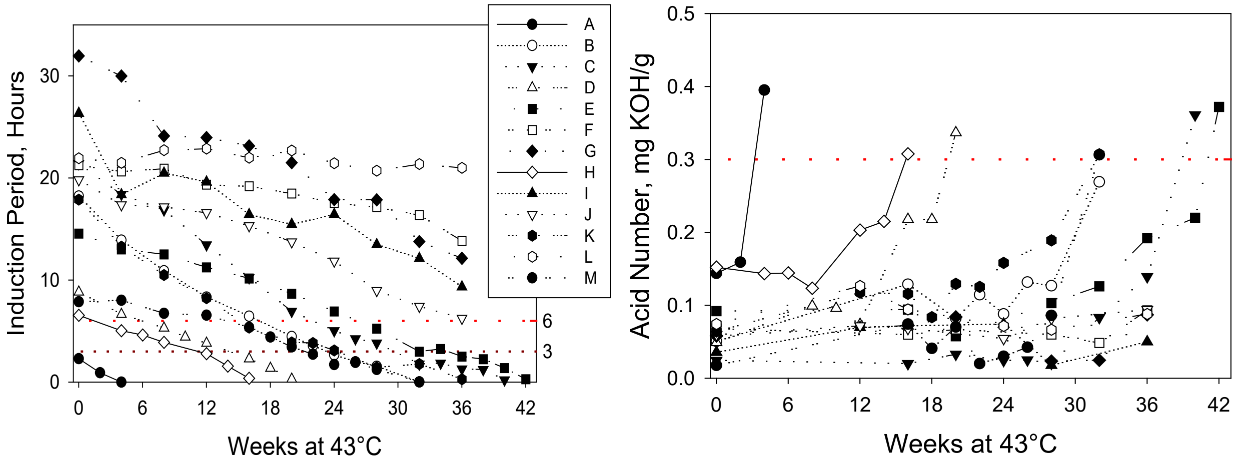

Figure 2: Induction periods and acid numbers of as-received blends during accelerated aging

Five of the 13 samples had very high storage stability and still met the IP ≥ 6 hr specification at 36 weeks (simulated 3 years). Initial and final stability properties of these samples are provided in Table 2. Acid numbers of these samples were well below 0.3 mg KOH/g and no measurable insoluble material was detected when the test was terminated (values were

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within the precision of the method). These fuels were still well within limits for acid number and IP, indicating they would be fit for use in an engine beyond the amount of time they were stored. The potential storage lives of these fuels were therefore longer than 3 years. Given their high storage stability, these samples were not re-additized.

Table 2: Initial and final properties of highest stability B20s

Sample ID	Initial IP (hr)	Final IP (hr)	Initial acid number (mg KOH/g)	Final acid number (mg KOH/g)	Initial Peroxide (ppm)	Final Peroxide (ppm)	Total Insolubles (mg/100 mL)
F	21.3	13.8	0.07	0.09	4.9	19.7	< 4
G	32.0	12.1	0.06	0.09	2.3	62.4	< 4
I	26.4	9.3	0.04	0.05	1.4	45.4	< 4
J	19.8	6.3	0.06	0.09	3.4	109.2	< 4
L	21.9	21.0	0.07	0.09	4.1	14.9	< 4

3.2 Re-additized B20s

The remaining eight samples fell below the first re-additization IP threshold of < 4 hr within 36 weeks. The number of weeks taken by each sample to fall below the IP thresholds/point of re-additization is provided in Table 3. Individual aliquots were re-additized with BHT upon reaching the thresholds and placed back in the test oven for continued aging and monitoring. The amount of BHT required to re-additize the B20s to ≥ 6 hr IP varied, but was considerably higher for the < 2 hr IP interval in every case. On average it took approximately 4 times the amount of BHT to increase IP to ≥ 6 hr after reaching < 2 hr compared to < 4 hr. Concentrations of BHT at the time of re-additization and at the end of aging are shown in Figure 3.

Given that Sample A was received with an initial IP < 4 hr, accelerated aging to the first IP threshold was not applicable. This sample was considered aged in the field, and a subsample was re-additized for aging alongside the as-received sample. Except for Sample B, by the time

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the B20s reached an IP of < 0.5 hr, the acid number was above the limit of 0.3 mg KOH/g. Therefore, only Sample B allowed for a third re-additized sample for study.

Table 3: Timeframes for B20 samples to reach IP thresholds when aged at 43°C

Sample ID	Initial IP (hr)	Weeks to IP < 4	Weeks to IP < 2	Weeks to IP < 0.5	Weeks to acid number > 0.3 mg KOH/g
A	2.3	--	2	4	4
B	18.2	22	28	32	>32
C	21.4	28	32	40	40
D	8.8	12	18	20	20
E	14.6	32	40	42	42
H	6.6	8	14	16	16
K	17.9	20	28	32	32
M	7.9	20	24	32	32

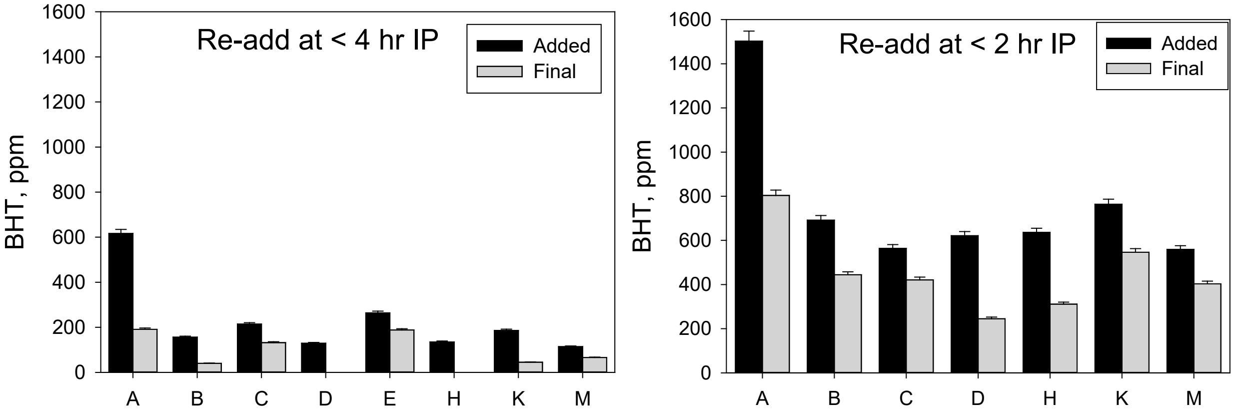

Figure 3: BHT concentrations measured by GC-MS at point of treatment to reach 6 hr IP and at the end of aging. The limit of quantitation of the analysis was 40 parts per million.

Re-additized samples were monitored for changes in IP, acids, and peroxides during continued aging to determine impacts on storage stability. The results of these experiments are summarized in Table 4. The amount of time taken to reach acid number > 0.3 mg KOH/g is expressed as potential storage life in months (the number of weeks of accelerated aging). The final acid number, final IP, final peroxides, and insolubles contents are included for the as-received and the re-additized samples. Re-additization at < 4 hr IP increased potential storage life to 36 months or longer in every case studied. Re-additization at < 2 hr IP was also effective at

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extending storage life relative to the as-received, but tended to be less effective than re-additization at < 4 hr. The only instance of re-additization at < 0.5 hr IP was ineffective at increasing storage life.

Table 4: Re-additization impacts on potential storage life of B20s

Sample ID	A	B	C	D	D Duplicate	E	H	K	M
Initial IP, hr	2.3	18.2	21.4	8.8	8.8	14.6	6.6	17.9	7.9
Aged As-received									
Potential Storage life, months	4	34	40	20	20	42	16	32	32
Total Insolubles, mg/100 mL	20	--	36	23	19	< 4	10	< 4	5
Final acid number, mg KOH/g	0.40	0.27	0.36	0.34	0.28	0.37	0.31	0.31	0.31
Final Peroxide, ppm	1196	1069	1369	978	762	920	826	811	1200
Final IP, hr	0.0	0.0	0.2	0.3	0.4	0.3	0.4	0.3	0.0
Aged and Re-additized at < 4 hr IP									
Potential Storage life, months	> 36	> 48	> 48	36	36	> 48	> 40	> 44	> 48
Total Insolubles, mg/100 mL	< 4	< 4	< 4	42	41	< 4	< 4	< 4	< 4
Final acid number, mg KOH/g	0.26	0.21	0.07	1.02	1.09	0.16	0.26	0.20	0.07
Final Peroxide, ppm	162	417	268	2173	2460	298	608	398	145
Final IP, hr	2.7	1.7	4.7	0.0	0.0	4.1	1.0	1.6	3.5
Aged and Re-additized at < 2 hr IP									
Potential Storage life, months	30	> 48	> 48	36	36	44	36	> 40	> 48
Total Insolubles, mg/100 mL	5	< 4	< 4	< 4	< 4	8	< 4	< 4	< 4
Final acid number, mg KOH/g	0.31	0.23	0.16	0.35	0.31	0.40	0.31	0.27	0.10
Final Peroxide, ppm	321	402	370	368	343	913	294	405	270
Final IP, hr	4.1	3.6	4.8	2.0	3.0	8.2	3.7	4.5	4.9
Aged and Re-additized at < 0.5 hr IP									
Potential Storage life, months	--	34	--	--	--	--	--	--	--
Total Insolubles, mg/100 mL	--	11	--	--	--	--	--	--	--
Final acid number, mg KOH/g	--	0.43	--	--	--	--	--	--	--
Final Peroxide, ppm		848							
Final IP, hr	--	6.4	--	--	--	--	--	--	--

As previously noted, Sample B was the only blend examined that reached < 0.5 hr IP before having acid number ≥ 0.3 mg KOH/g. Detailed storage stability results for this sample are provided in Figure 4. Re-additization attempts at both < 4 and < 2 hr IP resulted in the sample remaining below the limit for acid number when the test was terminated at 48 weeks (simulated 4 years). Re-additization at IP < 0.5 hr was not successful at elongating storage life. After re-

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additization with 2,200 ppm BHT, the IP was brought back up to ≥ 6 hr, but 2 weeks later the acid number was above the limit and continued to rise despite the IP remaining nearly constant. Total insolubles had increased to 11 mg/100 mL when this test was terminated at 40 weeks. It is notable that as the acid number of this sample rapidly increased, the peroxide number rapidly decreased, which indicates the peroxides that formed prior to re-additization decomposed, generating acids and insoluble polymers [7,9].

When re-additization was conducted at < 2 hr, the peroxide content was considerably higher than that of the as-received fuel at the beginning of aging, having reached 475 ppm, yet less than half that of the sample re-additized at < 0.5 hr. After re-additization growth in peroxide number was stopped, similar to the case with re-additization at < 0.5 hr. However, in this case the peroxide concentration remained relatively constant, decreasing slowly to 402 ppm 16 weeks after re-additization. The acid number of this sample increased slowly over time in conjunction with the slow rate of peroxide decrease, though this did not reach the 0.3 mg KOH/g acid number limit and insoluble material was not detected when the sample was filtered.

Peroxide formation was stalled after re-additization due to the fact that hindered phenolic antioxidants like BHT stabilize FAME peroxy radicals which are the primary products of FAME oxidation. FAME peroxy radicals propagate the oxidation chain reaction by removing a proton from another unsaturated FAME, forming a peroxide and another radical. These radicals can also react with one another to form higher molecular weight degradation products or decompose into lower molecular weight radicals and stable oxidation products such as alcohols, aldehydes, and carboxylic acids. Antioxidants readily donate a proton forming a stable unreactive antioxidant radical and a peroxy or hydroxy FAME, thus preventing propagation of the chain reaction. When

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in the presence of peroxy FAMEs these antioxidants can also act as peroxide destroyers that slow peroxide decomposition through the formation of more stable hydroxy FAMEs and lower molecular weight alcohols [42]. This process of preventing radical generation and slowing peroxide decomposition delays the formation of carboxylic acids and insoluble polymers. In the case of the sample re-additized at < 0.5 hr the peroxide concentration (and thus the concentration of radical species) was sufficiently high to lead to substantial degradation of the fuel substrate after re-additization, while re-additization at > 0.5 hr IP was conducted prior to the formation of such a high concentration of radicals, allowing for extended storage life of the fuel via stabilization. The potential storage life of this sample without re-additization was approximately 34 months. This was increased to greater than 4 years with re-additization when IP was less than 4 hr but greater than 0.5 hr and the peroxide concentration was less than 1,000 ppm.

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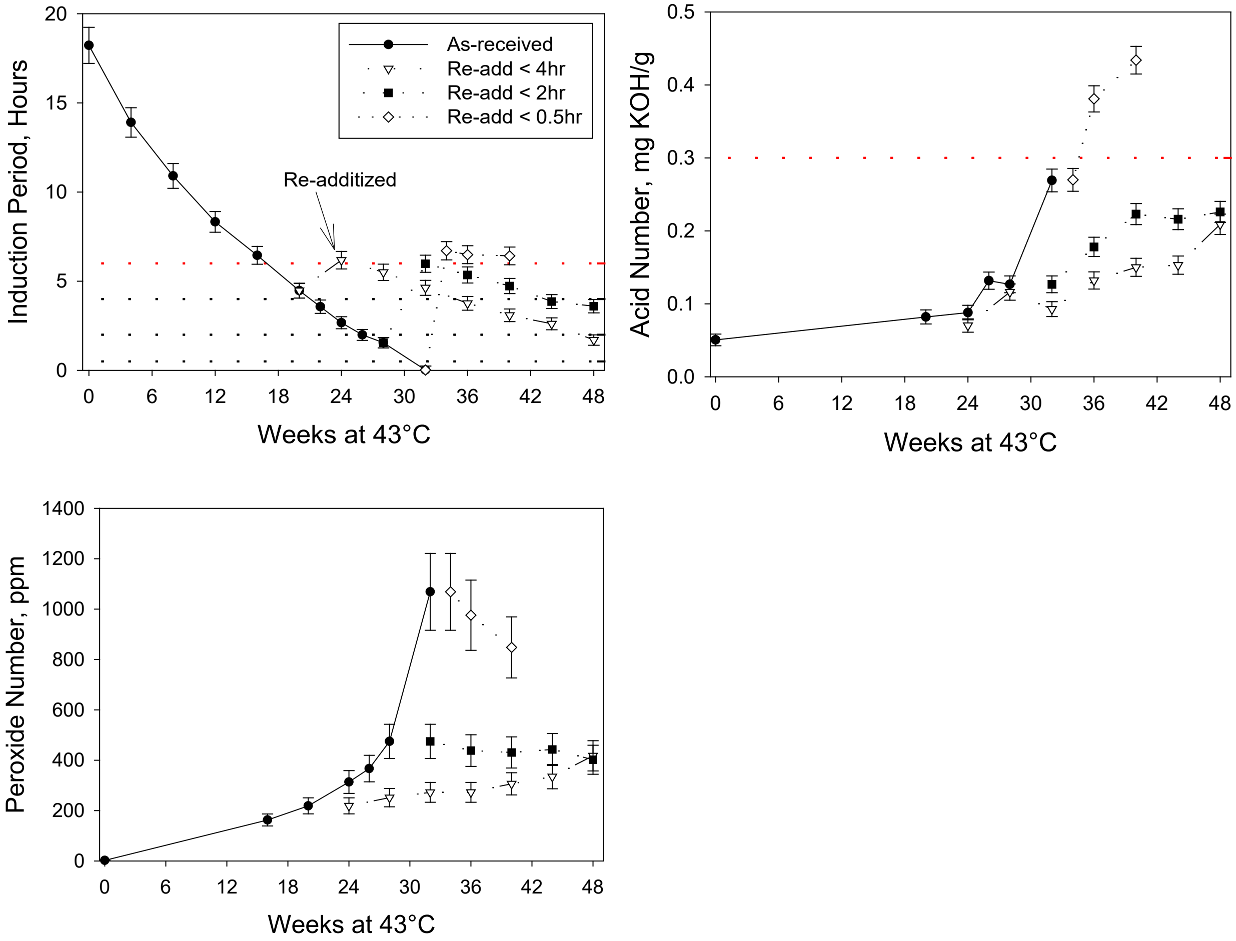

Figure 4: Sample B IP, acid number, and peroxide measured throughout aging experiments. Error bars for IP and acid number were calculated from the reported repeatability (r) of the test methods (EN 15751 and ASTM D664, respectively). Error bars for peroxide number represent the in-house determined repeatability.

Sample A was the only B20 collected that was below the 6-hr IP minimum. The cause of this fuel being out of specification is unknown; however, this allowed an opportunity to examine the effectiveness of re-additization on fuel that had been aged in the field rather than under accelerated conditions. Storage stability results for Sample A are provided in Figure 5. As noted above, this sample became unstable within 4 weeks of aging at which point insolubles, acid number, and peroxides had reached high values. When Sample A was re-additized with BHT to ≥ 6 hr (prior to any laboratory aging), the rate of IP decrease was much slower and storage life was increased significantly. By 40 weeks post re-additization, the acid number remained < 0.3

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mg KOH/g, and peroxides and insolubles remained low. Re-additization of this low-stability B20 increased the potential storage life from 4 months or less to greater than 3 years.

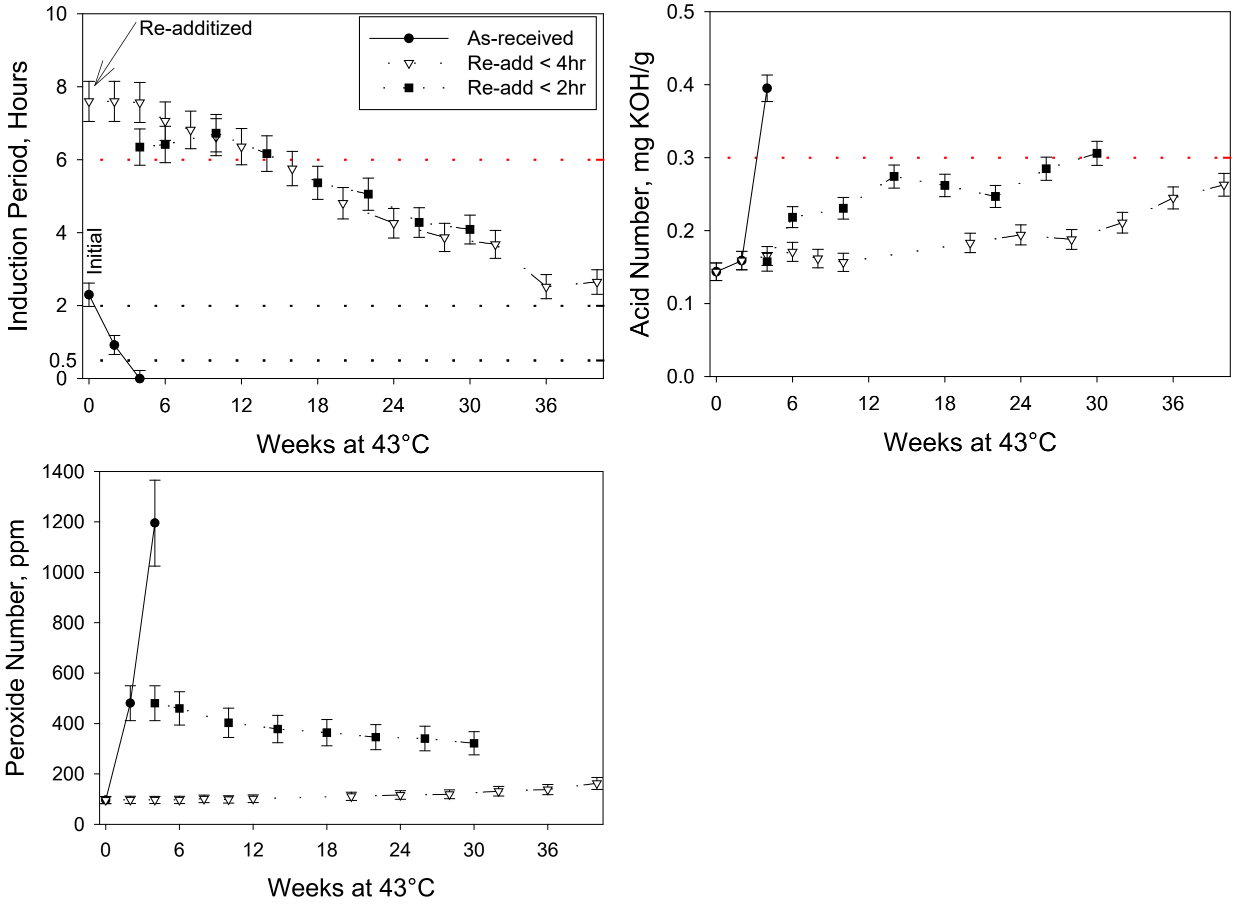

Figure 5: Sample A IP, acid number, and peroxide measured throughout aging experiments. Error bars for IP and acid number were calculated from the reported repeatability (r) of the test methods (EN 15751 and ASTM D664, respectively). Error bars for peroxide number represent the in-house determined repeatability.

Re-additization of Sample A after aging to < 2 hr IP is also shown in Figure 5. The IP was reduced well below 2 hr in 2 weeks, at which point the peroxide number had increased to 480 ppm, but the acid number had not significantly changed from the initial value. Addition of BHT stopped the increase in peroxides, but acid number continued to increase gradually, reaching 0.3 mg KOH/g at 30 weeks. The storage life of the second re-additized sample was

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significantly increased from the as-received sample; however, re-additization at this lower IP value was less effective at preventing acid formation over time.

While most of the B20 samples examined exceeded the minimum IP by > 1 hr (and in many cases several hours), Sample H was received with initial IP just meeting the 6-hr specification (6.6 hr). Storage stability results of this B20 are provided in Figure 6. This sample reached acid number > 0.3 mg KOH/g by 16 weeks. The inherent oxidation reserve of this sample allowed potential storage life longer than a year prior to problematic changes. Re-additizing this fuel resulted in storage life increased to 36 weeks or more, increasing potential storage life to approximately 3 years. Given the higher acid number of the second re-additized sample at 36 weeks, it appears re-additization at a lower IP value was again less effective than at higher IP.

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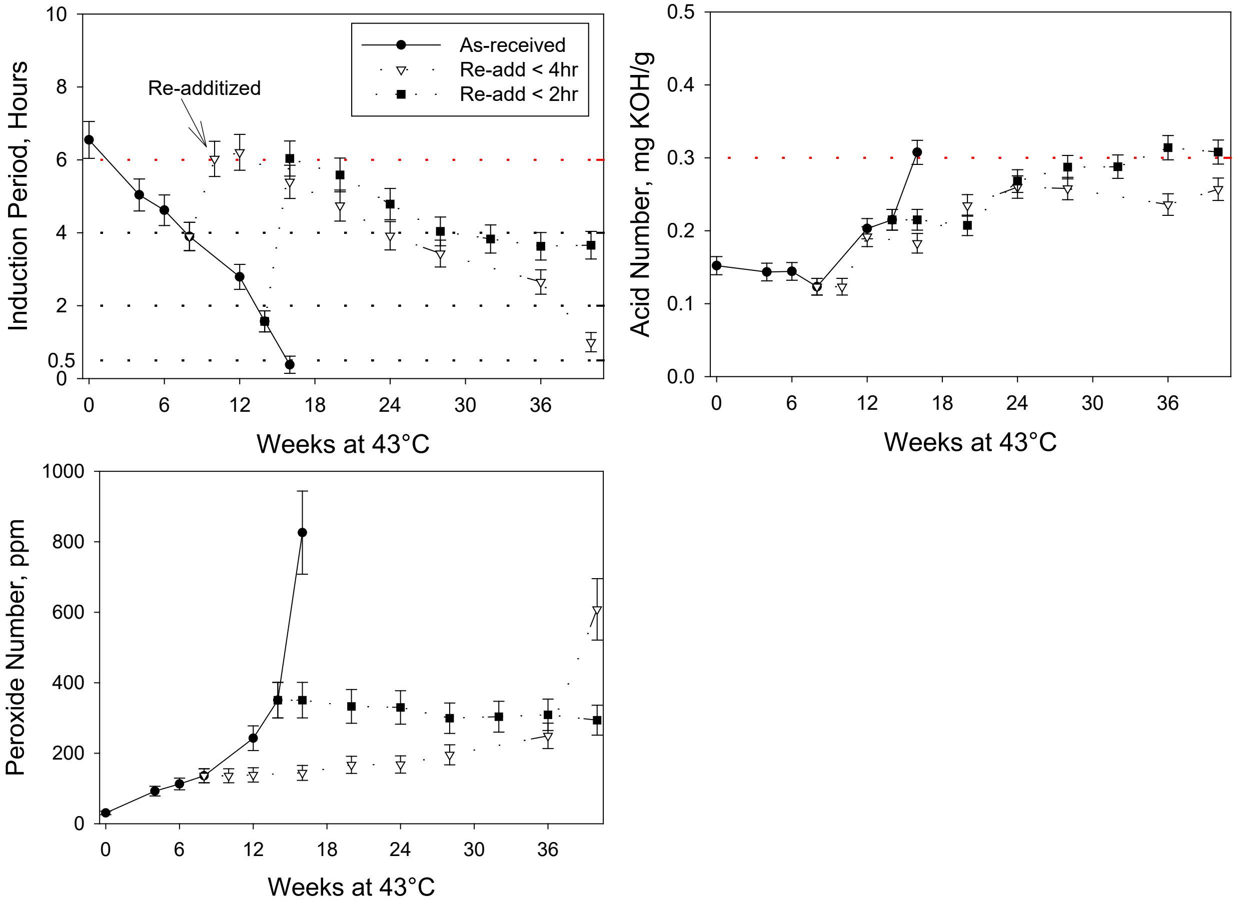

Figure 6: Sample H IP, acid number, and peroxide measured throughout aging experiments. Error bars for IP and acid number were calculated from the reported repeatability (r) of the test methods (EN 15751 and ASTM D664, respectively). Error bars for peroxide number represent the in-house determined repeatability.

Except for Sample C, all the B20 samples received with an initial IP ≥ 20 hr still met the specification for IP by 36 weeks of accelerated aging. Unlike the other high-IP samples, this one fell to < 4 hr by 28 weeks. Notably, this sample also contained the highest BAPE biodiesel (and was therefore the least stable) of the B20s with ≥ 20 hr IP. Storage stability results for Sample C are shown in Figure 7. The acid number of the as-received increased above the maximum value by 40 weeks. Re-additization of this sample at both < 4 hr and < 2 hr IP resulted in the acid number remaining below 0.3 mg KOH/g at 48 weeks, when the test was terminated. Potential storage life of this sample was just over 3 years but was increased to greater than 4 years with re-additization.

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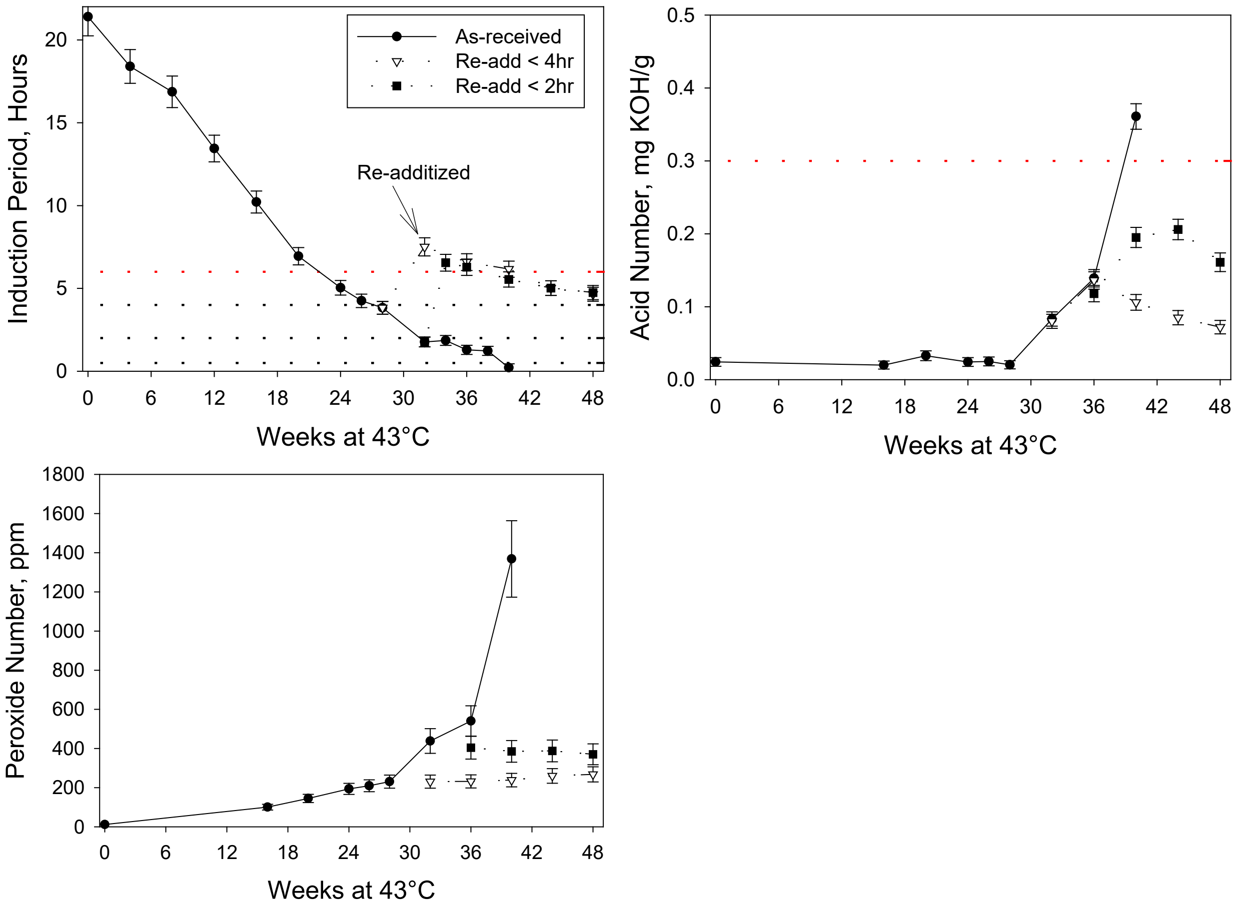

Figure 7: Sample C IP, acid number, and peroxide measured throughout aging experiments. Error bars for IP and acid number were calculated from the reported repeatability (r) of the test methods (EN 15751 and ASTM D664, respectively). Error bars for peroxide number represent the in-house determined repeatability.

Stability results in Table 4 show that the longest potential storage lives tended to be observed with the highest initial IP values; however, storage life and IP did not directly correlate. For example, Sample M had an initial IP of 7.9 hr, but had the same storage life as Sample K which had an initial IP of 17.9 hr. Figure 8 shows the initial IP vs. potential storage life for the base B20 samples. This figure also includes data for B20 blends from previous studies by McCormick and Westbroook [8] and Christensen [28] that reached acid number > 0.3 mg KOH/g during D4625 storage. A lack of correlation between Rancimat IP and shelf life has been

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recognized in application of this test to oils and fats; therefore, it is commonly used to rate oils and antioxidant effectiveness, but not to predict storage behavior [42,43]. Similarly, the results presented here show the lack of predictive capability of IP measurement for the storage behavior of B20 blends. Despite a lack of storage life prediction, these results highlight the applicability of a minimum IP value to provide a probable minimum storage life. IPs above 6 hr resulted in potential storage lives of more than 6 months in the data shown in Figure 8. In all but one case (from the early study by McCormick and Westbrook [8]), this minimum IP allowed for potential storage of greater than 12 months.

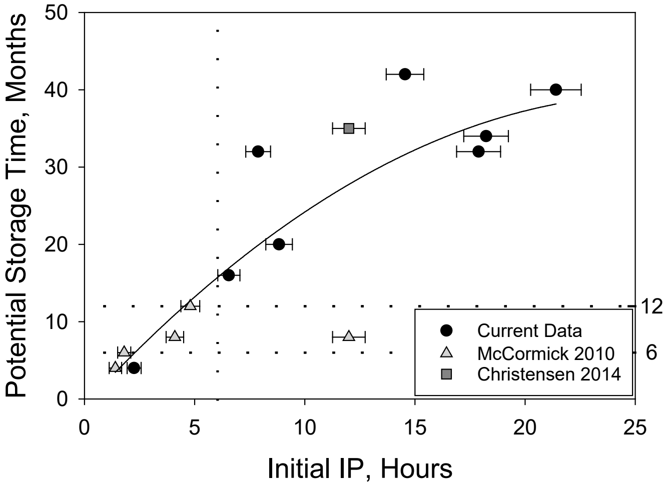

Figure 8: Initial IP of B20 samples vs. storage life (time to acid number > 0.3 mg KOH/g)

Although high-IP samples were stable for long periods during this experiment, it must be stressed that storage conditions greatly influence storage stability. The lack of predictability of storage life based on initial IP along with potential environmental influences on stability highlight the importance of monitoring properties during long-term storage. Re-additizing to increase storage life was found to be effective when antioxidants were added while IP was above 0.5 hr. Re-additizing at higher IP values tended to be more effective at extending storage life.

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Long-term storage of biodiesel blends is possible with sufficiently high initial IP, property monitoring during storage, and re-additizing if low IP is detected.

4. Conclusions

Based on ASTM D4625 storage stability results, all nominally B20 samples meeting the 6-hr minimum IP are expected to have a potential storage life of greater than 6 months and likely greater than 1 year. Higher IP values allowed for much longer storage lives, with fuels still meeting the 6-hr minimum at 3 years (simulated). Re-additization—the adding of an antioxidant during storage—can be effective at increasing storage life of B20s. Re-additizing is more effective and requires less antioxidant additive when applied at higher IP. Once the IP of a B20 has fallen to < 0.5 hr, it is probable that the fuel will have no oxidation reserve remaining. This fuel may soon produce high concentrations of acids and insoluble materials, making it unfit for use; therefore, re-additization will no longer be applicable. Monitoring IP and acid number at regular intervals during storage can detect changes in oxidation reserve before acid number goes out of specification and insoluble materials are formed. Using this information, re-additization can be applied prior to problematic changes in fuel properties. Initial IP does not predict long-term storage behavior, fuel monitoring during long-term storage is necessary to ensure high quality fuel at the time of use.

Acknowledgement

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Supporting Information Available

Additional data are provided. This information is available free of charge via the Internet at http://www.sciencedirect.com.

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Supporting information for:

Re-Additization of Commercial Biodiesel Blends During Long-Term Storage

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BHT Quantification Method

Samples were prepared by diluting with heptane at a concentration of 100 mg/mL. An internal standard was added to each sample, 2,4-dimethylphenol, at a concentration of 450 ppm. An Agilent 7890A GC equipped with a split/splitless injection port coupled with a 5975C MSD was used for BHT quantification. The column used was a DB-5MS column (5% phenyl polydimethylsiloxane phase) of dimensions 30 m x 250 µm x 0.25 µm. Helium was used as a carrier gas with column flow was set to 1 mL/min. The injection port temperature was 275°C, split ratio was 50:1, and injection volume was 1.0 µL. The initial oven temperature was 100°C; temperature ramp rate was 15°C/min to a final temperature of 325°C held for 2 minutes. The MS transfer line temperature was 325°C. The MS source temperature was 230°C and the quadrupole was set to 120°C. MS analysis was conducted by selected ion monitoring, measuring m/z 122, 205, and 220. The instrument was calibrated using BHT dissolved in heptane containing 2,4-dimethylphenol internal standard. The resulting linear calibration had an R2 of 0.999. Triplicate analysis of a B20 sample had a relative standard deviation of 1.5%.

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Table S1: Blendstock properties for in-house blended B20 sample

Property	ASTM Test Method	Units	B0	B100
Flash Point	D93	°C	61	176
Water and Sediment	D2709	vol%	< 0.005	< 0.005
Water	D6304	µg/g	37	115
Distillation Temp	D86	°C	330	--
Distillation Temp	D1160	°C	--	352
Viscosity at 40°C	D445	cSt	2.663	3.972
Ash	D482	wt%	<0.001	--
Sulfated Ash	D874	wt%	--	<0.001
Sulfur	D5453	µg/g	6.2	0.6
Copper Strip Corrosion	D130		1A	1A
Aromatics, Olefins, Saturates	D1319	vol%	31.6	--
Carbon Residue	D524	wt%	0.08	--
Carbon Residue	D4530	wt%	--	0.03
Lubricity	D6079		492	--
Conductivity	D4308	pS/m	210	--
Oxidation Stability	EN 15751	Hr	--	2.5
Total Acid Number	D664	mg KOH/g	0.08	0.12
Peroxide Value	AOCS Cd 8b-90	mg/kg	1.0	80.3
Cold Soak Filterability	D7501	seconds	--	81
Free Glycerin	D6584	wt%	--	0.007
Total Glycerin	D6584	wt%	--	0.011
Monoglycerides	D6584	wt%	--	0.017
Calcium	D7111	µg/g	<0.1	<0.1
Magnesium	D7111	µg/g	<0.1	<0.1
Sodium	D7111	µg/g	2.0	<1
Potassium	D7111	µg/g	1.1	1.7
Phosphorus	D4951	wt%	--	<5

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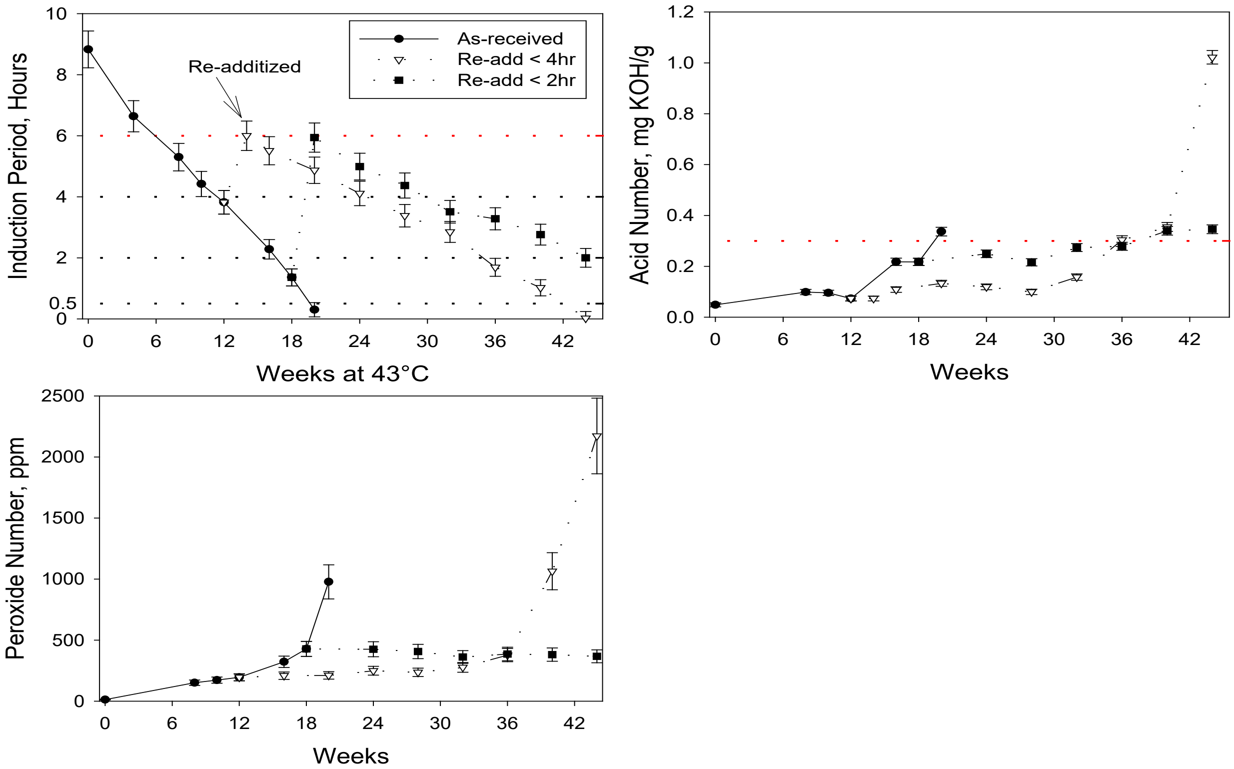

Figure S1: Sample D induction period, acid number, and peroxide measured throughout aging experiments

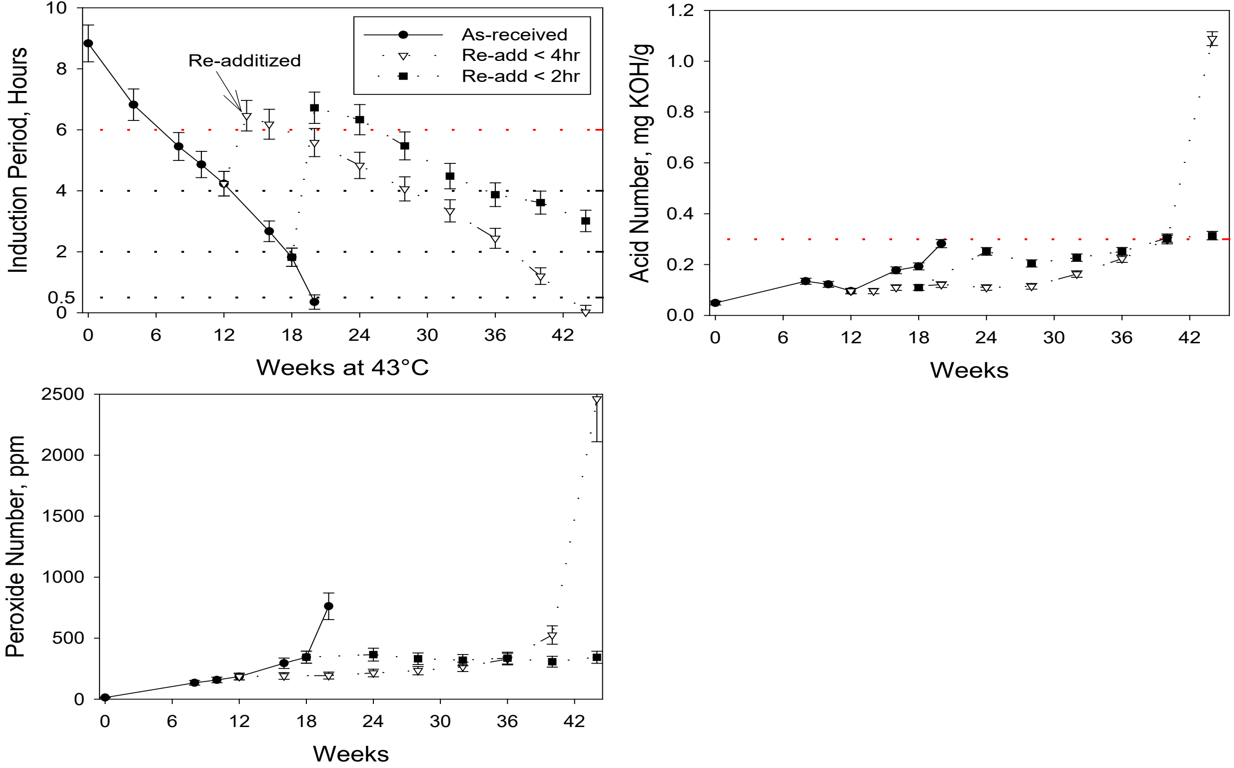

Figure S2: Sample D duplicate induction period, acid number, and peroxide

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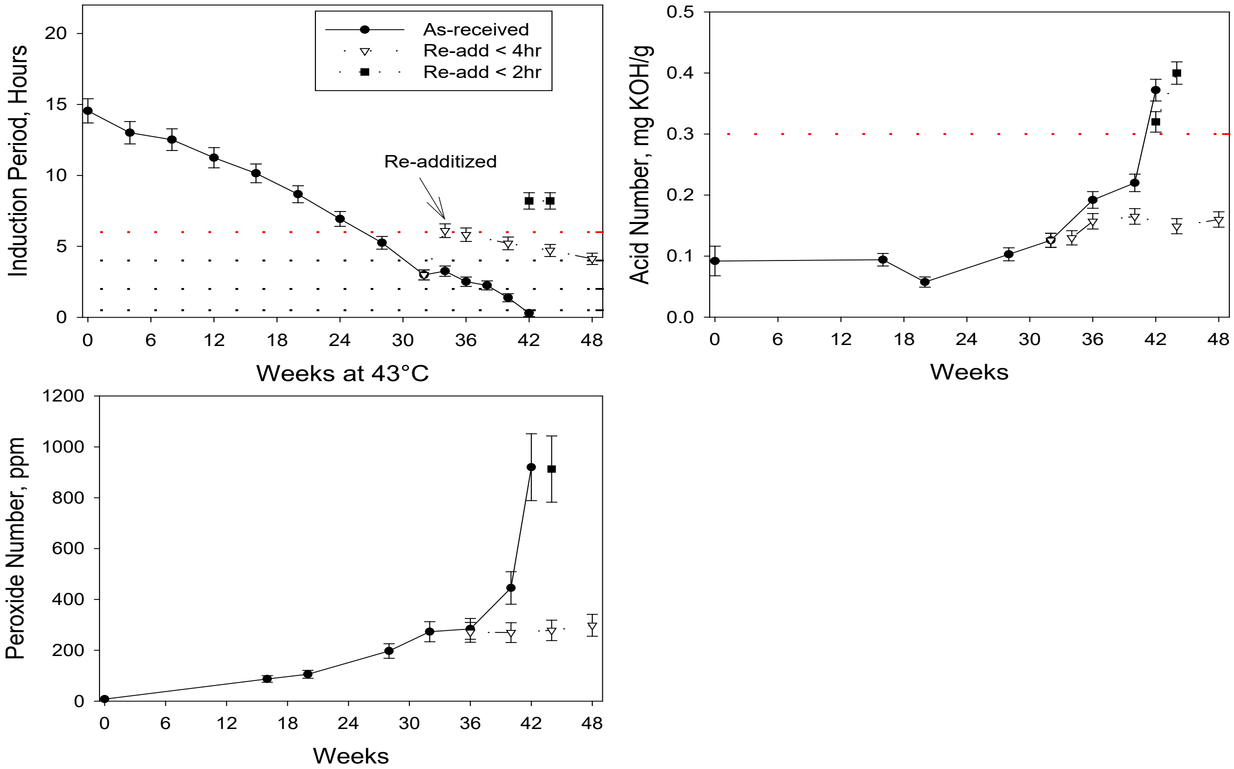

Figure S3: Sample E induction period, acid number, and peroxide measured throughout aging experiments

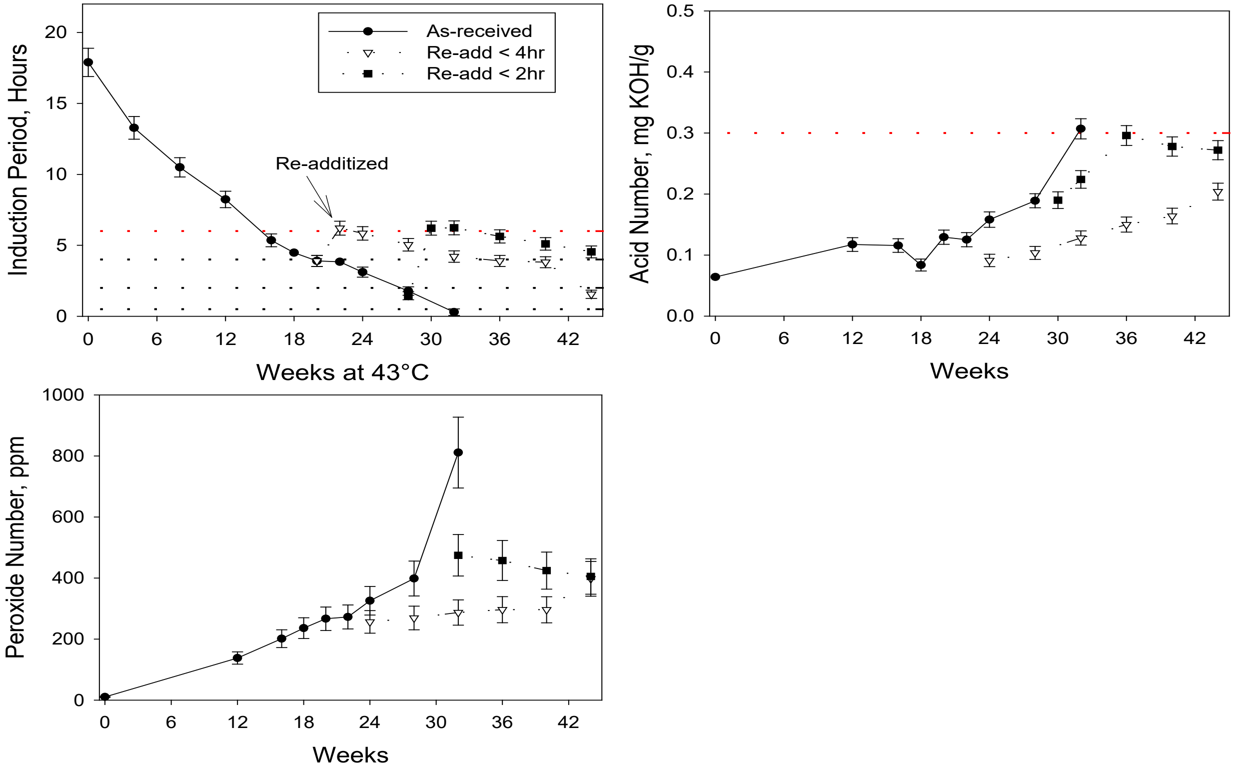

Figure S4: Sample K induction period, acid number, and peroxide measured throughout aging experiments

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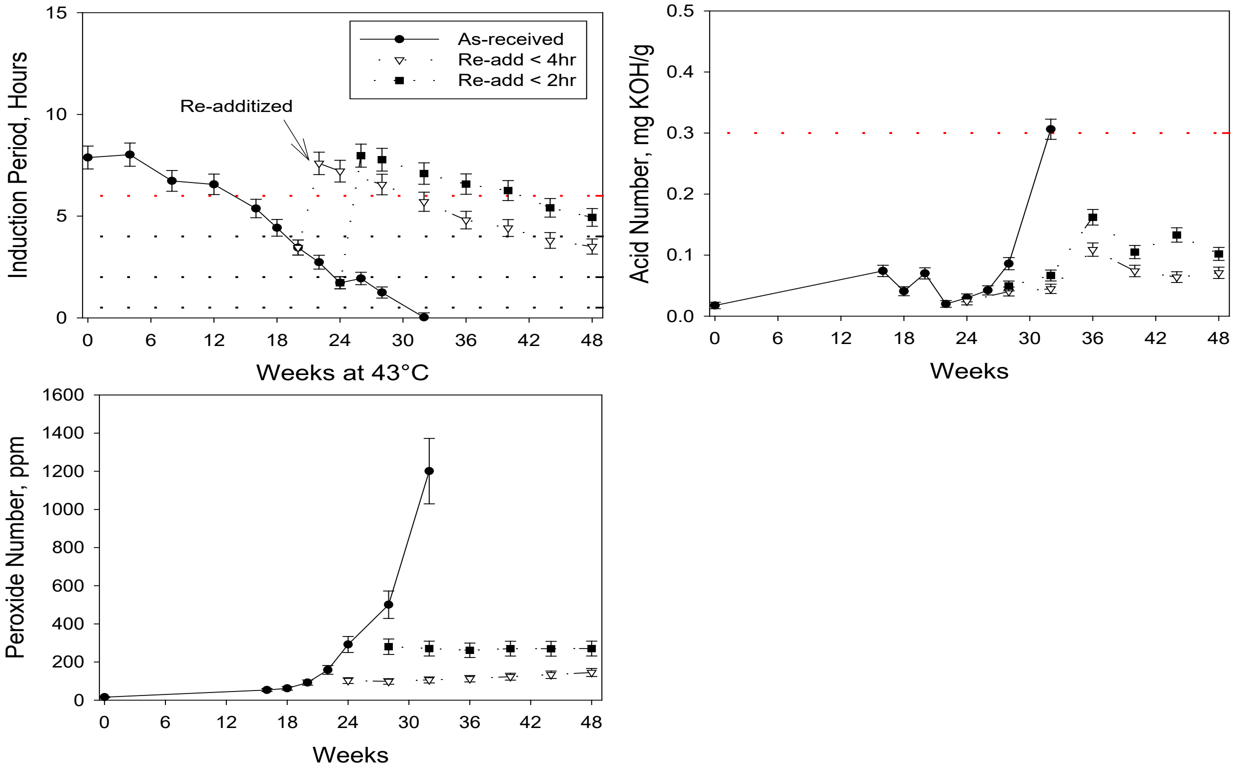

Figure S5: Sample M induction period, acid number, and peroxide measured throughout aging experiments

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