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Empirical Study of the Stability of Biodiesel and Biodiesel Blends

Milestone Report

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Golden, Colorado

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Executive Summary

In support of the U.S. Department of Energy Fuels Technologies Program Multiyear Program Plan goal of identifying fuels that can displace 5% of petroleum diesel by 2010, the National Renewable Energy Laboratory (NREL), in collaboration with the National Biodiesel Board (NBB) and with subcontractor Southwest Research Institute, performed a study of biodiesel oxidation stability. The objective of this work was to develop a database that supports specific proposals for a stability test and specification for biodiesel and biodiesel blends. B100 samples from 19 biodiesel producers were obtained in December of 2005 and January of 2006 and tested for stability. Eight of these samples were then selected for additional study, including long-term storage tests and blending at 5% and 20% with a number of ultra-low sulfur diesel (ULSD) fuels. These blends were also tested for stability. The study used accelerated tests as well as tests that were intended to simulate three real-world aging scenarios: (1) storage and handling, (2) vehicle fuel tank, and (3) high-temperature engine fuel system. Several tests were also performed with two commercial antioxidant additives to determine whether these additives improve stability. This report documents completion of NREL's Fiscal Year 2007 Annual Operating Plan Milestone 10.1.

The B100 samples examined show a broad distribution of stability on accelerated tests, with oil stability index (OSI) or Rancimat induction time results ranging from less than 1 hour to more than 9 hours and ASTM D2274 total insolubles ranging from less than 2 mg/100 ml to nearly 18 mg/100 ml. The accelerated test data indicate that if the B100 stability is above roughly a 3-hour induction time, blends prepared from that B100 appear to be stable on the OSI and D2274 tests.

The D4625 long-term storage results for B100 indicate that most biodiesel samples, regardless of initial induction time, will begin to oxidize immediately during storage. If induction time is near or below the 3-hour limit, the B100 will most likely go out of specification for either stability or acid value within 4 months. Even B100 with induction times longer than 7 hours will be out of specification for oxidation stability at only 4 months, although these samples may not have shown a significant increase in acidity or in deposit formation. The 3-hour B100 induction time limit appears to be adequate to prevent oxidative degradation for both B5 and B20 blends in storage for up to 12 months.

For tests that simulated fuel tank aging and high temperature stability, we conclude that stable B100 (longer than 3 hours induction time) leads to stable B5 blends. For B20, the results are less definitive, but provide considerable evidence that B100 with induction time of at least 3 hours produces stable B20 blends, but the test cannot differentiate between intermediate and highly stable samples for acid number increase or sediment formation under these worst-case test conditions. Additional work is required to confirm this finding and to determine whether an additional stability test for the B20 blend is required.

These results indicate that B100 stability is the main factor that affects the stability of B5 and B20 blends, independent of diesel fuel aromatic content, sulfur level, or stability. An antagonism between unstable B100 and diesel fuel was observed. For B100 with an induction time lower than 3-hours, the level of deposits formed on the D2274 stability test was well above what would be expected based on the B100 deposit level and the percentage of biodiesel in the fuel. This antagonistic effect was significantly greater for B20 than for B5. The hindered phenolic antioxidants tested here prevented oxidative degradation of B100 in the storage simulation, and prevented degradation of biodiesel blends in the storage, fuel tank, and high-temperature simulations.

We recommend that additional tests be performed with real equipment to validate these conclusions.

Acronyms and Abbreviations

ASTM	ASTM International, a standards setting organization
Bxx	designation of biodiesel or biodiesel blend (B100 is pure biodiesel, B20 is a 20% blend, for example)
EN	European Normalisation
ISO	International Standards Organization
KOH	potassium hydroxide
NBB	National Biodiesel Board
NREL	National Renewable Energy Laboratory
OSI	oil stability index (also called Rancimat induction time)
PV	peroxide value
RME	rapeseed methyl ester
T90	90% boiling temperature
ULSD	ultra-low sulfur diesel

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Introduction

In support of the U.S. Department of Energy Fuels Technologies Program Multiyear Program Plan Goal of identifying fuels that can displace 5% of petroleum diesel by 2010, the National Renewable Energy Laboratory (NREL), in collaboration with the National Biodiesel Board (NBB) and with subcontractor Southwest Research Institute, performed a study of biodiesel oxidation stability. The objective of this work was to develop a database to support specific proposals for a stability test and specification for biodiesel and biodiesel blends. B100 samples from 19 biodiesel producers were obtained during December 2005 and January 2006 and tested for stability. Eight of these samples were then selected for additional study, including long-term storage tests and blending at 5% and 20% with a number of ultra-low sulfur diesel (ULSD) fuels. These blends were also tested for stability. The study employed accelerated tests as well as tests intended to simulate three real-world aging scenarios: (1) storage and handling, (2) vehicle fuel tank, and (3) high-temperature engine fuel system. Results were analyzed to determine whether ensuring B100 stability was adequate to ensure the stability of B5 and B20 blends. Several tests were also performed with two commercial antioxidant additives to determine whether these additives might improve stability. This report documents completion of the NREL Fiscal Year 2007 Annual Operating Plan Milestone 10.1.

Background

Biodiesel produced from vegetable oils and other feedstocks can be more prone to oxidation than a typical petroleum diesel unless it is modified or treated with additives. The purpose of this project is to provide data that define how stable a biodiesel or biodiesel blend should be to prevent the formation of acids or sediment during transportation, storage, and use; and subsequent vehicle operational and maintenance problems.

The general mechanism of fat (or lipid) oxidation is reasonably well understood.[1,2] The fatty acid alkyl chains have varying numbers of double bonds. When multiple double bonds are present they are in allylic configuration, which means that they are separated by a single methylene group called a *bis*-allylic carbon or position. For biodiesel made from common feedstocks, such as oils from soy, rapeseed, and palm, as well as lard and tallow, the fatty acid chains contain primarily 16 or 18 carbon atoms and from zero to three double bonds. Eighteen-carbon chains contain one double bond for oleic acid, two for linoleic acid, and three for linolenic acid. The relative oxidation rates for these C18 esters are linolenic > linoleic >> oleic[3] because the di- and tri- unsaturated fatty acids contain the most reactive sites for initiating the auto-oxidation chain reaction sequence. Oxidation rate correlates with the total number of bis-allylic sites (the methylene CH directly adjacent to the two double bonds), not with the total number of double bonds.[4] These sites have the highest reactivity for the formation of free radicals that can react directly with oxygen to form peroxide radicals. This is the initial step in the classic auto-oxidation mechanism with the chain reaction steps of initiation, propagation, chain branching, and termination.[1,2] The allylic position (a methylene adjacent to a single double bond) is much less reactive, explaining the much lower oxidation rate of oleic acid. Also, the radicals formed at the bis-allylic sites immediately isomerize to form a more stable conjugated structure. The peroxide radicals can cleave to form acids and aldehydes, or can react with another fatty acid chain to form a dimer. Peroxide can form via this route even at ambient temperature.

Several studies have examined biodiesel stability. Westbrook[5] used the ASTM D4625 test wherein the subject fuel or blending component is held for 12 weeks at 43ºC in a capped but vented glass bottle, and oxidation effects (the amount of sediment formed, acidity, and change in viscosity) are periodically measured. Wide variations of insolubles formation, acid number, and viscosity increase were observed; the least stable samples exhibited unacceptable levels of insolubles and acidity 4 to 8 weeks into the test. To more fully understand the causes of these differences, McCormick and coworkers[6] examined the stability characteristics of biodiesel samples that were commercially available at blenders and distributors during 2004 and showed that the stability range results primarily from differences in fatty acid makeup and natural antioxidant content. However, samples containing high out-of-specification levels of glycerides (unconverted or partly converted feedstock) also tend to form deposits. Storage conditions can have a large impact on the degree of oxidation. Thus, for real-world samples containing impurities, the correlation of oxidation rate or tendency with the number of bis-allylic sites may be skewed or overshadowed by other factors such as natural antioxidant content.

Bondioli and coworkers[7] stored several drum quantity samples of biodiesel at ambient conditions for 1 year. One sample was "shaken" once per week to promote intimate contact with air. Over this period the quiescent samples exhibited little or no change in properties, including only minor reductions in Rancimat induction time. This contrasts strongly with results of studies conducted at higher temperatures (for example 43ºC as in ASTM D4625), which have shown large changes in acid value and other parameters.[5,8] Additionally, the agitated sample exhibited significant increase in peroxide and acid values and a large reduction in Rancimat induction time because of the increased exposure to dissolved oxygen. Mittelbach and Gangl also stored biodiesel produced from rapeseed oil and used frying oil under different conditions for up to 200 days.[9] Degradation caused by oxidation began immediately, as shown by the formation of peroxides and reduction in Rancimat induction time. However, even at the end of the storage period, limits for viscosity and acidity were not exceeded.

Fang and McCormick[10] showed that dimerization of the peroxide species is not the only mechanism for molecular weight growth and deposit formation in biodiesel, and identified several other mechanisms by which biodiesel can degrade. In particular, aldehydes formed by peroxide decomposition could also polymerize via aldol condensation. However, all pathways to deposit formation involved peroxide formation as the initial step, highlighting the importance of preventing peroxide formation at the point of biodiesel manufacture and throughout the biodiesel distribution chain. Fang and McCormick also showed an antagonistic or synergistic effect on deposit formation for biodiesel blends. The formation of deposits under oxidative stressing was higher than predicted for biodiesel blends based on the weight percent biodiesel and the deposits formed from the diesel fuel or biodiesel alone. This effect was most significant for blends in the 20% to 30% range.

Vegetable oils contain naturally occurring antioxidants that can cause oxidation stability to vary over a wide range, even for samples with similar fatty acid makeup.[6] The most common antioxidants are tocopherols. For example, soy oils contain 500 to 3000 ppm tocopherols, along with other antioxidants such as sterols and tocotrienols,[11] which may not be affected by the ester preparation process.[12] However, some production processes include steps to purify the methyl esters that can remove antioxidants. Biodiesel produced using distillation to purify the product, for example, typically contains little or no natural antioxidant and is less stable than biodiesel that does. The stability of biodiesel prepared by distillation, as well as biodiesel that contains natural antioxidants, can be improved by adding synthetic antioxidants.[2] Westbrook[5] has shown that several antioxidants, including proprietary antioxidants developed for petroleum fuels, can improve biodiesel oxidation stability.

High levels of oxidation can cause operational problems for engine fuel system components. Terry and coworkers[13] showed that at very high levels of oxidation, biodiesel blends can separate into two phases to cause fuel pump and injector operational problems or lacquer deposits on fuel system components. Blassnegger performed 500-hour fuel injector bench tests with rapeseed methyl ester (RME) (B100) samples that had a range of stability.[14] Lower stability B100, with a Rancimat induction time of 1.8 to 3.5 hours, produced injector deposits and reduced the amount of fuel injected per stroke. Tsuchiya et al demonstrated that the formation of high levels of acids, which can be generated from unstable biodiesel during extended fuel recirculation, can corrode metal vehicle fuel tanks.[15] Thus, there are strong arguments for ensuring the stability of biodiesel and biodiesel blends. We conducted this empirical study, which is directed at defining a performance-based standard, because of the numerous factors can affect oxidation

Methods

B100 and Diesel Fuel Properties

During December of 2005 and January of 2006 a single drum of B100 was obtained from each of 14 biodiesel production sites in the United States and two more from Canadian production facilities. Additionally, three drums of European rapeseed-derived biodiesel (RME) were obtained. The 19 B100 drums were nitrogen purged, and blanketed, and stored in a dark room at room temperature. All B100 samples were tested initially for:

- Total acid number (or acid value), ASTM D664
- Free and total glycerin, ASTM D6584.

Detailed characterization was performed on a subset of eight fuels that were selected for more detailed testing:

- Total particulate contamination, ASTM D6217
- Flash point, ASTM D93
- Peroxide value, ASTM D3703
- Karl Fischer moisture, ASTM D6304
- Iso-octane insoluble, (based on a 4:1 dilution of the sample with iso-octane followed by filtration using the modified ASTM D2274 procedures described below)
- Kinematic viscosity @ 40°C, ASTM D 445
- Polymer content, ISO 16931 (high performance size-exclusion chromatography)
- Metals (P, Na, K, Ca, Mg, Cu, Zn), ASTM D5185.

In addition, six samples (two drums each) of petroleum-derived diesel fuel were obtained from petroleum refiners in the United States and Canada. These include one 500-ppm sulfur fuel, and five others meeting the 15-ppm sulfur limit (ULSD). The diesel fuels were characterized with the following tests:

- Total particulate contamination, ASTM D6217
- Flash point, ASTM D93
- Sulfur, ASTM D5453
- T90/carbon residue, ASTM D86/D524
- Total acid number (or acid value), ASTM D664
- Peroxide value, ASTM D3703
- Ash content, ASTM D482
- Supercritical fluid chromatography aromatics, ASTM D5186.

Peroxide is measured by D3703, a method developed for aviation fuels with peroxide contents in the range of 1 to 5 ppm. The D3703 method is therefore not wholly applicable to samples with the high peroxide numbers found in many B100 and biodiesel blend samples. An interlaboratory study is underway to determine the applicability of this method to biodiesel. The absolute accuracy of the test for biodiesel is currently unknown, but we believe it is adequate for showing trends over time.

Accelerated Stability Tests

All samples, B100 and blends, were analyzed under the same conditions per standard test method EN 14112 Fat and oil derivatives—Fatty acid methyl esters (FAME)—Determination of Oxidation Stability. The Rancimat apparatus was used and tests were performed at 110ºC. The Rancimat utilizes a proprietary computer algorithm to analyze the conductivity results and determine the induction period. All samples were tested in duplicate and the average induction period was reported. If the results for the replicates differed by more than approximately 10% of the mean, a third test was conducted and the two results closest to each other were averaged.

Significant problems were often encountered when analyzing blends, especially B5 blends. For most blends, the petroleum diesel fraction was sufficiently volatile to evaporate and condense in either the air tubes or the measuring vessel. Some of the plastic components of the Rancimat were incompatible with the petroleum diesel. This caused swelling of the parts and resultant air leaks. We had to replace these parts on a frequent basis. The standard air tube would soften and restrict the flow of air to the measuring vessel. We found that standard Tygon™ laboratory tubing was an acceptable replacement for the original air tubing. As of this writing, the manufacturer is evaluating replacement parts that are compatible with petroleum for the analysis of blends.

Also, the test results for the blends were found to be far less repeatable. In many cases, the B5 samples would run for several days before an induction period was determined. This was due to the lower amount of biodiesel in the sample (compared to B100) and varied with the stability of the original B100. For the purposes of this project, we manually stopped Rancimat tests once the induction period was found to be greater than 12 hours.

Oxidation stability as determined by ASTM D2274 was modified for use with biodiesel by substituting glass fiber filters for the cellulose ester filters used with petroleum fuels, as described by Stavinoha and Howell.[16] Additionally, we attempted to keep the filtration time as consistent as possible. Iso-octane insolubles of the filtrate were determined by adding 100 ml of the filtered, post-D2274 B100 to 400 ml of prefiltered iso-octane. This was thoroughly mixed and allowed to set for at least 1 hour before filtering to determine insolubles. These insolubles or precipitates are a potential measure of oxidation products that remain soluble in the very polar B100, but could be insoluble in a diesel fuel blend. Acid value of the filtrate was also measured by D664 for some samples.

Thermal stability as determined by ASTM D6468 was performed at 150ºC for 180 minutes. In addition to measurement of filter reflectance, this test was modified to use the same gravimetric insoluble measurement procedures used for D2274 (both total and iso-octane). Duplicate 50-ml samples were tested; results for reflectance were reported as the average. Gravimetric results are reported as the sum of the duplicate samples in mg/100 ml. An additional modification to D6468 was examined in preliminary scoping tests to purge the ullage or space above the heated liquid with air to ensure that a highly unstable material would not consume all the oxygen and thereby produce an invalid result. Results of these scoping tests are shown in Table 1, which shows that ullage purge had no significant effect on the results, and thus was not used in subsequent tests.

Table 1. Results of D6468 Ullage Purge Scoping Tests

Sample Identification	AL-27131-F[(1)]		AL-27070-F[(2)]	
Modified ASTM D6468[(3)]	with air flow	without air flow	with air flow	without air flow
filterable insolubles, mg/100 ml	0.03	0.14	0.77	1.1
adherent insolubles, mg/100 ml	0.09	0.06	0.14	0.14
total insolubles, mg/100 ml	0.11	0.2	0.9	1.2

[1] Soy-based B100
[2] Low-sulfur No. 2 diesel fuel
[3] 350 ml; 150°C; 180 minutes with and without air flow within ullage

Oxidation stability as determined by ASTM D525 Standard Test Method for Oxidation Stability of Gasoline (Induction Period Method), measures an induction time for the start of oxygen consumption. This test was shown in a recent study[17] to correlate well with Rancimat induction time.

Simulation of Real-World Aging Scenarios

We envision three scenarios where oxidative degradation of biodiesel or biodiesel blends might occur.

Storage and Handling

Biodiesel and biodiesel blends must be stored and handled before they are dispensed into vehicle fuel tanks. For research purposes there seems to be general agreement that ASTM D4625 (43°C/12 weeks) adequately simulates this situation.* The method employs the glass vessel shown in Figure 1. Individual glass vessels are stored for 4, 8, and 12 weeks so that an independent sample is evaluated at each time interval (as opposed to removing an aliquot from one vessel at each time interval). In this study the procedures were modified to employ glass fiber filters to determine insolubles. For biodiesel and blends, acid value, peroxide value, polymer content, and viscosity, as well as total insolubles, were measured during this test. For B100, iso-octane insolubles were also measured.

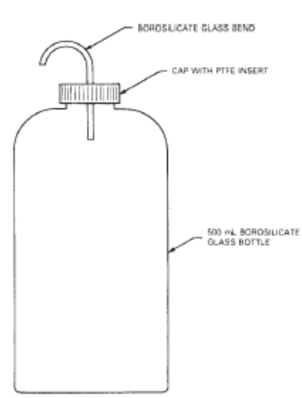

Figure 1. Glass vessel used for D4625 stability test

*However, the correspondence of 1 week on D4625 to 1 month of underground storage at 21ºC that is typically assumed for petroleum diesel has not been established for biodiesel.

The goals for this test are to:

- Determine whether there is an accelerated test that predicts D4625 results.
- Assess the potential of a B100 accelerated stability measurement to predict blend stability in this scenario.
- Reveal how antioxidants can affect storage stability.

Vehicle Fuel Tank

Biodiesel blends will ultimately be pumped into a vehicle fuel tank and will be subject to periodic heating to higher than ambient temperatures. This can be due to recirculation of hot fuel back into the fuel tank, or simply exposure to hot climates. The ASTM Biodiesel Stability Working Group discussed the possibility of storing the fuel for about 6 days at 80°C to simulate a type of worst-case situation. Although there is no ASTM test with this time and temperature duration, the ASTM D4625 procedures and apparatus to can be modified slightly to determine total insolubles at the end of this period. The measurement of acid value, peroxide value, polymer content, and viscosity may also prove valuable. Because the biodiesel is already blended with diesel fuel, the measurement of iso-octane insolubles is not likely to be informative. This is not a standard test, so results should be interpreted with caution.

A scoping study was performed to ensure that this test is not being conducted under oxygen-deficient conditions. Specifically, the D4625 apparatus (see Figure 1) was modified to allow a slow air purge of the bottle ullage during tests of a B100 and a diesel fuel. A comparison of these results is shown in Table 2. The results indicate that significantly higher levels of insolubles are obtained with the B100 when air purging is used. Because a real vehicle fuel tank will be agitated by vehicle motion and is open to the air, ullage purging will be employed in this 6-day test. This test is similar to a 24-hour storage stability test proposed by Bondioli and coworkers.[18]

Table 2. Results of D4625 (6-Day, 80ºC Modification) Ullage Purge Scoping Tests

Sample identification	AL-27131-F(1)		AL-27070-F(2)	
Modified ASTM D4625(3)	with air flow	without air flow	with air flow	without air flow
filterable insolubles, mg/100 ml				
replicate 1	1.3	0.14	0.20	0.17
replicate 2	2.1	0.11	0.20	0.20
adherent insolubles, mg/100 ml				
replicate 1	1.7	0.80	0.31	0.14
replicate 2	2.0	0.80	0.20	0.20
total insolubles, mg/100 ml				
replicate 1	3.0	0.94	0.51	0.31
replicate 2	4.1	0.91	0.40	0.40
average total insolubles, mg/100 ml	3.6	0.93	0.46	0.36

1 Soy-based B100
2 Low-sulfur No. 2 diesel fuel
3 500-ml; 80°C; 1 week storage with and without air flow within ullage

This test was performed on duplicate 500-ml samples. A 50-ml aliquot was removed from each bottle at the end of 1 week of storage. These were combined to make 100 ml and filtered to obtain a total insoluble result. The goals for this test are to:

- Determine whether there is an accelerated test that predicts simulated tank stability results.
- Assess the potential of a B100 accelerated stability measurement to predict blend stability in this scenario.
- Reveal how antioxidants can affect blend stability in the vehicle tank situation

High-Temperature Fuel System Environment

Biodiesel blends are subjected to temperatures as high as 150°C for short periods in the engine's fuel system. A substantial fraction of this fuel is recirculated to the vehicle fuel tank. Proposing a standard test that simulates this environment is somewhat more challenging. One possibility is ASTM D6468 (150°C and 180 minutes) but modified to make a gravimetric measurement of deposits. This test can be run on fresh fuel to simulate potential thermal stability in or around the injector (mentioned in the discussion of accelerated stability tests), or with aged fuel that has been in the fuel system for some time.

A worst-case scenario would be to test a fuel for 6 days at 80°C with the modified D4625, and then perform D6468. In this study one 50-ml aliquot was taken from each duplicate bottle after 1 week of storage. These were combined, and then split into two 50-ml samples for the D6468 test. Both 50-ml aliquots were filtered through the same filter to determine insolubles in mg/100 ml. The goals for this test are to:

- Determine whether there is an accelerated test that predicts simulated high-temperature zone stability.
- Assess the potential of a B100 accelerated stability measurement to predict blend high-temperature stability in this scenario.
- Reveal how antioxidants and other additives can effect high temperature stability.

This test, like the vehicle fuel tank simulation test, is not standard, and results should be interpreted with caution.

Results: Stability of B100

Accelerated Testing and Characterization

Table 3 lists the 19 B100 samples obtained, their feedstocks, and preliminary characterization results. These samples appear to cover the full range of feedstocks currently used in North America. Two samples failed the ASTM D6751 specification for biodiesel: one because of high acid value and the other because of high total glycerin. These samples are included in the accelerated stability tests, but were not considered for any additional testing in this study because of their poor quality. The samples that were selected for additional study were characterized much more extensively.

Table 3. Biodiesel Samples Obtained and Preliminary Characterization (values in bold exceed specification limits)

Sample Identification	Feedstock	Total Acid Number, mg KOH/g	Total Glycerin, %(mass)	Free Glycerin, %(mass)
		ASTM D664	ASTM D6584	ASTM D6584
	ASTM D6751-03a Limit:	*0.80*[1]	*0.240*	*0.02*
AL-27128-F	Canola	0.23	0.103	0.009
AL-27129-F	Palm Stearin	0.41	0.081	<0.001
AL-27137-F	Soy	0.05	0.144	0.002
AL-27138-F	Soy	0.33	0.016	0.002
AL-27140-F	Soy	0.20	0.022	0.015
AL-27141-F	Soy	0.13	0.121	0.005
AL-27142-F	Soy	0.07	0.216	0.003
AL-27144-F	Soy	0.39	0.221	0.004
AL-27145-F	Soy	0.49	0.192	0.005
AL-27146-F	Rapeseed	0.08	0.161	<0.001
AL-27148-F	Grease	0.69	0.121	<0.001
AL-27152-F	Rapeseed	0.09	0.15	0.001
AL-27153-F	Rapeseed	0.08	0.15	0.001
AL-27154-F	Grease	***1.31***	0.132	0.003
AL-27155-F	Soy	0.29	***0.298***	0.007
AL-27157-F	Soy	0.11	0.225	0.015
AL-27158-F	Soy	0.51	0.158	0.001
AL-27160-F	Tallow	0.46	0.188	0.002
AL-27161-F	Grease	0.37	0.151	0.003

[1] This limit was reduced to 0.50 mg KOH/g in mid-2006.

Oxidation stability data for the 19 B100 samples are tabulated in Appendix A. Figure 2 shows a histogram for OSI induction time measured for these samples. The samples show a broad distribution with results ranging from less than 1 to more than 9 hours. Figure 3 compares the OSI induction time results to ASTM D525 induction time results. Based on an earlier report, we anticipated that these tests would correlate to some extent.[17] The circled data points indicate that no oxidation was observed after 780 minutes, and the results are simply plotted as 780 minutes. Figure 3 indicates a poor correlation between these methods (r^2 of 0.4). Subsequent testing showed that D525 results were not predictive of B100 or blend performance. Consequently, D525 results are not discussed further.

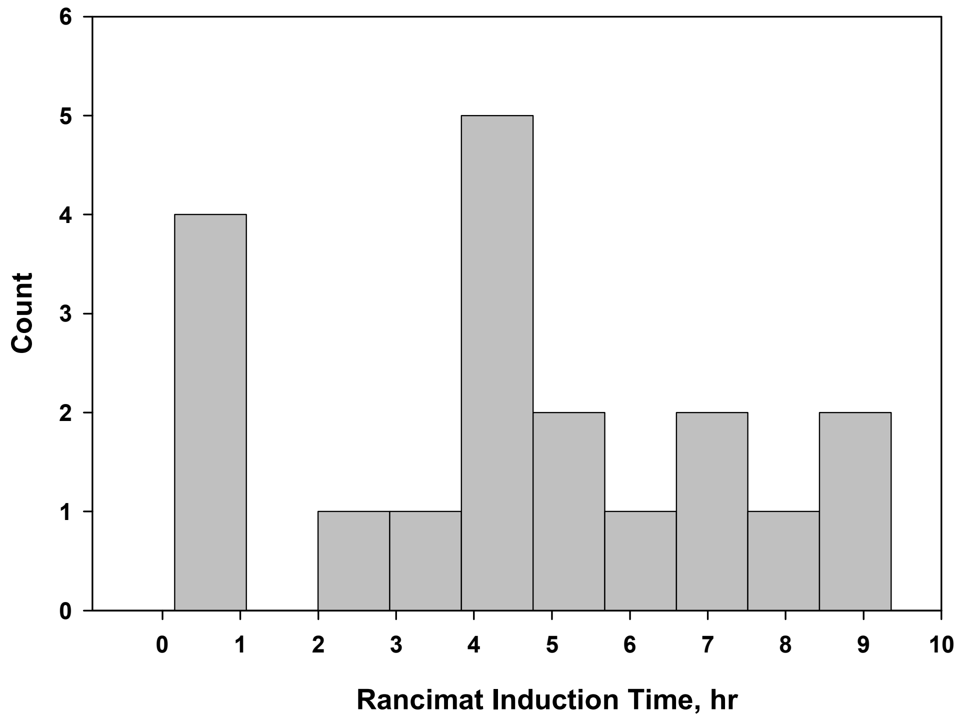

Figure 2. Histogram for B100 OSI or Rancimat induction time

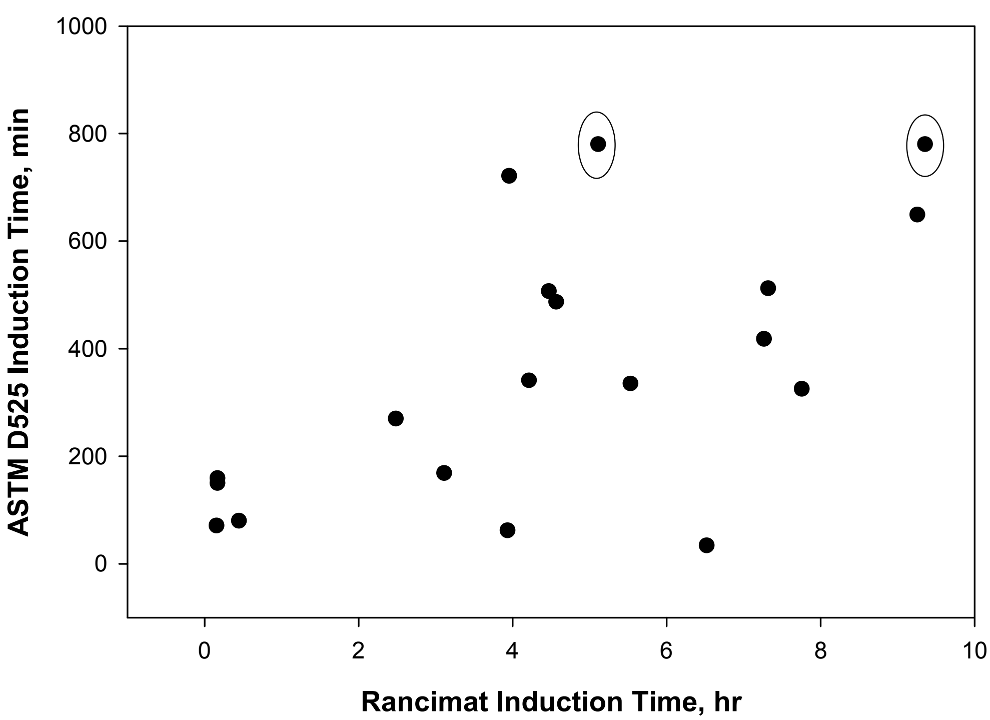

Figure 3. Relationship between B100 OSI or Rancimat induction time and ASTM D525 results. Circled data points indicate that no oxidation was observed after 780 minutes and the results are simply plotted as 780 minutes

Figure 4 shows a histogram for the ASTM D2274 deposit test. Ten of the 19 samples tested show deposits of less than 2 mg/100 ml; deposits for the other nine fuels cover the range to nearly 18 mg/100 ml. As observed previously,[19] the amount of adherent insolubles was 2 to 4 times higher than the amount of filterable insolubles. Figure 5 shows the inverse relationship between induction time and D2274 total insolubles. This is very similar to the relationship observed previously,[19] and in an approximate sense shows the expected inverse correlation. The filtrate from this test was also mixed with iso-octane to precipitate materials that are insoluble in nonpolar solvents. Fourteen of the samples exhibited less than 20 mg/100 ml; the balance ranged to 200 mg/100 ml. Figure 6 shows the relationship between total insolubles and iso-octane insolubles. The correlation is not perfect, but the only samples that produced very high levels of iso-octane insolubles also produced very high levels of total insolubles. This suggests that little new information is acquired by measuring iso-octane insolubles. Finally, the acid value of the filtered liquid was also measured and ranged from less than 1 to more than 5 mg KOH/g. Change in acid value over D2274 is closely correlated with total insolubles and inversely correlated with induction time, as shown in Figures 7 and 8.

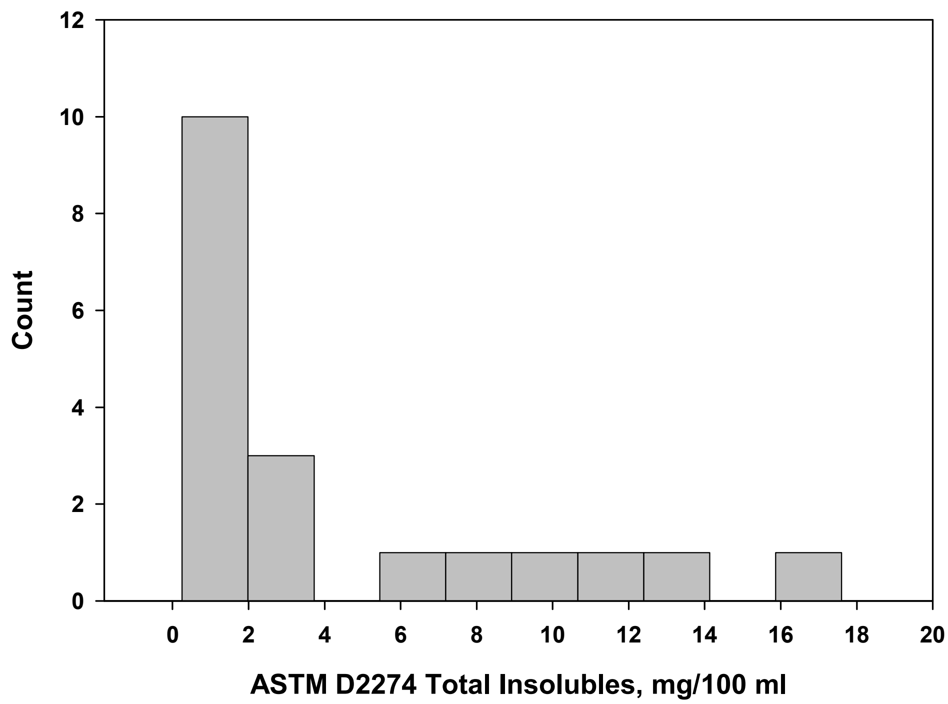

Figure 4. Histogram for B100 ASTM D2274 total insolubles

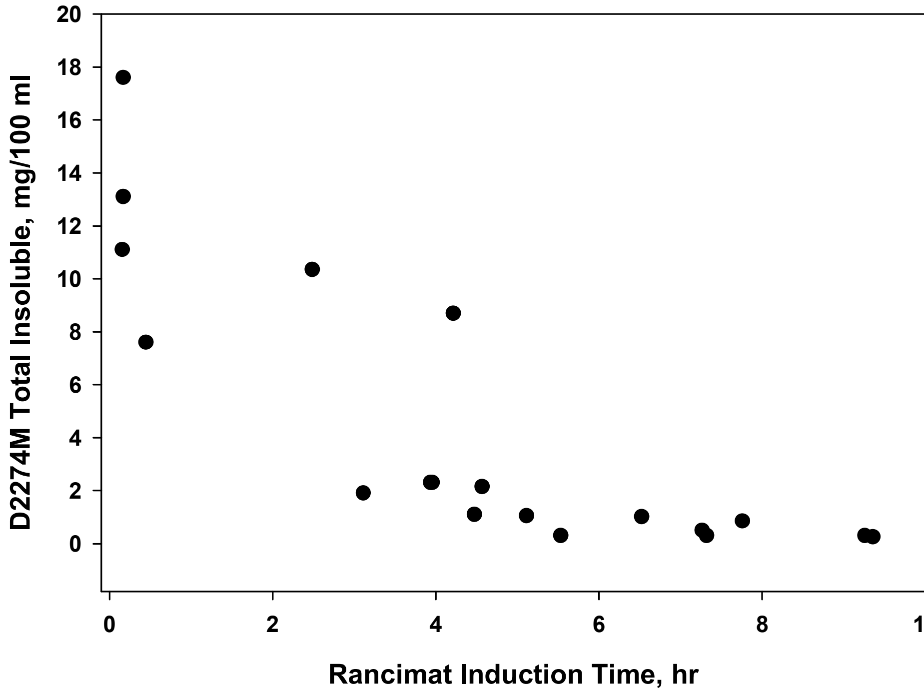

Figure 5. Relationship between B100 OSI or Rancimat induction time and D2274 total insolubles

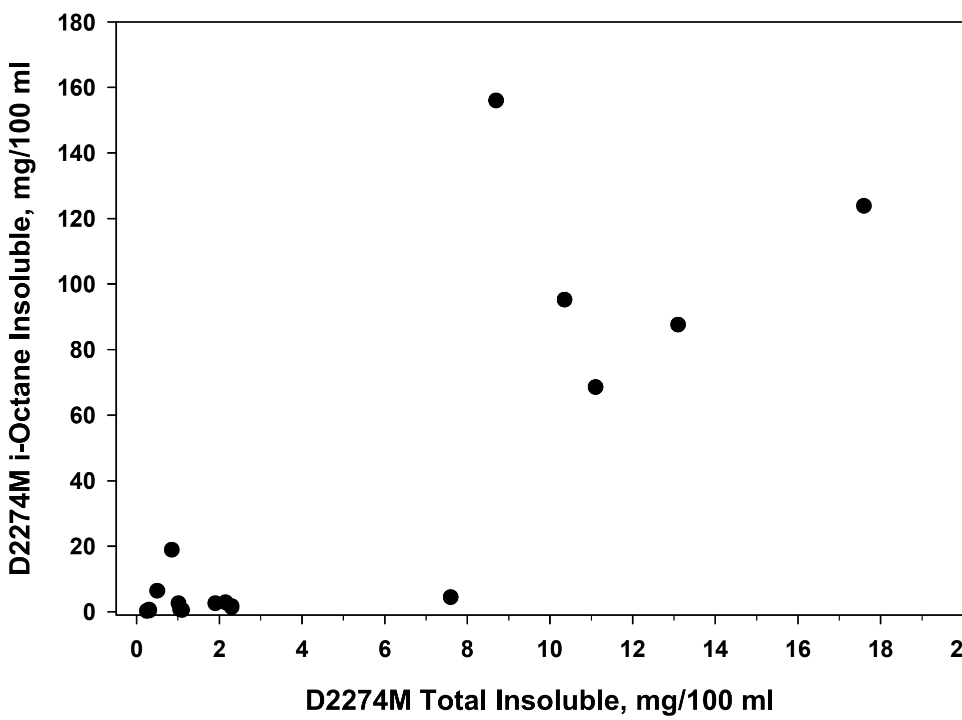

Figure 6. Relationship between B100 D2274 total insoluble and iso-octane insoluble

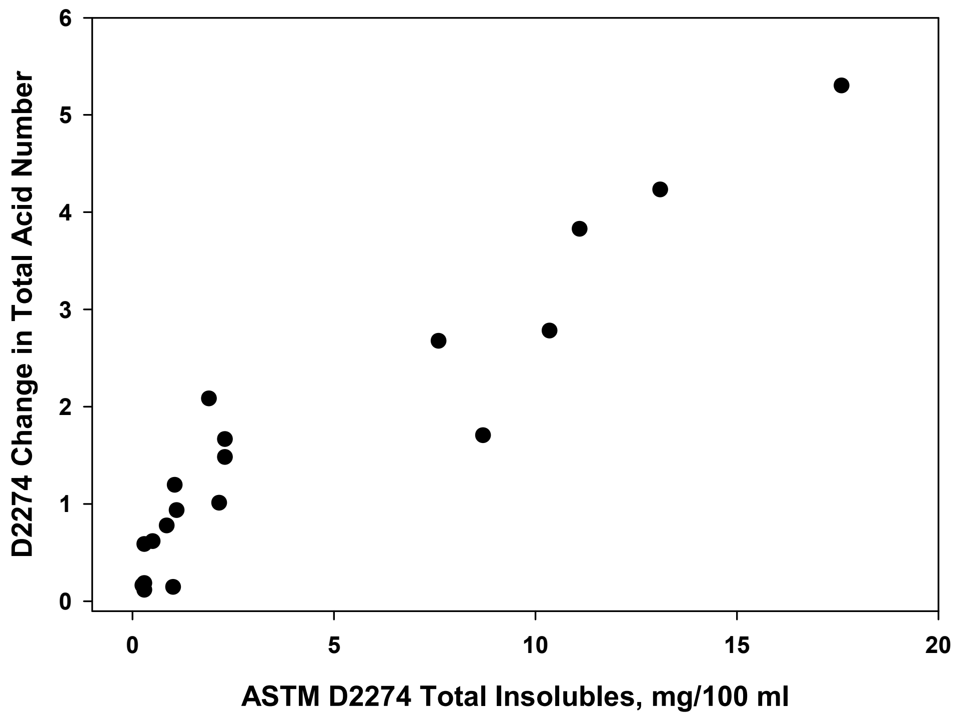

Figure 7. Change in total acid number on D2274 versus D2274 total insolubles for B100 samples

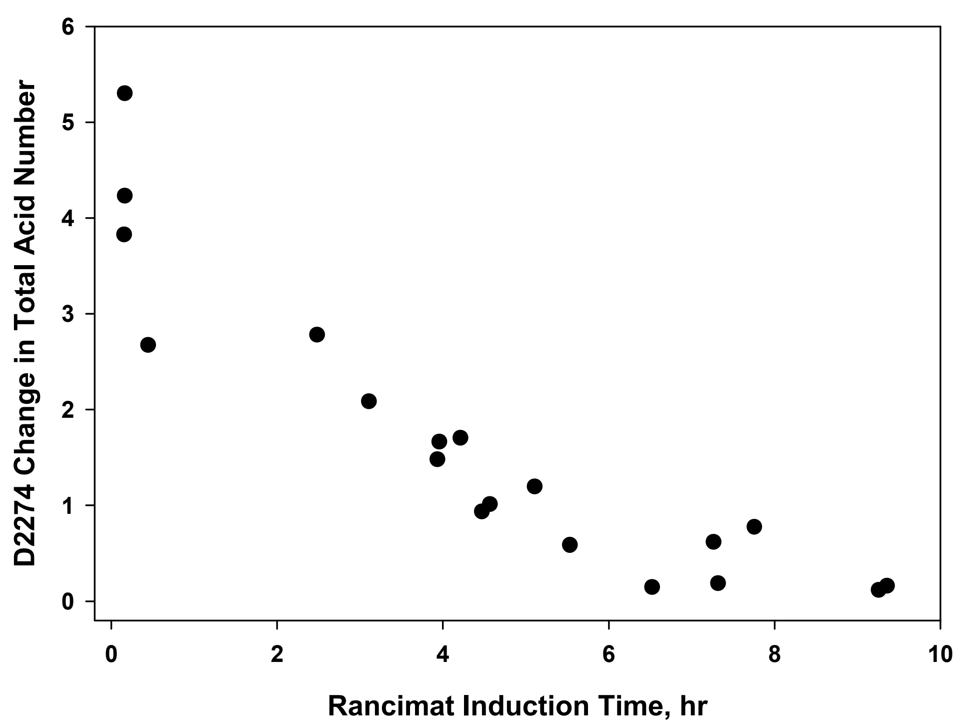

Figure 8. Change in total acid number on D2274 versus OSI or Rancimat induction time for B100 samples

Table 4 lists results for the ASTM D6468 thermal stability test modified for gravimetric measurement of deposits. All samples produced low levels of deposits, and there is little discrimination among the samples.

Table 4. Results of ASTM D6468 Performed on B100 Samples at 150°C/180 Minutes and Modified for Gravimetric Determination of Deposits

Sample Identification	ASTM D6468 Modified
	Thermal Stability, deposit, mg
AL-27128-F	0.3
AL-27129-F	0.1
AL-27137-F	0.3
AL-27138-F	0.3
AL-27140-F	0.4
AL-27141-F	0.2
AL-27142-F	0.3
AL-27144-F	0.4
AL-27145-F	0.4
AL-27146-F	0.5
AL-27148-F	0.4
AL-27152-F	0.1
AL-27153-F	0.5
AL-27154-F	0.1
AL-27155-F	0.3
AL-27157-F	0.3
AL-27158-F	0.6
AL-27160-F	0.5
AL-27161-F	0.2

Based on these results, eight samples were selected for more detailed characterization, long-term storage tests (D4625 for 12 weeks), and for preparation of B5 and B20 blends. The downselection was based on covering the full range (high, medium, low) of values for each of the accelerated tests and on trying to include the full range of feedstocks. However, results for D6468 showed low levels of deposits (gravimetric) for all samples, so that test is not considered here. Additionally, the two B100 samples that failed to meet specifications for either acid value or total glycerin were not considered. The samples selected are shown in Table 5. Some compromises were made to meet all the study objectives, including covering all feedstocks. These eight samples were subjected to more extensive characterization tests. Results of these tests are shown in Table 6. All samples met the D6751 requirements for which they were tested.

Table 5. B100 Samples Selected for Long-Term Storage and Blending Studies

	Feedstock	OSI/Rancimat	D2274 Total	D2274 i-Octane
Observed Range		0.2–9.4 h	0.3–17.6 mg/100 ml	0.6–198 mg/100 ml
AL-27128-F	Canola	4.2 (med)	6.5 (med)	198 (high)
AL-27129-F	Palm stearin	3.1 (med)	1.9 (low)	2.6 (low)
AL-27137-F	Soy	6.5 (high)	1.0 (low)	2.6 (low)
AL-27138-F	Soy	0.5 (low)	7.6 (med)	4.4 (low)
AL-27141-F	Soy	5.5 (high)	0.3 (low)	0.6 (low)
AL-27148-F	Grease	7.8 (high)	0.9 (low)	19 (med)
AL-27152-F	Rapeseed	7.3 (high)	0.5 (low)	6.4 (low)
AL-27160-F	Tallow	0.2 (low)	17.6 (high)	124 (high)

Table 6. Characterization Results for B100 Samples Downselected for Further Study and Blending*

	Test Method	Units	AL-27128	AL-27129	AL-27137	AL-27138	AL-27141	AL-27148	AL-27152	AL-27160
Particulate Contamination	D6217, mod	mg/l	14.7	0.2	103.9	0.8	3.5	19.5	5.1	17.6
Total Water	D6304	ppm	656	217	149	562	131	118	298	1092
Flash Point	D93	°C	160	177	179	155	152	131	169	178
Elemental Analysis	D5185	ppm								
	P		<1	<1	<1	<1	<1	<1	<1	<1
	Na		<5	<5	<5	<5	<5	<5	5	5
	K		<5	<5	<5	<5	<5	<5	<5	<5
	Ca		1	<1	<1	<1	<1	<1	<1	2
	Mg		<1	<1	<1	<1	<1	<1	<1	<1
	Cu		<1	<1	<1	<1	<1	<1	<1	<1
	Zn		<1	<1	<1	<1	<1	<1	<1	<1
	Mg		<1	<1	<1	<1	<1	<1	<1	<1
Iso-Octane Insoluble	D4625, mod	mg/100 ml	3.9	0.1	1.9	1.1	2.3	0.1	0.1	0.5
Peroxide Value	D3703		217	105	12	50	98	9	44	17
Viscosity @ 40°C	D445		4.45	5.12	4.10	4.32	4.09	4.67	4.47	4.86
Polymer Content	ISO16931		2.63	0.17	0.82	0.22	1.03	1.46	2.17	4.91
Total Acid No.	D664	mg KOH/g	0.23	0.41	0.05	0.33	0.13	0.69	0.09	0.46
Free Glycerin	D6584	wt%	0.009	<0.001	0.002	0.002	0.005	<0.001	0.001	0.002
Total Glycerin	D6584	wt%	0.103	0.081	0.144	0.016	0.121	0.121	0.150	0.188

* At the time these samples were collected the acid value was limited to 0.80 mg KOH/g maximum. In mid-2006 this limit was reduced to 0.50 mg KOH/g.

Storage Stability of B100

Storage stability was assessed for the eight B100 samples by using ASTM D4625 (storage for 12 weeks at 43ºC), numerical results are in Appendix B. For petroleum-based diesel fuels, each week of testing correlates to approximately 1 month of storage at ambient conditions. Figure 9 shows how induction times change over this test. All these biodiesel samples exhibited induction times shorter than 3 hours after 4 weeks, and all declined to very low levels at 8 weeks. Figure 10 shows peroxide value over the test and indicates that all but one of the samples had clearly degraded, even at 4 weeks. Figure 11 shows how acid value changes over the D4625 test. All but the most stable samples show a small increase in acidity at 4 weeks, but all still meet the 0.80 mg KOH/g limit that was in place when these samples were acquired. By 8 weeks (simulated 8 months) acidity had increased to above the 0.80 mg KOH/g limit for all samples. Figure 12 shows total insolubles formation over 12 weeks (simulated 8 months). These results show acid value and total insolubles in a range similar to that observed in previous investigations that used this test.[5,8,16] The level of B100 total insoluble on this test that is indicative of an unacceptable fuel blending component, and the repeatability of this test for B100, are unknown. The acid number increase may be a more accurate indicator than sediment formation of deleterious changes in B100 under these conditions. The data can mainly be interpreted by looking for a large increase in insolubles or by comparing the samples in a relative sense. Generally all the samples are beginning to experience significant increases in insolubles formation at the 12-week point. At 4 and 8 weeks the samples with induction times shorter than 3 hours have the highest levels of insolubles. Data for iso-octane insoluble and polymer content have a similar pattern (not shown), although polymer content remains low through 8 weeks and increases only at 12 weeks. Viscosity does not appear to be a sensitive indicator of oxidation for these samples.

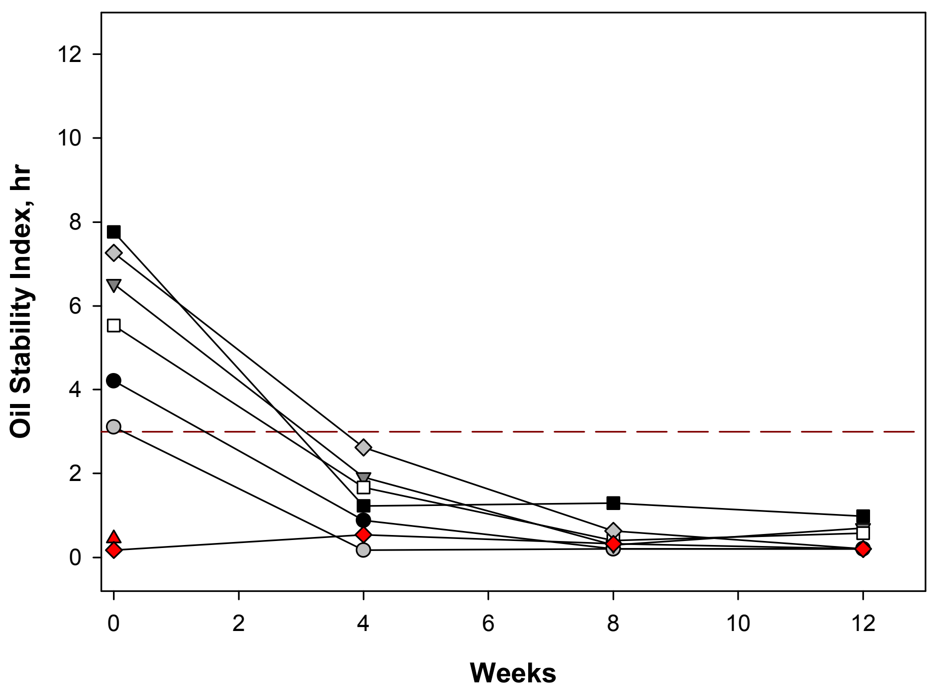

Figure 9. Change in OSI or Rancimat for B100 samples over 4 weeks in D4625 test

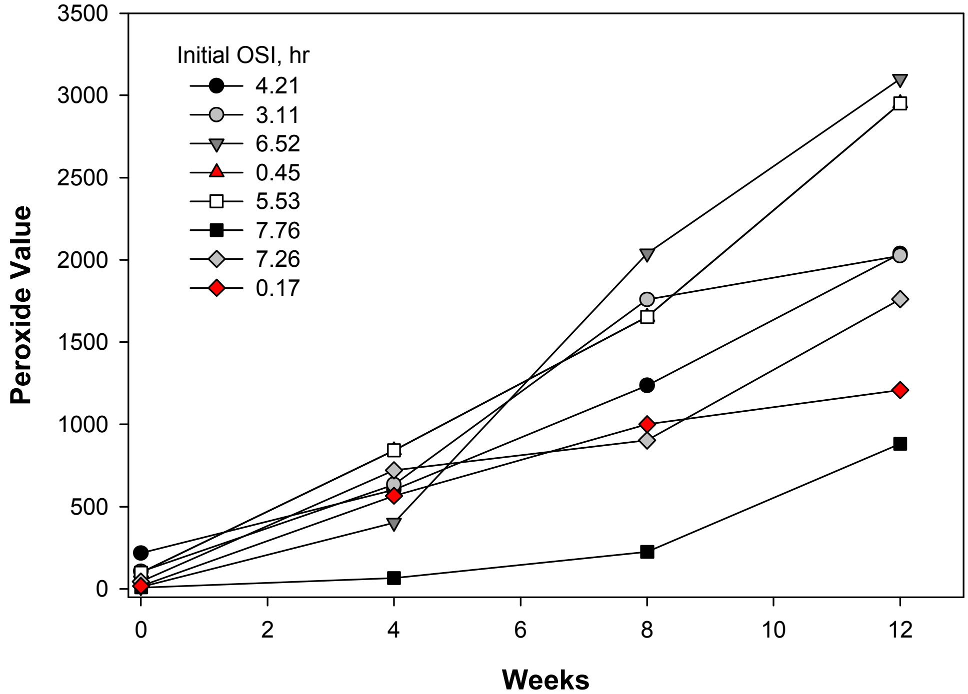

Figure 10. Peroxide value measured for B100 samples over the D4625 test

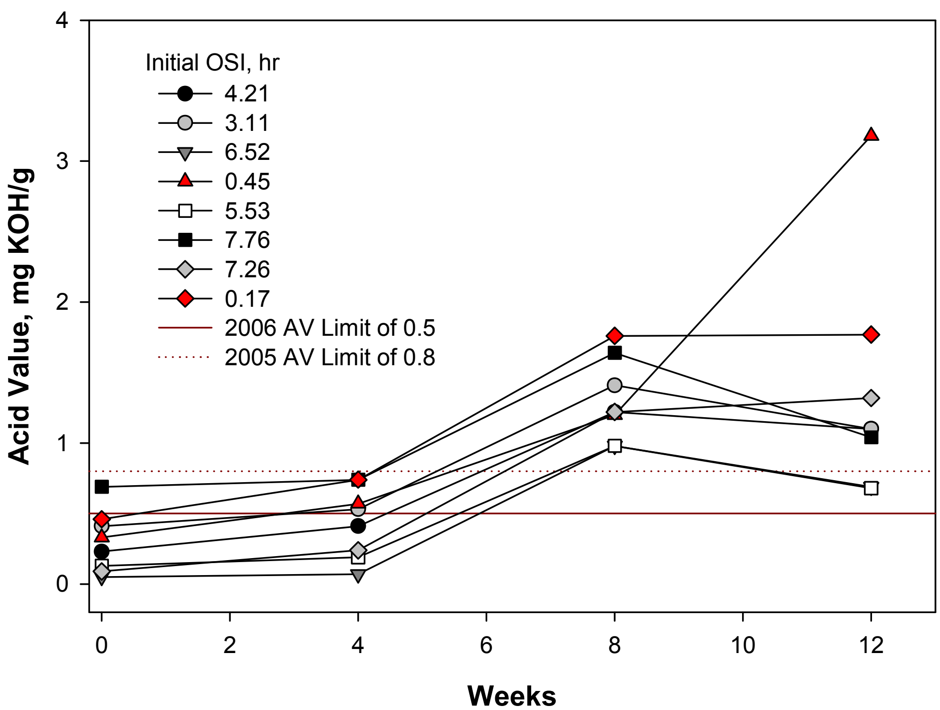

Figure 11. Change in acid value for B100 samples on the D4625 test

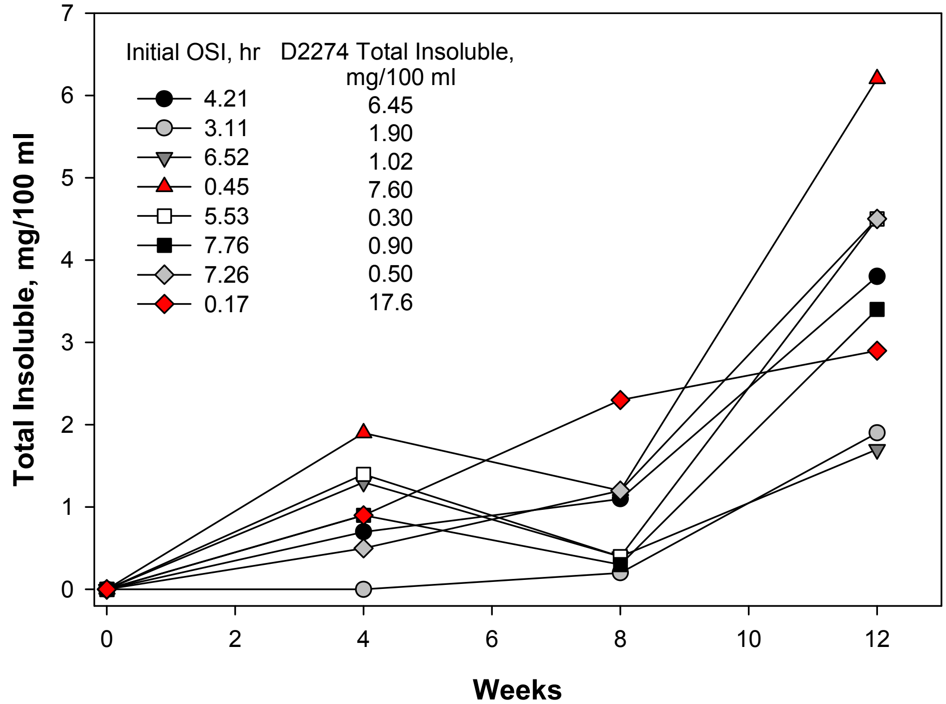

Figure 12. Total insoluble measured for B100 samples over the D4625 test

B100 Antioxidant Testing

Biodiesel samples AL-27129-F and AL-27138-F were treated with two commercial antioxidants. Antioxidant treat rates as well as Rancimat induction times and total insolubles from ASTM D2274 are given in Table 7. Both additives are effective at increasing induction time and reducing insolubles formation for these samples. The biodiesels were selected to represent unstable material (AL-27138-F) with an induction time of 0.45 hours and moderately stable material (AL-27129-F) with an induction time of 3.11 hours.

These samples were also tested for long-term storage stability with ASTM D4625; detailed results for these tests are reported in Appendix B. Results for total acid number are shown in Figure 13. The data indicate that both additives effectively prevented acid formation. Results for total insolubles are shown in Figure 14. Both antioxidants effectively suppressed insoluble formation in both biodiesel samples at both treat rates. Protection from insoluble and acid formation might have been achieved at lower treat rate.

Table 7. Results of Accelerated Stability Tests for Biodiesel Treated with Antioxidant Additives

Sample Number	Description	Rancimat Induction Time	ASTM D2274		
			Total Insoluble	i-Octane Insoluble	Acid Value
		h	mg/100 ml	mg/100 ml	mg KOH/g
	AL-27138 with no additive	0.45	7.6	4.4	3.01
06-0077	AL-27138 plus 1000 ppm additive A	3.18	6.5	1.0	2.35
06-0078	AL-27138 plus 2000 ppm additive A	5.73	0.3	1.6	0.40
06-0079	AL-27138 plus 1000 ppm additive B	1.67	3.0	0.6	2.49
06-0080	AL-27138 plus 2000 ppm additive B	2.64	0.8	0.3	1.28
	AL-27129 with no additive	3.11	1.9	2.6	2.50
06-0081	AL-27129 plus 1000 ppm additive A	22.8	0.1	0.5	0.45
06-0082	AL-27129 plus 1000 ppm additive B	6.87	0.2	0.1	0.47

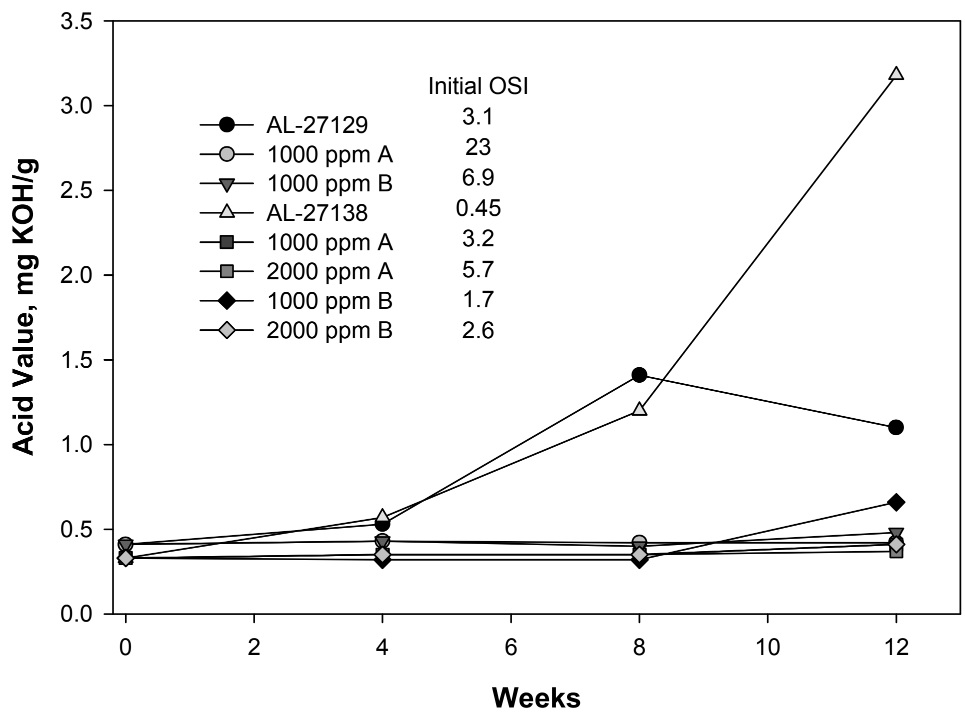

Figure 13. Total acid number results for D4625 long-term storage testing of antioxidant-treated B100 samples

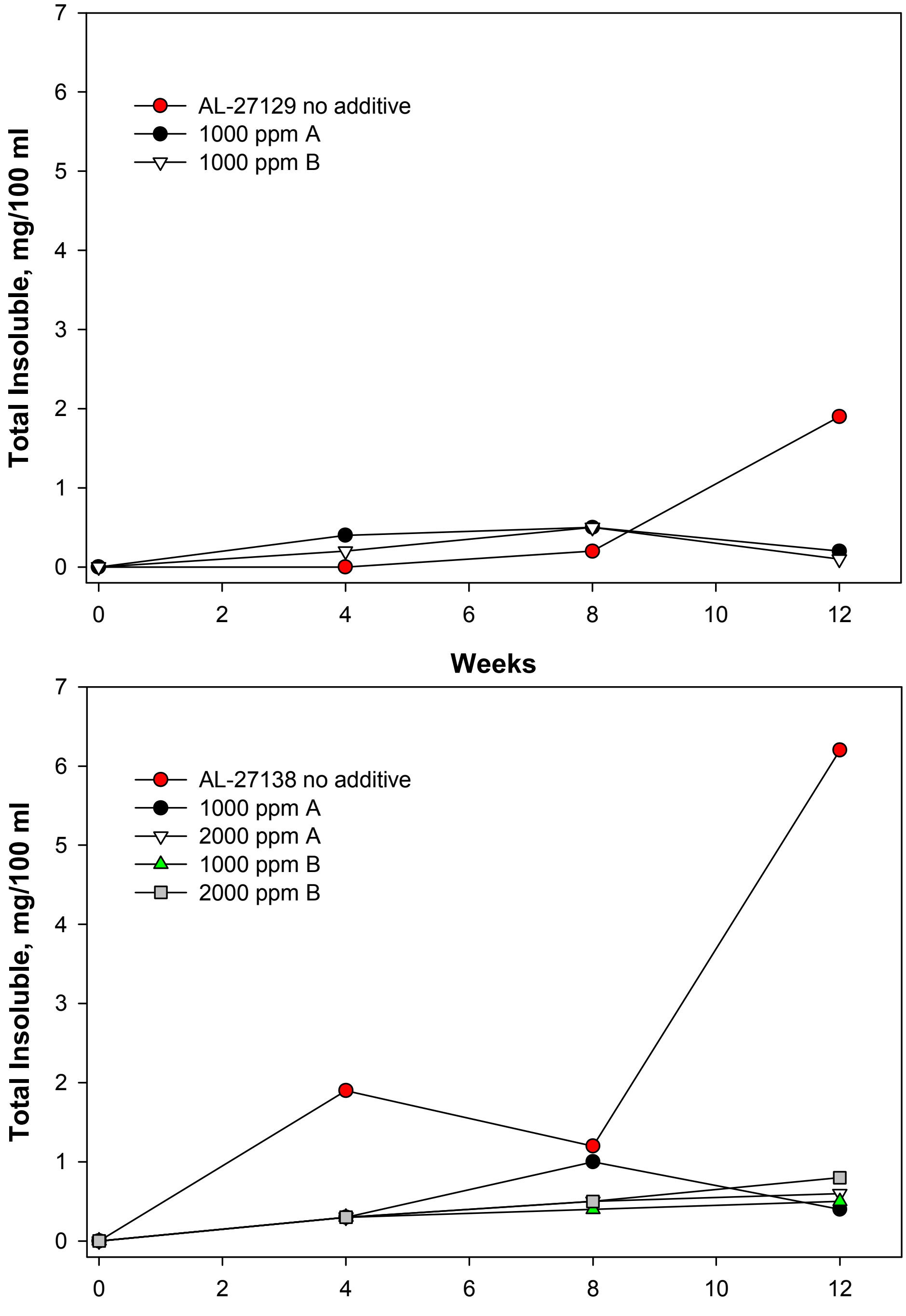

Figure 14. Total insoluble results of ASTM D4625 long-term storage test for antioxidant-treated B100 samples

Results: Stability of Biodiesel Blends

Diesel Fuel Properties and Stability

Characterization results for the six diesel fuel samples to be used for blending are shown in Table 8. Five are ULSD, and one is an on-road diesel fuel produced before ULSD was required. Based on the distillation T90, samples AL-27150F, AL-27166F, and AL-27176F are No. 1 diesel fuels; the others are No. 2 diesel fuels. Aromatic content is regarded as an important parameter for this study because fuels with higher aromatic content may be able to more readily solvate oxidized biodiesel molecules, which would otherwise precipitate as deposits in fuels with lower aromatic content. Total aromatics for the ULSD samples range from 8.2 to 22.1 mass percent. Because these ULSD were obtained in late 2005 they might not be representative of commercial ULSD in use today. All samples exhibited good stability on both D2274 and D6468.

These fuels were also tested for long-term storage stability by using D4625 with measurement of insolubles formation. Results are shown in Figure 15 where all diesel samples were stable at 8 weeks and one sample, AL-27175, showed the initiation of degradation at 12 weeks. This is a No. 2 ULSD with the lowest aromatic content of the samples in this set. Detailed results for D4625 are listed in Appendix C.

The diesel fuels were also tested by using the fuel tank aging simulation of 1 week in the D4625 glass vessel at 80ºC while the ullage was purged with air. Results are reported at the bottom of Table 8. These samples, after the 1 week of aging, were also tested with the D6468 thermal stability test but with gravimetric measurement of total insolubles. These results are also shown in Table 8. Because this test sequence is not standard, there is little information with which to compare these numbers. However, they do provide an important baseline for comparison with results for biodiesel blend samples.

Table 8. Characterization Results for Petroleum Diesel Samples To Be Used in Preparation of B5 and B20 Blends

	Sample	ASTM D975 Limit (No. 2 Diesel)	AL27150F	AL27151F	AL27166F	AL27171F	AL27175F	AL27176F
ASTM D93	Flash point, ºC	52	56	69	59	73	59	69
ASTM D5453	Sulfur, ppm	15 or 500	7.4	6.7	5.8	339.6	2.9	7.4
ASTM D86	T90, ºC	282 min 338 max	274	313	269	319	333	236
ASTM D524	Carbon residue (on 10% distillation residue), mass%	0.35	0.07	0.04	0.06	0.13	0.05	0.08
ASTM D664	Acid number, mg KOH/g	none	0.01	0.03	0.01	0.01	0.01	0.01
ASTM D3703	Peroxide number	none	<1	<1	<1	<1	<1	<1
ASTM D2709	Water and sediment, vol%	0.05	0.01	0.01	0.01	0.01	0.01	0.01
ASTM D482	Ash content, mass%	0.01	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
ASTM D5186	Total Aromatics, mass%	none	15.7	22.1	18.1	36.2	8.2	19.3
	Monoaromatics, mass%	none	14.4	19.9	17.1	27.6	7	17.4
	Polynuclear aromatics, mass%	none	1.3	2.1	1	8.7	1.2	1.9
ASTM D6217	Particulate contamination, mg/l	none	0.5	0.4	0.8	0.8	1.2	0.3
ASTM D2274	Total Insolubles, mg/100 ml	none	0.25	0.25	0.5	0.2	0.1	0.05
ASTM D6468	Thermal stability, 150ºC/180 min % reflectance	none	100	100	100	98	95	100
ASTM D4625	Modified, 80ºC, air purge, 1 week	none						
	Adherent insoluble, mg/100 ml		0.3	0.4	0.1	0.1	0.2	0.2
	Filterable insoluble, mg/100 ml		0.7	0.2	0.1	0.1	0.4	0.2
	Total insoluble		1.1	0.6	0.2	0.2	0.6	0.4
ASTM D6468	Modified, 150ºC/180 min, gravimetric on fuel from D4625, 1 week 80ºC, mg/100 ml	none	2.2	0.2	0.1	0.1	0.4	0.8

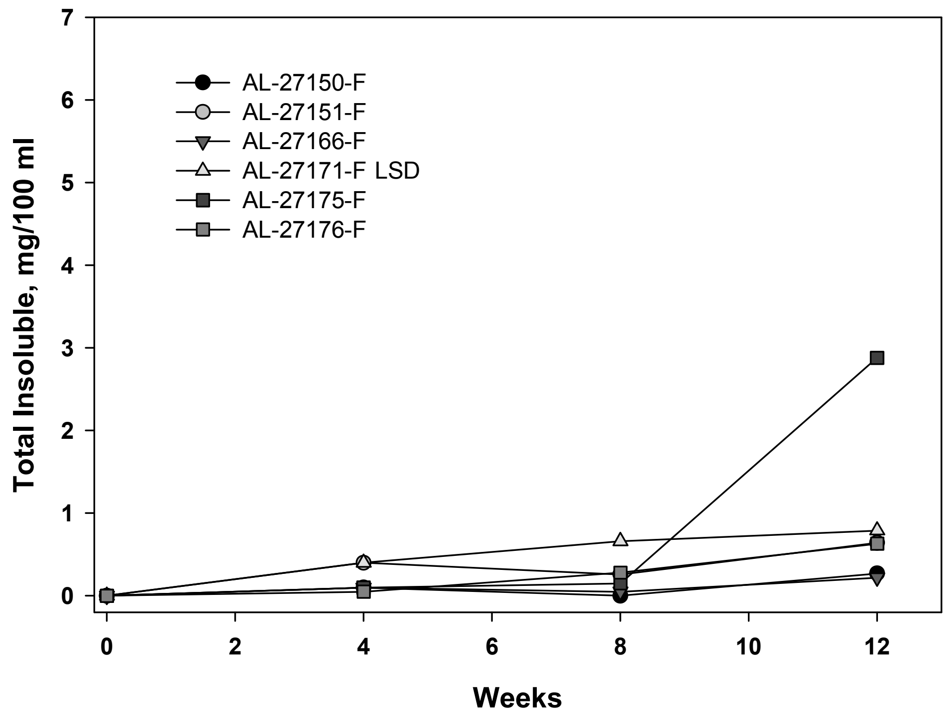

Figure 15. Total insolubles for petroleum diesel fuels on the D4625 test

Stability of B5 Blends

Accelerated Tests

Six diesel fuels were acquired, and eight B100 samples were selected from the original 19. These were used to prepare 48 B5 blends that have been tested by using the following accelerated stability tests:

- OSI/Rancimat induction time
- ASTM D2274 (biodiesel modification)
- ASTM D6468 percent reflectance and gravimetric modification.

Results for accelerated tests with B5 blends are in Appendix D. Figure 16 shows a histogram of the Rancimat induction time results. The samples fall into three categories: short, medium, and long induction times. Figure 17 shows the histogram for total insolubles measured on the D2274 test. Most of the samples are reasonably stable, with less than 2.5 mg/100 ml. There are also samples with intermediate and high levels of insolubles. Figures 18 and 19 show the reflectance and gravimetric results from the D6468 thermal stability test. Most samples are thermally stable, although several produce significant amounts of insolubles.

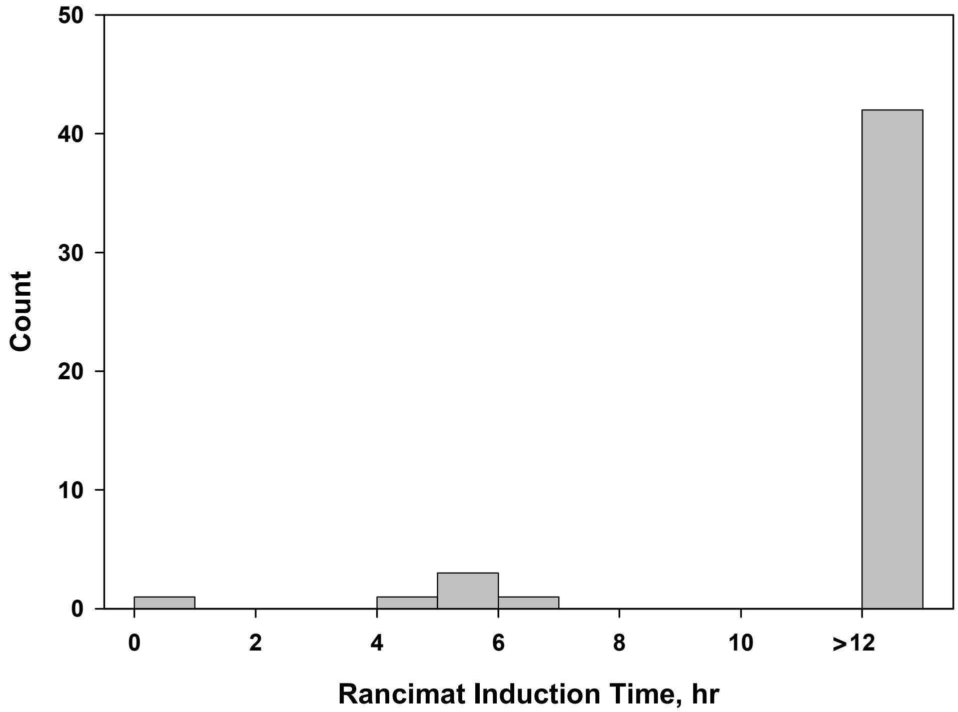

Figure 16. Histogram of OSI or Rancimat induction times for B5 samples

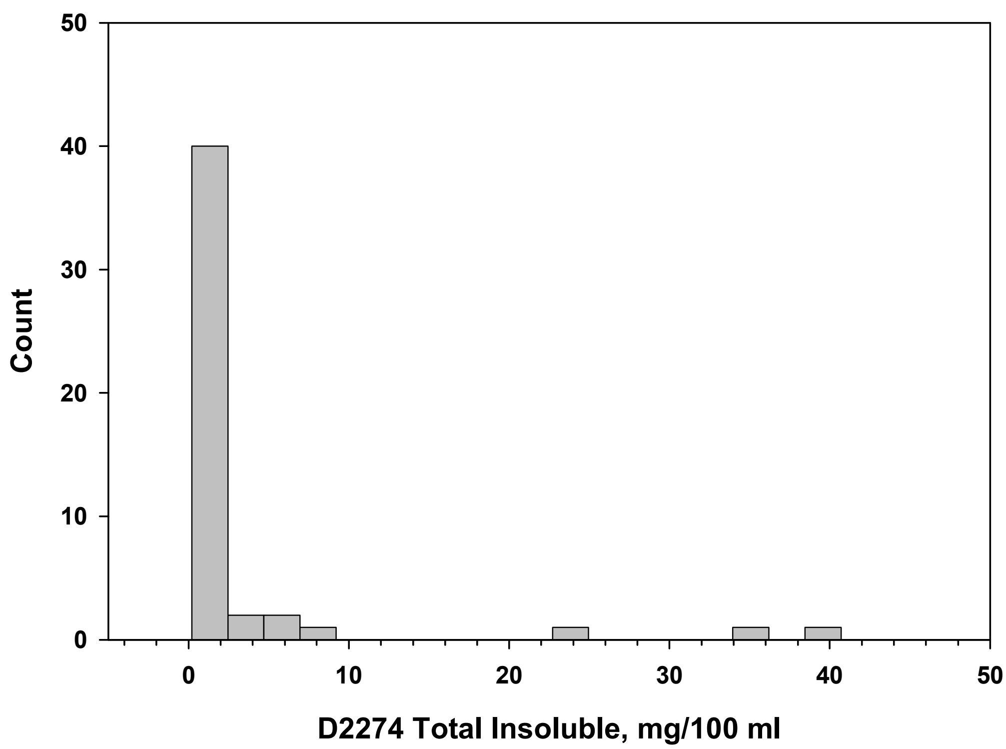

Figure 17. Histogram of D2274 (biodiesel modification) total insolubles results for B5 samples

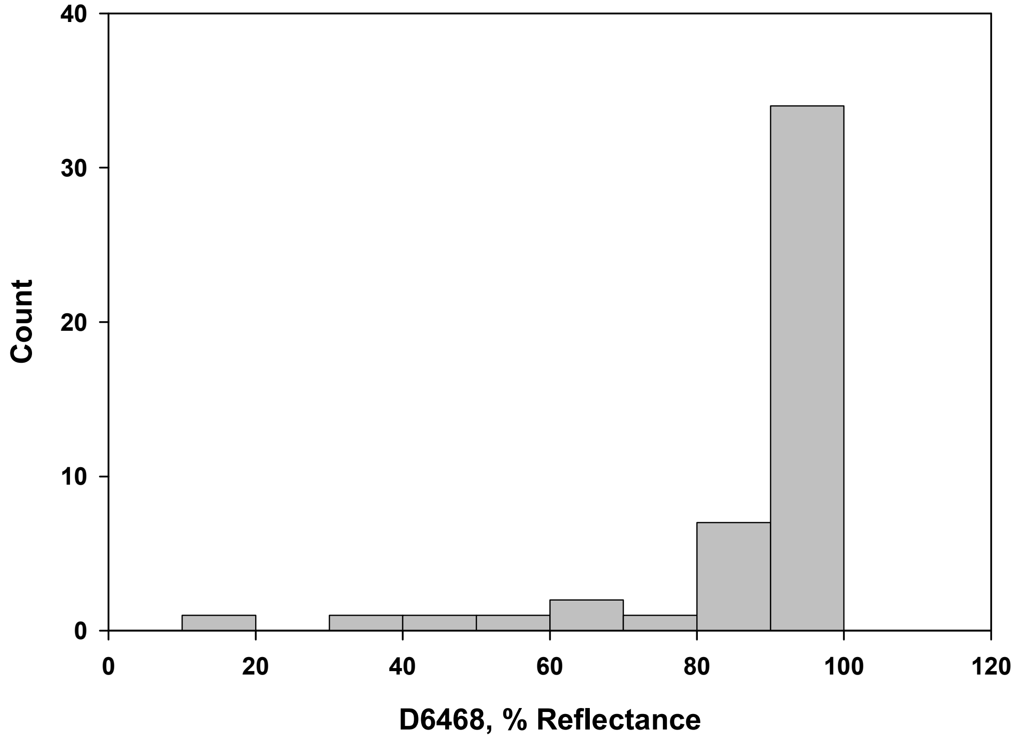

Figure 18. Histogram of D6468 percent reflectance results for B5 samples

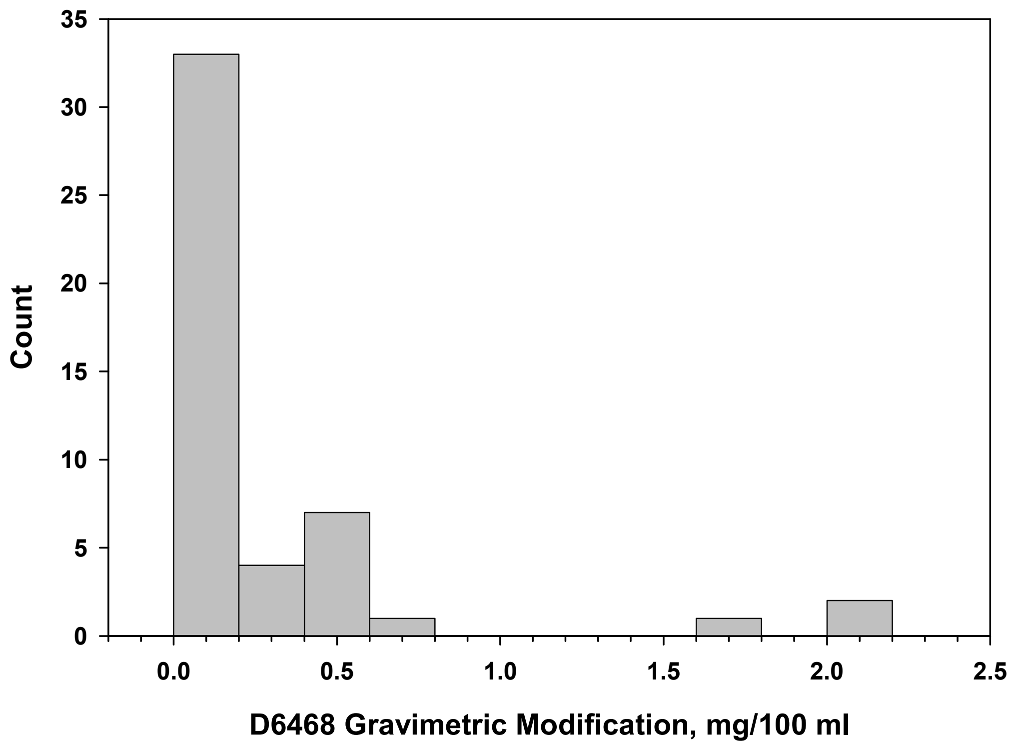

Figure 19. Histogram of D6468 gravimetric insoluble results for B5 samples

Based on these distributions, and so as not to exclude any one biodiesel or diesel fuel from the group, the B5 blend samples listed in Table 9 were selected for more detailed study. This included long-term storage testing, as well as tests to simulate aging in the vehicle fuel tank and degradation in the high-temperature environment of a diesel engine fuel injection system. Biodiesel AL-27138, an unstable material, produced a B5 blend with a short induction time and high D2274 insolubles, but is thermally stable. Biodiesel AL-27160, also unstable, produced a B5 blend with a short induction time and low D2274 deposits, but appears to be thermally unstable. These data confirm previous results and indicate that biodiesel and B5 blends are generally thermally stable,[16] and with the implementation of the 3-hour induction period there appears to be no additional information to be gained about blends from the thermal stability values of the B100.

Table 9. B5 Samples Downselected for More Detailed Study

Sample	**B100**	**Diesel**	**Rancimat** h	**D2274** mg/100 ml	**D6468** % Reflectance/Insoluble mg/100 ml
CL06-200	27128	27166	>12	5.5	98/0.1
CL06-215	27129	27176	>12	1.5	99/0.1
CL06-227	27137	27175	>12	0.3	94/0.1
CL06-235	27138	27150	4.8	40.7	88/0.1
CL06-252	27141	27175	>12	0.3	96/0.1
CL06-264	27148	27175	>12	0.4	93/0.2
CL06-273	27152	27151	>12	0.3	99/0.1
CL06-287	27160	27171	5.5	0.8	19/2.0

Several B5 samples were also treated with antioxidant additives and evaluated on accelerated tests. Results are shown in Table 10. Most of the B5 samples are fairly stable without additive on these tests. Antioxidants caused a large reduction in D2274 total insolubles for the one sample that exhibits significant instability and increased the induction time for all samples. Additive treat rates given are for addition to the B100 before it is blended.

Table 10. Accelerated Test Results for B5 Samples Treated with Antioxidant

Sample Number	Description	Rancimat Induction Time h	ASTM D2274 Total Insoluble mg/100 ml
06-236	5% AL-27138 in AL-27151 no additive	5.8	23.5
06-548	5% AL-27138 plus 1000 ppm additive A in AL-27151	9.0	_
06-331	5% AL-27138 plus 2000 ppm additive A in AL-27151	>12	0.3
06-332	5% AL-27138 plus 1000 ppm additive B in AL-27151	>12	0
06-333	5% AL-27138 plus 2000 ppm additive B in AL-27151	>12	0
06-211	5% AL-27129 in AL-27151 no additive	>12	1.0
06-334	5% AL-27129 plus 1000 ppm of additive A in AL-27151	>12	0
06-550	5% AL-27129 plus 1000 ppm of additive B in AL-27151	>12	_
06-214	5% AL-27129 in AL-27175 no additive	>12	0.6
06-552	5% AL-27129 plus 1000 ppm of additive B in AL-27175	>12	_
06-239	5% AL-27138 in AL-27175 no additive	6.9	0.2
06-552	5% AL-27138 plus 1000 ppm of additive A in AL-27175	>12	0.2
06-516	5% AL-27138 plus 2000 ppm additive A in AL-27175	>12	0.2
06-518	5% AL-27138 plus 1000 ppm additive B in AL-27175	>12	0
06-520	5% AL-27138 plus 2000 ppm additive B in AL-27175	>12	0.3

Storage Stability

The eight B5 blends listed in Table 9 were tested for long-term storage stability with ASTM D4625. Numerical results are given in Appendix E. Figure 20 shows results for peroxide value (PV). At 4 weeks, the peroxide value results indicate that some degradation is occurring for samples produced from B100 with an induction time shorter than 1 hour, and for one sample with a longer induction time. However, at 8 weeks all samples show low peroxides, and at 12 weeks the only sample with high peroxides was produced from an unstable B100. Acid value increase for B5 blends over the D4625 test is shown in Figure 21. The only B5 sample in which acid value increased significantly was blended from a B100 with an induction time of 0.5 hour. Total insoluble formation is shown in Figure 22. Again, the only sample in which insolubles increased significantly was blended from a B100 with an induction time of 0.5 hour (AL-27138). Figure 23 shows results for several B5 blends that were treated with antioxidants. Treatment of B5 blends containing AL-27138 eliminated the increase in insolubles observed at 12 weeks without antioxidant, with all results below 2 mg/100 ml. Antioxidant treatment also stabilized the induction time for all samples at more than 10 hours over the 12-week test.

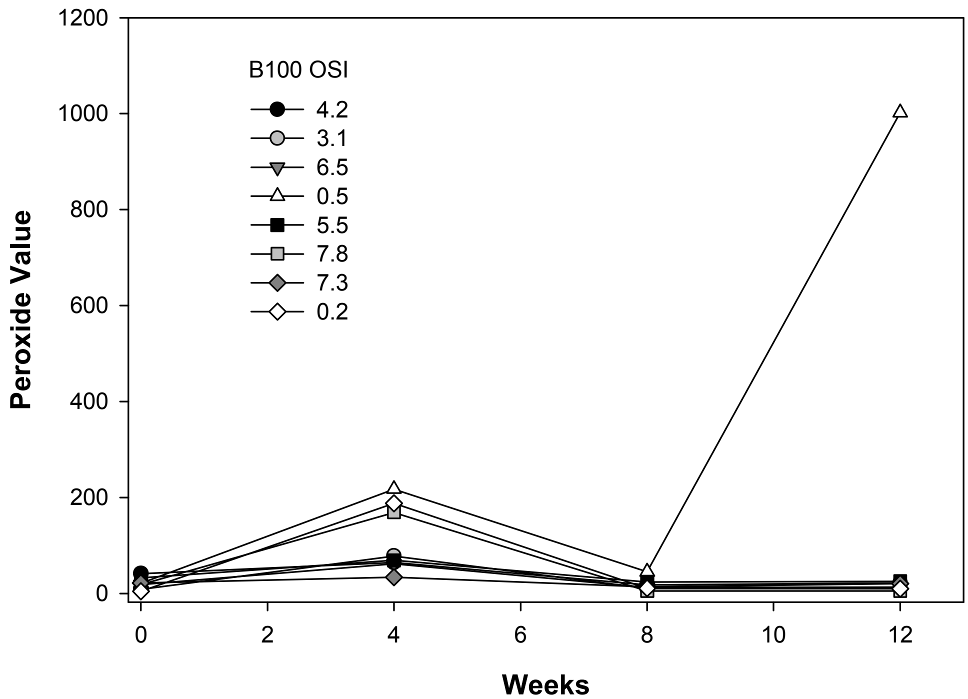

Figure 20. Peroxide value over the D4625 test for B5 samples

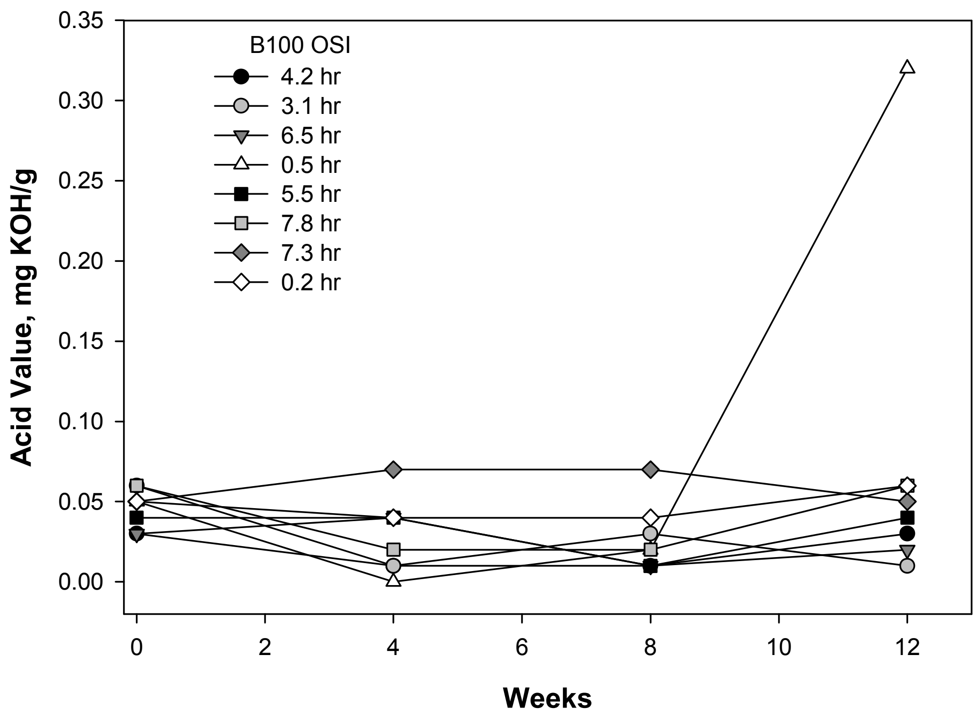

Figure 21. Acid value for B5 blends over the D4625 test

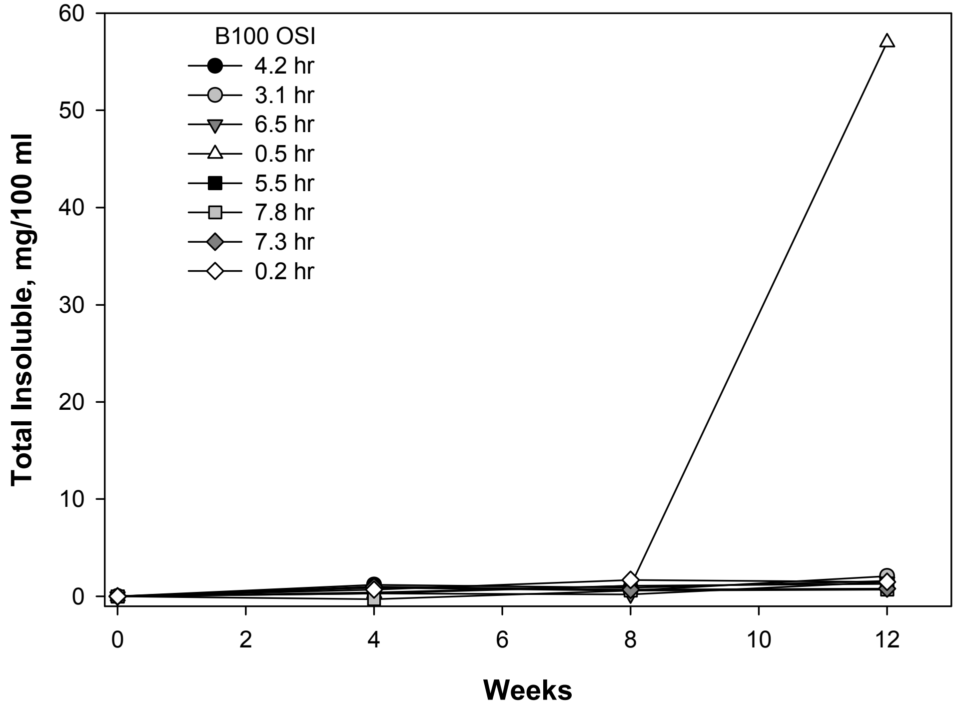

Figure 22. Total insolubles formation for B5 blends in the D4625 test

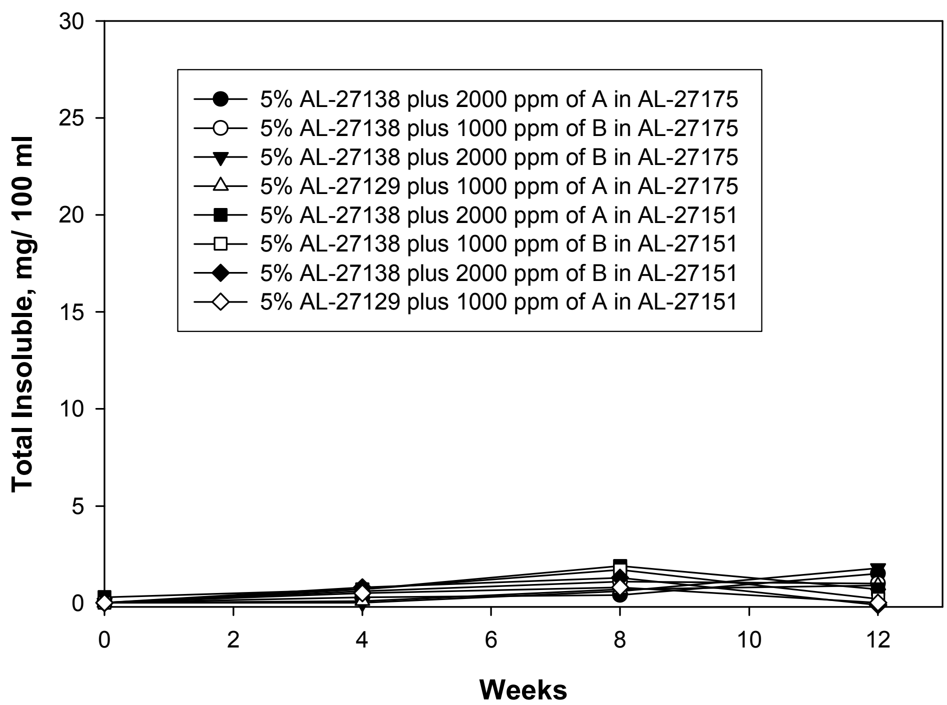

Figure 23. Total insolubles formation for B5 samples treated with antioxidant additives on the D4625 test

Simulated Vehicle Fuel Tank Aging

As described in the methods section, fuel tank aging was simulated by storing the biodiesel blend in the D4625 flask at 80ºC for 1 week with ullage purge, followed by measurement of peroxide number, acid number, and insolubles. Figures 24, 25, and 26 show results for peroxide, acid, and total insolubles, respectively, as a function of the B100 induction time. Detailed results are given in Appendix E. For all three measures, significant degradation occurs only for B100 induction times shorter than 1 hour. Similar plots could be made as a function of the B5 induction times (not shown) and indicate that degradation is not observed for B5 induction times longer than 6 hours. Although also not shown, antioxidant additives reduced insolubles formation on this test for the one biodiesel sample that generated high levels of insolubles.

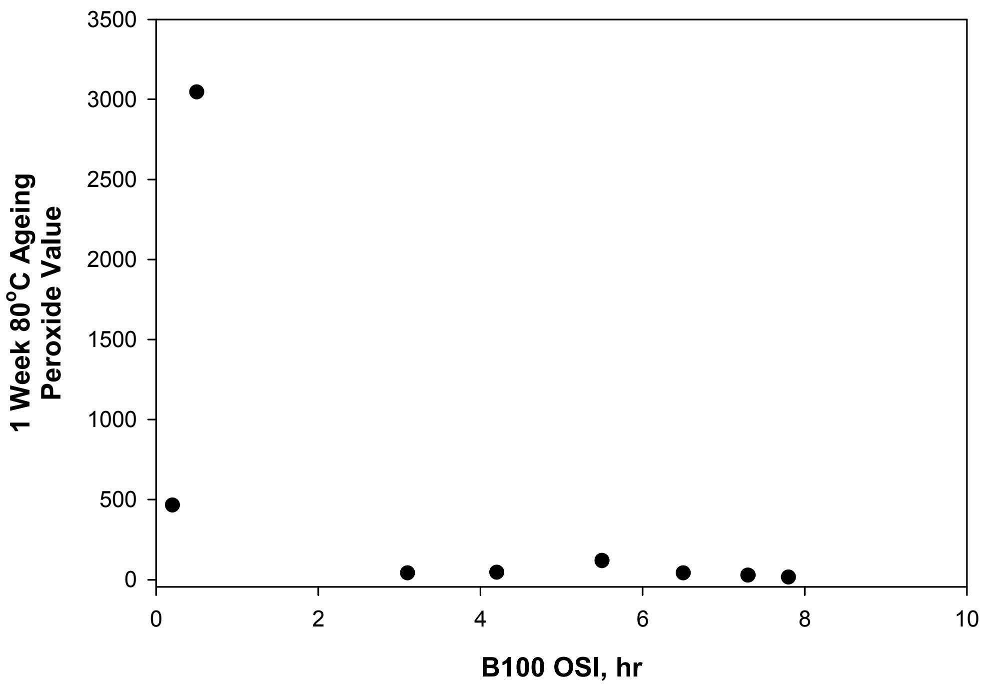

Figure 24. Peroxide value for B5 blends after 1 week aging at 80ºC, as a function of B100 OSI or Rancimat induction time

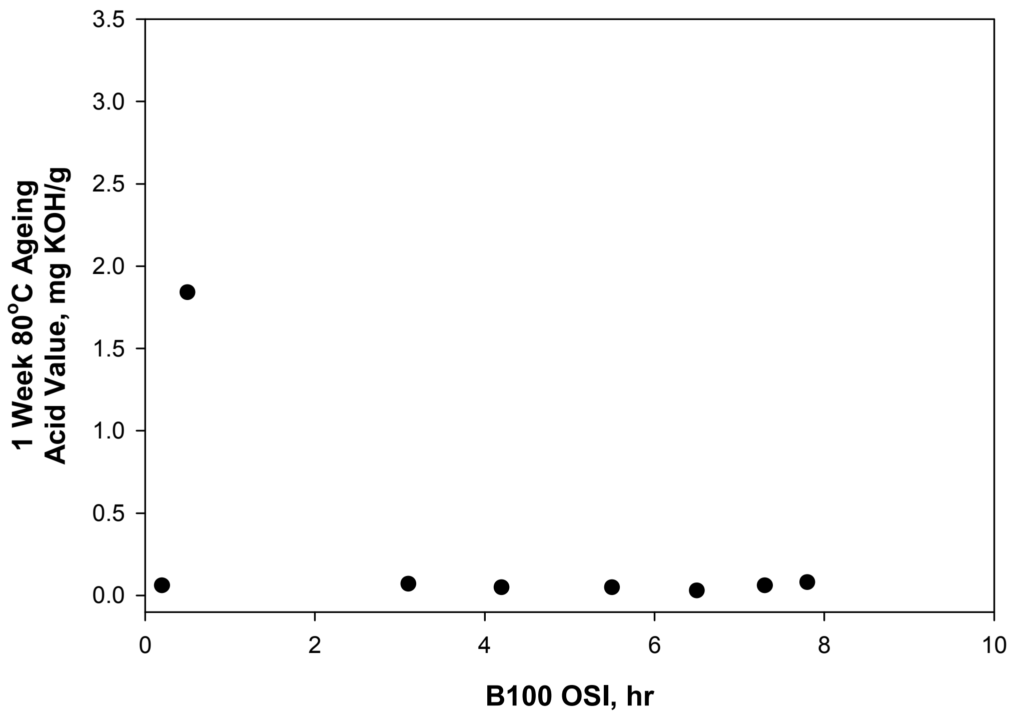

Figure 25. Acid value for B5 blends after 1 week aging at 80ºC, as a function of B100 OSI or Rancimat induction time

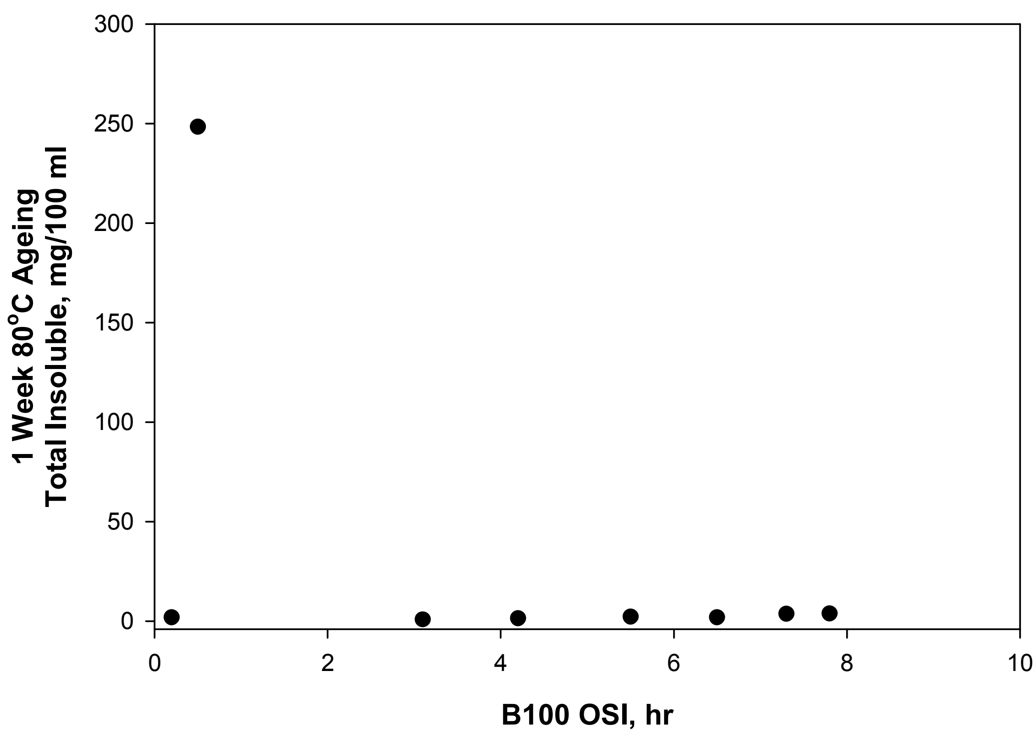

Figure 26. Total insoluble for B5 blends after 1 week aging at 80ºC, as a function of B100 OSI or Rancimat induction time

Simulated Vehicle Tank Aging Followed by High Temperature Testing

To simulate the stability in the high-temperature environment of a diesel engine fuel injection system, we subjected the samples that had been aged for 1 week at 80ºC (see previous section), then conducted the D6468 thermal stability test (150ºC for 180 minutes). In addition to measuring filter reflectance, the amount of deposits on the filter was also quantified gravimetrically by using procedures that are identical to those in D2274. Results are shown in Figure 27 as a function of the blending B100 induction time. Detailed results are listed in Appendix E. Low values of reflectance or high values of gravimetric insoluble occur only for B100 with induction times shorter than 1 hour. Treatment of this B100 with antioxidants eliminated the formation of insolubles for this sample (not shown). Notably, the B5 blend produced from AL-27160, which demonstrated poor thermal stability on the D6468 test before aging, does not generate high deposits on this test after 1 week of aging.

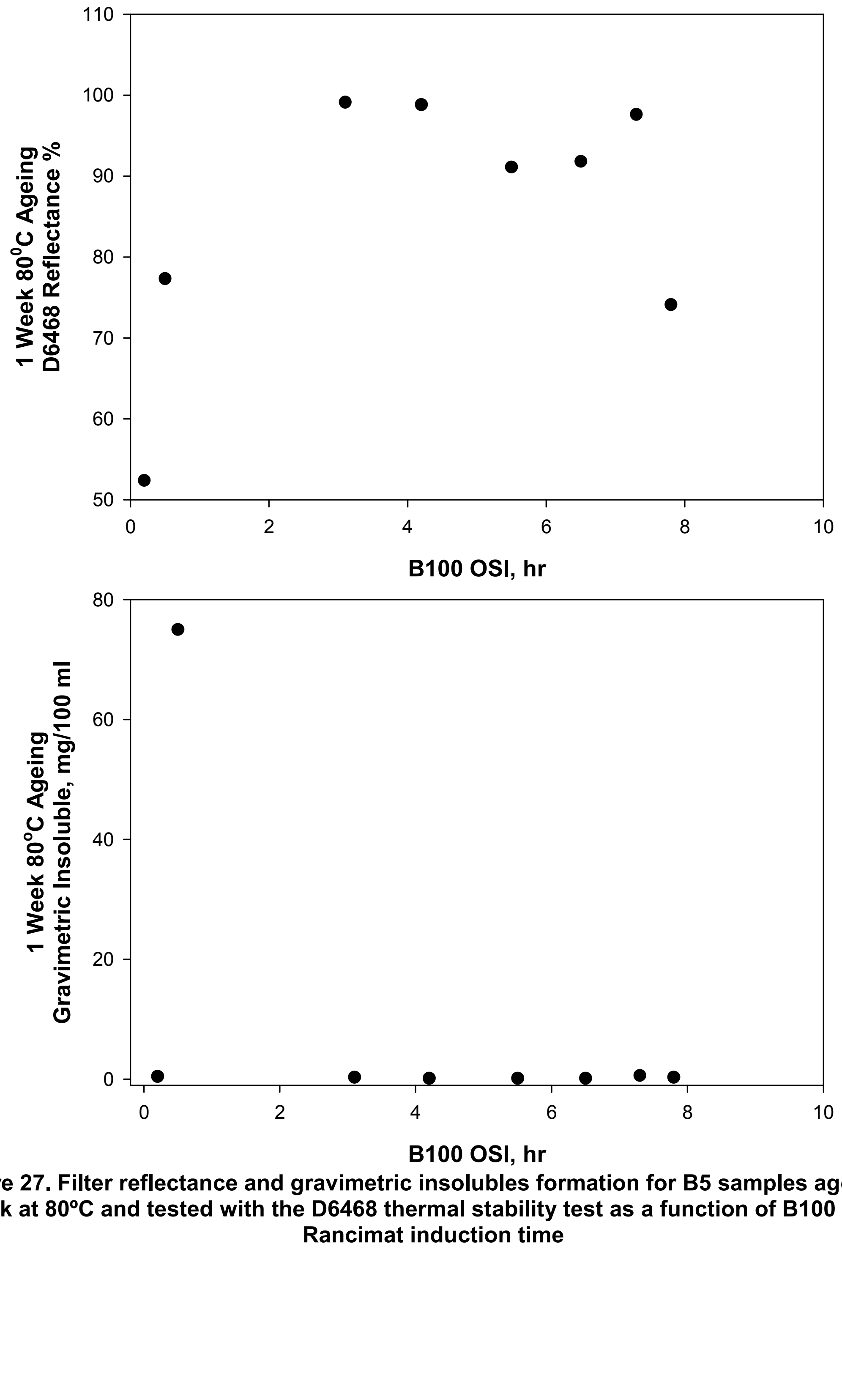

Figure 27. Filter reflectance and gravimetric insolubles formation for B5 samples aged for 1 week at 80ºC and tested with the D6468 thermal stability test as a function of B100 OSI or Rancimat induction time

Stability of B20 Blends

Accelerated Tests

Six diesel fuels were acquired, and eight B100 samples were selected from the original 19. These were used to prepare 48 B20 blends that were tested with the following accelerated stability tests:

- OSI/Rancimat induction time
- ASTM D2274 (biodiesel modification)
- ASTM D6468 percent reflectance and gravimetric modification.

Detailed results are listed in Appendix F. Figure 28 shows a histogram of the Rancimat induction time results. Figure 29 shows the histogram for total insolubles measured on the D2274 test. Most of the samples are stable, with less than 2.5 mg/100 ml. There are also samples with intermediate and high levels of insolubles. Figures 30 and 31 show the reflectance and gravimetric results from the D6468 thermal stability test. Only one sample exhibited poor D6468 reflectance values (below 70, the generally accepted level for petrodiesel). Although no generally accepted gravimetric value has been established for D6468, most values were below 1 mg/100 ml, and four samples gave higher results. There were fewer poor samples for D6468, but the sample set did contain samples that could be considered both stable and unstable on all the stability tests.

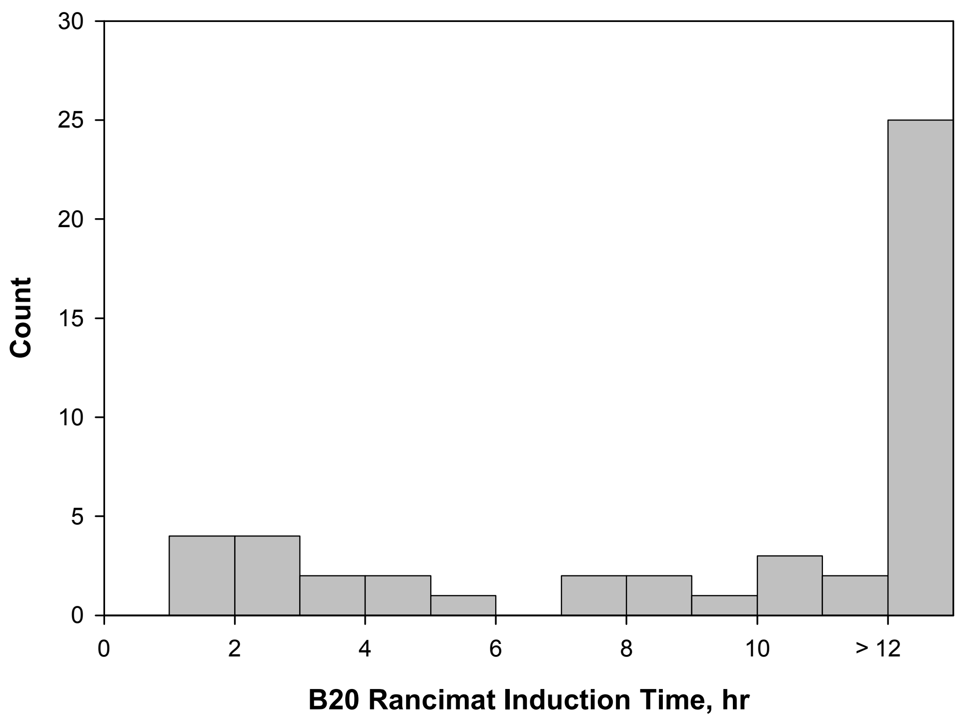

Figure 28. Histogram of OSI or Rancimat induction times for B20 samples

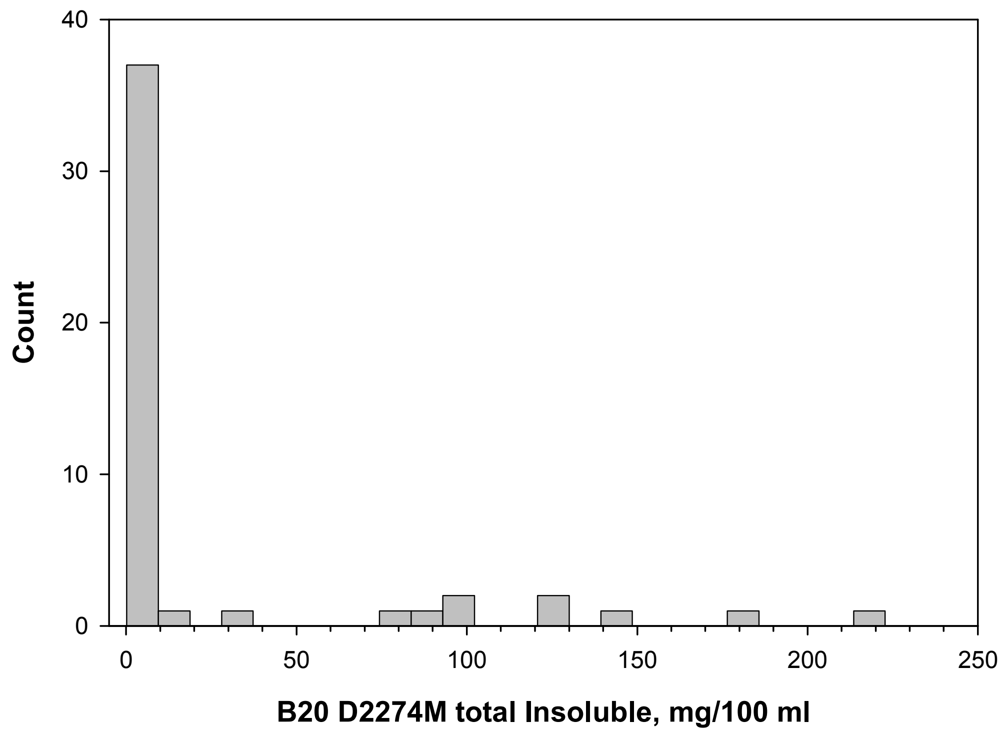

Figure 29. Histogram of D2274 (biodiesel modification) total insolubles results for B20 samples

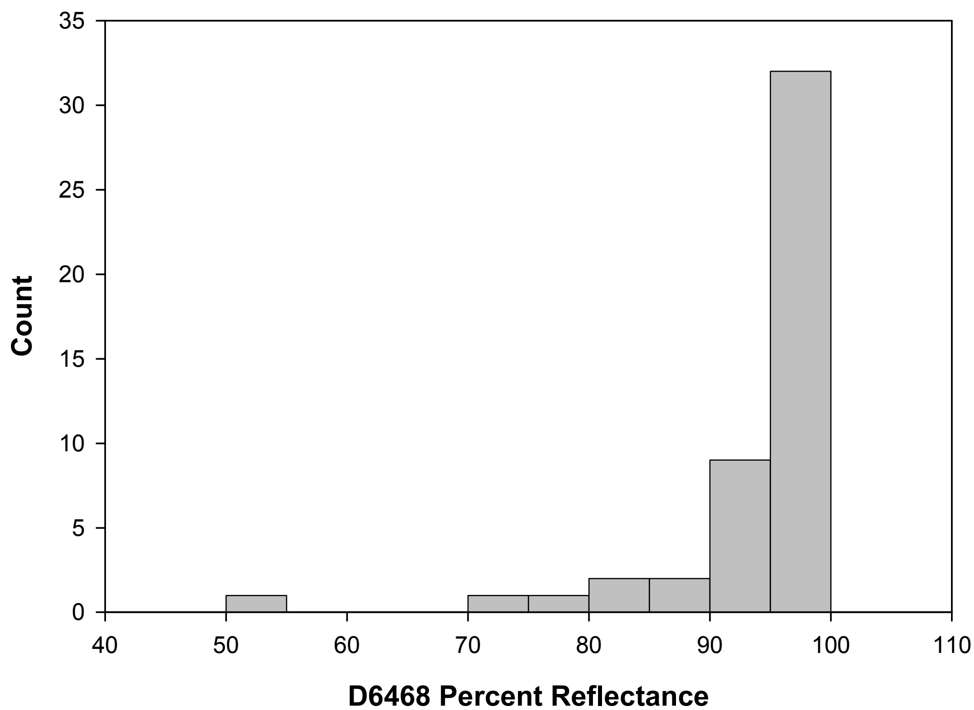

Figure 30. Histogram of D6468 percent reflectance results for B20 samples

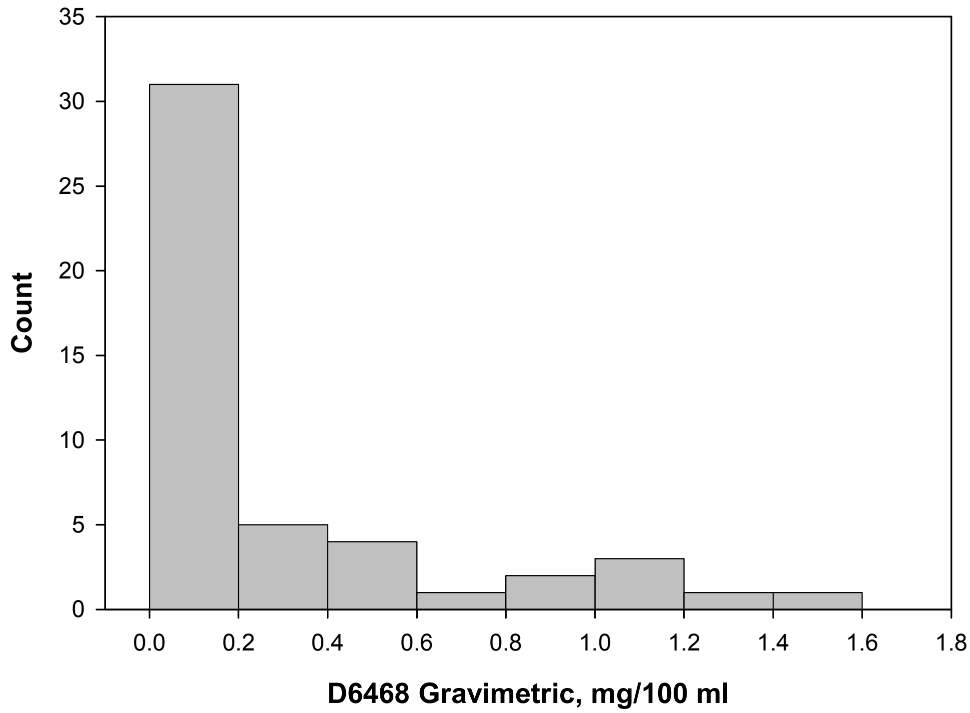

Figure 31. Histogram of D6468 gravimetric insoluble results for B20 samples

Based on these distributions, and so as not to exclude any one biodiesel or diesel fuel from the group, we selected the samples listed in Table 11 for further testing of long-term storage stability, stability conditions simulating a vehicle fuel tank, and conditions simulating the high-temperature conditions of a diesel engine fuel injection system.

Table 11. B20 Samples Downselected for More Detailed Study

Sample	B100	Diesel	Rancimat h	D2274 mg/100 ml	D6468 % Reflectance/Insolubles mg/100 ml
CL06-196	27128	27175	7.8	0.3	95/0.1
CL06-204	27129	27150	>12	0.4	98/0.1
CL06-237	27137	27171	>12	0.6	82/0.9
CL06-242	27138	27151	1.8	124.8	99/0.1
CL06-256	27141	27166	10.6	0.4	99/0.1
CL06-268	27148	27166	>12	0.3	97/0.2
CL06-282	27152	27175	>12	1.2	97/0.1
CL06-295	27160	27176	4.1	33.7	72/0.1

Several additional B20 samples prepared with antioxidant treated B100 were also tested for stability. Results are shown in Table 12. The antioxidants generally reduced insoluble levels effectively and increased induction time for the samples prepared from the highly unstable B100 AL-27138. Additive treat rates given are for adding antioxidant to the B100.

Table 12. Accelerated Test Results for B20 Samples Treated with Antioxidant

Sample Number	Description	Rancimat Induction Time h	ASTM D2274 Total Insolubles mg/100 ml
06-242	20% AL-27138 in AL-27151 no additive	1.8	124.8
06-549	20% AL-27138 plus 1000 ppm additive A in AL-27151	4.4	–
06-335	20% AL-27138 plus 2000 ppm additive A in AL-27151	9.4	0.5
06-336	20% AL-27138 plus 1000 ppm additive B in AL-27151	4.6	0.3
06-337	20% AL-27138 plus 2000 ppm additive B in AL-27151	7.0	0.1
06-205	20% AL-27129 in AL-27151 no additive	>12	0.3
06-338	20% AL-27129 plus 1000 ppm of additive A in AL-27151	>12	0.2
06-551	20% AL-27129 plus 1000 ppm of additive B in AL-27151	>12	–
06-208	20% AL-27129 in AL-27175 no additive	>12	0.3
06-553	20% AL-27129 plus 1000 ppm of additive B in AL-27175	>12	–
06-245	20% AL-27138 in AL-27175 no additive	1.7	222.8
06-523	20% AL-27138 plus 1000 ppm additive A in AL-27175	6.0	1.7
06-517	20% AL-27138 plus 2000 ppm of additive A in AL-27175	>12	0.2
06-519	20% AL-27138 plus 1000 ppm additive B in AL-27175	4.5	0.5
06-521	20% AL-27138 plus 2000 ppm additive B in AL-27175	6.6	0.2

Storage Stability

The eight B20 blends listed in Table 11 were tested with ASTM D4625 for long-term storage stability. Numerical results are given in Appendix G. Figure 32 shows results for peroxide value. The two unstable B100 samples, with induction times shorter than 1 hour, produced B20 blends that clearly degraded on this test. Acid value increase for B20 blends over the D4625 test is shown in Figure 33. B20 prepared from unstable B100 shows a significant increase in acidity. One other B100 (with an induction time of 6.5 hours) shows a small acidity increase, but this sample shows no increase in peroxide, so it may not actually be degrading. The acid number increase for this sample is also close to the reproducibility of the test method. Total insolubles formation is shown in Figure 34. The only sample that increased significantly in insolubles was blended from a B100 sample with an induction time of 0.5 hours (AL-27138). One B100 sample with a short induction time (0.2 hours) did not exhibit insolubles formation in B20 over the 12-week D4625 test. This indicates that the B100 induction period may be a conservative measurement of blend performance as the data indicate not all B100 failing the 3-hour induction period would form deleterious amounts of sediment when aged under these conditions.

Figure 35 shows results for several B20 blends treated with antioxidants, primarily B20 produced from the unstable B100, AL-27138. None of the antioxidant-treated samples showed a significant increase in insolubles formation. Antioxidant treatment also stabilized the induction time for these samples such that there was little change over the 12-week test. This result could indicate another potential solution to addressing stability with biodiesel and biodiesel blends, that being the mandatory addition of antioxidants. This would require further study, but confirmed use of antioxidants might be a better control strategy than any of the tests proposed here.

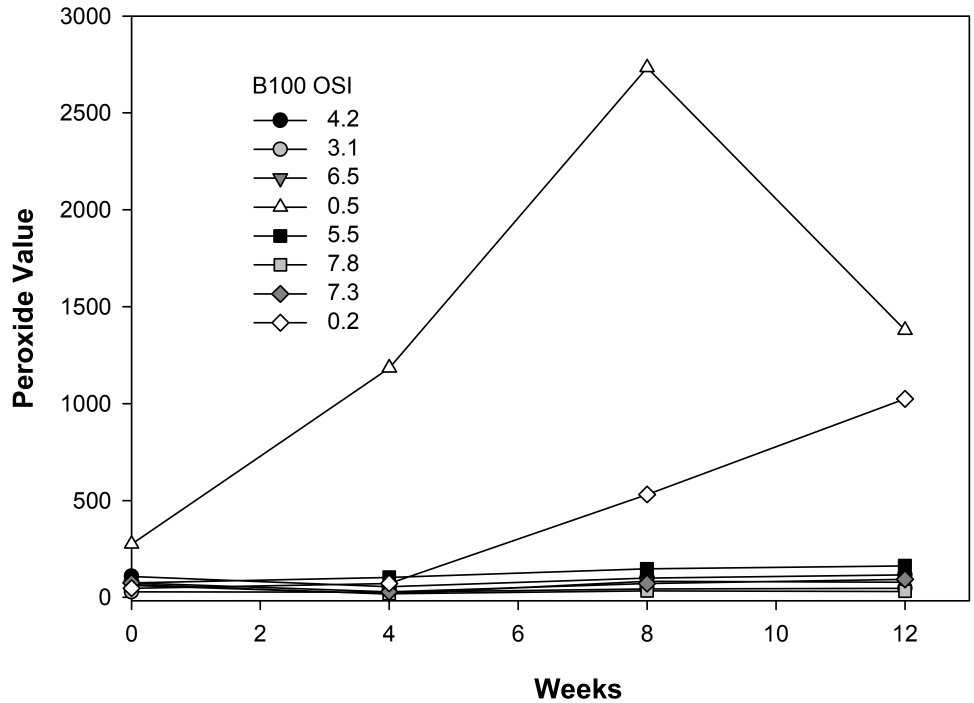

Figure 32. Peroxide value for B20 samples tested on D4625 test

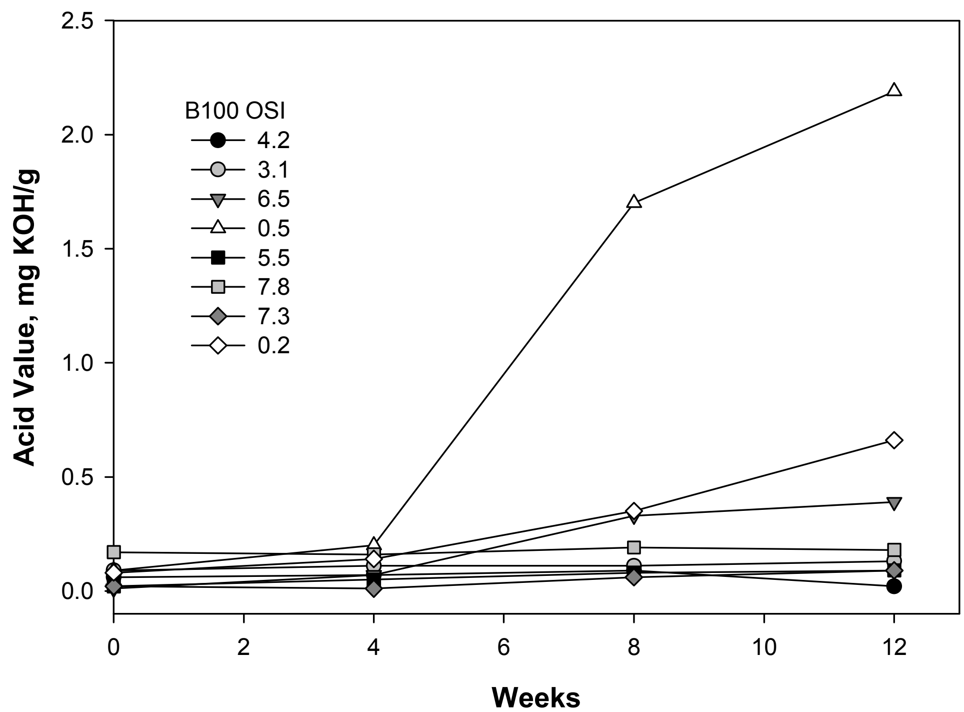

Figure 33. Acid value for B20 samples tested on the D4625 test

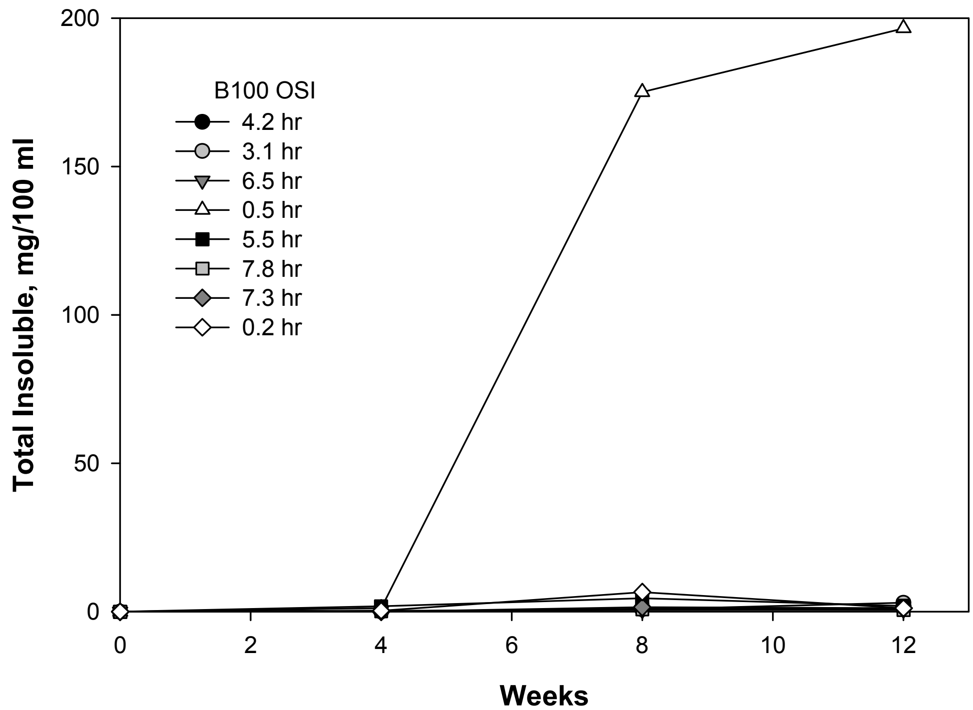

Figure 34. Total insolubles formed from B20 samples tested on the D4625 test

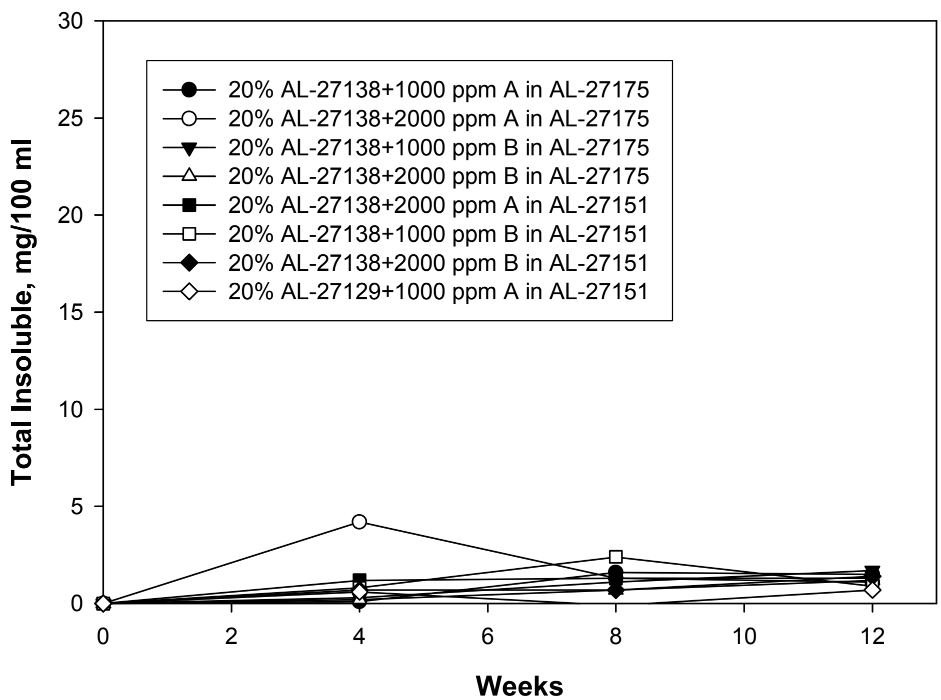

Figure 35. Total insolubles formation for B20 samples treated with antioxidant additives on the D4625 test

Simulated Vehicle Fuel Tank Aging

As described in the methods section, worst-case fuel tank aging was simulated by storing the biodiesel blend in the D4625 flask at 80ºC for 1 week with ullage purge, followed by measurement of peroxide number, acid number, and insolubles. This is not a standard test, and results should be interpreted with caution. Detailed results are given in Appendix G. An increase in peroxides is observed for all these B20 samples under these severe test conditions, as shown in Figure 36; however, the largest increase in acid value was observed for blends prepared from B100 with induction times shorter than 1 hour (Figure 37). B20 induction time is a somewhat better predictor of the final acidity on this test, as shown in Figure 38. The B100 induction time was not predictive of insolubles formation on this test for B20 samples as shown in Figure 39, nor was B20 induction time or B100 D2274 total insolubles (not shown). Antioxidant additives effectively reduced total insolubles formation on this test (not shown), although in some cases the additive treat rate may have been too low to completely eliminate insolubles (see Appendix G).

Because we cannot correlate results on this test to what actually happens in a vehicle fuel tank, the levels of insolubles shown in Figure 39, and the levels of acidity developed for the more stable B100 in Figure 37, may not indicate that these fuels would cause vehicle operational or durability problems. Interpretation would be more straightforward if we observed large differences for less stable versus more stable B100, as was the case for B5 blends. Neither anecdotal nor detailed field data on B20 show a propensity for significant vehicle fuel filter clogging, which should be the case if sediment actually forms at levels similar to this 1-week aging test in the field.[20]

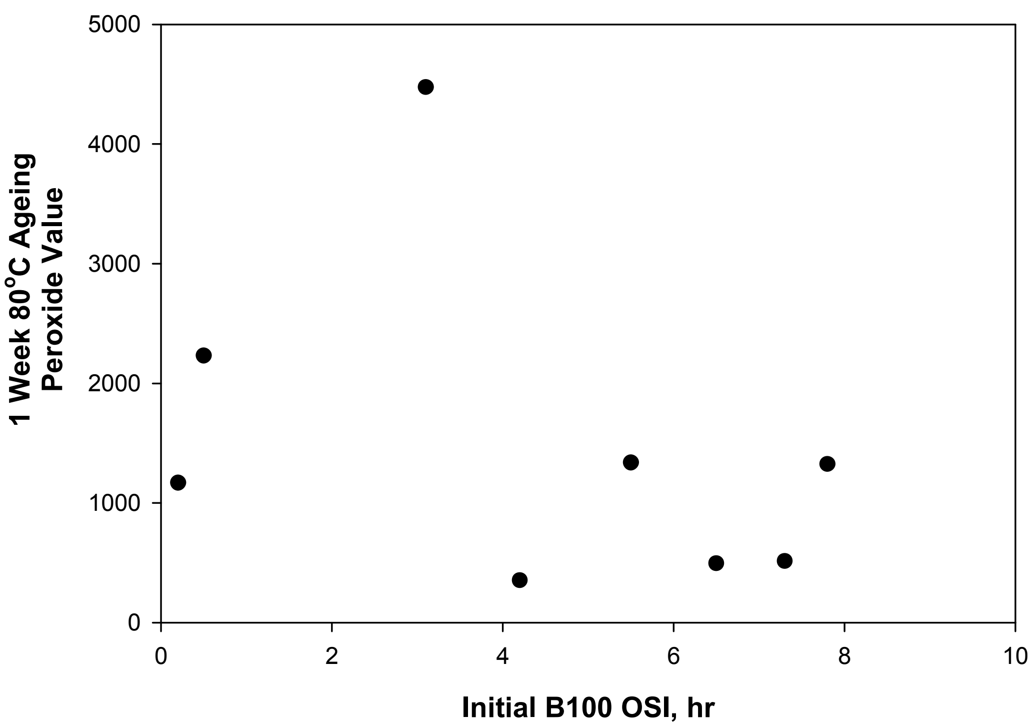

Figure 36. Peroxide value for B20 blends after 1 week aging at 80ºC, as a function of B100 OSI or Rancimat induction time

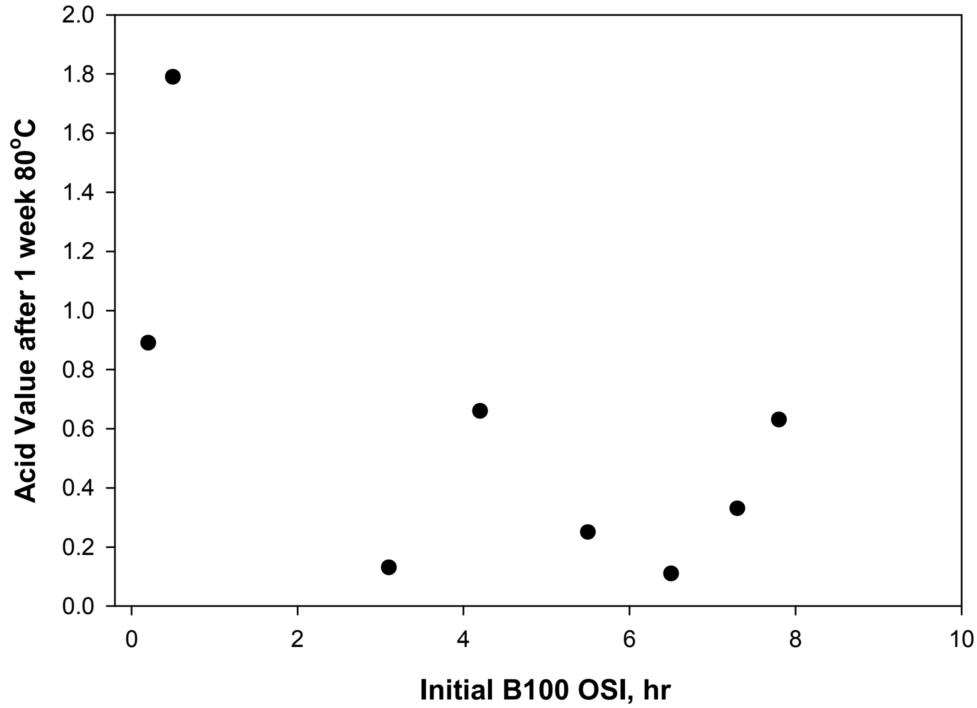

Figure 37. Acid value for B20 blends after 1 week aging at 80ºC, as a function of B100 OSI or Rancimat induction time.

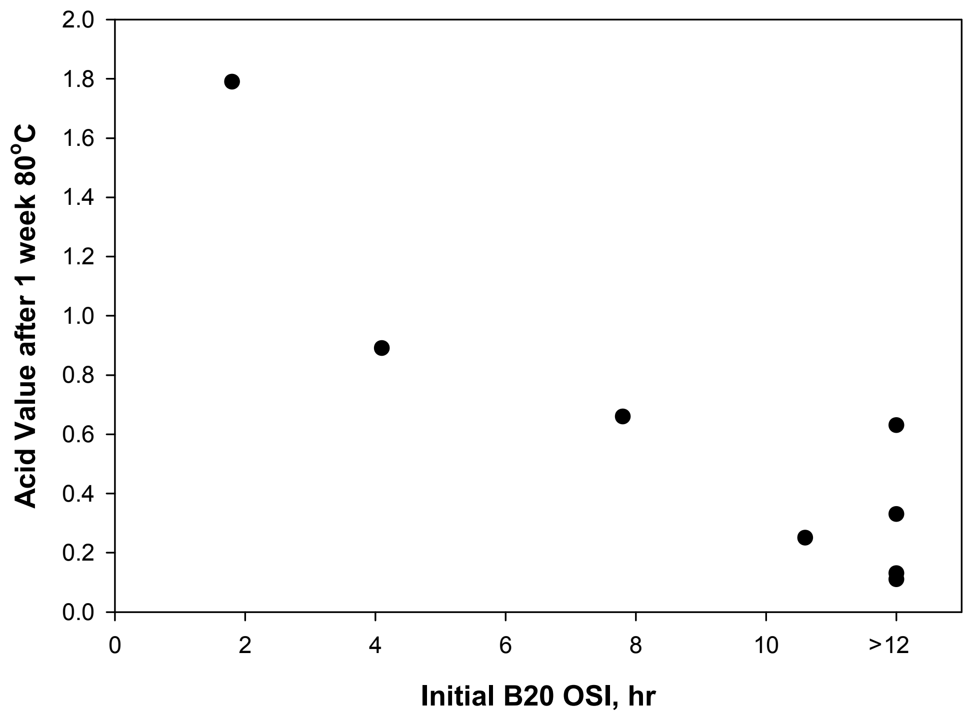

Figure 38. Acid value for B20 blends after 1 week aging at 80ºC, as a function of B20 OSI induction time

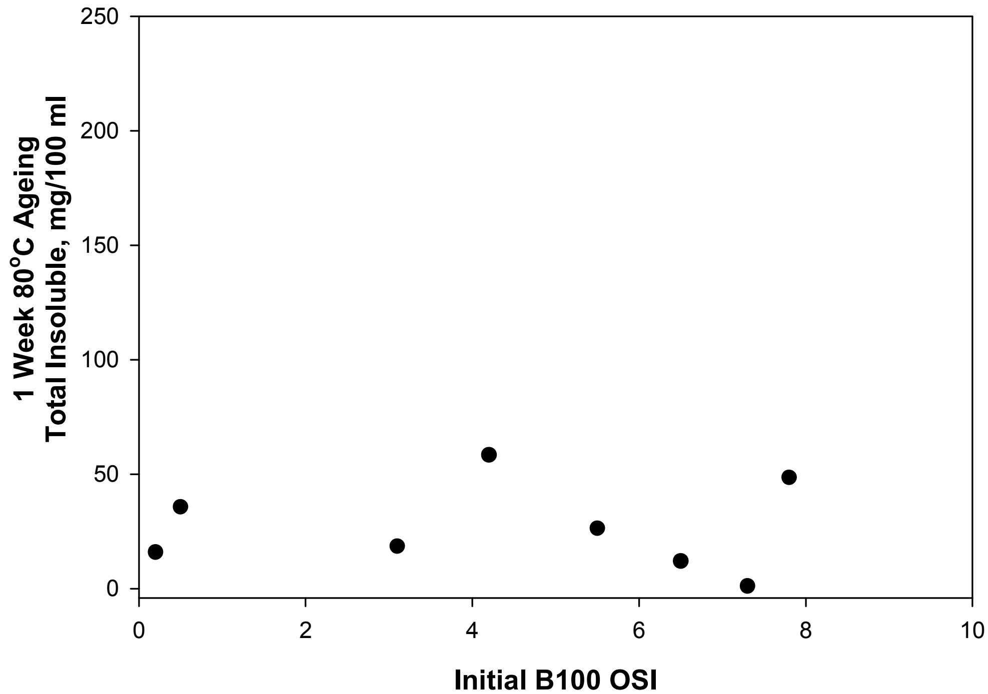

Figure 39. Total insolubles for B20 blends after 1 week aging at 80ºC, as a function of B100 OSI induction time

Simulated Vehicle Tank Aging Followed by High-Temperature Testing

Worst-case stability in the high-temperature environment of a diesel engine fuel injection system is simulated by subjecting the samples that had been aged for 1 week at 80ºC (see previous section) to the D6468 thermal stability test (150ºC for 180 minutes). We measured filter reflectance, and used procedures identical to those in D2274 to gravimetrically quantify the amount of deposits on the filter. Results are shown in Figure 40 as a function of the blending B100 induction time. Detailed results are listed in Appendix G. Low reflectance values are not observed for any of the B20 samples. High values of gravimetric insolubles occur only for B100 with induction times shorter than about 4 hours. Treating these B100 blends with antioxidants eliminated the formation of insolubles on this test (not shown). Notably, the B20 blend produced from AL-27160, which demonstrated marginal thermal stability on the D6468 test before aging, does not generate high deposits on this test after 1 week of aging. Similar results were observed for the B5 blend prepared from this B100.

As noted for the fuel tank simulation test, because we have no correlation of this test sequence (1 week at 80ºC followed by D6468 thermal stability testing) with performance in actual engine fuel systems, whether any of the fuels tested would actually cause engine operational or durability problems is unclear. The B100 induction time specification of 3 hours does, however, eliminate the highest sediment-forming blend under these test conditions. But overall this testing approach does not provide an obvious delineation between fuels that are stable and those that are not under these conditions.

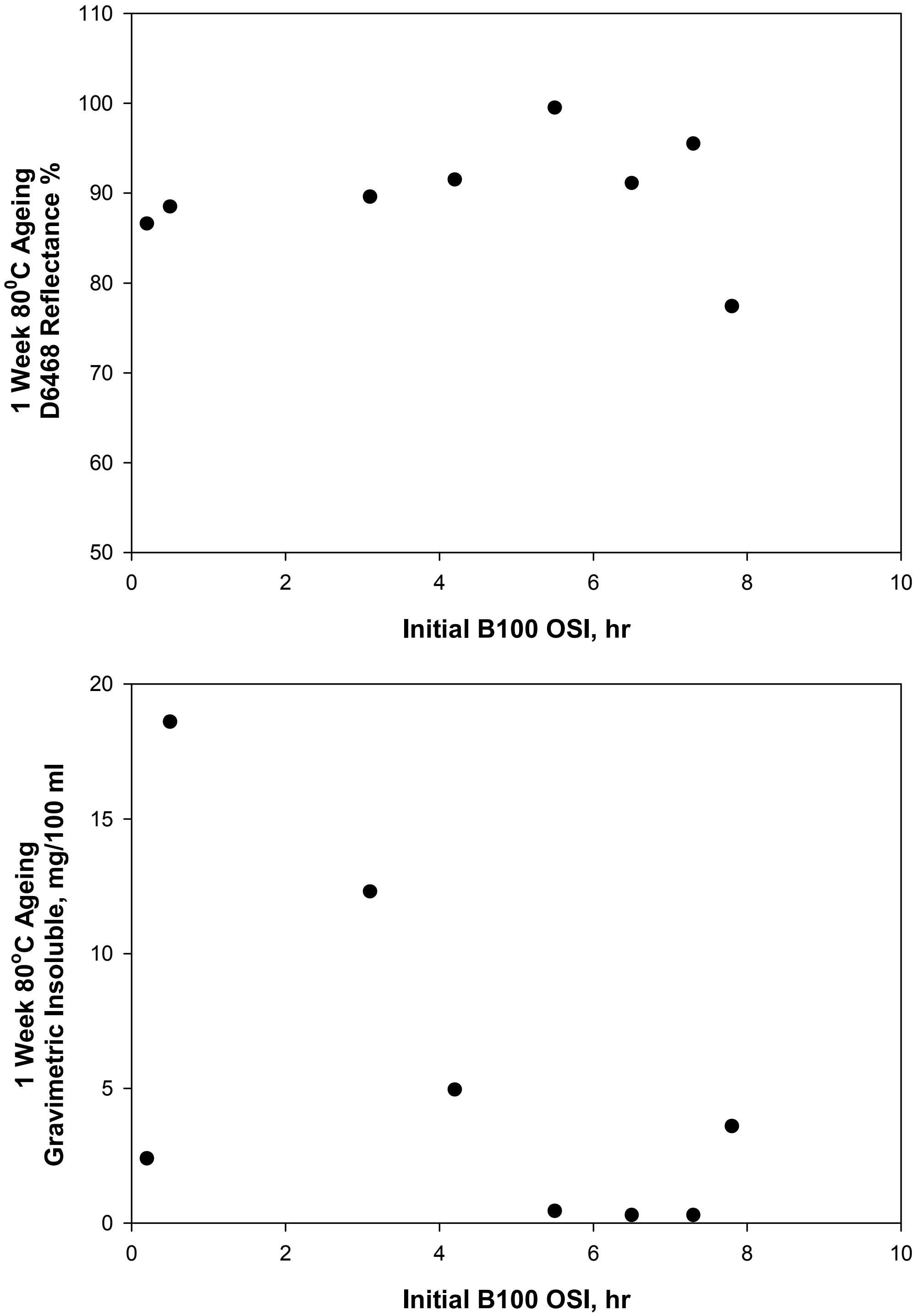

Figure 40. Filter reflectance and gravimetric insoluble formation for B20 samples aged for 1 week at 80ºC and tested in the D6468 thermal stability test

Discussion

Do Accelerated Tests Predict B100 Storage Stability?

The D4625 storage data for B100 at 8 and 12 weeks indicate that none of the accelerated tests are good—or even average—predictors of the degree of biodiesel degradation on this test at these storage times. Almost all samples at both 4 and 8 weeks had sediment formation below 2 mg/100 ml, which indicates fairly low sediment formation on this test, but all samples exhibited an increase in acid number at 8 weeks to out-of-specification levels. Attempts to correlate biodiesel degradation at 4 weeks with results of initial stability tests were slightly more successful. Figure 41 shows that initial induction time is a rough predictor ($r^2 = 0.55$) of induction time at 4 weeks. Figure 42 suggests that if the initial degree of oxidative degradation (as measured by the peroxide number or value) is low, the peroxide number will be low at 4 weeks. However, the curve is very steep at low peroxide levels. Nevertheless, this confirms that exposure of the biodiesel to oxidative conditions that cause peroxide formation should be avoided. Figure 43 shows the change in acid value over 4 weeks as a function of the initial induction time. Samples with longer induction times in general experience a smaller change in acid value, although clearly other factors affect the results. Operating on the idea that the initial degree of degradation (peroxide number) combined with some measure of stability (induction time or D2274 insoluble) might be a better predictor, we performed simple multiple regression analysis, but r^2 values for these regressions were quite low.

Real-world experience and common sense suggest that samples with longer induction times or lower levels of D2274 deposits are more stable, but the results of these accelerated tests are not strong predictors of storage stability on the D4625 test at 4, 8, or 12 weeks. One possibility not examined here is that even at 4 weeks these samples have degraded so far that their initial state is no longer predictive of their condition. Storage results for a shorter period (2 weeks, for example) might yield stronger correlations. However, the data in Figure 9 show that if induction time is near or below the 3-hour limit, B100 will most likely fail to meet its specification for stability before 4 months. Even samples with induction times longer than 6 hours are out of specification for oxidation stability at 4 weeks on this test, suggesting that any B100 not treated with antioxidant should not be stored for more than 2 or 3 months. The B100 could be stored significantly longer before it goes out of specification for acid value or before significant levels of deposits form.

The D4625 test condition of 43ºC may not be appropriate for B100. This test was developed to provide slightly accelerated conditions for assessing the stability of petroleum-derived fuels. For these fuels reactions that occur at typical storage temperatures are apparently the same as those that occur at 43ºC. This may not be the case for B100. For example, Bondioli and coworkers[18] compared the results from D4625 tests[8] and storage for 1 year in drums at ambient conditions.[7] They observed only modest degradation in the 1-year storage study, but for D4625 storage they saw significant increases in peroxide value and insolubles at only 4 weeks, along with significant increases in acidity at 8 to 12 weeks. These results suggest that degradation reactions that occur in B100 are accelerated much more by increasing the temperature to 43ºC than are those that occur in conventional diesel fuels at this temperature.

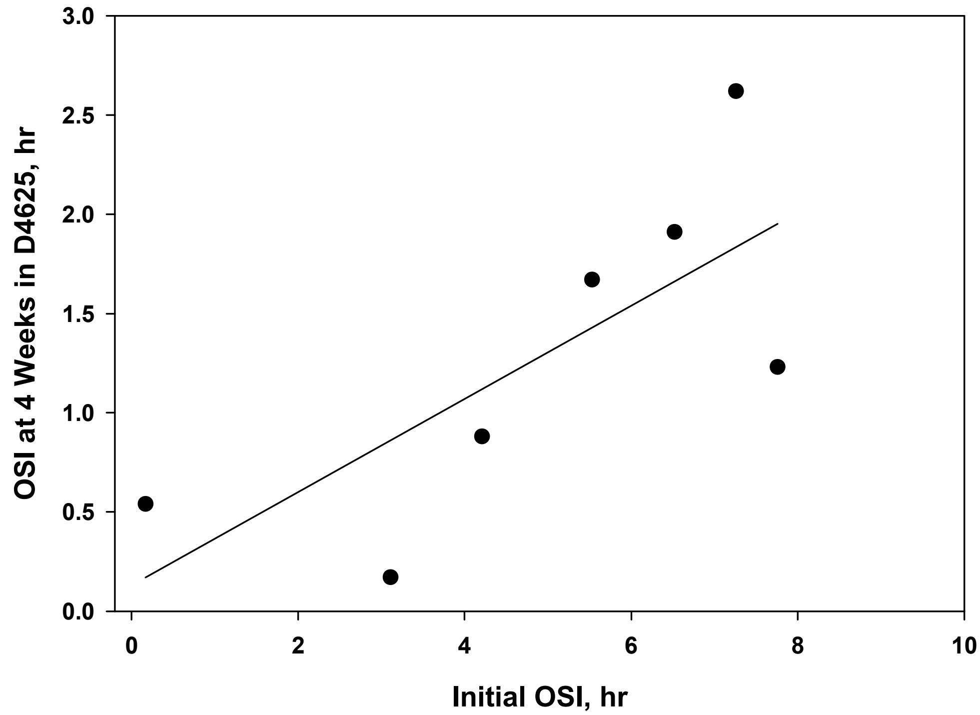

Figure 41. B100 OSI or Rancimat induction period at 4 weeks on the D4625 test as a function of initial induction time

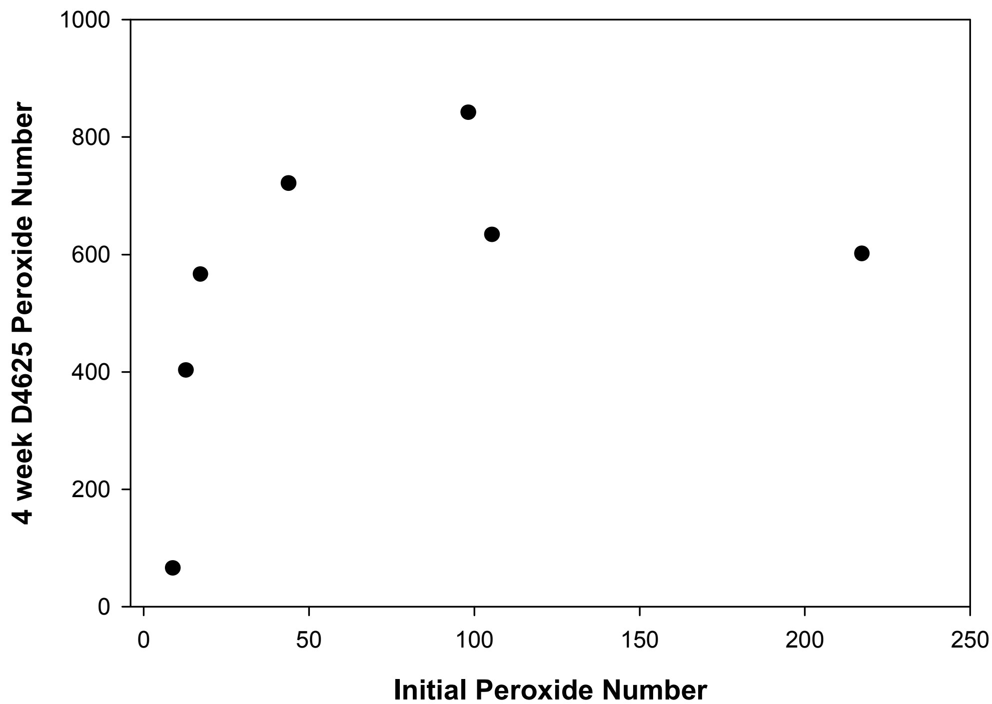

Figure 42. Peroxide number at 4 weeks on the D4625 test for B100 samples, as a function of initial peroxide number

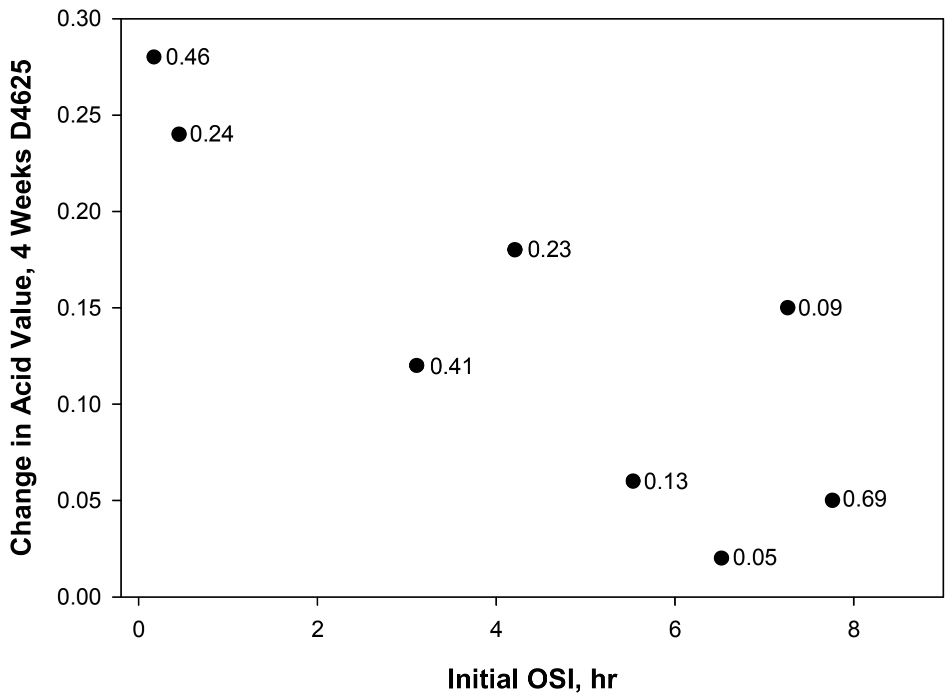

Figure 43. Change in acid value at 4 weeks on D4625 as a function of initial OSI or Rancimat induction time for B100 samples. Data labels indicate initial acid value

Is B100 Stability a Predictor of Blend Stability?

Accelerated Tests

The accelerated test data indicate that B100 stability is, in some sense, a good predictor of blend stability for both B5 and B20 blends. For B5 blends the B5 induction time as a function of the B100 induction time is shown in Figure 44. The experiment was ended at 12 hours for B5 blends. If the B100 has an induction time of about 3 hours or longer, the B5 blend is guaranteed to have a 12-hour or longer induction time. A similar plot for B5 D2274 total insolubles is shown in Figure 45. Again, if the B100 has an induction time longer than about 3 hours, the B5 blend will always have D2274 deposits of less than 2.5 mg/100 ml. For less stable B100, high levels of insolubles—in fact, much higher than those observed for the B100 used to make the blend—can form. Another way to look at the data is to compare B5 D2274 total insolubles with B100 D2274 total insolubles as shown in Figure 46. If the B100 total insolubles are less than about 6 mg/100 ml, the B5 blend produces total insolubles below 2.5 mg/100 ml. The 2.5 mg/100-ml level was chosen because it is used as a stability requirement for diesel fuels in several pipeline systems.

Figure 47 compares B20 induction time to B100 induction time. For all but one of 48 samples, if the B100 induction time is longer than about 3 hours, the B20 induction time will exceed 6 hours. Figure 48 shows that if B100 induction time is longer than about 3 hours, the B20 D2274 total insolubles will be below 2.5 mg/100 ml. If B100 induction time is shorter than 3 hours, high levels of insolubles can form, much higher than those observed for the B100 that was used to make the blend. Figure 49 shows that if B100 D2274 total insolubles are below about 6 mg/100 ml, B20 total insolubles will be below 2.5 mg/100 ml.

Thus, accelerated tests do not show a direct proportionality or correlation between B100 stability and blend stability, but if the B100 stability is above a certain level (roughly a 3-hour induction time), blends prepared from that B100 appear to be stable. Based in part on these results, ASTM has recently included a 3-hour minimum induction time requirement in the D6751 specification for B100 (this was originally included in D6751-06b).

Fang and McCormick recently reported on a negative synergism or antagonism for deposit formation from biodiesel blends on the D2274 test.[10] As noted in the Background chapter, blends in the B20 to B30 range produced much higher levels of deposits than would be predicted from a weighted average of the results obtained for the diesel and biodiesel blending components. Figures 45 and 48 also show this effect, here even for B5 blends, although deposit levels are much higher for B20 blends.

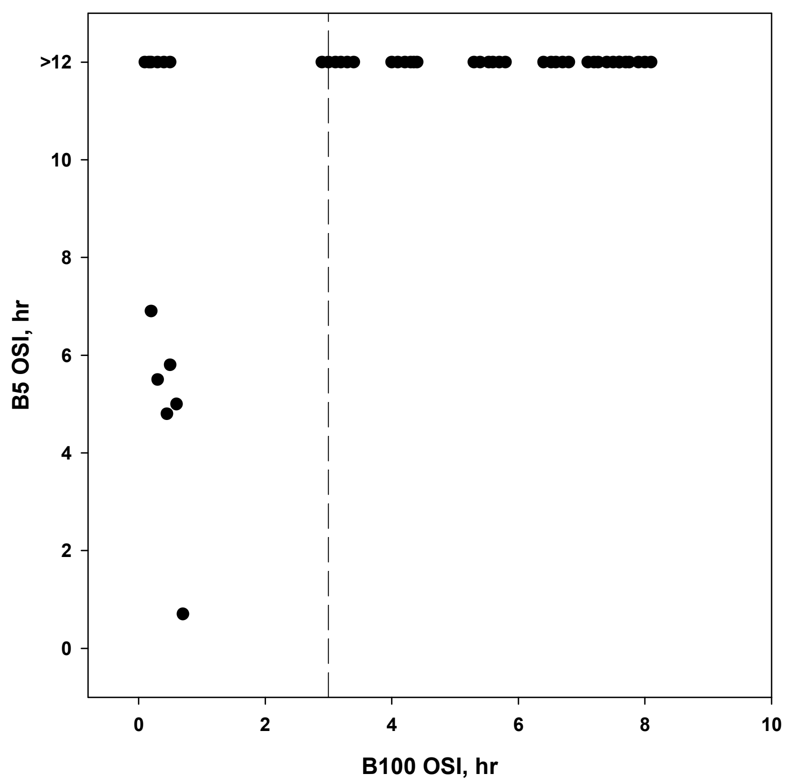

Figure 44. B5 OSI induction time as a function of B100 OSI induction time

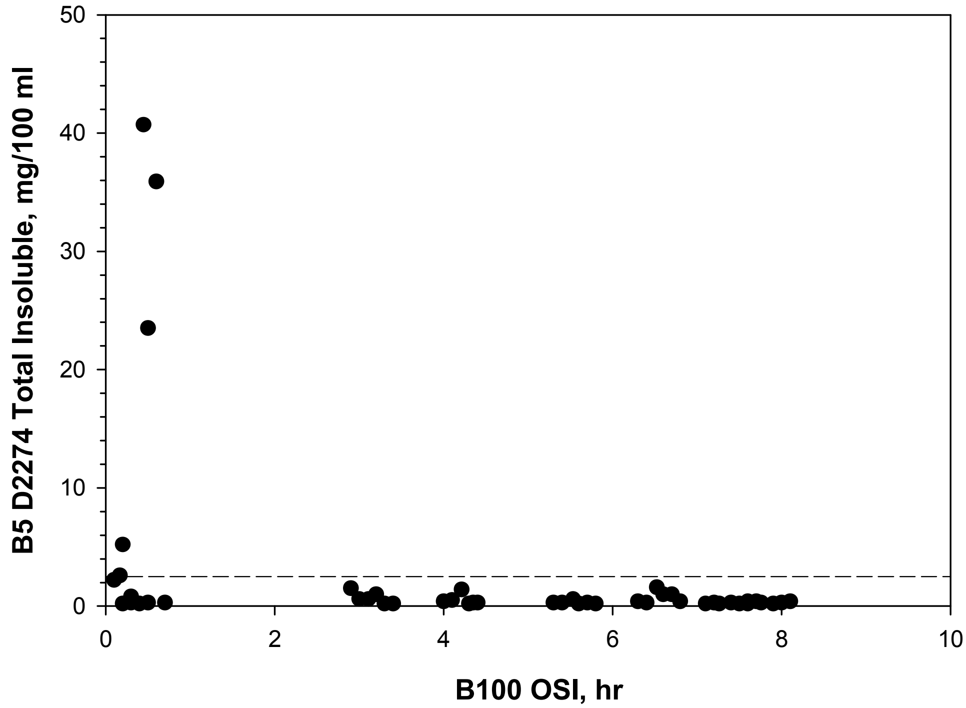

Figure 45. B5 D2274 total insoluble as a function of B100 OSI or Rancimat induction time

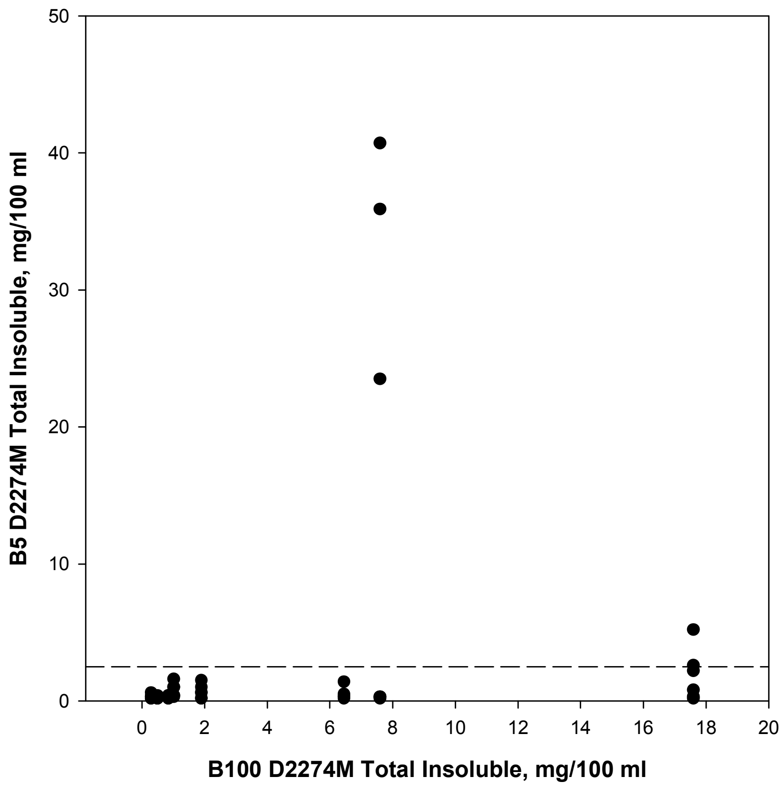

Figure 46. B5 D2274 total insoluble as a function of B100 D2274 total insoluble

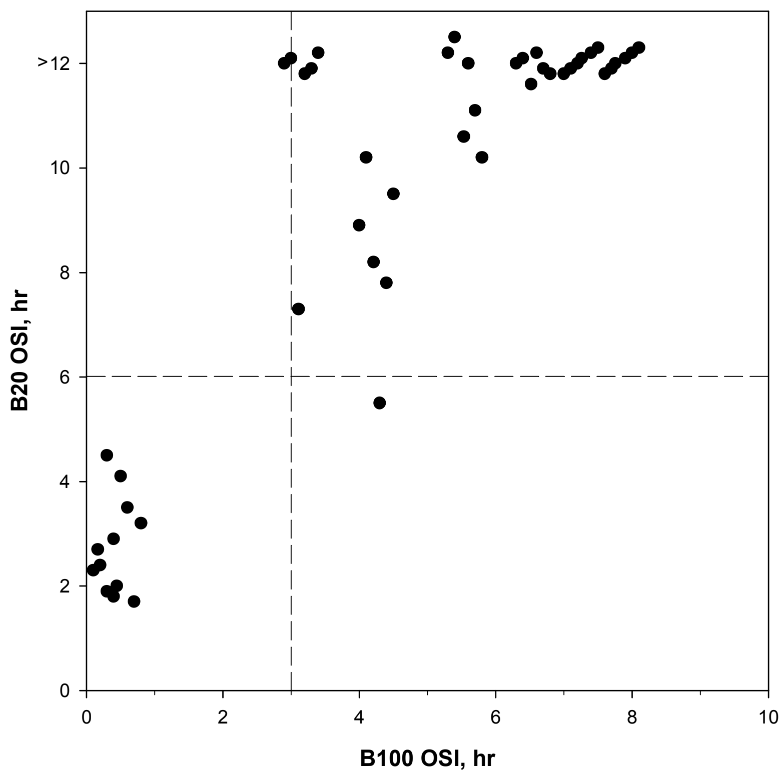

Figure 47. B20 OSI induction time as a function of B100 OSI induction time

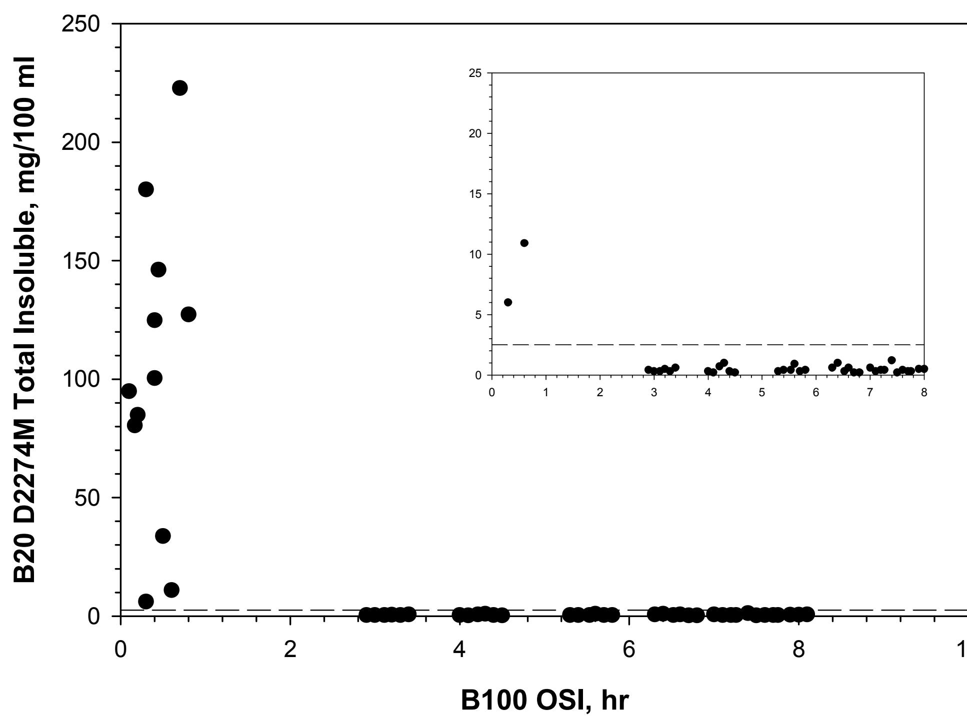

Figure 48. B20 D2274 total insoluble as a function of B100 OSI or Rancimat induction time

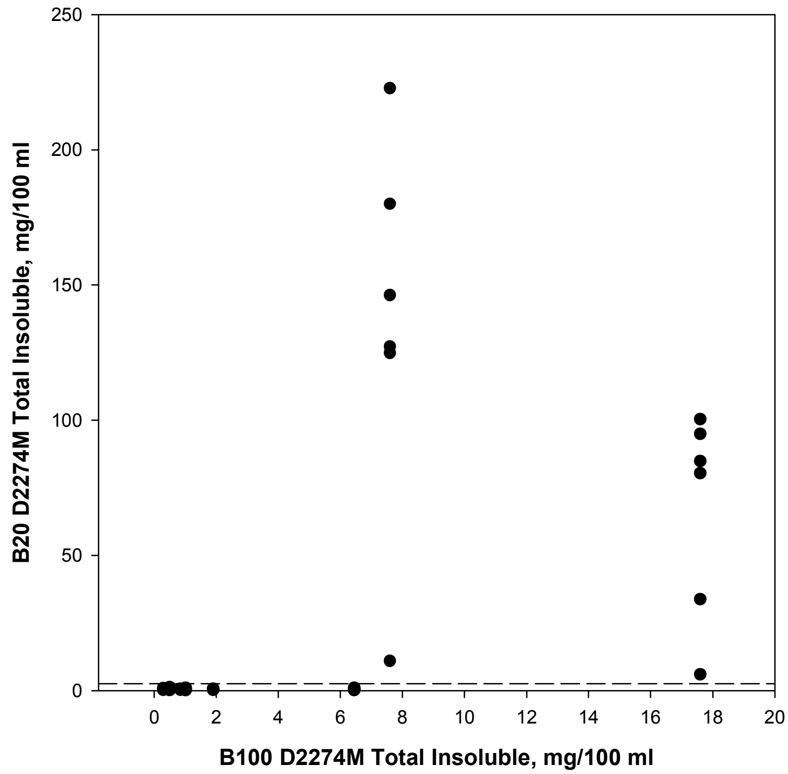

Figure 49. B20 D2274 total insoluble as a function of B100 D2274 total insolubles

Aging and In-Use Scenario Tests (Storage, Vehicle Tanks, High-Temperature Environment)

These tests include the D4625 12-week storage test, the 1 week at 80ºC test, and the subsequent high-temperature thermal stability test. B100 stability on accelerated tests seems to be a reasonable predictor of stability of B5 and B20 blends on the D4625 test. As shown in Figures 20, 21, and 22; the only B5 blend that exhibited oxidative deterioration on this test was prepared from a B100 with an induction time of 0.5 hours. Similarly for B20, Figures 32, 33, and 34 show that only B20 prepared from B100 with short induction times (in this case 0.5 and 0.2 hours) exhibited oxidative degradation. So, although questions remain about the suitability of the 43ºC storage test for B100 and about whether 1 week of storage on this test for biodiesel and biodiesel blends equates to 1 month of real-world storage (as is generally assumed for petroleum-derived fuels), biodiesel blends prepared from B100 with 3-hour or longer induction times do not appear to degrade under these conditions.

For the worst-case simulated fuel tank aging test (1 week at 80ºC) Figures 24, 25, and 26 show significant oxidative degradation only for B5 blends prepared from a B100 with 0.5 hour induction time. The picture is less clear cut for B20, where Figures 36 through 39 indicate little relationship between B100 induction time and oxidative degradation under these conditions. However, B20 induction time was reasonably predictive of the acid value (and acid value increase) on this test. Thus we conclude that for these test conditions stable B100 will lead to stable B5 blends. We may also reasonably conclude that stable B100 will eliminate the most unstable B20 as measured by acid value, but the test cannot differentiate between intermediate and highly stable samples for acid number or sediment formation under these worst-case test conditions. This may be because these test conditions are too severe for B20 blends, such that stable and unstable blends are degraded. Additionally, because we cannot correlate results on this test to what actually happens in a vehicle fuel tank, it is not clear that the levels of insolubles shown in Figure 39, or the levels of acidity developed for the more stable B100 in Figure 37, actually indicate that these B20 blends would cause problems.

Blends were aged for 1 week at 80ºC, then tested for thermal stability with D6468 (150ºC for 180 minutes) to simulate reaction of the fuel in the high-temperature environment of the fuel injection system. Filter reflectance was measured and insolubles were quantified gravimetrically. For B5 blends the only sample exhibiting significant deposits was produced from a B100 with an induction time of 0.5 hours (see Figure 27). As shown in Figure 40, none of the B20 samples exhibited thermal instability based on reflectance. Most samples with B100 induction times of roughly 4 hours or less exhibited higher gravimetric deposits than other samples. We conclude that for B5 blends a stable B100 will lead to a thermally stable B5 blend, based on these test conditions, even after aging. For B20 blends additional data may be required, or the test conditions may be so severe that we cannot distinguish between stable and unstable samples. And as before, because we have no correlation of this test sequence (1 week at 80ºC followed by D6468 thermal stability testing) with performance in actual engine fuel systems, we cannot be certain that any of the fuels tested would actually cause engine operational problems. This testing approach does not provide a clear performance delineation between fuels that are stable and those that are not under these conditions.

An important caveat is that these tests have all been conducted in glassware. We recommend that additional tests be performed in real equipment to validate these conclusions. For storage this might be accomplished by storing the fuels in drums at ambient conditions; for the fuel tank simulation perhaps blends from biodiesel of varying stability levels could be examined in stand-alone vehicle fuel systems, similar to the approach taken by Tsuchiya and coworkers.[15] Unfortunately, there is no standard engine test for assessing the impact of fuel stability on fuel system and injector deposits and durability. Nevertheless, some testing with blends of varying stability in real fuels systems is required to validate these results.

How Do Diesel Fuel Properties Effect Stability?

Diesel fuel properties that might affect biodiesel blend stability include:

- Aromatic content. Higher aromatic fuels may be better able to hold polar biodiesel and diesel fuel oxidation products in solution.
- Sulfur content. Sulfur compounds can function as antioxidants.
- Diesel fuel oxidative and thermal stability.

Table 8 and Figure 15 show property and stability data for the diesel fuels used in this study. Total aromatic content ranges from about 8 to about 36 mass percent. One fuel (AL-27171) contains 340 ppm of sulfur; the remaining five contain less than 10 ppm. D2274 and D6468 indicate all six fuels are stable with little to distinguish one from another. Aging for 12 weeks in D4625 showed one fuel (AL-27175) beginning to show instability at 12 weeks. Notably this is the diesel fuel with the lowest aromatic content of 8%. Aging for 1 week at 80ºC indicated little difference between the diesel fuels.

Examining accelerated test data, Figures 50 and 51 show how diesel fuel aromatic content affects D2274 total insolubles for B5 and B20 blends, respectively. In both cases the only samples exhibiting high levels of insolubles were prepared from B100 with induction times shorter than 1 hour, independent of fuel aromatic content. D4625 storage data for B5 blends show one sample with instability at 12 weeks (Figures 20–22, Appendix E). This fuel was prepared from an unstable B100 and the low-sulfur diesel fuel (AL-27171) with 36% aromatic content. This B5 blend was also unstable in simulated fuel tank aging and in high-temperature stability tests. A B20 blend prepared from these same blending components, as well as a second B20 prepared from an unstable biodiesel and a ULSD with 16% aromatic content also demonstrated instability on D4625.

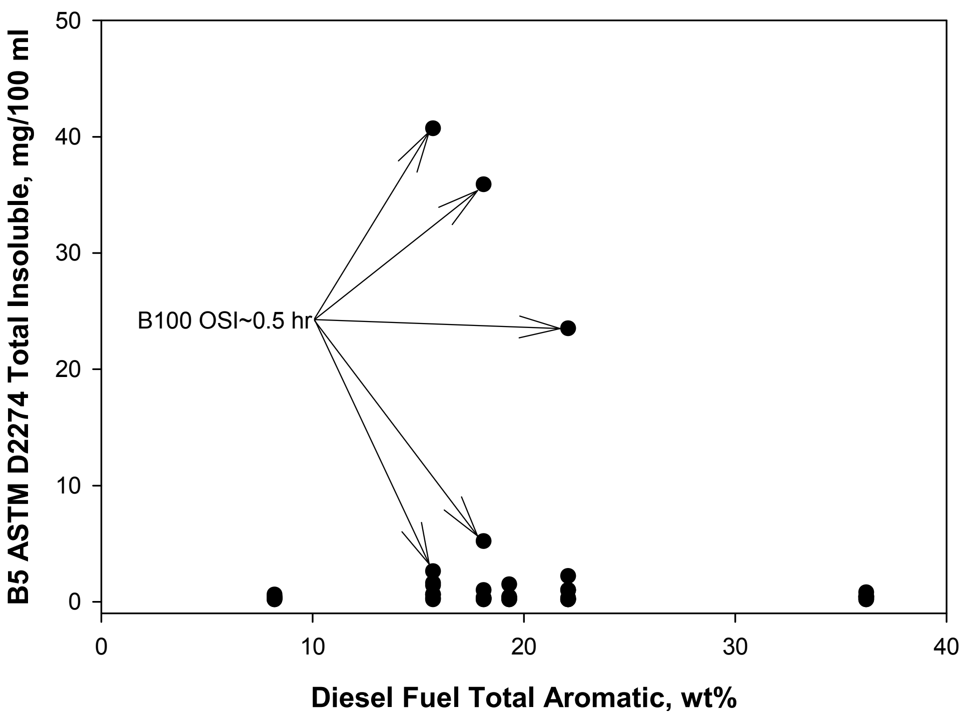

Figure 50. Diesel fuel aromatic content affect on D2274 total insolubles for B5 blends

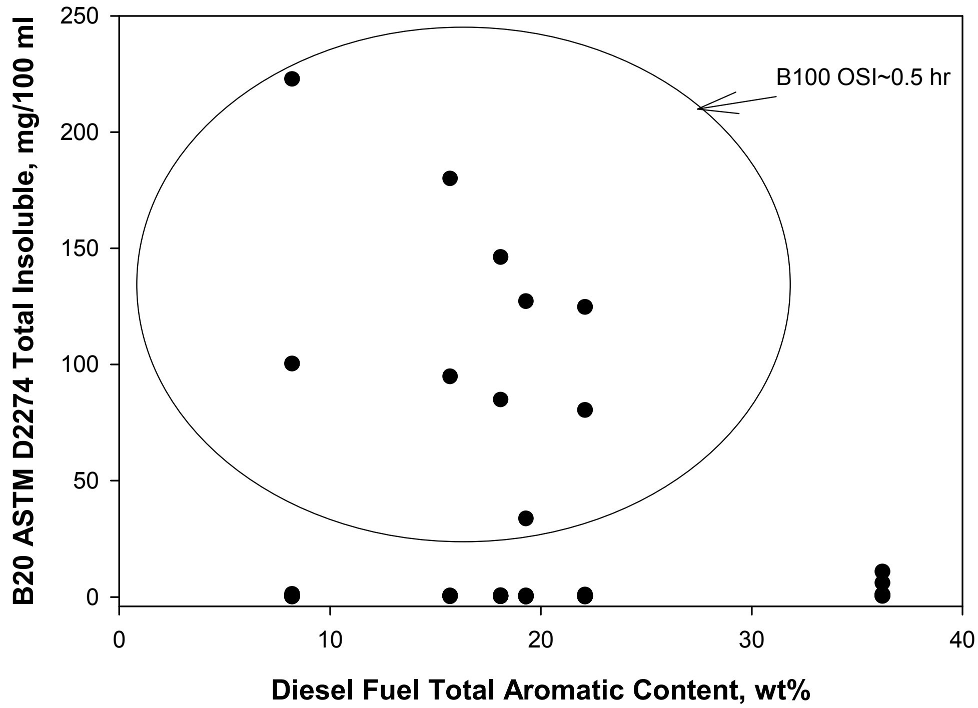

Figure 51. Diesel fuel aromatic content affect on D2274 total insolubles for B20 blends

To examine the issue of diesel fuel aromatic content in more detail, an unstable B100 (AL-27138) was blended with each diesel fuel at 20% and tested on the fuel tank aging and high-temperature stability simulation tests. Results are shown in Figure 52. Four of the six samples produced total insolubles after 1 week of aging above 100 mg/100 ml, somewhat higher than observed when a range of B20 samples from various biodiesels were subjected to this test (Figure 39). A blend of AL-27138 (B100) and AL-27151 (ULSD) was tested twice, once in November 2006 for the dataset shown in Figure 39 and again in April 2007 for the dataset shown in Figure 52. In November this sample produced 35.7 mg/100 ml; in April it generated 200 mg/100 ml, suggesting that the already unstable B100 had aged further in the intervening months. Nevertheless, these tests show no correlation between stability and diesel fuel aromatic content.

Our results suggest that diesel fuel aromatic content does not play a role in the stability of biodiesel blends and that B100 stability is the most important factor, consistent with the discussion in the previous section. However, we have noted the antagonistic effect where D2274 deposits for biodiesel blends are much higher than would be predicted based on the individual stability of the petroleum and biodiesel blend components. The cause of this antagonism is unknown, but based on these results does not appear to be related to aromatic content. The antagonism requires an unstable biodiesel, however, and perhaps unstable biodiesel degrades to produce polar components that are soluble in oxidized B100 but insoluble in any diesel fuel, independent of aromatic content.

The impact of diesel fuel sulfur content is less easily assessed because the dataset consists of essentially five samples with very low sulfur content (below 10 ppm) and one with 340 ppm.

The accelerated and real-world simulation results show that when an unstable B100 is blended with the 340 ppm sulfur diesel fuel an unstable blend is formed. Because there was little difference between the diesel fuels for stability, the impact of diesel stability on biodiesel blend stability cannot be assessed from these data. These results also support the idea that B100 stability is the main factor that affects the stability of B5 and B20 blends. However, an important caveat is that the diesel fuels included here were obtained before ULSD was mandated in the United States. Confirmatory testing should be conducted with fuels that are more representative of in-use fuels today.

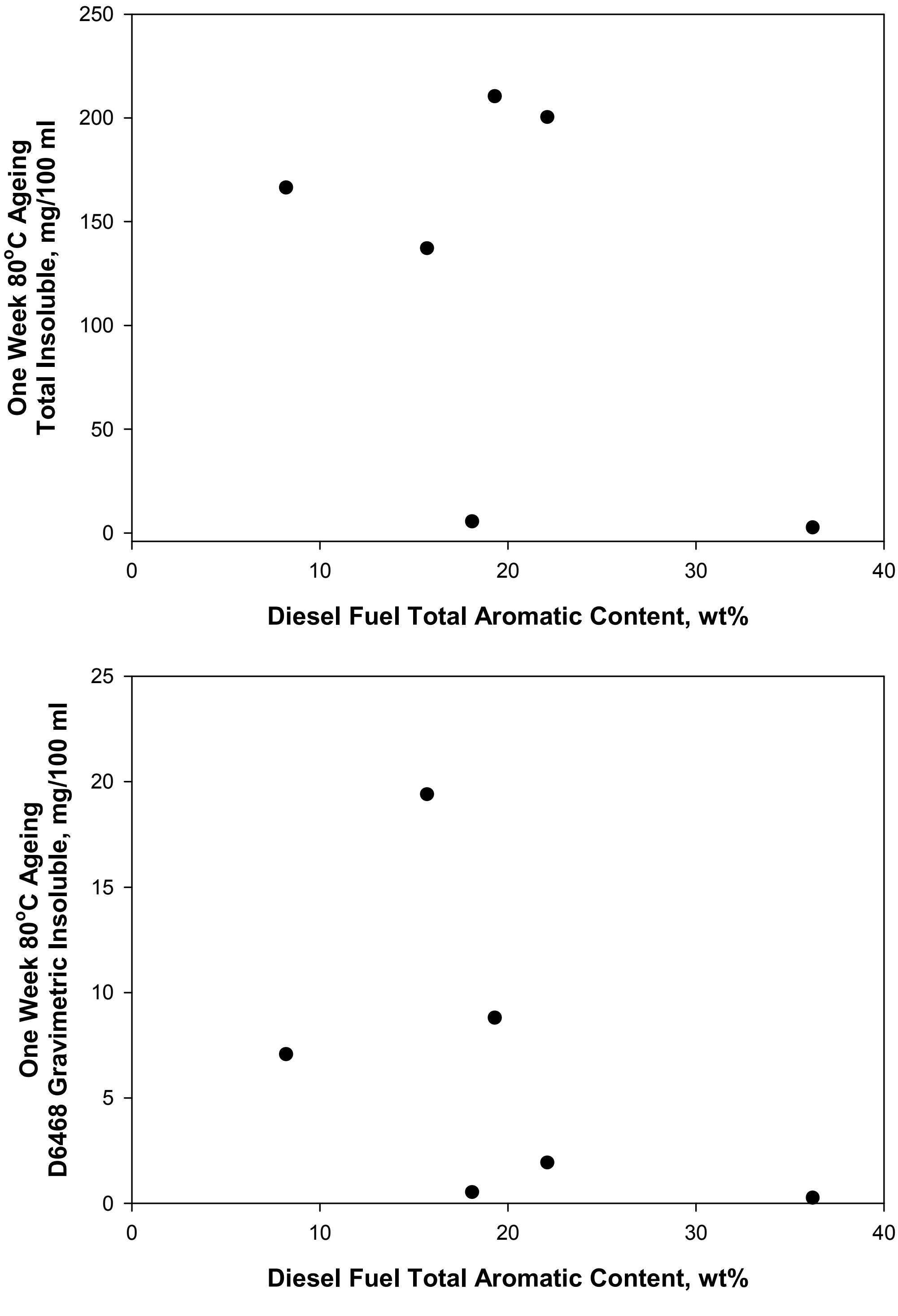

Figure 52. Results of 1 week at 80ºC aging test followed by D6468 thermal stability test for B20 samples prepared from B100 AL-27138 and all diesel samples

How Do Antioxidant Additives Affect Stability?

The hindered phenolic antioxidants tested here prevented oxidative degradation of B100 in the storage simulation, and prevented degradation of biodiesel blends in the storage, fuel tank, and high-temperature simulations. The dramatic suppression in insoluble formation for the highly unstable B100 AL-27138 (Figure 14), and for B5 (Figure 23) and B20 (Figure 35) blends produced from it, during the 12-week storage test is striking, even for cases where the antioxidant did not increase B100 induction times to longer than 3 hours. For B5 blends, antioxidants also prevented insolubles from forming in the fuel tank and high-temperature simulations. In some B20 cases the additive treat rates were too low to prevent insolubles from forming for the fuel tank and high-temperature stability simulations, but did reduce insolubles formation. In these cases, a higher treat rate eliminated insolubles. No effort was made to optimize additive treat rate. Additionally, the amount of active ingredient in the additives is unknown. So the results mainly confirm that additives can be effective, but individual producers and blenders will have to select appropriate additives and determine optimal treat rates for their specific situations.

Is a 3-Hour B100 Induction Time Adequate?

Beginning with the publication of ASTM D6751-06b in January 2007, B100 is required to have a minimum 3-hour induction time. This requirement is largely based on the accelerated stability data and analysis presented in the section titled, Is B100 Stability a Predictor of Blend Stability? Additional data are now available from the aging simulation tests (storage, vehicle fuel tank, and high temperature) and the extent to which these new data support the 3-hour minimum induction time requirement is of interest.

Storage Stability

As discussed, none of the accelerated stability tests were particularly strong predictors of the stability of B100 on the D4625 test at 43ºC. However, as indicated in Figure 43, having a minimum induction time of 3 hours limits acid value increase over 4 weeks of storage on this test to less than 0.2 mg KOH/g. Figure 11 shows that at 4 weeks the only samples that had gone out of specification for acid value had initial induction times of 3.1 hours or lower. Our experience agrees with that of other researchers,[5,7,8,9,14,15,17] that B100 samples with longer induction times are more stable in real-world settings. Thus, we take these results to mean that most biodiesel samples, regardless of initial induction time, will begin to oxidize immediately during storage. If induction time is near or below the 3-hour limit, the B100 will most likely go out of specification for either stability or acid value within 4 months. For longer induction times the biodiesel might be stored for several months. However, the results in Figure 9-12 indicate that even B100 with induction times longer than 7 hours will be out of specification for oxidation stability at only 4 months, although these samples may not have shown a significant increase in acidity or in deposit formation. The 3-hour limit appears to be adequate to prevent oxidative degradation for B5 and B20 blends in storage for up to 12 months (assuming that we accept the relationship that 1 week on D4625 is equivalent to 1 month of real-world storage at 21ºC for blends).

Given these observations, we recommend that the 3-hour limit be considered as adequate to protect B100 and blends in storage, and that additional data on B100 storage be acquired at more realistic storage temperatures and for longer periods. Blenders of biodiesel and others who need to store B100 should be made aware of limitations on the number of months this material can be stored. In developing a follow-up testing plan, the actual B100 storage conditions should be considered. In many cases, B100 may be stored in aboveground tanks that are heated to roughly 15ºC during the winter months, but might experience higher temperatures during the summer months.

Stability in Simulated Vehicle Fuel Tank and High-Temperature Environments

The results of B5 testing shown in Figures 24 to 27 clearly indicate that B100 with a 3-hour or longer induction time produced B5 blends that were stable on the testing protocols employed here. Even if these test conditions are later found to have been too severe, the B5 blends did not exhibit instability if the B100 had at least a 3-hour induction time.

For B20 blends the situation is less clear cut. For the most part there was little to distinguish blends produced from minimum 3-hour induction time B100 from blends produced from less stable biodiesel. As shown in Figure 38, the B20 induction time was a better predictor of acid formation on the fuel tank aging simulation, as B20 induction time of roughly 4 hours was adequate to prevent a large increase in acidity.

Compared to the fuel tank aging simulation test, the D2274 test is conducted at conditions of 95ºC with bubbling of oxygen through the fuel for 16 hours, in some ways more severe than the 80ºC for 1 week test conditions. Increased contact of B100 and air via mixing or bubbling has been shown to produce a dramatic increase in oxidation rates.[7] Figure 48 shows that B100 with a minimum 3-hour induction time produces stable B20 on this test. The accelerated test results shown in Figure 48 strongly support the conclusion that the B100 minimum 3-hour induction time produces B20 that is stable in the vehicle fuel tank and high-temperature environments. In other ways the 1-week storage test conditions may be more severe. Temperature and air contacting are less severe than D2274, but the test lasts more than 10 times longer (168 hours versus 16 hours). Perhaps we could better discriminate between stable and unstable B20 by reducing the test time from 1 week to 2 or 3 days, especially given that the test temperature of 80ºC is likely higher than would be encountered in a real vehicle fuel tank over extended periods without being fueled with fresh fuel. Also, because Figure 47 indicates that if B100 induction time is longer than 3 hours, B20 induction time is almost always longer than 6 hours; therefore, the idea of a separate stability requirement for B20 may not provide additional protection. So although additional data are needed to confirm, the picture emerging from the available data is that B20 blends prepared from B100 with a minimum 3-hour induction time are stable in vehicle fuel tank and high-temperature engine fuel system environments.

Conclusions and Recommendations

The B100 samples examined here show a broad distribution of stability on accelerated tests, with induction time (OSI) results ranging from less than 1 hour to more than 9 hours and ASTM D2274 total insolubles ranging from less than 2 mg/100 ml to nearly 18 mg/100 ml. Samples that produce very high levels of iso-octane insolubles on the D2274 test also produced very high levels of total insolubles. This suggests that little new information is acquired by measuring iso-octane insolubles. The change in acid value of the filtered liquid over the D2274 test was closely correlated with total insolubles and the initial induction time. The accelerated test data indicate that if the B100 stability is above a roughly 3-hour induction time, blends prepared from that B100 appear to be stable on the OSI and D2274 tests.

The D4625 long-term storage results for B100 indicate that most biodiesel samples, regardless of initial induction time, will begin to oxidize immediately during storage. If induction time is near or below the 3-hour limit, the B100 will most likely go out of specification for either stability or acid value within 4 months. Even B100 with induction times longer than 7 hours will be out of specification for oxidation stability at only 4 months, although these samples may not have shown a significant increase in acidity or in deposit formation. B100 should probably not be stored longer than several months in any case unless it is treated with a synthetic antioxidant. Blenders of biodiesel and others who need to store B100 should be made aware of limitations on the number of months this material can be stored.

The 3-hour B100 induction time limit appears to be adequate to prevent oxidative degradation for both B5 and B20 blends in storage for up to 12 months. Questions remain as to whether 1 week of storage on the D4625 test for biodiesel and biodiesel blends equates to 1 month of real world storage, as is generally assumed for petroleum-derived fuels.

For tests that simulated fuel tank aging and high-temperature stability, we conclude that stable B100 (longer than 3 hour OSI) leads to stable B5 blends. For B20, considering the entire dataset available today, we provisionally conclude that stable B100 (longer than 3 hour OSI) leads to stable B20 blends, but the test cannot differentiate between intermediate and highly stable samples for acid number or sediment formation under these worst-case test conditions. Anecdotal and detailed field data collections on B20 do not show a propensity for significant vehicle fuel filter clogging. Additional work is required to confirm this or to determine whether an additional stability test is required for the B20 blend.

These results support the idea that B100 stability is the main factor that affects the stability of B5 and B20 blends, independent of diesel fuel aromatic content, sulfur level, or stability. However, the diesel fuels included here were obtained before ULSD was mandated in the United States. Confirmatory testing should be conducted with fuels that are more representative of actual in-use fuels. Additionally, the factors leading to the negative antagonism for deposit formation that occurs with blending of unstable B100 in to diesel fuel remain unknown, and future studies should endeavor to understand this phenomenon.

The hindered phenolic antioxidants tested here prevented oxidative degradation of B100 in the storage simulation, and prevented degradation of biodiesel blends in the storage, fuel tank, and high-temperature simulations. Individual producers, blenders, and additive suppliers will have to select appropriate additives and determine optimal treat rates for their specific situations.

We recommend that additional data be acquired in real equipment to verify these conclusions. For storage this might be accomplished with storage in drums at ambient conditions; for the fuel tank simulation perhaps blends from biodiesel of varying stability levels could be examined in stand-alone vehicle fuel systems or more intense monitoring and measurement of fuel in actual use. Unfortunately there is no standard engine test to assess the impact of fuel stability on fuel system and injector deposits and durability. Nevertheless, some testing with blends of varying stability in real fuel systems is required to confirm these results.

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Appendix A: B100 Characterization and Stability Test Data

Sample Identification	Method	AL-27128-F	AL-27129-F	AL-27137-F	AL-27138-F	AL-27140-F	AL-27141-F
Oxidation Stability, hours	EN 14112						
Replicate 1		4.22	3.09	6.41	0.13	0.17	5.74
Replicate 2		4.18	3.10	6.55	0.62	0.17	5.75
Replicate 3		4.24	3.14	6.61	0.59	0.13	5.11
Mean		4.21	3.11	6.52	0.45	0.16	5.53
Oxidation Stability, mg/ 100 ml	Modified ASTM D2274						
Replicate 1							
Filterable insolubles		4.7	1.3	0.7	6.1	7.6	0.2
Adherent Insolubles		1.6	1.0	1.1	0.9	2.1	0.1
Total Insolubles		6.3	2.3	1.8	7.0	9.7	0.3
Iso-Octane Insolubles		197.4	4.7	2.4	4.0	64.1	0.7
Replicate 2							
Filterable insolubles		5.0	1.0	0.2	6.9	10.5	0.2
Adherent Insolubles		1.6	0.5	0.0	1.3	2.0	0.1
Total Insolubles		6.6	1.5	0.2	8.2	12.5	0.3
Iso-Octane Insolubles		198.0	0.4	2.8	4.8	73.0	0.5
Mean Total Insolubles		6.5	1.9	1.0	7.6	11.1	0.3
Mean Iso-Octane Insolubles		197.7	2.6	2.6	4.4	68.6	0.6
Oxidation Stability, Pressure Vessel	ASTM D525						
Induction Period Method, minutes		341	169	34	80	71.0	335.0
Thermal Stability, deposit, mg	ASTM D6468 Modified	0.3	0.1	0.3	0.3	0.4	0.2
Total Acid Number, mg KOH/g	ASTM D664	0.23	0.41	0.05	0.33	0.2	0.13
Total Acid Number after D2274, mg KOH/g							
Replicate 1		1.84	2.92	0.24	2.75	3.83	0.79
Replicate 2		2.03	2.07	0.15	3.26	4.22	0.64
Mean		1.94	2.50	0.20	3.01	4.03	0.72
Total Glycerin, %(mass)	ASTM D6584	0.103	0.081	0.144	0.016	0.022	0.121
Free Glycerin, %(mass)	ASTM D6584	0.009	<0.001	0.002	0.002	0.015	0.005

Sample Identification	Method	AL-27142-F	AL-27144-F	AL-27145-F	AL-27146-F	AL-27148-F	AL-27152-F
Oxidation Stability, hours	EN 14112						
Replicate 1		4.56	3.69	3.70	9.28	7.82	7.24
Replicate 2		4.46	4.02	4.01	9.33	7.76	7.24
Replicate 3		4.40	4.10	4.16	9.16	7.69	7.31
Mean		4.47	3.94	3.96	9.26	7.76	7.26
Oxidation Stability, mg/ 100 ml	Modified ASTM D2274						
Replicate 1							
Filterable insolubles		0.9	2.0	2.0	0.3	0.8	0.4
Adherent Insolubles		0.2	0.3	0.4	0.1	0.1	0.1
Total Insolubles		1.1	2.3	2.4	0.4	0.9	0.5
Iso-Octane Insolubles		0.3	1.4	2.7	0.4	22.1	6.2
Replicate 2							
Filterable insolubles		0.9	2.2	2.0	0.2	0.7	0.3
Adherent Insolubles		0.2	0.1	0.2	0.0	0.1	0.2
Total Insolubles		1.1	2.3	2.2	0.2	0.8	0.5
Iso-Octane Insolubles		0.7	1.3	0.7	0.4	15.7	6.5
Mean Total Insolubles		1.1	2.3	2.3	0.3	0.9	0.5
Mean Iso-Octane Insolubles		0.5	1.4	1.7	0.4	18.9	6.4
Oxidation Stability, Pressure Vessel	ASTM D525						
Induction Period Method, minutes		507	62	721	649	325	418
Thermal Stability, deposit, mg	ASTM D6468 Modified	0.3	0.4	0.4	0.5	0.4	0.1
Total Acid Number, mg KOH/g	ASTM D664	0.07	0.39	0.49	0.08	0.69	0.09
Total Acid Number after D2274, mg KOH/g							
Replicate 1		1.11	1.91	2.18	0.19	1.56	0.73
Replicate 2		0.90	1.83	2.13	0.20	1.37	0.68
Mean		1.01	1.87	2.16	0.20	1.47	0.71
Total Glycerin, %(mass)	ASTM D6584	0.216	0.221	0.192	0.161	0.121	0.15
Free Glycerin, %(mass)	ASTM D6584	0.003	0.004	0.005	<0.001	<0.001	0.001

Sample Identification	Method	AL-27153-F	AL-27154-F	AL-27155-F	AL-27157-F	AL-27158-F	AL-27160-F
Oxidation Stability, hours	EN 14112						
Replicate 1		9.36	0.14	2.60	4.67	7.18	0.18

Replicate 2		9.36	0.18	2.59	4.56	7.26	0.14
Replicate 3		9.35	0.18	2.27	4.47	7.52	0.18
Mean		9.36	0.17	2.49	4.57	7.32	0.17
Oxidation Stability, mg/ 100 ml	Modified ASTM D2274						
Replicate 1							
Filterable insolubles		0.2	12.3	9.4	1.5	0.2	11.0
Adherent Insolubles		0.1	1.3	1.5	0.5	0.1	2.1
Total Insolubles		0.3	13.6	10.9	2.0	0.3	13.1
Iso-Octane Insolubles		0.2	87.6	94.6	2.8	0.5	120.9
Replicate 2							
Filterable insolubles		0.2	11.1	8.5	1.5	0.2	18.0
Adherent Insolubles		0.0	1.5	1.3	0.8	0.1	4.1
Total Insolubles		0.2	12.6	9.8	2.3	0.3	22.1
Iso-Octane Insolubles		0.2	ND	95.8	2.8	0.0	126.7
Mean Total Insolubles		0.3	13.1	10.4	2.2	0.3	17.6
Mean Iso-Octane Insolubles		0.2	87.6	95.2	2.8	0.3	123.8
Oxidation Stability, Pressure Vessel	ASTM D525						
Induction Period Method, minutes		No break	150	270	487	512	159
Thermal Stability, deposit, mg	ASTM D6468 Modified	0.5	0.1	0.3	0.3	0.6	0.5
Total Acid Number, mg KOH/g	ASTM D664	0.08	**1.31**	0.29	0.11	0.51	0.46
Total Acid Number after D2274, mg KOH/g							
Replicate 1		0.21	5.54	3.21	1.05	0.70	5.12
Replicate 2		0.27	ND	2.93	1.19	0.69	6.40
Mean		0.24	5.54	3.07	1.12	0.70	5.76
Total Glycerin, %(mass)	ASTM D6584	0.15	0.132	**0.298**	0.225	0.158	0.188
Free Glycerin, %(mass)	ASTM D6584	0.001	0.003	0.007	0.015	0.001	0.002

Sample Identification	Method	AL-27161-F
Oxidation Stability, hours	EN 14112	
Replicate 1		5.13
Replicate 2		5.11
Replicate 3		5.09
Mean		5.11
Oxidation Stability, mg/ 100 ml	Modified ASTM D2274	
Replicate 1		
Filterable insolubles		1.0
Adherent Insolubles		0.1
Total Insolubles		1.1
Iso-Octane Insolubles		0.60
Replicate 2		
Filterable insolubles		0.8
Adherent Insolubles		0.2
Total Insolubles		1.0
Iso-Octane Insolubles		0.80
Mean Total Insolubles		1.1
Mean Iso-Octane Insolubles		0.7
Oxidation Stability, Pressure Vessel	ASTM D525	
Induction Period Method, minutes		No break
Thermal Stability, deposit, mg	ASTM D6468 Modified	0.2
Total Acid Number, mg KOH/g	ASTM D664	0.37
Total Acid Number after D2274, mg KOH/g		
Replicate 1		1.63
Replicate 2		1.50
Mean		1.57
Total Glycerin, %(mass)	ASTM D6584	0.151
Free Glycerin, %(mass)	ASTM D6584	0.003

Appendix B: D4625 Results for B100 Samples

				AL-27128	AL-27129	AL-27137	AL-27138	AL-27141	AL-27148	AL-27152	AL-27160
0 Weeks	IsoOctane Insoluble	D 4625, mod	mg/100 ml	3.9	0.1	1.9		2.3	0.1	0.1	0.5
	Peroxide Value	D 3703		217	105	12		98	8	43	17
	Viscosity @ 40°C	D 445		4.45	5.12	4.10		4.09	4.67	4.47	4.86
	Polymer Content	ISO 16931		2.63	0.17	0.82		1.03	1.46	2.17	4.91
	Total Acid No.	D 664	mg KOH/g	0.23	0.41	0.05	0.33	0.13	0.69	0.09	0.46
	Total insoluble	D2274	mg/100ml	6.45	1.9	1.015	7.6	0.3	0.9	0.5	17.6
	IsoOctane Insols	D2274	mg/100ml	197.7	2.6	2.6	4.4	0.6	18.9	6.4	123.8
	Rancimat IP		h	4.21	3.11	6.52	0.45	5.53	7.76	7.26	0.17
4 Weeks	Filterable Insols	D 4625, mod	mg/100 ml	0.7	0.1	1.03	1.8	0.4	0.9	0.4	0.7
	Adherent Insols	D 4625, mod	mg/100 ml	0	0	0	0.1	1	0	0.1	0.2
	Total Insols	D 4625, mod	mg/100 ml	0.7	0	1.3	1.9	1.4	0.9	0.5	0.9
	IsoOctane Insols	D 4625, mod		14.8	0.7	3.3	0.2	4	1.2	3.8	10.3
	Peroxide Value	D 3703		601	633	403		841	65	721	566
	Viscosity @ 40°C	D 445		5.5	4.78	4.13		4.22	4.69		5.08
	Polymer Content	ISO 16931		2.8	0.49	0.89		1.26	1.5	2.29	5.63
	Total Acid No.	D 664	mg KOH/g	0.41	0.53	0.07	0.57	0.19	0.74	0.24	0.74
	Rancimat IP		h	0.88	0.17	1.91		1.67	1.23	2.62	0.54
8 Weeks	Filterable Insols	D 4625, mod	mg/100 ml	1	0.1	0.3	1.1	0.3	0.2	1.1	2.2

	Adherent Insols	D 4625, mod	mg/100 ml	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Total Insols	D 4625, mod	mg/100 ml	1.1	0.2	0.4	1.2	0.4	0.3	1.2	2.3
	IsoOctane Insols	D 4625, mod		59.7	0.5	3.6	1.9	3.6	1.9	28.5	55.3
	Peroxide Value	D 3703		1237	1759	2039		1654	225	903	1000
	Viscosity @ 40°C	D 445		5.75	5.03	4.54		4.49	4.73	4.81	5.36
	Polymer Content	ISO 16931		3.59	1.33	1.92		2.01	1.54	2.82	7.2
	Total Acid No.	D 664	mg KOH/g	1.22	1.41	0.98	1.2	0.98	1.64	1.22	1.76
	Rancimat IP		h	>12	>12	>12		0.4	1.29	0.63	0.32
12 Weeks	Filterable Insols	D 4625, mod	mg/100 ml	3.1	1.4	1	5.9	4.1	3.2	4.2	2.8
	Adherent Insols	D 4625, mod	mg/100 ml	0.7	0.5	0.7	0.3	0.4	0.2	0.3	0.1
	Total Insols	D 4625, mod	mg/100 ml	3.8	1.9	1.7	6.2	4.5	3.4	4.5	2.9
	IsoOctane Insols	D 4625, mod		17.6	1.1	7.3		6.4	13.1	74.7	97.4
	Peroxide Value	D 3703		2037	2026	3099		2951	881	1762	1208
	Viscosity @ 40°C	D 445		4.83	4.93	4.72		4.67	4.84	5.04	5.53
	Polymer Content	ISO 16931		4.45	1.99	3.07		3.26	2.02	4.18	8.42
	Total Acid No.	D 664	mg KOH/g	1.10	1.10	0.69	3.18	0.68	1.04	1.32	1.77
	Rancimat IP		h	>12	>12	>12		0.58	0.98	>12	>12

B100 Storage with Antioxidants			AL-27138 Neat	AL-27138 + 1000 ppm A	AL-27138 + 2000 ppm A	AL-27138 + 1000 ppm B	AL-27138 + 2000 ppm B	AL-27129 + 1000 ppm A	AL-27129 + 1000 ppm B
After 4 Weeks Storage at 43°C									
Filterable Insolubles	**D 4625, mod**	**mg/100 ml**	**1.8**	**0.2**	**0.2**	**0.2**	**0.2**	**0.3**	**0.1**
Adherent Insolubles	**D 4625, mod**	**mg/100 ml**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**
Total Insolubles	**D 4625, mod**	**mg/100 ml**	**1.9**	**0.3**	**0.3**	**0.3**	**0.3**	**0.4**	**0.2**
Isooctane Insolubles	**D 4625, mod**	**mg/100 ml**	**0.2**	**0.4**	**0.7**	**0.2**	**0.2**	**0.2**	**0.2**
Total Acid Number	**D 664**	**mg KOH/g**	**0.57**	**0.35**	**0.35**	**0.32**	**0.35**	**0.43**	**0.43**
After 8 Weeks Storage at 43°C									
Filterable Insolubles	**D 4625, mod**	**mg/100 ml**	**1.1**	**0.3**	**0.3**	**0.3**	**0.3**	**0.4**	**0.4**
Adherent Insolubles	**D 4625, mod**	**mg/100 ml**	**0.1**	**0.7**	**0.2**	**0.1**	**0.2**	**0.1**	**0.1**
Total Insolubles	**D 4625, mod**	**mg/100 ml**	**1.2**	**1.0**	**0.5**	**0.4**	**0.5**	**0.5**	**0.5**
Isooctane Insolubles	**D 4625, mod**	**mg/100 ml**	**1.9**	**1.6**	**1.8**	**1.6**	**5.8**	**0.5**	**0.3**
Total Acid Number	**D 664**	**mg KOH/g**	**1.20**	*	**1.28**	**1.29**	**1.23**	**0.42**	**0.40**
After 12 Weeks Storage at 43°C									
Filterable Insolubles	**D 4625, mod**	**mg/100 ml**	**5.9**	**0.3**	**0.4**	**0.3**	**0.4**	**0.1**	**0.1**
Adherent Insolubles	**D 4625, mod**	**mg/100 ml**	**0.3**	**0.1**	**0.2**	**0.2**	**0.4**	**0.1**	**0**
Total Insolubles	**D 4625, mod**	**mg/100 ml**	**6.2**	**0.4**	**0.6**	**0.5**	**0.8**	**0.2**	**0.1**
Isooctane Insolubles	**D 4625, mod**	**mg/100 ml**		**1.4**	**3.2**	**1.5**	**2.1**	**0.7**	**0.6**
Total Acid Number	**D 664**	**mg KOH/g**	**3.18**	**0.41**	**0.37**	**0.66**	**0.41**	**0.42**	**0.48**

Appendix C: D4625 Results for Petroleum-Derived Diesel Fuels

				AL-27150	AL-27151	AL-27166	AL-2717	AL-27175	AL-27176
4 Weeks	**Filterable Insols**	**D 4625, mod**	**mg/100 ml**	**0.0**	**0.1**	**< 0.1**	**0.3**	**0.1**	**< 0.1**
	Adherent Insols	**D 4625, mod**	**mg/100 ml**	**0.1**	**0.3**	**< 0.1**	**0.1**	**< 0.1**	**0.0**
	Total Insols	**D 4625, mod**	**mg/100 ml**	**0.1**	**0.4**	**0.1**	**0.4**	**0.1**	**< 0.1**
8 Weeks	**Filterable Insols**	**D 4625, mod**	**mg/100 ml**	**0.0**	**0.1**	**0.1**	**0.3**	**0.1**	**0.1**
	Adherent Insols	**D 4625, mod**	**mg/100 ml**	**0.0**	**0.2**	**0.0**	**0.4**	**0.0**	**0.1**
	Total Insols	**D 4625, mod**	**mg/100 ml**	**0.0**	**0.3**	**0.1**	**0.7**	**0.2**	**0.3**
12 Weeks	**Filterable Insols**	**D 4625, mod**	**mg/100 ml**	**0.0**	**0.1**	**0.1**	**0.2**	**2.6**	**0.3**
	Adherent Insols	**D 4625, mod**	**mg/100 ml**	**0.3**	**0.6**	**0.2**	**0.6**	**0.3**	**0.3**
	Total Insols	**D 4625, mod**	**mg/100 ml**	**0.3**	**0.6**	**0.2**	**0.8**	**2.9**	**0.6**

Appendix D: Accelerated Test Results for B5 Blends

CL#	Biodiesel	%	Diesel	Diesel	Rancimat	D2274, mod, mg/100 ml			D525*	D6468	
				IBP, °C	IP, h	Filt Insols	Adh Insols	Tot Insols	IP, h	Reflectance, %	mg/100 ml
CL06-198	**27128**	**95**	**27150**	**154**	**>20**	**0.8**	**0.6**	**1.4**	**No break**	**97.6**	**<0.1**
CL06-199	**27128**	**95**	**27151**	**167**	**>20**	**0.2**	**0.3**	**0.5**	**No break**	**99.0**	**0.2**
CL06-200	**27128**	**95**	**27166**	**165**	**>20**	**0.3**	**0.3**	**0.6**	**No break**	**97.8**	**<0.1**
CL06-201	**27128**	**95**	**27171**	**190**	**>20**	**0.5**	**0.2**	**0.7**	**No break**	**84.1**	**<0.1**
CL06-202	**27128**	**95**	**27175**	**164**	**>20**	**0.2**	**0.2**	**0.4**	**No break**	**93.8**	**<0.1**
CL06-203	**27128**	**95**	**27176**	**183**	**>20**	**0.2**	**0.1**	**0.3**	**No break**	**98.9**	**<0.1**
CL06-210	**27129**	**95**	**27150**	**154**	**>20**	**0.2**	**0.4**	**0.6**	**No break**	**95.9**	**<0.1**
CL06-211	**27129**	**95**	**27151**	**167**	**>20**	**0.8**	**0.2**	**1.0**	**No break**	**98.3**	**<0.1**
CL06-212	**27129**	**95**	**27166**	**165**	**>20**	**0.1**	**0.1**	**0.2**	**No break**	**98.7**	**<0.1**
CL06-213	**27129**	**95**	**27171**	**190**	**>20**	**0.1**	**0.1**	**0.2**	**No break**	**85.5**	**<0.1**
CL06-214	**27129**	**95**	**27175**	**164**	**>20**	**0.5**	**0.1**	**0.6**	**No break**	**95.3**	**0.1**
CL06-215	**27129**	**95**	**27176**	**183**	**>20**	**0.1**	**1.4**	**1.5**	**1.8**	**98.7**	**<0.1**
CL06-223	**27137**	**95**	**27150**	**154**	**>20**	**0.2**	**1.4**	**1.6**	**No break**	**97.0**	**<0.1**
CL06-224	**27137**	**95**	**27151**	**167**	**>20**	**0.1**	**0.9**	**1.0**	**No break**	**98.8**	**<0.1**
CL06-225	**27137**	**95**	**27166**	**165**	**>20**	**0.1**	**0.9**	**1.0**	**No break**	**98.6**	**0.1**

CL06-226	27137	95	27171	190	>20	0.3	0.1	0.4	No break	91.5	<0.1
CL06-227	27137	95	27175	164	>20	0.2	0.1	0.3	No break	94.1	<0.1
CL06-228	27137	95	27176	183	18.5	0.3	0.1	0.4	No break	98.9	0.4
CL06-235	27138	95	27150	154	4.8	39	1.7	40.7	8.3	87.7	0.1
CL06-236	27138	95	27151	167	5.8	23	0.5	23.5	No break	98.3	<0.1
CL06-237	27138	95	27166	165	5.0	32	3.9	35.9	No break	90.3	0.3
CL06-238	27138	95	27171	190	>12	0.2	0.1	0.3	No break	32.1	0.3
CL06-239	27138	95	27175	164	6.9	0.1	0.1	0.2	No break	93	<0.1
CL06-240	27138	95	27176	183	0.7	0.2	0.1	0.3	No break	98.4	0.4
CL06-248	27141	95	27150	154	>12	0.1	0.5	0.6	No break	97.5	<0.1
CL06-249	27141	95	27151	167	>12	0.1	0.1	0.2	No break	99.0	<0.1
CL06-250	27141	95	27166	165	>12	0.2	0.1	0.3	No break	96.4	<0.1
CL06-251	27141	95	27171	190	>12	0.1	0.1	0.2	No break	87.7	<0.1
CL06-252	27141	95	27175	164	>12	0.2	0.1	0.3	No break	95.6	<0.1
CL06-253	27141	95	27176	183	>12	0.2	0.1	0.3	No break	99.3	<0.1
CL06-260	27148	95	27150	154	>12	0.2	0.1	0.3	No break	89.6	0.1
CL06-261	27148	95	27151	167	>12	0.1	0.1	0.2	No break	91.4	0.1
CL06-262	27148	95	27166	165	>12	0.2	0.1	0.3	No break	91.0	0.6

CL06-263	27148	95	27171	190	>12	0.1	0.3	0.4	No break	84.4	0.4
CL06-264	27148	95	27175	164	>12	0.2	0.2	0.4	No break	93.4	0.2
CL06-265	27148	95	27176	183	>12	0.1	0.1	0.2	No break	87.6	0.4
CL06-272	27152	95	27150	154	>12	0.1	0.1	0.2	No break	97.9	<0.1
CL06-273	27152	95	27151	167	>12	0.1	0.2	0.3	No break	99.1	<0.1
CL06-274	27152	95	27166	165	>12	0.1	0.1	0.2	No break	99.0	0.1
CL06-275	27152	95	27171	190	>12	0.1	0.3	0.4	No break	91.7	0.1
CL06-276	27152	95	27175	164	>12	0.1	0.2	0.3	No break	96.0	<0.1
CL06-277	27152	95	27176	183	>12	0.1	0.1	0.2	No break	99.2	0.1
CL06-284	27160	95	27150	154	>12	2.4	0.2	2.6	No break	48.6	2.0
CL06-285	27160	95	27151	167	>12	2.0	0.2	2.2	No break	72.0	0.5
CL06-286	27160	95	27166	165	>12	4.6	0.6	5.2	No break	65.1	0.7
CL06-287	27160	95	27171	190	5.5	0.6	0.2	0.8	No break	19.3	2.0
CL06-288	27160	95	27175	164	>12	0.1	0.1	0.2	No break	55.7	0.5
CL06-289	27160	95	27176	183	>12	0.2	0.1	0.3	No break	68.1	1.6

Appendix E: B5 Blend Storage, Fuel Tank, and High Temperature Stability Results

				CL06-462	CL06-463	CL06-464	CL06-465	CL06-466	CL06-467	CL06-468	CL06-469
				5% AL-27128 in 95% AL-27166	**5% AL-27129 in 95% AL-27176**	**5% AL-27137 in 95% AL-27175**	**5% AL-27138 in 95% AL-27150**	**5% AL-27141 in 95% AL-27175**	**5% AL-27148 in 95% AL-27175**	**5% AL-27152 in 95% AL-27151**	**5% AL-27160 in 95% AL-27171**
0 Weeks	**Peroxide Value**	**D 3703**		**41.24**	**8.14**	**18.79**	**21.16**	**32.27**	**18.75**	**21.56**	**4.17**
	Viscosity@40 C	**D 445**		**1.72**	**1.61**	**2.37**	**1.67**	**2.31**	**2.34**	**2.36**	**3.04**
	Total Acid No.	**D 664**	**mg KOH/g**	**0.03**	**0.06**	**0.03**	**0.05**	**0.04**	**0.06**	**0.05**	**0.05**
4 Weeks	**Filterable Insols**	**D 4625, mod**	**mg/100 ml**	**0.2**	**0.3**	**0.1**	**-0.2**	**0.2**	**0.1**	**0**	**0.5**
	Adherent Insols	**D 4625, mod**	**mg/100 ml**	**1**	**0.6**	**0.2**	**0.5**	**0.2**	**-0.4**	**1**	**0.2**
	Total Insols	**D 4625, mod**	**mg/100 ml**	**1.2**	**0.9**	**0.3**	**0.3**	**0.4**	**-0.3**	**1**	**0.7**
	Peroxide Value	**D 3703**		**64.71**	**77.97**	**61.58**	**217.33**	**68.75**	**168.66**	**33.53**	**187.67**
	Viscosity@40 C	**D 445**		**1.76**	**1.6**	**2.33**	**1.66**	**2.31**	**2.34**	**2.38**	**3.01**
	Total Acid No.	**D 664**	**mg KOH/g**	**0.01**	**0.01**	**0.04**	**0**	**0.04**	**0.02**	**0.07**	**0.04**
8 Weeks	**Filterable Insols**	**D 4625, mod**	**mg/100 ml**	**0.3**	**0.5**	**0.2**	**0.5**	**0.3**	**0.3**	**0.2**	**0.9**
	Adherent Insols	**D 4625, mod**	**mg/100 ml**	**0.6**	**0.1**	**0**	**0.6**	**0.8**	**0.3**	**0.5**	**0.8**
	Total Insols	**D 4625, mod**	**mg/100 ml**	**0.9**	**0.6**	**0.2**	**1.1**	**1.1**	**0.6**	**0.7**	**1.7**
	Peroxide Value	**D 3703**		**17.58**	**10.38**	**12.39**	**44.71**	**23.92**	**4.79**	**13.98**	**10.8**
	Viscosity@40 C	**D 445**		**1.73**	**1.61**	**2.37**	**1.67**	**2.33**	**2.35**	**2.36**	**3.07**

	Total Acid No.	**D 664**	**mg KOH/g**	**0.01**	**0.03**	**0.01**	**0.02**	**0.01**	**0.02**	**0.07**	**0.04**
12 Weeks	**Filterable Insols**	**D 4625, mod**	**mg/100 ml**	**0.3**	**1.4**	**0.2**	**34.3**	**0.3**	**0.2**	**0.2**	**0.7**
	Adherent Insols	**D 4625, mod**	**mg/100 ml**	**1.3**	**0.7**	**1.3**	**22.7**	**1**	**0.5**	**0.6**	**0.8**
	Total Insols	**D 4625, mod**	**mg/100 ml**	**1.6**	**2.1**	**1.5**	**57**	**1.3**	**0.7**	**0.8**	**1.5**
	Peroxide Value	**D 3703**		**21.98**	**10.79**	**12.79**	**1001.99**	**25.18**	**4.80**	**20.37**	**9.59**
	Viscosity@40 C	**D 445**		**1.73**	**1.58**	**2.31**	**1.69**	**2.31**	**2.36**	**2.34**	**2.98**
	Total Acid	**D 664**	**mg KOH/g**	**0.03**	**0.01**	**0.02**	**0.32**	**0.04**	**0.06**	**0.05**	**0.06**
1 Week	**Filterable Insols**	**D 4625, mod @ 80C**	**mg/100 ml**	**0.4**	**0.4**	**1.3**	**98.9**	**1.3**	**3.2**	**3**	**1.2**
	Adherent Insols	**D 4625, mod @ 80C**	**mg/100 ml**	**0.9**	**0.4**	**0.6**	**149.5**	**0.9**	**0.6**	**0.7**	**0.7**
	Total Insols	**D 4625, mod @ 80C**	**mg/100 ml**	**1.3**	**0.8**	**1.9**	**248.4**	**2.2**	**3.8**	**3.7**	**1.9**
	Peroxide Value	**D 3703**		**45.99**	**42.38**	**41.56**	**3046.12**	**118.73**	**16.37**	**27.92**	**465.02**
	Viscosity@40 C	**D 445**		**2.31**	**1.85**	**3.73**	**2.71**	**3.69**	**3.6**	**2.94**	**3.6**
	Gravimetric	**D 6468**	**% Reflectance**	**98.8**	**99.1**	**91.8**	**77.3**	**91.1**	**74.1**	**97.6**	**52.4**
			Heptane Rinse mg/150ml	**0.15**	**0.3**	**0.15**	**75**	**0.15**	**0.3**	**0.6**	**0.45**
	Total Acid No.	**D 664**	**mg KOH/g**	**0.05**	**0.07**	**0.03**	**1.84**	**0.05**	**0.08**	**0.06**	**0.06**

Antioxidant Treated B5 Blends				CL06-331	CL06-332	CL06-333	CL06-334	CL06-516	CL06-518	CL06-520	CL06-522
				5% 27138 + 2000 ppm A 95% 27151	**5% 27138 + 1000 ppm B 95% 27151**	**5% 27138 + 2000 ppm B 95% 27151**	**5% 27129 + 1000 ppm A 95% 27151**	**5% 27138 +2000ppm A, 95% 27175**	**5% 27138 +1000ppm B, 95% 27175**	**5% 27138 +2000ppm B, 95% 27175**	**5% 27138 +1000ppm A, 95% 27175**
0 Weeks	**Filterable Insols**	**D 2274, mod**	**mg/100 ml**	**0.1**	**0**	**0**	**0**	**0.0**	**0.0**	**0.2**	**0.1**
	Adherent Insols	**D 2274, mod**	**mg/100 ml**	**0.2**	**0**	**0**	**0**	**0.2**	**0.0**	**0.1**	**0.1**
	Total Insols	**D 2274, mod**	**mg/100 ml**	**0.3**	**0**	**0**	**0**	**0.2**	**0.0**	**0.3**	**0.2**
	Rancimat IP		**h**	**>12**	**>12**	**>12**	**>12**	**>12**	**>12**	**>12**	**>12**
4 Weeks	**Filterable Insols**	**D 4625, mod**	**mg/100 ml**	**0.2**	**0.2**	**0.2**	**0.2**	**0.1**	**0.1**	**0.0**	**0.1**
	Adherent Insols	**D 4625, mod**	**mg/100 ml**	**0.5**	**0.5**	**0.6**	**0.3**	**0.2**	**0.5**	**0.0**	**0.0**
	Total Insols	**D 4625, mod**	**mg/100 ml**	**0.7**	**0.7**	**0.8**	**0.5**	**0.3**	**0.6**	**0.0**	**0.1**
	Rancimat IP		**h**	**7.75**	**9.57**	**10.46**	**0**	**>12**	**>12**	**>12**	**>12**
	Total Acid No.	**D 664**	**mg KOH/g**	**0.93**	**0.92**	**0.91**	**0.93**				
8 Weeks	**Filterable Insols**	**D 4625, mod**	**mg/100 ml**	**0.2**	**0.2**	**0.2**	**0.1**	**0.2**	**0.4**	**0.2**	**0.4**

	Adherent Insols	**D 4625, mod**	**mg/100 ml**	**1.7**	**1.5**	**1.1**	**0.7**	**0.2**	**0.7**	**0.4**	**0.3**
	Total Insols	**D 4625, mod**	**mg/100 ml**	**1.9**	**1.7**	**1.3**	**0.8**	**0.4**	**1.1**	**0.6**	**0.7**
	Rancimat IP		**h**	**>12**	**9.87**	**>12**	**>12**	**>12**	**>12**	**>12**	**>12**
	Total Acid No.	**D 664**	**mg KOH/g**	**>12**	**9.91**	**>12**	**>12**				
12 Weeks	**Filterable Insols**	**D 4625, mod**	**mg/100 ml**	**0.2**	**0.2**	**0.1**	**0.2**	**0.3**	**0.3**	**1.1**	**0.6**
	Adherent Insols	**D 4625, mod**	**mg/100 ml**	**0.5**	**0**	**-0.2**	**-0.2**	**1.2**	**0.7**	**0.7**	**0.3**
	Total Insols	**D 4625, mod**	**mg/100 ml**	**0.7**	**0.2**	**-0.1**	**0**	**1.5**	**1.0**	**1.8**	**0.9**
	Rancimat IP		**h**	**11.27**	**10.74**	**>12**	**>12**				
	Total Acid No.	**D 664**	**mg KOH/g**	**0.08**	**0.08**	**0.06**	**0.09**				
1 Weeks	**Filterable Insols**	**D 4625, mod**	**mg/100 ml**	**0.4**	**0.6**	**0.8**	**0.8**	**2.1**	**1.6**	**4.5**	**1.8**
80C	**Adherent Insols**	**D 4625, mod**	**mg/100 ml**	**0.3**	**0.4**	**0.1**	**0.3**	**0.5**	**-0.2**	**0.0**	**11.9**
	Total Insols	**D 4625, mod**	**mg/100 ml**	**0.7**	**1.0**	**0.9**	**1.1**	**2.6**	**1.4**	**4.5**	**13.7**
	Thermal Stability	**D 6468**	**% Reflectanc e**	**99.0**	**99.2**	**99.0**	**98.1**	**91.0**	**92.6**	**90.9**	**89.2**
			Heptane Rinse mg/100ml	**0.15**	**0.15**	**0.15**	**0.15**	**0.15**	**0.15**	**0.15**	**0.15**

Additional Antioxidant Treated B5 Blends				**CL06-546**	**CL06-548**	**CL06-550**	**CL06-552**
				5% 27138 + 1000 ppm A 95% 27175	5% 27138 + 1000 ppm A 95% 27151	5% 27129 + 1000 ppm B 95% 27151	5% 27129 + 1000 ppm B 95% 27175

1 Weeks	Filterable Insols	D 4625, mod	mg/100 ml	21.5	89	2.5	13.4
80C	Adherent Insols	D 4625, mod	mg/100 ml	0.7	11	0.2	0.2
	Total Insols	D 4625, mod	mg/100 ml	22.2	100	2.7	13.6
	Thermal Stability	D 6468	% Reflectance	77.5	92	98	88
			Heptane Rinse mg/100ml	2.1	10.5	0.15	0.15

Appendix F: Accelerated Test Results for B20 Blends

CL#	Biodiesel	%	Diesel		Rancimat	D2274, mod, mg/100 ml			D525	D6468	
					IP, h	Filt Insols	Adh Insols	Tot Insols	IP, h	Reflectance, %	mg/100 ml
CL06-192	**27128**	**80**	**27150**		**8.9**	**0.1**	**0.2**	**0.3**	**No break**	**97.9**	**<0.1**
CL06-193	**27128**	**80**	**27151**		**10.2**	**0.1**	**0.1**	**0.2**	**No break**	**99.1**	**<0.1**
CL06-194	**27128**	**80**	**27166**		**8.2**	**0.2**	**0.5**	**0.7**	**No break**	**98.4**	**0.5**
CL06-195	**27128**	**80**	**27171**		**5.5**	**0.8**	**0.2**	**1**	**No break**	**91.0**	**<0.1**
CL06-196	**27128**	**80**	**27175**		**7.8**	**0.2**	**0.1**	**0.3**	**No break**	**94.7**	**<0.1**
CL06-197	**27128**	**80**	**27176**		**9.5**	**0.1**	**0.1**	**0.2**	**No break**	**98.9**	**<0.1**
CL06-204	**27129**	**80**	**27150**		**>12**	**0.3**	**0.1**	**0.4**	**11.5**	**97.6**	**<0.1**
CL06-205	**27129**	**80**	**27151**		**>12**	**0.2**	**0.1**	**0.3**	**No break**	**98.4**	**<0.1**
CL06-206	**27129**	**80**	**27166**		**>12; 7.3**	**0.2**	**0.1**	**0.3**	**11.9**	**95.9**	**<0.1**
CL06-207	**27129**	**80**	**27171**		**>12**	**0.2**	**0.3**	**0.5**	**No break**	**89.4**	**1.2**
CL06-208	**27129**	**80**	**27175**		**>12**	**0.1**	**0.2**	**0.3**	**No break**	**97.9**	**<0.1**
CL06-209	**27129**	**80**	**27176**		**>12; 12**	**0.2**	**0.4**	**0.6**	**No break**	**99.0**	**<0.1**
CL06-229	**27137**	**80**	**27150**		**>12**	**0.2**	**0.4**	**0.6**	**No break**	**98.2**	**<0.1**
CL06-230	**27137**	**80**	**27151**		**>12**	**0.4**	**0.6**	**1**	**No break**	**98.8**	**<0.1**
CL06-231	**27137**	**80**	**27166**		**11.6**	**0.1**	**0.2**	**0.3**	**No break**	**99.0**	**0.2**
CL06-232	**27137**	**80**	**27171**		**>12**	**0.2**	**0.4**	**0.6**	**No**	**82.1**	**0.9**

									break		
CL06-233	27137	80	27175		>12	0.1	0.1	0.2	No break	98.0	<0.1
CL06-234	27137	80	27176		>12; 12	0.1	0.1	0.2	No break	98.9	<0.1
CL06-241	27138	80	27150		1.8	47.6	132.4	180	1.5	91.1	1.5
CL06-242	27138	80	27151		1.8	42.4	82.4	124.8	1.4	99.2	<0.1
CL06-243	27138	80	27166		1.9	36.8	109.4	146.2	2.2	91.3	0.2
CL06-244	27138	80	27171		3.5	6.1	4.8	10.9	No break	54.1	1.1
CL06-245	27138	80	27175		1.7	51.7	171.1	222.8	2.4	97.8	<0.1
CL06-246	27138	80	27176		3.2	42.2	85	127.2	4.3	99.3	<0.1
CL06-254	27141	80	27150		12.2	0.2	0.1	0.3	No break	98.2	0.1
CL06-255	27141	80	27151		12.5	0.3	0.1	0.4	No break	99.3	0.1
CL06-256	27141	80	27166		10.6	0.3	0.1	0.4	No break	98.7	<0.1
CL06-257	27141	80	27171		>12	0.8	0.1	0.9	No break	94.2	<0.1
CL06-258	27141	80	27175		11.1	0.2	0.1	0.3	No break	98.8	<0.1
CL06-259	27141	80	27176		10.2	0.3	0.1	0.4	No break	99.3	0.3
CL06-266	27148	80	27150		>12	0.3	0.1	0.4	No break	97.3	<0.1
CL06-267	27148	80	27151		>12	0.2	0.1	0.3	No break	97.1	<0.1
CL06-268	27148	80	27166		>12	0.2	0.1	0.3	No break	97.1	0.1
CL06-269	27148	80	27171		>12	0.4	0.1	0.5	No break	92.6	<0.1
CL06-270	27148	80	27175		>12	0.4	0.1	0.5	No break	87.6	0.4
CL06-271	27148	80	27176		>12	0.5	0.1	0.6	No break	97.0	0.3

CL06-278	27152	80	27150		>12	0.5	0.1	0.6	No break	98.5	0.1
CL06-279	27152	80	27151		>12	0.2	0.1	0.3	No break	99.5	<0.1
CL06-280	27152	80	27166		>12	0.3	0.1	0.4	No break	99.0	0.2
CL06-281	27152	80	27171		>12	0.3	0.1	0.4	No break	96.0	0.4
CL06-282	27152	80	27175		>12	1.1	0.1	1.2	No break	97.2	<0.1
CL06-283	27152	80	27176		>12	0.1	0.1	0.2	No break	99.4	0.5
CL06-290	27160	80	27150		2.3	34	60.9	94.9	3.9	93.7	0.1
CL06-291	27160	80	27151		2.7	38.8	41.6	80.4	3.3	90.3	<0.1
CL06-292	27160	80	27166		2.3	40.4	44.5	84.9	3.2	84.0	1.4
CL06-293	27160	80	27171		4.5	5.7	0.3	6	No break	90.5	0.8
CL06-294	27160	80	27175		2.9	48.1	52.2	100.3	No break	78.9	0.7
CL06-295	27160	80	27176		4.1	31.7	2	33.7	7.5	71.5	1.0

Appendix G: B20 Blend Storage, Fuel Tank, and High-Temperature Stability Results

				CL06-480	CL06-481	CL06-482	CL06-483	CL06-484	CL06-485	CL06-486	CL06-487
				20%AL-27128 in AL-27175-F	**20%AL-27129 in AL-27150-F**	**20%AL-27137 in AL-27171-F**	**20%AL-27138 in AL-27151-F**	**20%AL-27141 in AL-27166-F**	**20%AL-27148 in AL-27166-F**	**20%AL-27152 in AL-27175-F**	**20%AL-27160 in AL-27176-F**
0 Weeks	**Peroxide Value**	**D 3703**		**108.51**	**28.52**	**66.07**	**274.84**	**75.37**	**61.45**	**74.30**	**46.91**
	Viscosity@40C	**D 445**		**2.56**	**1.89**	**3.10**	**2.51**	**1.92**	**1.94**	**2.56**	**1.91**
	Total Acid No.	**D 664**	**mg KOH/g**	**0.06**	**0.09**	**0.01**	**0.09**	**0.02**	**0.17**	**0.02**	**0.08**
4 Weeks	**Filterable Insols**	**D 4625, mod**	**mg/100 ml**	**0.2**	**0.1**	**0.3**	**0.5**	**1.3**	**0.2**	**0.1**	**0.6**
	Adherent Insols	**D 4625, mod**	**mg/100 ml**	**<0.1**	**0**	**0.1**	**0.7**	**0.5**	**<0.1**	**<0.1**	**<0.1**
	Total Insols	**D 4625, mod**	**mg/100 ml**	**0.1**	**0.1**	**0.4**	**1.2**	**1.8**	**<0.1**	**0**	**0.3**
	Peroxide Value	**D 3703**		**55.56**	**26.36**	**17.19**	**1183.43**	**103.15**	**17.99**	**27.96**	**71.91**
	Viscosity @ 40°C	**D 445**		**2.53**	**1.93**	**3.14**	**2.62**	**1.94**	**1.96**	**2.56**	**1.88**
	Total Acid No.	**D 664**	**mg KOH/g**	**0.07**	**0.11**	**0.07**	**0.2**	**0.05**	**0.16**	**0.01**	**0.14**
8 Weeks	**Filterable Insols**	**D 4625, mod**	**mg/100 ml**	**0.2**	**0.1**	**0.2**	**64.8**	**0.3**	**0.3**	**0.3**	**4**
	Adherent Insols	**D 4625, mod**	**mg/100 ml**	**0.8**	**0.7**	**0.4**	**110.3**	**4.3**	**0.5**	**1.2**	**2.6**
	Total Insols	**D 4625, mod**	**mg/100 ml**	**1**	**0.8**	**0.6**	**175.1**	**4.6**	**0.8**	**1.5**	**6.6**
	Peroxide Value	**D 3703**		**99.11**	**43.96**	**82.73**	**2733.56**	**147.48**	**33.46**	**72.33**	**531.11**
	Viscosity@40C	**D 445**		**2.57**	**1.92**	**3.11**	**2.91**	**1.96**	**1.98**	**2.54**	**1.92**
	Total Acid No.	**D 664**	**mg KOH/g**	**0.09**	**0.11**	**0.33**	**1.7**	**0.08**	**0.19**	**0.06**	**0.35**
12 Weeks	**Filterable Insols**	**D 4625, mod**	**mg/100 ml**	**0.8**	**0.4**	**0.3**	**55.1**	**0.8**	**0.5**	**0.8**	**0.8**

	Adherent Insols	**D 4625, mod**	**mg/100 ml**	**0.3**	**2.6**	**0.4**	**141.5**	**1.2**	**0.1**	**0.4**	**0.4**
	Total Insols	**D 4625, mod**	**mg/100 ml**	**1.1**	**3.0**	**0.7**	**196.6**	**2.0**	**0.6**	**1.2**	**1.2**
	Peroxide Value	**D 3703**		**115.45**	**47.18**	**77.41**	**1379.57**	**162.24**	**30.39**	**93.49**	**1024.25**
	Viscosity @ 40°C	**D 445**		**2.52**	**1.93**	**3.14**	**3.02**	**1.95**	**1.99**	**2.56**	**1.93**
	Total Acid No.	**D 664**	**mg KOH/g**	**0.02**	**0.13**	**0.39**	**2.19**	**0.09**	**0.18**	**0.09**	**0.66**
1 Weeks	**Filterable Insols**	**D 4625, mod @80C**	**mg/100 ml**	**56**	**17.7**	**10**	**26.1**	**25.4**	**48.3**	**0.8**	**15.3**
	Adherent Insols	**D 4625, mod @80C**	**mg/100 ml**	**2.4**	**0.8**	**2**	**9.6**	**0.9**	**0.2**	**0.3**	**0.6**
	Total Insols	**D 4625, mod @80C**	**mg/100 ml**	**58.4**	**18.5**	**12**	**35.7**	**26.3**	**48.5**	**1.1**	**15.9**
	Peroxide Value	**D 3703**		**353.15**	**4474.52**	**494.89**	**2230.16**	**1336.25**	**1325.35**	**513.02**	**1167.71**
	Viscosity @ 40°C	**D 445**		**5.38**	**5.16**	**4.09**	**5.00**	**3.66**	**3.54**	**4.99**	**3.93**
	Gravimetric	**D 6468**	**% Reflectance**	**91.5**	**89.6**	**91.1**	**88.5**	**99.5**	**77.4**	**95.5**	**86.6**
			Heptane Rinse mg/150ml	**4.95**	**12.3**	**0.3**	**18.6**	**0.45**	**3.6**	**0.3**	**2.4**
	Total Acid No.	**D 664**	**mg KOH/g**	**0.66**	**2.88**	**0.11**	**1.79**	**0.25**	**0.63**	**0.33**	**0.89**
Antioxidant Treated B20 Blends				CL06-335	CL06-336	CL06-337	CL06-338	CL06-517	CL06-519	CL06-521	CL06-523
				20% 27138 + 2000 ppm A 80% 27151	**20% 27138 + 1000 ppm B 80% 27151**	**20% 27138 + 2000 ppm B 80% 27151**	**20% 27129 + 1000 ppm A80% 27151**	**20% 27138 +2000pp m A 80% 27175**	**20% 27138 +1000pp m B, 80% 27175**	**20% 27138 +2000pp m B, 95% 27175**	**20% 27138 +1000pp m A, 80% 27175**
0 Weeks	**Filterable Insols**	**D 2274, mod**	**mg/100 ml**	**35.7**	**0.3**	**0.1**	**0**	**0.1**	**0.6**	**0.2**	**58.6**

	Adherent Insols	**D 2274, mod**	**mg/100 ml**	**65.1**	**0**	**0**	**0.2**	**0.1**	**0.1**	**0**	**89.5**
	Total Insols	**D 2274, mod**	**mg/100 ml**	**100.8**	**0.3**	**0.1**	**0.2**	**0.2**	**0.5**	**0.2**	**148.1**
	Rancimat IP		**h**	**9.35**	**4.63**	**6.98**	**>12**	**>12**	**4.47**	**6.63**	**5.95**
4 Weeks	**Filterable Insols**	**D 4625, mod**	**mg/100 ml**	**0.8**	**0.5**	**0.3**	**0.3**	**0.1**	**0.2**	**0.1**	**0.1**
	Adherent Insols	**D 4625, mod**	**mg/100 ml**	**0.4**	**0.3**	**0.4**	**0.3**	**4.1**	**0.1**	**0.1**	**0**
	Total Insols	**D 4625, mod**	**mg/100 ml**	**1.2**	**0.8**	**0.7**	**0.6**	**4.2**	**0.3**	**0.2**	**0.1**
	Rancimat IP		**h**	**4.75**	**3.25**	**5.46**	**>12**	**8.27**	**4.34**	**5.84**	**6.29**
	Total Acid No.	**D 664**	**mg KOH/g**	**0.94**	**1.01**	**1.02**	**1.02**				
8 Weeks	**Filterable Insols**	**D 4625, mod**	**mg/100 ml**	**0.5**	**1**	**0.4**	**0.2**	**0.2**	**0.4**	**0.3**	**1.3**
	Adherent Insols	**D 4625, mod**	**mg/100 ml**	**0.8**	**1.4**	**0.3**	**0.3**	**1.1**	**0.7**	**0.4**	**0.3**
	Total Insols	**D 4625, mod**	**mg/100 ml**	**1.3**	**2.4**	**0.7**	**-0.1**	**1.3**	**1.1**	**0.7**	**1.6**
	Rancimat IP		**h**	**7.78**	**3.43**	**5.86**	**>12**	**8.65**	**4**	**7**	**5.25**
	Total Acid No.	**D 664**	**mg KOH/g**	**0.94**	**1.01**	**1.02**	**1.02**				
12 Weeks	**Filterable Insols**	**D 4625, mod**	**mg/100 ml**	**0.2**	**0.2**	**0.2**	**0.1**	**0.5**	**0.8**	**0.9**	**1.1**
	Adherent Insols	**D 4625, mod**	**mg/100 ml**	**1.1**	**0.7**	**1.2**	**0.6**	**0.6**	**0.9**	**0.3**	**0.4**
	Total Insols	**D 4625, mod**	**mg/100 ml**	**1.3**	**0.9**	**1.4**	**0.7**	**1.1**	**1.7**	**1.2**	**1.5**
	Rancimat IP		**h**	**6.66**	**3.47**	**5.81**	**>12**				
	Total Acid No.	**D 664**	**mg KOH/g**	**0.06**	**0.08**	**0.11**	**0.11**				
1 Weeks	**Filterable Insols**	**D 4625, mod**	**mg/100 ml**	**0.6**	**1.1**	**0.8**	**0.5**	**2.2**	**6.4**	**2.3**	**10.9**
80C	**Adherent Insols**	**D 4625, mod**	**mg/100 ml**	**0.1**	**0.4**	**0.1**	**0.3**	**-0.3**	**-0.6**	**0.0**	**0.1**
	Total Insols	**D 4625, mod**	**mg/100 ml**	**0.7**	**1.5**	**0.9**	**0.8**	**1.9**	**5.8**	**2.3**	**11.0**

	Thermal Stability	**D 6468**	**% Reflectance**	**99.3**	**99.5**	**97.1**	**99**	**97.6**	**91.6**	**97.4**	**91.4**
			Heptane Rinse mg/150ml	**1.05**	**0.45**	**0.45**	**0.6**	**0.15**	**4.8**	**0.15**	**4.05**

Additional Antioxidant Treated B20 Blends				CL06-547	CL06-549	CL06-551	CL06-553
				20% 27138 + 1000 ppm A 80% 27175	**20% 27138 + 1000 ppm A 80% 27151**	**20% 27138 + 1000 ppm B 80% 27151**	**20% 27138 + 2000 ppm B 80% 27175**
1 Weeks	**Filterable Insols**	**D 4625, mod**	**mg/100 ml**	**4.3**	**15.5**	**0.7**	**11.9**
80C	**Adherent Insols**	**D 4625, mod**	**mg/100 ml**	**0.7**	**0.6**	**0.1**	**0.2**
	Total Insols	**D 4625, mod**	**mg/100 ml**	**5.0**	**16.1**	**0.8**	**12.1**
	Thermal Stability	**D 6468**	**% Reflectance**	**89**	**97**	**99**	**96**
			Heptane Rinse mg/150ml	**7.8**	**19.8**	**0.15**	**0.15**

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The objective of this work was to develop a database that supports specific proposals for a stability test and specification for biodiesel and biodiesel blends. B100 samples from 19 biodiesel producers were obtained in December of 2005 and January of 2006 and tested for stability. Eight of these samples were then selected for additional study, including long-term storage tests and blending at 5% and 20% with a number of ultra-low sulfur diesel fuels.

15. SUBJECT TERMS
biodiesel; database; B100; biodiesel blend; storage test

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